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Synthesis and characterization of novel and smart hydrogels for uranyl ions uptake under saline conditions

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ABSTRACT

In the present paper we report the synthesis and characterization of two copolymeric hydrogels based on acrylic acid (AAc) and methacrylic acid (MAAc) with acrylamide (AAm) for use in the removal and sorption of the uranyl ions from saline conditions. In a novel research plan, the hydrogels were synthesized by polymerizing AAm separately with equimolar amount of AAc and MAAc using ammonium persulphate (APS) as initiator and ethylene glycol dimethacrylate (EGDMA) as crosslinker to get crosslinked bifunctional hydrogels namely poly(AAm-co-AAc) hydrogel and poly(AAm-co-MAAc) hydrogel respectively. The hydrogels are bifunctional and have both amide and acid functional groups. For comparison, reference poly(acrylic acid) hydrogel [Poly(AAc) hydrogel] and poly(methacrylic acid) [Poly(MAAc) hydrogel] were also prepared. The hydrogels were characterized by nitrogen analysis, FTIR and SEM. Swelling studies of hydrogels were carried out as a function of time, temperature, pH and in 5% NaCl solution. These hydrogels respond quickly to the changes in their external environment and are pH and temperature sensitive and moderately salt tolerant. These hydrogels have been successfully used for uptake of uranyl ions from saline conditions. Uranyl ion uptake was studied as a function of concentration of uranyl ions in the presence of 0.1 N Na_2CO_3 *and three different concentrations of NaCl (1%, 2% and 3%) for three different time intervals (1h, 2h and 4h) at* 25^oC *to* 45^oC*. It is very interesting to observe that even in the presence of strong electrolytic salts percent swelling and percent uptake of uranyl ions is appreciable thereby indicating the salt tolerance of the hydrogels.*

Key words: hydrogels; percent uptake; salt tolerance; swelling; temperature sensitive.

INTRODUCTION

Many methods have been proposed for separation, enrichment and removal of metal ions [1-3]. Chemical precipitation has been traditionally proposed to remove metal ions from aqueous solutions. However, metal ions removal in the precipitation-coagulation systems in many cases is insufficient to meet strict regulatory requirements and create waste of another kind, which may be difficult to dispose off. Removal of metal ions by adsorption or sorption has been shown to be an efficient alternative [4,5]. However many exchange materials have been reported which not only are more effective in removal and separation of metal ions but also can be reused time and again [6-13]. Many ion specific resins, which under proper operating conditions are selective for one ionic species only have also been reported [14-18].

Synthetic polymers have almost entirely replaced inorganic carriers in the separation of heavy metal ions. Ability of resins containing amides, amine and carboxylic groups to bind metal ions has been reported [19-23]. The selectivity in the metal ion uptake of the polymers strongly depends on the crosslinking density [24-26]. Hydrogels sorb ionic species in bulk and can exchange protons. The presence of the water solubilizing functional groups is essential for metal ion uptake [27-28]. A number of factors including binding degree, pH value, solution composition and interaction of the polymeric ligands with metal ions influence interactions between the ligands and metal ions, which includes lanthanides, actinides, other transition metals and also alkali and alkaline earth metals ions [29]. The formation of complexes between linear poly(Acrylic Acid) [poly(AAc)] and uranyl ions [poly(AAc)/UO^{2+}] in aqueous solutions was studied [30]. Adsorption of uranyl ions by poly(N-Vinyl pyrrolidone-*g*-tartaric acid) hydrogels has been reported to be dependent mainly on the pH as well as on the amount of tartaric acid in the hydrogel and lesser dependence was reported on the ionic strength and temperature [31]. The complexing ability of the poly(AAc-*co*-vinylsulfonic acid) was determined by the relative amount of carboxylic acid groups [32].

Cellulose-*g*-poly(AAc)-*cl*-N,N-methylenebisacrylamide has been used for the competitive removal of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions from the aqueous solution [33]. Formation of a very stable tris-carboxylate coordinate complex by the Gd^{3+} ions and modified poly(Methacrylic acid)[poly(MAAc)] microparticles has been reported [34]. Poly(Acrylamide-*co*-AAc) hydrogels [Poly(AAm-*co*-AAc)] can be used as sorbent for water pollutants such as dyes and treatment of these organics from the wastewater [35]. A terpolymer prepared by reacting p-hydroxybenzoic acid with diamines and formaldehyde in presence of 2M HCl as catalyst, proved to be selective chelating ion-exchange resins for Fe^{3+},Cu^{2+}, Ni^{2+},Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} ions employing a batch equilibrium method. The terpolymer showed higher selectivity for Fe^{3+},$Cu^{2+}$and Ni^{2+}ions than for Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions [36]. The chelating ion-exchange properties of terpolymer resin synthesized by the condensation of p-Cresol and oxamide with formaldehyde in the presence of 2M HCl as catalyst was studied for Fe (III), Cu (II), Ni (II), Co (II), Zn (II), Cd (II) and Pb (II) ions by batch equilibrium method .The terpolymer showed a higher selectivity for Fe (III), Cu (II), and Ni (II) ions than for Co (II), Zn (II), Cd (II) and Pb (II) ions [37]. Sorption of metal ions namely Cd^{2+},Mn^{2+}, Zn^{2+} and Mg^{2+} by modified lignin was investigated. Soda and peroxyacid lignins precipitated from produced black liquor from cotton stalks pulping with soda and peroxyacid pulping process followed by hydrolysis using 10% HCl and incorporation of different functional groups by carboxylation and phosphorylation reactions and cross linking by using epichlorohydrine [38].

In the present communication, we report synthesis and characterization of two novel and smart hydrogels based on AAc and MAAc with AAm for the removal and sorption of the uranyl ions (UO_2^{2+}) as a function of different environmental factors like temperature and pH from moderately saline conditions. The reference crosslinked poly(AAc) and poly(MAAc) was also studied for swelling and UO_2^{2+} ions 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 ion exchangers. The hydrogels were characterized by nitrogen analysis, FTIR, SEM and water uptake studies as a function of time, temperature, pH, and in the presence of 5% NaCl.

MATERIALS AND METHODS

Materials

Acrylic acid, acrylamide, methacrylic acid, ammonium persulphate, sodium chloride, sodium carbonate and buffer tablets (4.0, 7.0 and 9.2) (S.D. Fine, Mumbai, India), Ethylene glycol dimethacrylate, Uranyl nitrate [$UO_2(NO_3)_2.6H_2O$], (Merck, Schuchardt, Germany) were used as received. Solvents were distilled before use.

Synthesis of Hydrogels

Known amount of AAm was treated with equimolar amount of AAc using ammonium persulphate (APS) (1% of the combined weight of two monomers) as initiator and ethylene glycol dimethacrylate (EGDMA) (2.5% of the total weight of the two monomers and pre-dissolved in water) as crosslinker. The reaction system was mixed by stirring to get a homogeneous mixture. The mixture was transferred to a glass vial and filled in fine capillaries by creating vacuum in the vial. The capillaries were sealed and kept in a hot water bath maintained at 70°C for three hours. The capillaries were broken to get the thread like hydrogel. The crosslinked hydrogel was washed repeatedly with distilled water to remove all soluble fraction completely. The hydrogel was dried at 50°C for one week to get constant weight. Then these threads were cut in small beads of equal size. The crosslinked hydrogel was heated in hot air oven at 60^0C to obtain constant weight.

