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### RADIATION CROSSLINKED POLY(ACRYLAMIDE/2-HYDROXYPROPYL METHACRYLATE/MALEIC ACID) AND THEIR USABILITY IN THE UPTAKE OF URANIUM

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**RADIATION CROSSLINKED  
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**ABSTRACT**

The terpolymeric poly(acrylamide/2-hydroxy propylmethacrylate/maleic acid) (AAM/HPMA/MA) hydrogels in the rod form have been prepared by  $\gamma$  radiation of quaternary mixtures of acrylamide/2-hydroxy propylmethacrylate/maleic acid/water. Spectroscopic and thermal analyses of AAM/HPMA/MA were made. The hydrogels were used in experiments on swelling, diffusion and adsorptions of uranyl ions from aqueous uranyl acetate solutions. For the hydrogels, the parameters of swelling and diffusion were calculated. In the experiment of uranyl ions adsorption, Type L (*Langmuir*) adsorption isotherm in Giles classification system was found. Binding parameters such as the initial binding constant ( $K_i$ ), the equilibrium binding constant ( $K$ ), monolayer coverage ( $n$ ), site-size ( $u$ ), maximum fractional occupancy ( $\theta$ ) were calculated for hydrogel/uranyl ion system by using the linearization methods such as Klotz, Scatchard and Langmuir methods. Thermodynamic parameters such as

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adsorption free energy ( $\Delta G$ ), adsorption enthalpy ( $\Delta H$ ) and adsorption entropy ( $\Delta S$ ) were also calculated. Finally, the effect of MA contents of the hydrogel and irradiation doses was studied on the adsorption of uranyl ion from its aqueous solution.

*Key Words:* Radiation; Hydrogel; Poly(acrylamide/2-hydroxy propylmethacrylate/maleic acid); Uranyl ion; Adsorption

## INTRODUCTION

Radiation chemical studies of polymeric materials, especially for water-soluble monomers that can be crosslinked by ionizing radiation resulting in the formation of hydrogels, are current interest. Use of ionizing radiation can result in a dramatic change in such properties as mechanical behavior, solubility and swelling. Applications of the gels are being probed in variety of areas such as recyclable absorbents, drug delivery systems, robotics and as mechano-chemical actuators.<sup>[1]</sup>

Uranium is one of the most seriously threatening heavy metals because of its toxicity and some radioactivity. Excessive amounts of uranium have found their ways into the environment through the activities associated with the nuclear industry. Uranium contamination poses a threat in some surface and ground waters.<sup>[2]</sup> To recover uranium from seawater, mining water or wastewater, many different minerals and clays,<sup>[3–5]</sup> bacteria,<sup>[6–8]</sup> biomass,<sup>[2,9]</sup> natural polymers,<sup>[10]</sup> ion exchange resins<sup>[11]</sup> and polymeric chelates were used,<sup>[12–14]</sup> but, there are relatively fewer studies related with hydrogels designed and synthesized for the uranyl ion adsorption from aqueous solutions.<sup>[15,16]</sup> For the separation, in the use of chelating functional group containing hydrogels, some features of adsorbent such as durability, reusability, and practical applicability are very important. In this aspect, hydrogels have some advantages over other systems.<sup>[17]</sup> For the purpose of uranyl ion adsorption from aqueous solutions, we have synthesized different functional groups containing acrylamide-based hydrogels with radiation technique or chemical initiation.<sup>[18–20]</sup>

In this study, novel terpolymeric hydrogels from acrylamide, 2-hydroxypropyl methacrylate and maleic acid were prepared by gamma radiation and, used to increase of adsorption capacity of acrylamide hydrogels for uranyl ions. The hydrophilicities of acrylamide containing amide group and maleic acid containing carboxyl groups is higher than 2-hydroxypropyl methacrylate containing alkyl, hydroxyl and ester groups. At the same time, acrylamide is non-ionic in character while maleic acid is ionic in character in the aqueous media.

## EXPERIMENTAL

The three monomers used in this work, namely, acrylamide (AAm), 2-hydroxypropyl methacrylate (HPMA) and maleic acid (MA) were obtained from BDH (Poole, UK). Uranyl acetate (UA) and sodium salicylate were purchased from Merck (Darmstadt, Germany). All materials were used as received.

Aqueous solutions of monomers of 1 g AAm, 1 g HPMA and 0, 20, 40, 60, 80, 100, and 120 mg MA were prepared in 2 mL of distilled water. Monomer solutions thus prepared were placed in the PVC straws of 3 mm diameter and irradiated to 2, 3, 4, 5, and 6 kGy at air in ambient temperature in a Gammacell 220 type  $\gamma$  irradiator at a fixed dose rate of 0.45 kGy h<sup>-1</sup>. Hydrogels obtained in long cylindrical shapes were cut into pieces of 4–5 mm long, washed and, dried first in air and then in vacuum.

FTIR spectra of homopolymeric AAm, copolymeric AAm/HPMA and terpolymeric AAm/HPMA/MA hydrogel containing 100 mg maleic acid and irradiated to 5 kGy were recorded on a Nicolet 520 model a FTIR spectrophotometer. Spectra were taken with a resolution of 1 cm<sup>-1</sup>. Samples were thoroughly ground with exhaustively dried KBr and discs were prepared by compression under vacuum.