Hydrogel of AAm with MAAc was also synthesized in the same manner. Reference poly(AAc) hydrogel and poly(MAAc) hydrogel were also synthesized on the similar lines except the addition AAm.

Characterization of Hydrogels

FTIR spectra were recorded on Nicollete 5700 FTIR Spectrophotometer in KBr. SEMs were taken on Jeol JSM-6100 scanning electron microscope; and nitrogen analysis was carried on Carlo Erba EA-1108**.**

Water uptake / Swelling 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 ºC - 45 ºC in a temperature-controlled bath (accuracy ±0.1 ºC). 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). The effect of pH on swelling was studied at optimum temperature, *i.e.*, 35 ºC. 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 ºC. Percent Swelling (P_s) of the hydrogels were calculated as follows:

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

Sorption of Uranyl ions by Hydrogels

Known weight of the dried hydrogel was subjected to swell in the solution of desired concentration of uranyl nitrate (0.0025, 0.005, 0.01, 0.02, 0.03, 0.04 and 0.05 m mol/L) in different concentrations of sodium chloride solution (1%, 2% and 3%) and 0.1 M sodium carbonate solution. The hydrogels were immersed in 50 ml solution of uranyl nitrate for different time intervals (1h, 2h and 4h) at five different temperatures i.e. 25^{o}C, 30^{o}C, 35^{o}C, 40^{o}C and 45^{o}C. The rejected filtrate of each solution was spectroscopically analyzed on Cary 300 UV-Spectrophotometer at an absorption maxima 215 nm.

P_u of the hydrogels have been calculated by the expression:

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

RESULTS AND DISCUSSION

The hydrogels prepared have been characterized by different methods as discussed.

FTIR Spectra of Hydrogels

FTIR spectrum of poly(AAm-*co*-AAc) hydrogel shows peaks at 3463 cm^{-1} (O-H and NH stretching), 2975 cm^{-1} (C-H stretching), 1722 cm^{-1} (C=O stretching of CO_2H), 1656 cm^{-1} (C=O stretching of amide), 1467 cm^{-1} (CH_2 bending) and so on (Fig.1.1). FTIR spectrum of poly(AAm-*co*-MAAc) hydrogel shows peaks at 3460 cm^{-1} (O-H and NH stretching), 2956 cm^{-1} (C-H stretching), 1719 cm^{-1} (C=O stretching of CO_2H), 1654 cm^{-1} (C=O stretching of amide), 1467 cm^{-1} (CH_2 bending) and so on (Fig. 1.2). FTIR spectra of reference poly(AAc) hydrogel and reference poly(MAAc) hydrogel also show their respective peaks.

Nitrogen Analysis of Hydrogels

The high percent of nitrogen has been found in both the hydrogels. A comparison of the % N present in a known weight of each of the hydrogels analyzed is given in Table 1. In both the hydrogels % N was found slightly less than the theoretical values, thereby indicating equal amount of AAm and AAc/MAAc in the coploymeric hydrogels.

Table 1: Nitrogen Analysis of the Hydrogels

Hydrogel	Wt. of sample (g)	Observed wt. of N (g)	Theoretical wt. of N (g)
Poly(AAm-*co*- AAc) hydrogel	2.347	0.2201	0.2297
Poly(AAm-*co*- MAAc) hydrogel	2.455	0.2111	0.2189

Scanning Electron Micrography (SEM)

SEMs of the hydrogels are shown in Fig. 2.1 and 2.2. SEMs of poly(AAm-*co*-AAc) hydrogel shows intense crosslinking and numerous pores of different sizes are visible. SEMs of poly(AAm-*co*-MAAc) hydrogel has more intense crosslinking and hence smaller pores.

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. In the present study, hydrogels 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 hydrogels.

Swelling Behaviour as a Function of Time and Temperature

Swelling was studied at seven different time intervals, *i.e.*, 30 min, 60 min, 120 min, 240 min, 360 min, 480 min and 720 min at five different temperatures, *i.e.*, 25ºC, 30ºC, 35ºC, 40ºC and 45ºC. The effect of swelling time on swelling behaviour of different hydrogels is exemplified by Fig. 3.1 at 35 ºC. Trends at all other temperatures are exactly the same. In general P_s increases till 480 min and thereafter remains almost constant in most of the cases or decreases gradually in other cases at all the five temperatures. The effect of swelling temperature on swelling behaviour of different hydrogels is exemplified by Fig. 3.2 at 480 min. P_s increase with the increase in temperature from 25ºC to 35ºC in most of the cases and from 25ºC to 40ºC in some cases. There after it decreases gradually in most of the cases and remains almost constant in other cases.

For poly(AAm-*co*-AAc) hydrogel, maximum P_s (7822) was observed at 35ºC and 480 min and minimum (1791) at 25ºC and 30 min. For poly(AAm-*co*-MAAc) hydrogel maximum P_s has been found to be 1515 at 35ºC and 360 min whereas minimum P_s has been found to be 692 at 25ºC and 30 min. For reference poly(AAc) hydrogel, P_s varies from 578 (30 min and 25°C) to 844 (480 min and 35°C). For reference poly(MAAc) hydrogel P_s varies from 256 (30 min and 25°C) to 419 (720 min and 35°C). The order of P_s for different hydrogels is: poly(AAm-*co*-AAc) hydrogel > poly(AAm-*co*-MAAc) hydrogel > poly(AAc) hydrogel > poly(MAAc) hydrogel.

It is interesting to observe that copolymerization of AAc and MAAc with AAm, increases P_s to a large extent. Some of the hydrogels exhibit thermosensitivity as these show rapid swelling transitions with the increase in temperature. For example, poly(AAm-*co*-AAc) hydrogel swells dramatically from 4202 to 6112 (when swelling time is 120 min), from 5023 to 6713 (when swelling time is 240 min) and from 5719 to 7454 (when swelling time is 360 min) when temperature is increased from 30ºC to 35 ºC. It also follows that swelling is much higher for poly(AAm-*co*-AAc) hydrogel as compared to poly(AAm-*co*-MAAc) hydrogel. It can be concluded that the swelling time and temperature largely affect P_s of all the hydrogels. P_s increases with time until the equilibrium is attained (480 min in most of the hydrogels) and thereafter it tends to decrease or remains constant. Similarly, P_s increases with increase in temperature till the equilibrium (35ºC or 40ºC) and thereafter it tends to decrease or remains almost constant.

Swelling Behaviour as a Function of pH

The effect of pH on swelling behaviour of different hydrogels is exemplified by Fig. 3.3 when swelling was carried out at 35ºC and 480 min. On variation of *p*H in the range 4, 7.0 and 9.2, P_s increases sharply with the increase in *p*H from 4.0 to 7.0 and thereafter it decreases, but decrease is less drastic. This behaviour is almost common for all the hydrogels. Here again, same trends have been observed as those for swelling as a function of time and temperature. These trends in behaviour originate from the suppression of any ionized carboxylic groups at low pH and result is some shriveling of the hydrogels. However, it has been also reported that at pH < 3.75, strong hydrogen bonding interpolymer complexation between the side chains of the network in semi dilute solution results in the formation of a transient hydrogel of the hydrogen bonded complex [39]. Such complex formation makes the water solubilizing groups less available for formation of hydrogen bonds with water. In the alkaline pH (*i.e.*, 9.2 in the present case), the hydrogels interact with the basic species again restricting the interaction of water molecules with those of acids.