Dynamic thermal analysis was carried out with a Dupont 990 thermal analyzer. Thermogravimetric analyses were performed with 10 mg samples under nitrogen atmosphere with a nominal gas flow rate of 5 mL. Experiments were made at a heating rate of 10°C min<sup>-1</sup> until 600°C.

AAm hydrogel, AAm/HPMA hydrogel and AAm/HPMA/MA hydrogel containing 100 mg maleic acid and irradiated to 5 kGy were swelled in the distilled water and in 100 mg L<sup>-1</sup> uranyl acetate solution at 25°C to determine the parameters of swelling and diffusion. Swollen gels removed from the water bath at regular intervals were dried superficially with filter paper, weighed and placed in the same bath. The radii of cylindrical swollen gels were measured by a micrometer.

About 0.1 g AAm/HPMA/MA hydrogel containing 100 mg MA and irradiated to 5 kGy were transferred into 50 mL of solutions of UA in the concentration range of 25–250 mg U L<sup>-1</sup>, allowed the equilibrate for 24 h at 25°C. The pHs of the aqueous solutions of UA were in the ranges of 5–6, and the changes in pH were not significant during the experiments. These aqueous solutions were separated by decantation from the hydrogels. 2 mL of solution of sodium salicylate in the concentration of 1 g L<sup>-1</sup>, into 2 mL of U solutions were added and, waited 30 min for the complex formation.

Spectrophotometric measurements were carried out using a HITACHI VIS spectrophotometer at ambient temperature. The absorbance of these U-complex solutions was recorded at a wavelength of 327 nm. Distilled water was chosen as the reference. The influences of MA content and irradiation

dose were investigated for binding of uranyl ions to AAm/HPMA/MA hydrogels. Hydrogel samples weighing 0.1 g and prepared with different MA content and irradiation doses were added to 50 mL of  $100 \text{ mg L}^{-1}$  of uranyl acetate solutions. The samples left in the solution for one day at  $25^\circ\text{C}$ , and the absorbance of the solutions was measured spectrophotometrically.

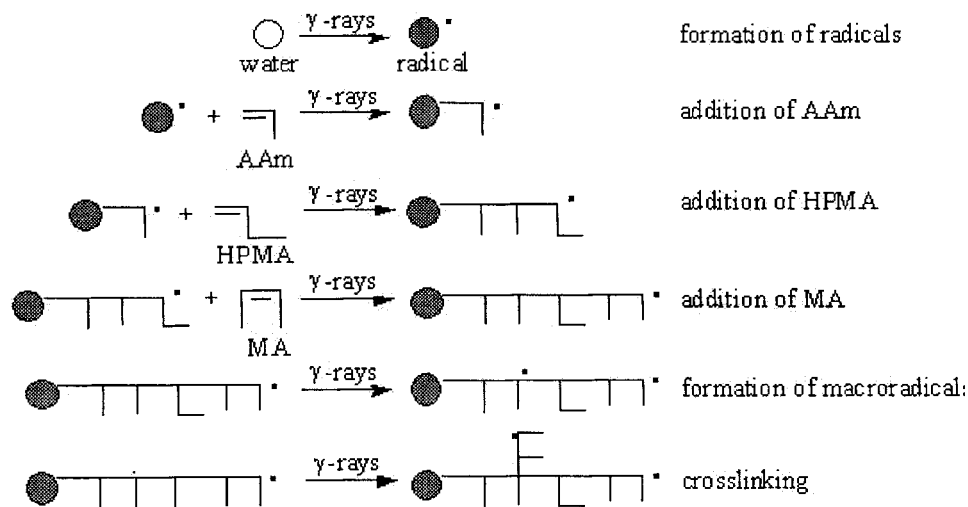
Uranyl ions-laden hydrogels were left in 50 mL of distilled water for 3 days at  $25^\circ\text{C}$  to investigate of desorption.

## RESULTS AND DISCUSSION

### Preparation of Hydrogels

A radiation technique was used to prepare of AAm, AAm/HPMA and AAm/HPMA/MA polymers. When monomers of AAm, HPMA and MA were irradiated together with ionizing rays,  $\gamma$ -rays, weak  $\pi$  bonds of  $-\text{C}=\text{C}-$  on the monomers were broken by ionization irradiation and free radicals are generated. These free radicals react with each other, and a polymer is produced. For the polymerization and crosslinking of poly(AAm/HPMA/MA) by  $\gamma$ -irradiation, a possible mechanism is proposed in Fig. 1. During the irradiation of AAm, HPMA, MA and water quaternary mixtures, the polymer chains crosslinks and gel is obtained. It is reported that complete gelation of AAm is 2 kGy of  $\gamma$ -rays irradiation at ambient temperature.<sup>[21]</sup> So, a minimum dose of 2 kGy of  $\gamma$  rays is used for preparation of AAm/HPMA/MA hydrogels.

Dried AAm/HPMA/MA polymers are glassy form and very hard, but swollen gels are very soft. The crosslinked polymers are obtained in the form

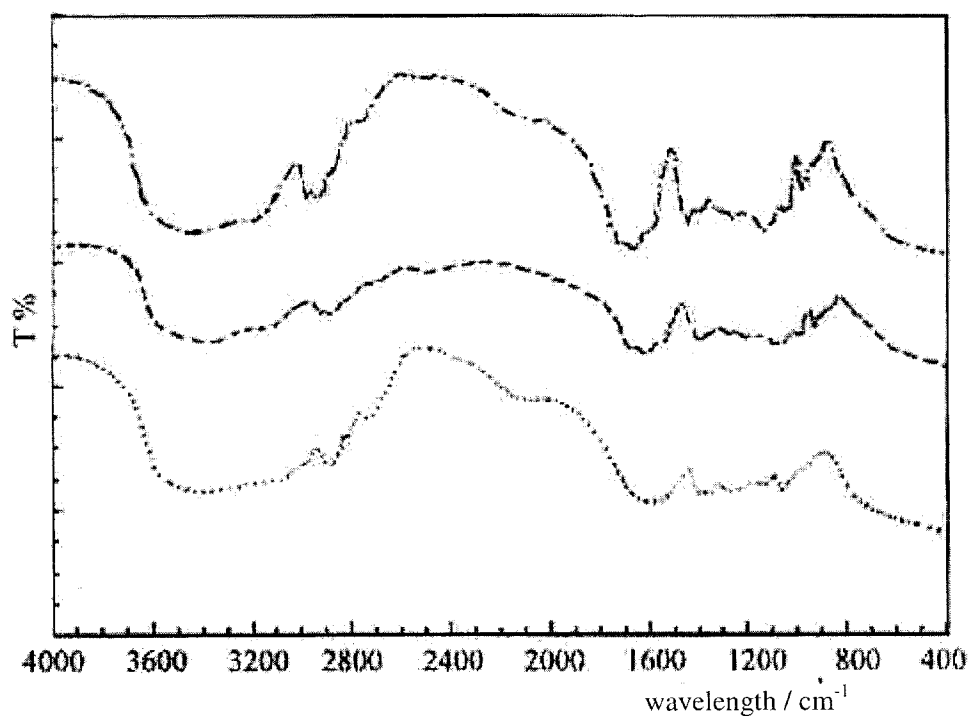


**Figure 1.** Possible mechanism of radiation crosslinked terpolymeric AAm/HPMA/MA hydrogel.

of cylinder rods. Upon swelling, the hydrogels were strong enough to retain their shape.

### Spectroscopic Analysis

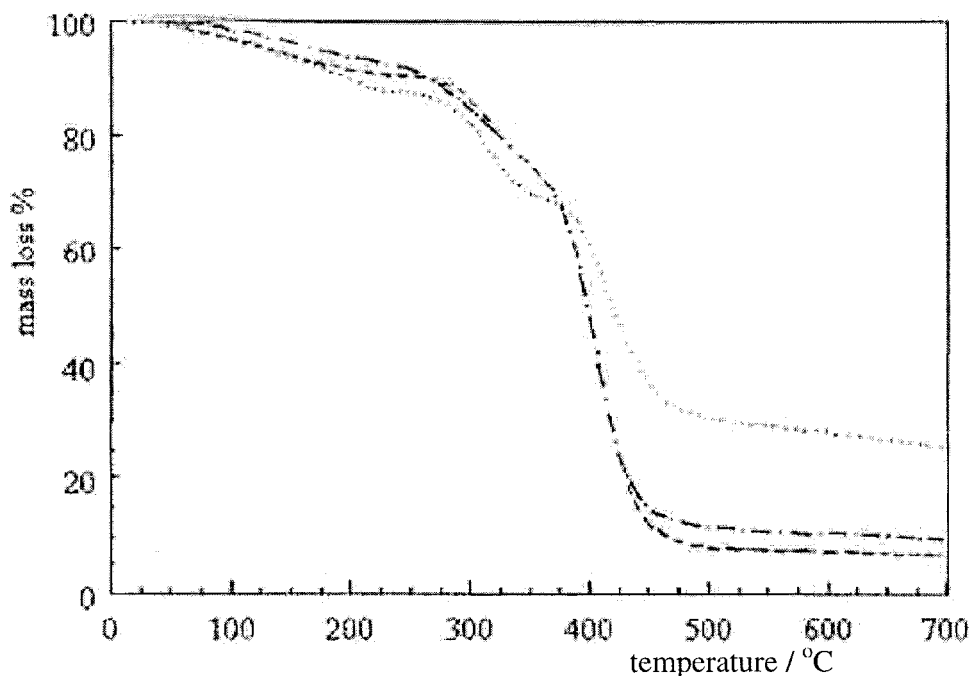
To understand the formation of poly(AAm/HPMA/MA) hydrogels, obtained from AAm, HPMA and MA monomers, FTIR spectra of AAm, AAm/HPMA and AAm/HPMA/MA were evaluated and are presented in Fig. 2. In these spectra, the bands appearing in the range of  $3200\text{--}3600\text{ cm}^{-1}$  are due to  $\text{--NH}_2$  bands and  $\text{--COOH}$  groups may be explained the reason of this wide band. When MA is introduced into these copolymers, these peaks have increased gradually with the increasing of  $\text{--COOH}$  groups. It has been also observed similar situations in AAm/HPMA and AAm/HPMA/MA hydrogels. The peak at  $1650\text{ cm}^{-1}$  is of the  $\text{--CONH}_2$  and  $\text{--COOH}$  group absorption and has increased in the case incorporation of HPMA and MA to these hydrogels.  $\text{--CH}_2\text{--}$  groups on the chain give absorption at  $1450\text{--}1500\text{ cm}^{-1}$  interval. The peaks at  $1000\text{--}1200\text{ cm}^{-1}$  can be attributed to  $\text{--C--N}$  absorption. These data indicated that synthesized terpolymer was AAm/HPMA/MA hydrogel.