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. Swelling is much higher for poly(AAm-*co*-AAc) hydrogel than poly(AAm-*co*-MAAc) hydrogel.

Study of Salt Tolerance of Hydrogels in the Presence of NaCl

Hydrogels do not swell appreciably in the presence of electrolyte salts due to the exosmosis as even the swollen hydrogels shrink dramatically in the presence of salt. High water uptake by hydrogels in the presence of salt is important from technological point of view. Hydrogels shriveling result from the loss of hydrophilic-hydrophobic balance of networks in the presence of electrolyte salts. Thus the pre-swollen gels shrink quickly and regain their original shape and weight by deswelling when they are subjected to electrolyte salt solution. In the present study, hydrogels show a small, yet significant swelling and hence salt tolerance in 5 % NaCl (w/v) solution (Fig. 3.4). The order of salt tolerance of different hydrogels is the same as is their swelling behaviour in pure water. Copolymerization and crosslinking of AAc and MAAc with AAm improves salt tolerance. Poly(AAm-*co*-AAc) hydrogel shows higher P_s (hence more salt tolerance) as compared to poly(AAc) hydrogel whereas poly(AAm *co*-MAAc) hydrogel shows higher P_s (hence more salt tolerance) as compared to poly(MAAc) hydrogel (Fig. 3.4).

It can be concluded from the foregone discussion that copolymerization and crosslinking of AAc/MAAc with AAm results in tremendous increase in the P_s of the hydrogels as compared to reference poly(AAc) hydrogel and poly(MAAc) hydrogel. Further, these hydrogels are more sensitive to the changes in their external environment and more salt tolerant as compared to reference hydrogels.

Uptake Uranyl Ion Studies

Uranyl ion uptake was studied as a function of concentration of uranium (0.0025, 0.0050, 0.010, 0.020, 0.030, 0.040 and 0.050 m mol/L) in the presence of 0.1 N Na_2CO_3 and three different concentrations of NaCl (1%, 2% and 3%) for three different time intervals (1h, 2h and 4h) at five different temperatures i.e. 25 ^oC, 30 ^oC, 35^oC, 40 ^oC and 45 ^oC. The results are described below.

P_u as a Function of Concentration of Uranium

For all the hydrogels, P_u increases sharply with increase in $[UO_2(NO_3)_2]$ from 0.0025 m mol/L to 0.020 m mol/L or 0.03 m mol/L followed by either constant value or a bit decrease in P_u with further increase in $[UO_2(NO_3)_2]$ (Fig. 4.1 to 4.5). From these results it may be concluded that at [0.020] m mol/L or [0.030] m mol/L, equilibrium sorption is reached and further increase in concentration does not affect the rate of sorption.

P_u as a Function of Time

The effect of time on swelling behaviour of different hydrogels is exemplified by Fig. 4.6 when swelling was carried out at 35ºC at 0.03 m mol/L concentration of $UO_2(NO_3)_2$. For all the cases, P_u increases with increase in sorption time from 1h to 2h and decreases thereafter or remains almost constant. Here again equilibrium sorption is reached in 2h and thereafter the rate of reverse process (desorption) increases resulting in decrease in P_u. Maximum P_u of 88% has been observed for poly(AAm-*co*-MAAC) hydrogel for 2h at 35^oC when concentration of $UO_2(NO_3)_2$ was 0.03 m mol/L and that of NaCl was 1%. The order of P_u is poly(AAm-*co*-MAAc) hydrogel > poly(AAm-co-AAc) hydrogel > poly(MAAc) hydrogel > poly(AAc) hydrogel.

P_u as a Function of concentration of NaCl

As has already been discussed that hydrogels have little tendency to swell in the presence of electrolyte salts as even the swollen hydrogels shrink dramatically in the presence of salts. So, as expected, P_s as well as P_u decreases with the increase in [NaCl] (Fig. 4.1 to 4.5). For example, for poly(AAm-*co*-AAC) hydrogel, maximum P_u is 77% in 1% [NaCl] (for 2h) that decreases to 59% in 2% [NaCl] and 56% in 3% [NaCl]. These results can easily be explained on the basis of the well known fact that with the increase in the [NaCl], charge on the hydrogels (responsible for their stability and expanded structure) is neutralized resulting in their partial flocculation and contraction in the network structure. This contraction decreases the accessibility of the binding sites on the networks for uranyl ions resulting in lesser P_u. In the present study it is very interesting to observe that even in the presence of strong electrolytic salts P_u is appreciable thereby indicating their salt resistant power.