*Figure 2.* FTIR spectra of the hydrogels. ....; AAm, ----; AAm/HPMA; -.-.-; AAm/HPMA/MA.

### Thermogravimetric Analysis of Hydrogels

Figure 3 shows the thermograms for the dried samples of AAm, AAm/HPMA and AAm/HPMA/MA hydrogels in nitrogen atmosphere a heated at  $10^{\circ}\text{C min}^{-1}$  from  $0^{\circ}\text{C}$  to  $600^{\circ}\text{C}$ . There are three types of the decomposition region on the thermograms of the hydrogels. It is reported that the first region ( $0\text{--}220^{\circ}\text{C}$ ) correspond to loss bound water, in the second region ( $220\text{--}340^{\circ}\text{C}$ ) to loss of  $\text{NH}_3$  by imidization (intra- and intermolecular), and  $\text{H}_2\text{O}$  by dehydration. The third region ( $>340^{\circ}\text{C}$ ) represents substantial mass loss, and is normally attributed to main chain break-down.<sup>[22]</sup> In order to determine the thermal stabilities of AAm, AAm/HPMA, and AAm/HPMA/MA hydrogels, the temperatures for the maximum mass loss ( $T_{\text{max}}/^{\circ}\text{C}$ ) were found directly from their thermograms given in Fig. 3. The temperatures for the maximum mass loss of AAm, AAm/HPMA and AAm/HPMA/MA hydrogels are  $408$ ,  $398$  and  $398^{\circ}\text{C}$ , respectively. Heating hydrogel at high temperatures than  $408^{\circ}\text{C}$  result in rapid decomposition to carbon dioxide and volatile hydrocarbons. It was observed that  $T_{\text{max}}$  of AAm hydrogel is higher than that of AAm/HPMA and AAm/HPMA/MA hydrogels. So, it is said that, AAm polymers in the case of adding HPMA and MA were rapidly decreased with the heating.



**Figure 3.** TGA thermograms of the hydrogels. ....; AAm, ----; AAm/HPMA; -.-.-; AAm/HPMA/MA.

### Swelling and Diffusion

Swelling behaviors of AAm, AAm/HPMA, and AAm/HPMA/MA hydrogel containing 100 mg MA, and irradiated at 5 kGy were followed gravimetrically. The swelling degree (S%) of the hydrogels was calculated from the following relation.

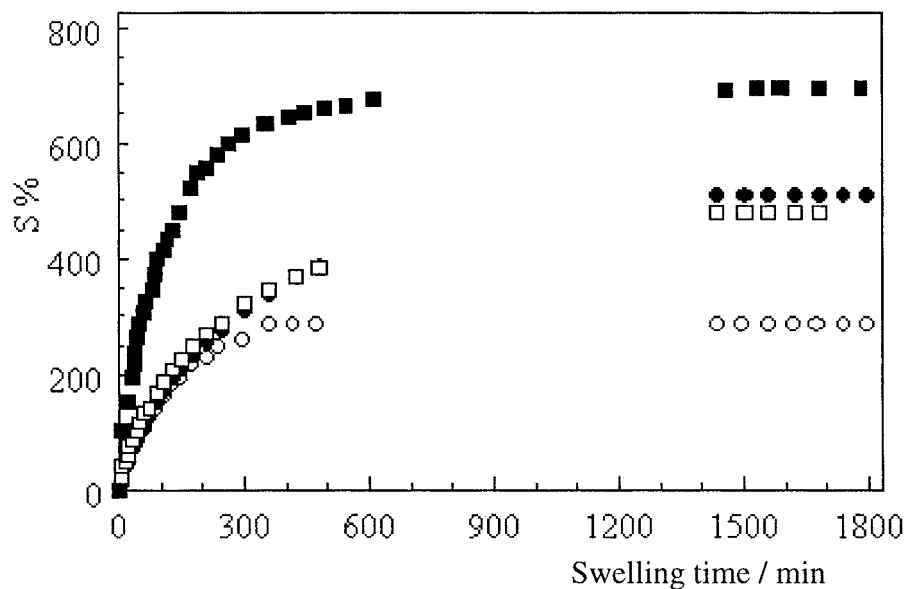
$$S\% = \frac{m_t - m_o}{m_o} \times 100 \quad (1)$$

where  $m_t$  is the mass of swollen gel at time  $t$  and  $m_o$  is the initial mass of the swollen gel. The dynamic swelling curves of the hydrogels in distilled water and the solution of uranyl acetate are shown in Fig. 4.

Figure 4 shows that, the swelling of the hydrogels in water is in following order:

$$\text{AAm} > \text{AAm/HPMA/MA} > \text{AAm/HPMA}.$$

Homopolymeric AAm hydrogel is the most hydrophilic of the other type, so, it swells higher than the others. Since HPMA is less hydrophilic than AAm and MA, the swelling degree was decreased with the incorporation of HPMA into AAm hydrogel. The swelling degree increased with the incorporation of MA into AAm/HPMA hydrogel.



**Figure 4.** The swelling curves of the hydrogels. ■; AAm, □; AAm/HPMA, ●; AAm/HPMA/MA in water, ○; AAm/HPMA/MA in the uranyl solution.



On the other hand, as can be seen from Fig. 4, the values of equilibrium swelling of AAm/HPMA/MA hydrogel are lower in uranyl solution than in water. This decrease was attributed to the absorption of uranyl ions in the gel system, and the exclusion of water molecules. In addition, the uranyl ions are interacted by the carboxyl groups of maleic acid in the hydrogel. So, carboxylic groups of the hydrogel are not bonded with water. Thus, the swelling of the hydrogel decreased in the solutions of the uranyl ions.

The pH response was investigated in AAm/HPMA/MA hydrogel that were allowed to swell to equilibrium in the universal (0.04 M  $\text{H}_3\text{BO}_3$  + 0.04 M  $\text{CH}_3\text{COOH}$  + 0.04 M  $\text{H}_3\text{PO}_4$  and 0.2 M NaOH) and phosphate (0.1 M citric acid and 0.2 M  $\text{Na}_2\text{HPO}_4$ ) buffer of varying pH at 25°C. Figure 4 shows the swelling behaviors of AAm/HPMA/MA hydrogel in two buffers at varying pH. As shown in Fig. 5, the swelling behavior of the gel is dependent on the type of buffer and pH. The values of swelling degree of the hydrogel are increased up to pH 6, and these values are decreased after pH 6 in two buffers. In addition, the swelling degrees of the hydrogel are lower in phosphate buffer than in universal buffer. These changes resulted from the contribution of various factors such as polymer-based, solution based, and polymer-solvent combination type parameters on the equilibrium degree of swelling of the hydrogel. In AAm/HPMA/MA hydrogel, the maximum extent of swelling was reached at pH 6, as a result of the complete dissociation of the acid groups of MA units at his pH. The first and second dissociation constants of the MA are  $\text{pK}_{a1} = 1.85$  and  $\text{pK}_{a2} = 6.06$ , respectively. Charged groups attached to the polymeric network structure played essential role in swelling properties.

For extensive swelling of polymers, the following relation can be written as:<sup>[23]</sup>

$$\frac{t}{S} = A + Bt, \quad (2)$$

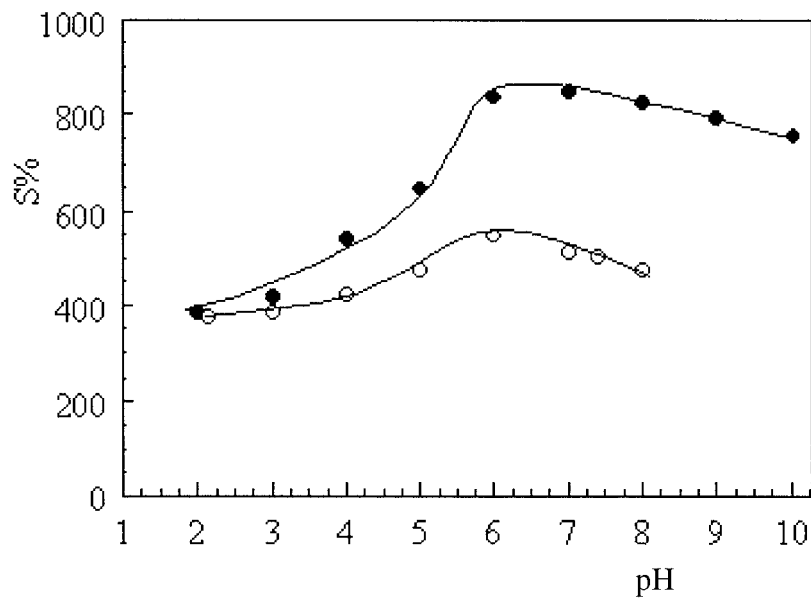
where S is the degree of the swelling at time t,  $B = 1/S_{\text{max}}$  is the inverse of the maximum or equilibrium swelling,  $A = 1/(dS/dt)_0$ , is the reciprocal of the initial swelling rate ( $r_0$ ) the gel. The relation represents second-order kinetics.

Figure 5 shows the linear regression of the swelling curves obtained by means of Eq. (2). The values of the initial swelling rate and maximum swelling of the hydrogels are calculated from the slope and intersection of the lines and, are presented in Table 1.

As can be seen from Table 2, the values of maximum swelling of the hydrogels are in accordance with the swelling behaviors. Swelling processes of the hydrogels in water are quicker than the swelling rate of the hydrogels in the aqueous solution of uranyl acetate.

The following equation is used to determine the nature of diffusion of water and uranyl ions into hydrogels:<sup>[24]</sup>

$$F = kt^n, \quad (3)$$



**Figure 5.** The pH-responsive swelling curves of AAm/HPMA/MA hydrogel. ○; AAm/HPMA/MA in the phosphate buffer solution, ●; AAm/HPMA/MA in the universal buffer solution.