Fig. 1.1: FTIR spectrum of poly (AAm-*co*-AAc) hydrogel

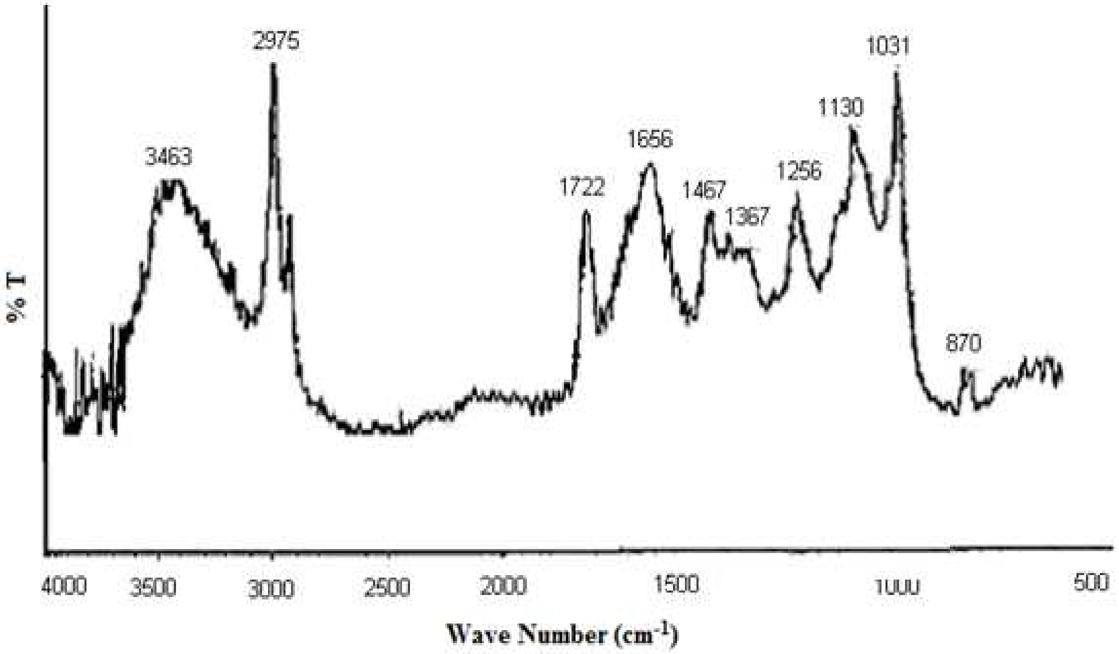


Fig. 1.2: FTIR spectrum of poly (AAm-*co*-MAAc) hydrogel

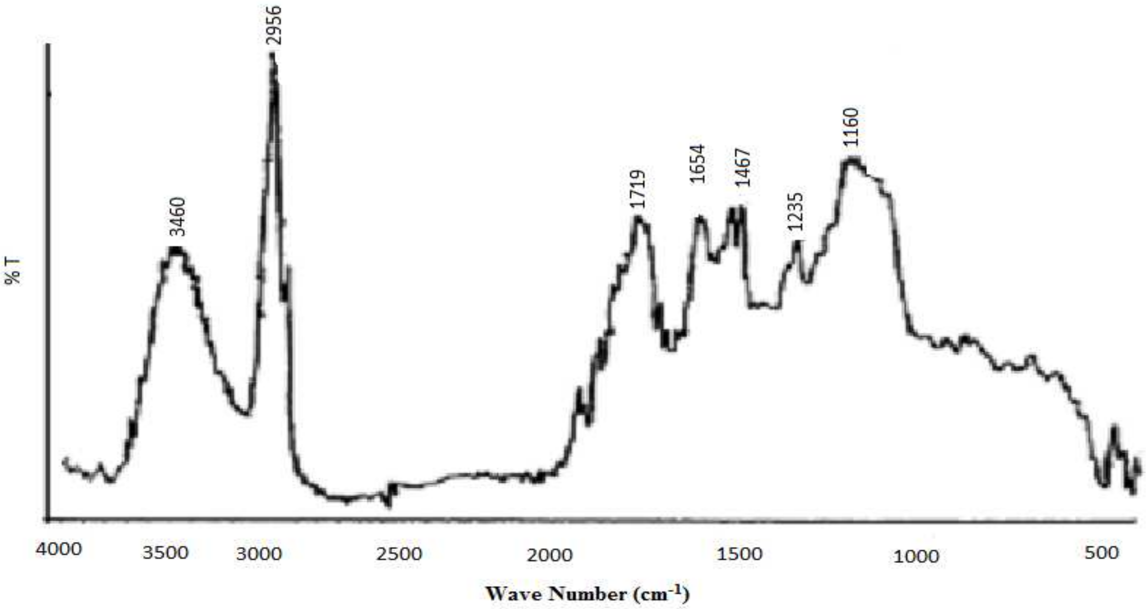


Fig. 2.1: SEMs of poly(AAm-*co*-AAc) hydrogel
(Magnifications are given in the SEMs)

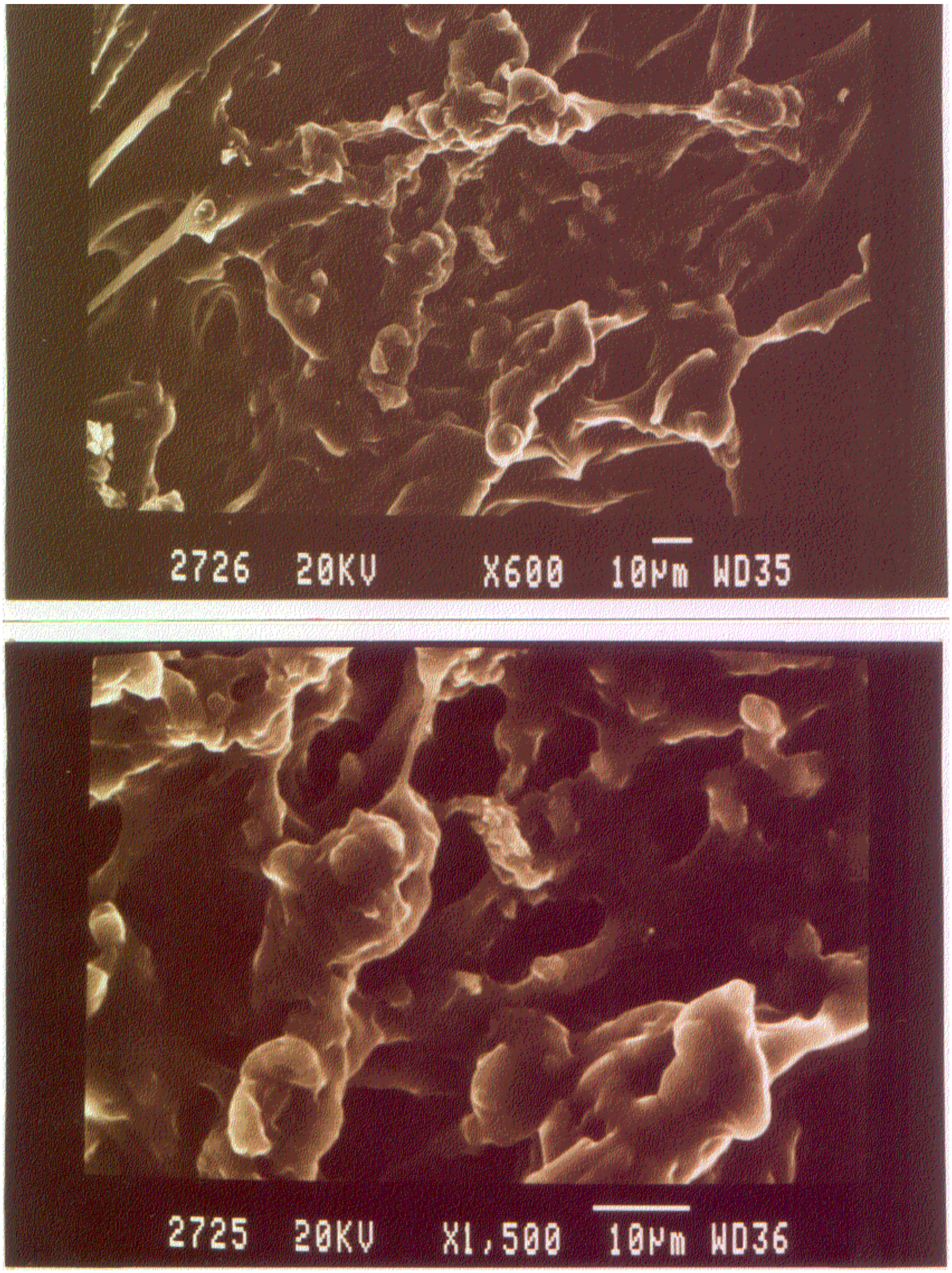
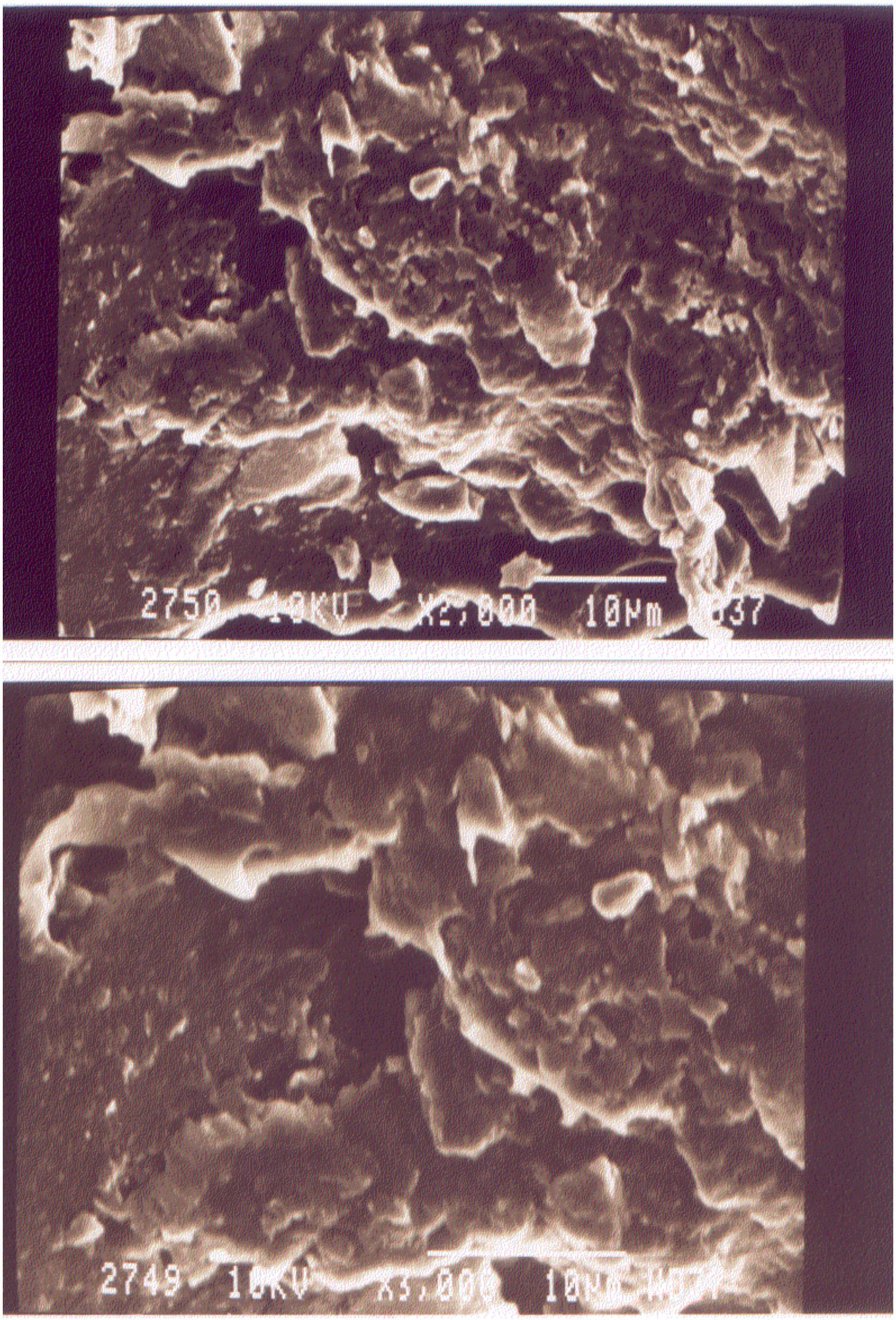


Fig. 2.2: SEMs of poly(AAm-*co*-MA Ac) hydrogen
(Magnifications are given in the SEMs)



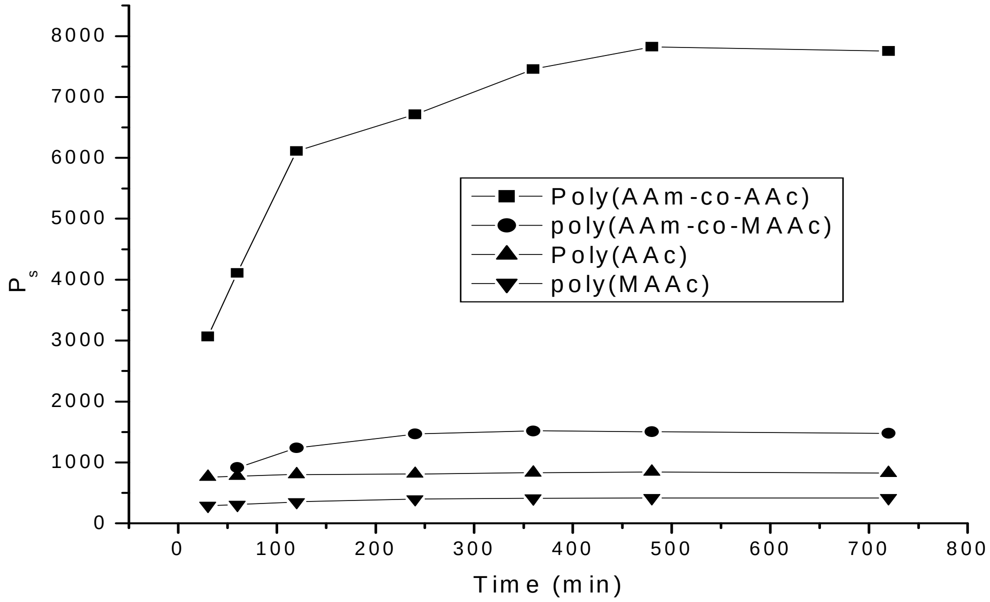


Fig. 3.1: P_s of hydrogels as a function of time at 35°C

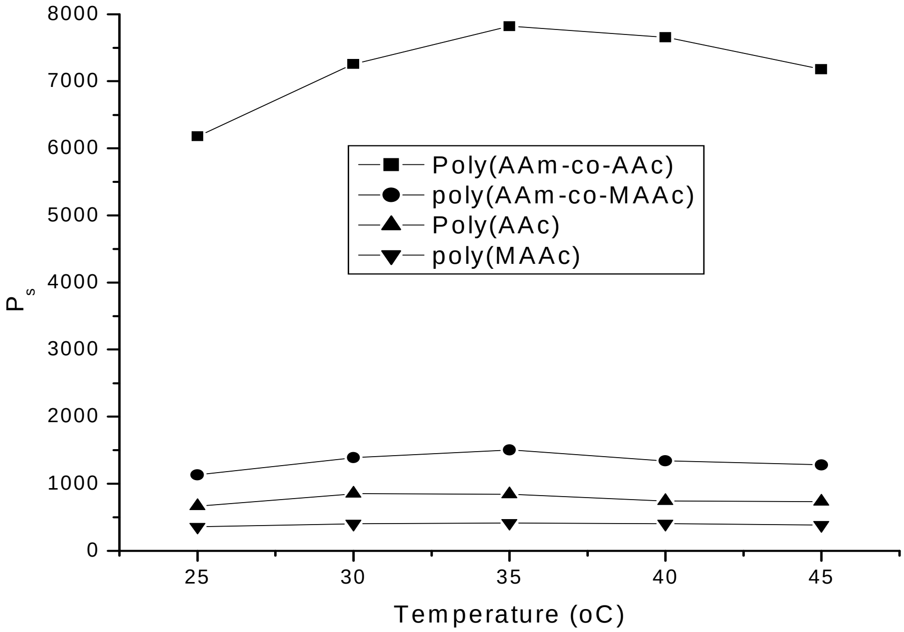


Fig. 3.2: P_s of hydrogels as a function of temperature (time = 480 min)