**Table 1.** Swelling and Diffusion Parameters of the Hydrogels

Hydrogel	$S_{eq}\%$	$S_{max}$	$r_0$	$n$	$D \times 10^7$
AAm in water	695	7.25	0.108	0.53	9.0
AAm/HPMA in water	480	5.32	0.031	0.67	3.2
AAm/HPMA/MA in water	510	5.83	0.025	0.69	3.2
AAm/HPMA/MA in uranyl solution	290	3.01	0.040	0.64	5.2

**Table 2.** Binding Parameters of AAm/HPMA/MA Hydrogel-Uranyl Ion Binding System

Method	$K_i$	$K$	$n/(\text{mmol U}) (\text{mol gel})^{-1}$	$u$	$\hat{\theta}$
Klotz	52.03	1258.8	41.33	24.20	0.47
Scatchard	50.53	1123.1	44.99	22.23	0.43
Langmiur	50.23	1105.8	45.42	22.02	0.43
Mean $\pm$ SD	$50.93 \pm 0.96$	$1162.6 \pm 83.8$	$43.91 \pm 2.25$	$22.82 \pm 1.20$	$0.44 \pm 0.02$

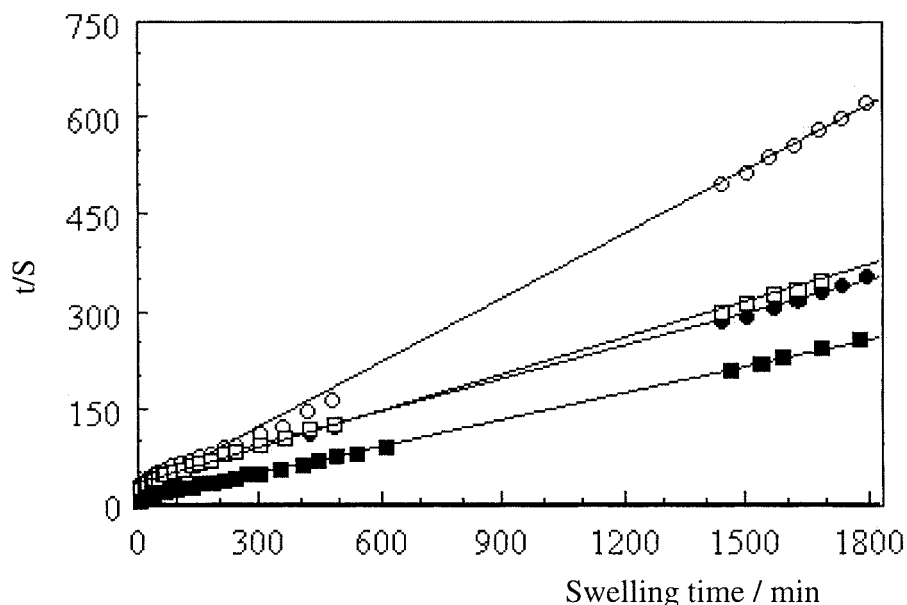
where  $F$  is the fractional uptake at time  $t$ ,  $k$  is a constant incorporating characteristic of the macromolecular network system and the penetrant, and  $n$  is the diffusional exponent, which is indicative of the transport mechanism. Equation 3 is valid for the first 60% of the fractional uptake. Fickian diffusion and Case II transport are defined by  $n$  valuing to  $1/2$  and  $1$ , respectively. Anomalous transport behavior (non-Fickian diffusion) is intermediate between Fickian and Case II. That is reflected on  $n$  between  $1/2$  and  $1$ .<sup>[24]</sup>

For the hydrogels,  $\ln F$  vs.  $\ln t$  graphs is plotted and is shown in Fig. 6.  $n$  exponents and  $k$  parameters are calculated from the slopes and intercepts of the lines, respectively, and are listed in Table 1.

Table 1 shows the number determining type of diffusion ( $n$ ) is over  $0.50$ . Hence the diffusion of water into the hydrogels is generally found as a *non-Fickian* character. When diffusion type is anomalous behavior, the relaxation and diffusion time are of the same order of magnitude. As the solvent diffuses into the hydrogel, rearrangement of chains does not occur immediately.

The diffusion coefficients  $D$  of the cylindrical hydrogels can be found by various ways. And one of the them is the short time approximation which is necessary arrangements the above equation:

$$F = kt^{1/2} \quad (4)$$



**Figure 6.** The swelling kinetics curves of the hydrogels. ■; AAm, □; AAm/HPMA, ●; AAm/HPMA/MA in water, ○; AAm/HPMA/MA in the uranyl solution.

where  $k=4(D/\pi l^2)^{1/2}$  and  $D$  in  $\text{cm}^2 \text{ s}^{-1}$ ,  $t$  in sec and  $l$  is the radius of cylindrical polymer sample. For the hydrogels,  $F$  vs.  $t^{1/2}$  plots were plotted, and are shown in Fig. 7.

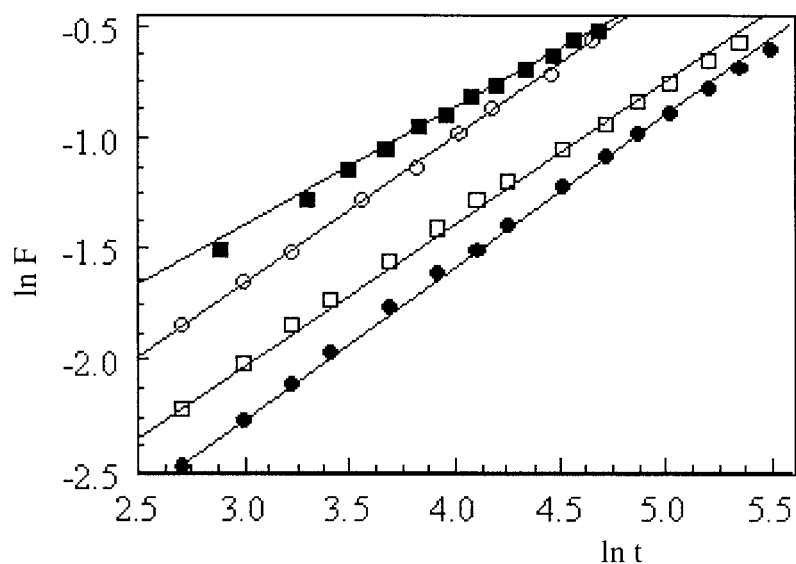
With the assessment of  $F$  vs.  $t^{1/2}$  graphs, the obtained diffusion coefficients were presented in Table 2. As shown from the table, the diffusion coefficients were varied from  $3.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  to  $9.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ .