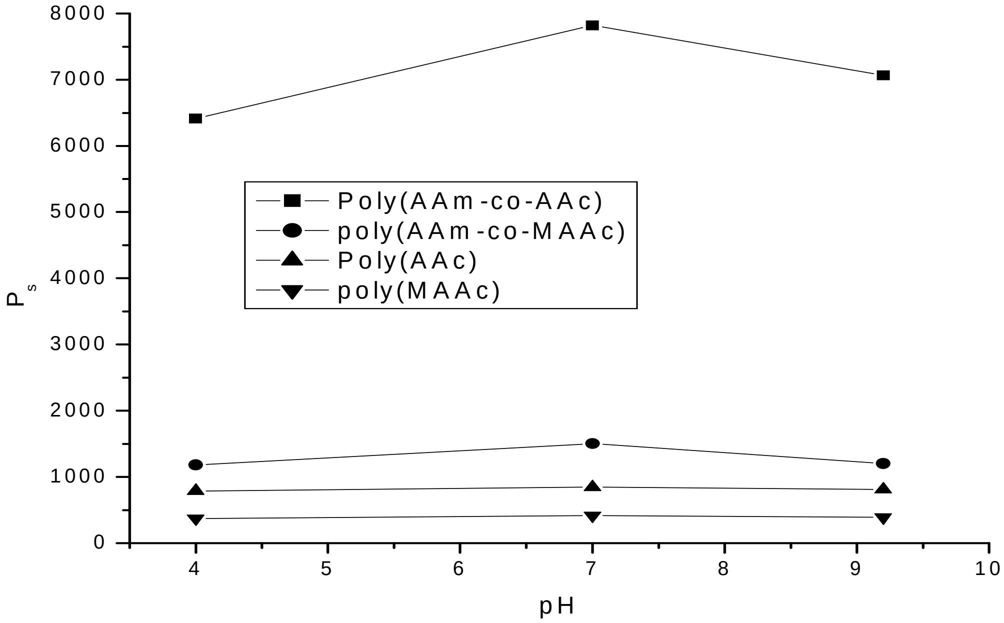


Fig. 3.3: P_s of hydrogels as a function of pH at 35°C (time = 480 min)

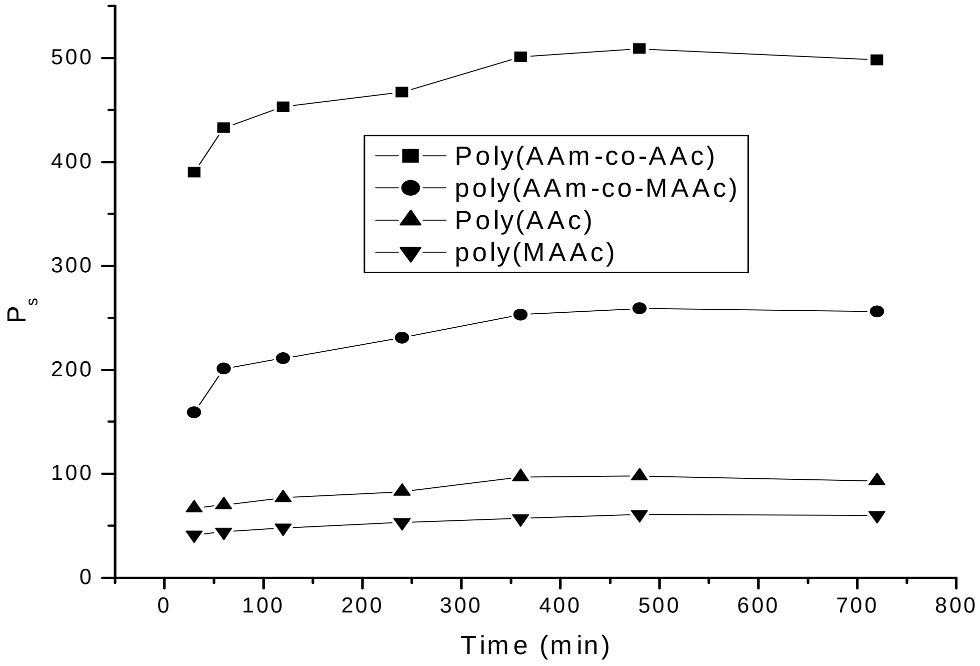


Fig. 3.4: P_s of hydrogels in 5% NaCl as a function of time at 35°C

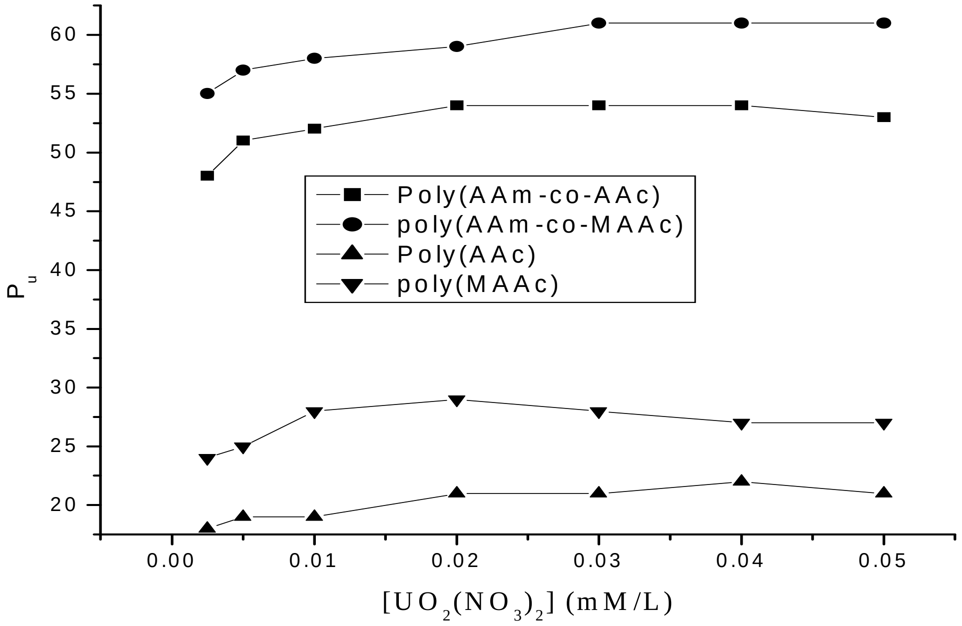


Fig.4.1: P_u of hydrogels as a function of [$UO_2(NO_3)_2$] at 25°C in presence of 0.1 N Na_2CO_3 and 1% NaCl (time = 1h)

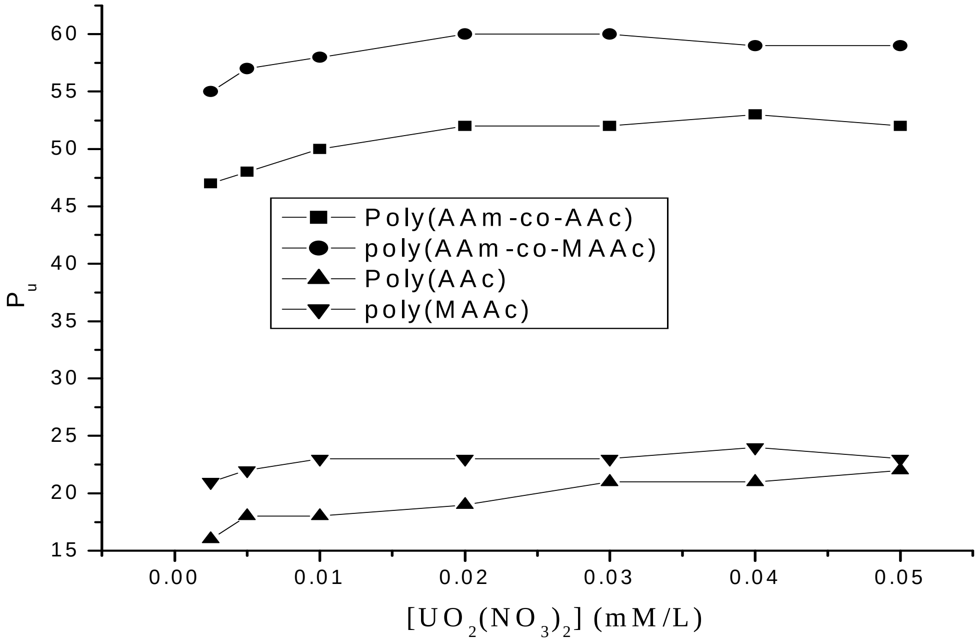


Fig.4.2: P_u of hydrogels as a function of [$UO_2(NO_3)_2$] at 25°C in presence of 0.1 N Na_2CO_3 and 2% NaCl (time = 2h)