### Uranyl Ions Uptake

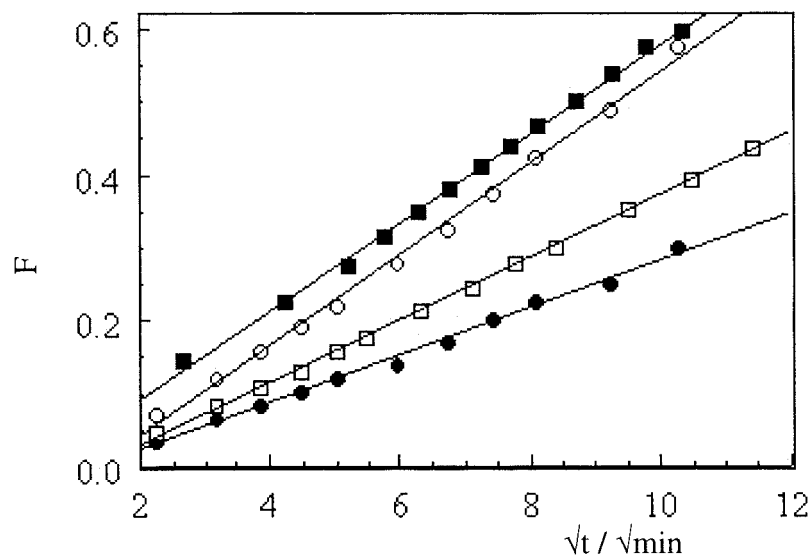
In second stage, it was purposed that investigation of uptake of uranyl ions onto the hydrogels and usability as a sorbent for uranyl ions.

To observe adsorption of uranyl ions, AAm, AAm/HPMA and AAm/HPMA/MA hydrogels were placed in the aqueous U solutions, and allowed to equilibrate for two days. At the end of this time, AAm/HPMA and AAm/HPMA/MA hydrogels in the solution of uranium acetate showed the dark colorations of the colors of the original solutions, while AAm has not sorbed any uranyl ions from the solutions.

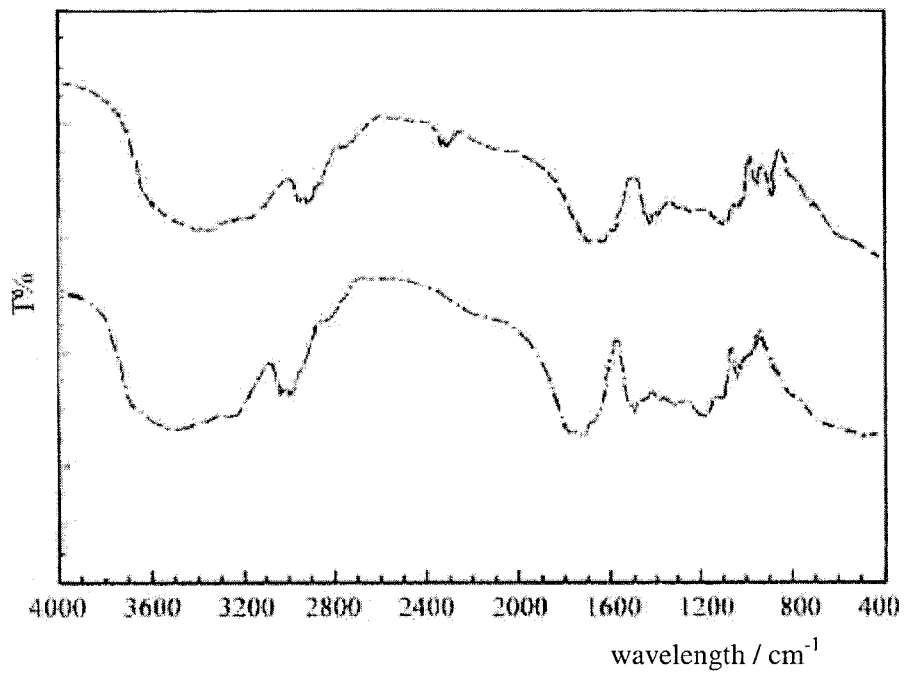
The FTIR spectra of AAm/HPMA/MA hydrogel before and after uranyl binding process are presented in Fig. 9. In the FTIR spectrum of AAm/HPMA/MA hydrogel after uranyl ions binding process, the most important peak which is linear  $\text{O}=\text{U}=\text{O}$  stretching vibration appears at  $930 \text{ cm}^{-1}$ .<sup>[20,25]</sup> This result explained that there is an interaction between AAm/HPMA/MA hydrogel and uranyl ions.



**Figure 7.** The plots of  $\ln F - \ln t$  of the hydrogels. ■; AAm, □; AAm/HPMA, ●; AAm/HPMA/MA in water, ○; AAm/HPMA/MA in the uranyl solution.