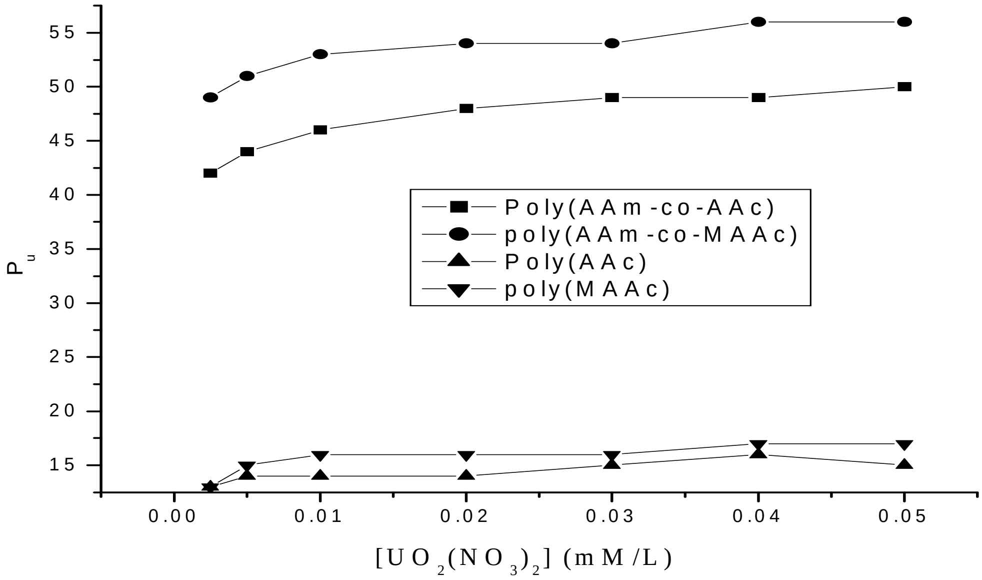


Fig.4.3: P_u of hydrogels as a function of $[UO_2(NO_3)_2]$ at 25°C in presence of 0.1 N Na_2CO_3 and 3% NaCl (time = 2h)

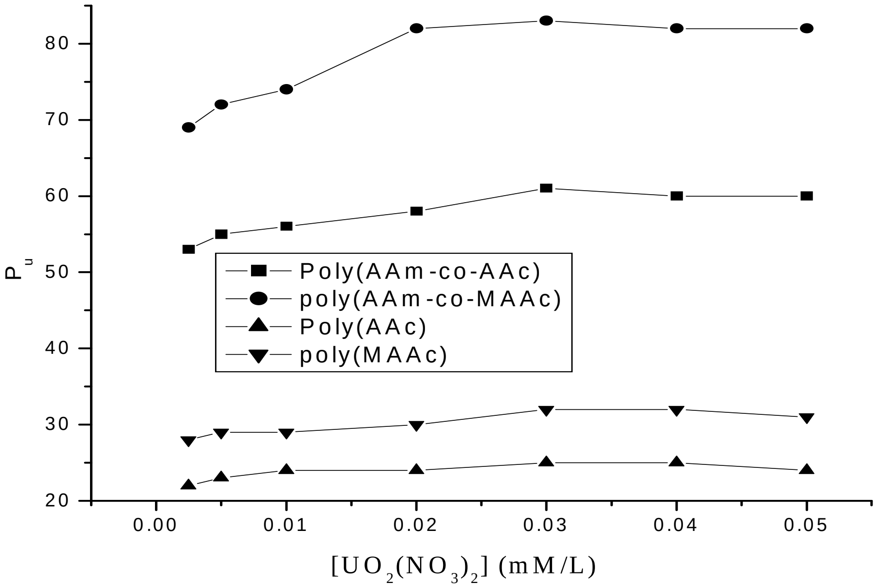


Fig.4.4: P_u of hydrogels as a function of $[UO_2(NO_3)_2]$ at 30°C in presence of 0.1 N Na_2CO_3 and 1% NaCl (time = 2h)

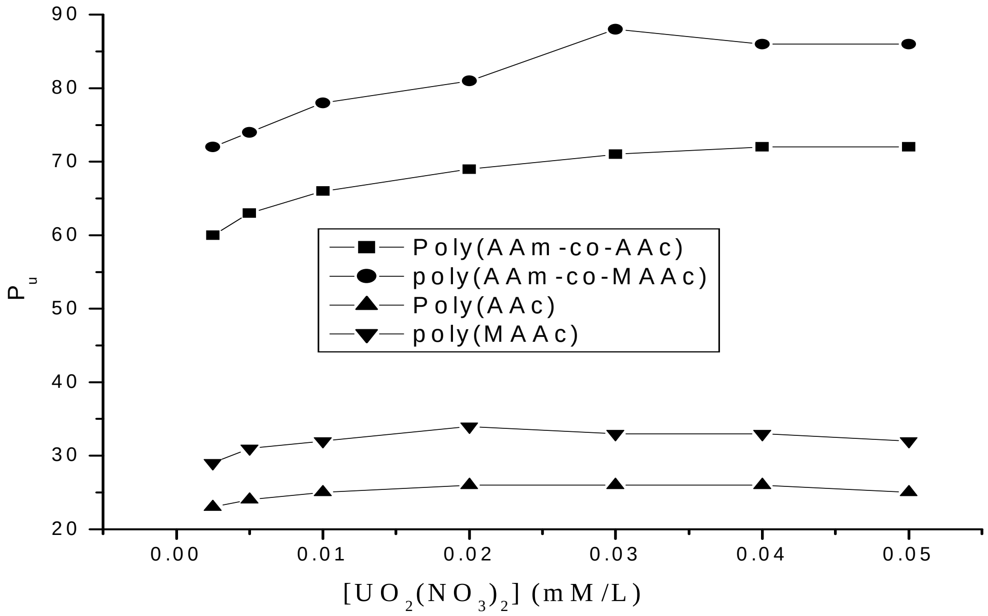


Fig.4.5: P_u of hydrogels as a function of $[UO_2(NO_3)_2]$ at 35°C in presence of 0.1 N Na_2CO_3 and 1% NaCl (time = 2h)

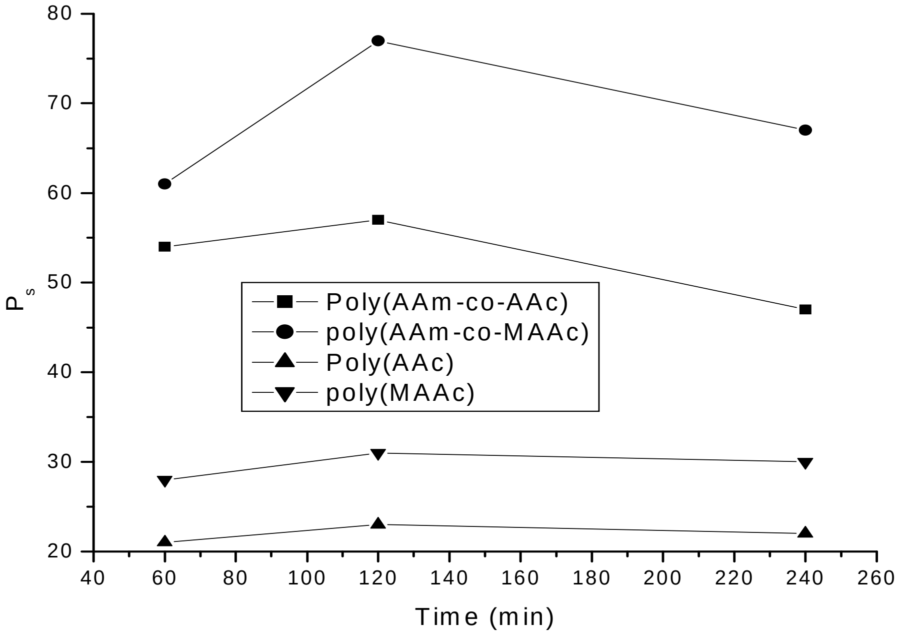


Fig.4.6: P_u of hydrogels as a function of time at 35°C in presence of 0.1 N Na_2CO_3 and 1% NaCl, $[UO_2(NO_3)_2$ = 0.03 m mol/L]

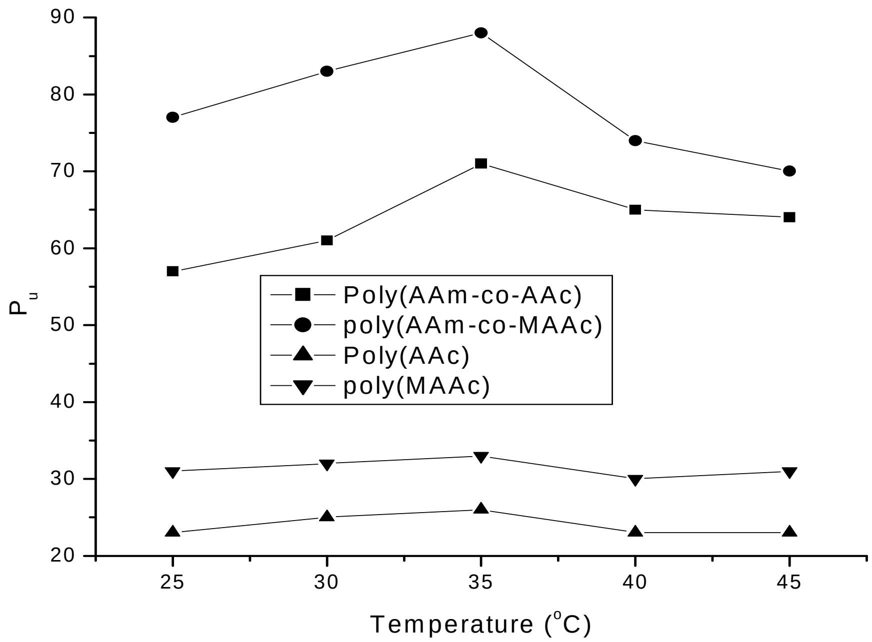


Fig.4.7: P_u of hydrogels as a function of temperature in presence of 0.1 N Na_2CO_3 and 1% NaCl ($[UO_2(NO_3)_2]$ = 0.03 mM/L, time = 2h) 45°C

High P_u of UO_2^{2+} ions by the hydrogels is due to the strong chelation between UO_2^{2+} and –COOH and $–CONH_2$ groups of the hydrogels. The formation of complexes between linear poly(AAc) and uranyl ions in aqueous solutions was studied with conductometry, potentiometry, thermal analysis, Fourier transform infrared (FTIR), and luminescence spectroscopy methods. All these studies proved strong interactions in poly(AAc)/UO_2^{2+} complexes [30]. The nature of adsorption depends upon several parameters, such as ionic charge, ionic strength, pH, temperature, ability to be hydrolyzed and formation of polynuclear species in the reaction.

Uranyl Ions Uptake as a Function of Temperature

The metal ion uptake study of synthesized hydrogels was carried out at different time intervals and at different temperatures (Figs. 4.1 to 4.7) at different concentrations of uranyl nitrate. As maximum P_u was found at 0.03 mM/L concentration of uranyl nitrate when sorption time was 2 hours and [NaCl] was 1%, therefore uranyl ion uptake was further studied at five different temperatures i.e. 25°C, 30°C, 35°C, 40°C and 45°C under these conditions.

It has been observed that P_u increases when temperature increases from 25 to 35°C, followed by an appreciable decrease in Pu from 35°C to 40°C. From 40 °C to 45°C, Pu remains almost constant or decreases slightly. The increase in temperature results, ionization of functional groups, such as -COOH, $-CONH_2$ and therefore, the chelation between the metal ion and these anions becomes more predominant at higher temperature. At the same time when temperature is raised from 25 to 35°C the higher temperature changes the morphology of the sorbent, enhances the diffusion of the metal ion inside the pores of the sorbent, and provide required binding energy for uptake [40,41]. The morphology could be the controlled shriveling/swelling of matrix due to presence of crosslinking agent affecting the diffusion path length and free volume inside the pores. The observed increase in uptake could be attributed to the combined effect of all above. At temperature higher than 35°C the reverse process of desorption also becomes more predominant, resulting decrease in the P_u of UO_2^{2+}.

It is evident from the foregone discussion that copolymerization and crosslinking of AAc/MAAc with AAm increases P_u of UO_2^{2+} tremendously. The structure of the hydrogel as well as the environment of the UO_2^{2+} in the solution phase, both act as the determinants of UO_2^{2+} uptake.

CONCLUSION

Well characterized temperature and pH responsive hydrogels for use as adsorbent for uranyl ions have been synthesized. It follows from the forgone discussion that the hydrogels reported in this communication respond very quickly to small changes in their external environment and are thus *smart or intelligent hydrogels*. The interaction of the hydrogel with water is affected by the environmental factors. The hydrogels synthesized have been successfully used for uptake of UO_2^{2+} ions from moderately saline conditions. The structure of the hydrogels as well as the environment of the UO_2^{2+} ions in the solution phase, both act as the determinants of UO_2^{2+} ions uptake. Further copolymerization and crosslinking of AAc/MAAc with AAm increases P_s and P_u of UO_2^{2+} many folds. It can, thus be concluded that the hydrogel have been effectively used to sorb UO_2^{2+} ions from water by employing less energy and low time intensive clean processes. It can also be concluded that copolymerization of AAc and MAAc with AAm results in the improvement of salt tolerance of these hydrogels significantly.

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