**Figure 8.** The plots of  $F-\sqrt{t}$  of the hydrogels. ■; AAm, □; AAm/HPMA, ●; AAm/HPMA/MA in water, ○; AAm/HPMA/MA in the uranyl solution.



**Figure 9.** FTIR spectra of AAm/HPMA/MA hydrogel before and after uranyl binding process. ....; before uranyl ion binding, ----; after uranyl ion binding.

AAm is a non-ionic polymer, and thus acrylamide hydrogel does not interact with many small molecules, ions and other chemical species. By the addition of MA to AAm, AAm/HPMA/MA hydrogel contains ionizable groups. These groups can interact with small molecules or ions and, these species bind to acrylamide copolymers with non-covalent or covalent bonds. In the uranyl ion/hydrogel system, uranyl ion has a cationic character and, can interact by electrostatic forces with the anionic carboxyl groups of maleic acid in the AAm/HPMA/MA hydrogel (Fig. 10). Therefore, the cationic character of ions may be important factor for binding to acrylamide hydrogels containing diprotic moieties.

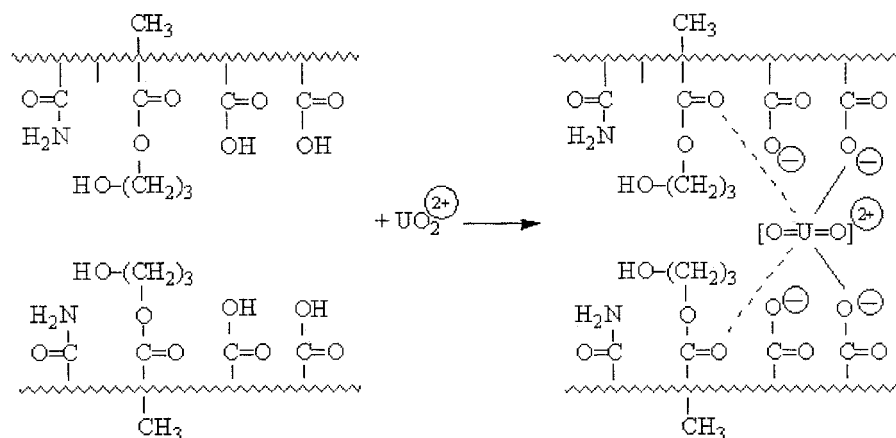
On the other hand, for a cationic ion to get bounded to AAm/HPMA/MA hydrogel, it has penetrated first outside aqueous layer and then the specifically bound water molecules for the sites. Not only that, the structure of crosslinked polymer in the three dimensional matrix would also change with changes in the water structure. Hence, any change in the amount of the water sorbed could affect the binding sites and hence, alter the type of interacting forces.

In a adsorption system at equilibrium, total solute concentration ( $C_I$ , mole  $L^{-1}$ ) is:<sup>[27]</sup>

$$C_I = C_B + C \quad (5)$$

where,  $C_B$  is the equilibrium concentration of the solute on the adsorbent in mol per liter (bound solute concentration) and  $C$  is the equilibrium concentrations of the solute in the solution in mol  $L^{-1}$  (free solute concentration). The binding ratio,  $r$ , defined by

$$r = C_B/P. \quad (6)$$



**Figure 10.** Possible electrostatic interaction between uranyl ions and AAm/HPMA/MA hydrogel.

Thus, with  $C_B$  in mole  $L^{-1}$  and  $P$  in base mole (moles of monomer units,  $P = m_p/M_r$ , where  $m_p$  is the mass of the polymer in g and  $M_r$  is the molecular mass of constitutional repeating units of polymer in g mole $^{-1}$ ) per liter,  $r$  then represents the average number of molecules of solute bound each monomer unit at that free solute concentration.

A plot of the binding isotherm of uranyl ion is shown in Fig. 10. The binding of uranyl ion to AAm/HPMA/MA hydrogel corresponds to L-type (*Langmuir type*) adsorption isotherms in the Giles classification system for adsorption of a solute from its solution<sup>[26]</sup> (Fig. 10).

The binding data were interpreted based on the uniform site-binding model (u.s.b.), which in statistical-thermodynamic terms corresponds to the formation of an ideal localized one-dimensional monolayer of solute on the polymer chains.<sup>[7]</sup> This leads to the hyperbolic (*Langmuir*) form of binding isotherm, which applies to many polymer/solute binding system:

$$r = \frac{nKC}{1 + KC} \quad (7)$$

where  $K$  is the binding constant, that is, the equilibrium constant and,  $n$  is the site density (i.e., the limiting value of  $r$  for “monolayer” coverage, which is thus a measure of the density of the sites along the polymer chain). The reciprocal of  $n$  is the site-size,  $u$ , which may be taken to represent either an average number of monomer units occupied by the bound solute molecule, or more generally the average spacing of solute molecules when the chain saturated. Initial binding constant,  $K_i$  is initial slope of the binding isotherm, and thus average binding strength of a solute molecule by a single monomer unit on an occupied chain. In the u. s. b. model, it is equal to the product  $Kn$ .

To get the best values of the binding parameters from the experimental data, some linearization methods of Eq. (6) have been developed by some researchers such as Klotz, Scatchard and Langmuir.<sup>[27]</sup>

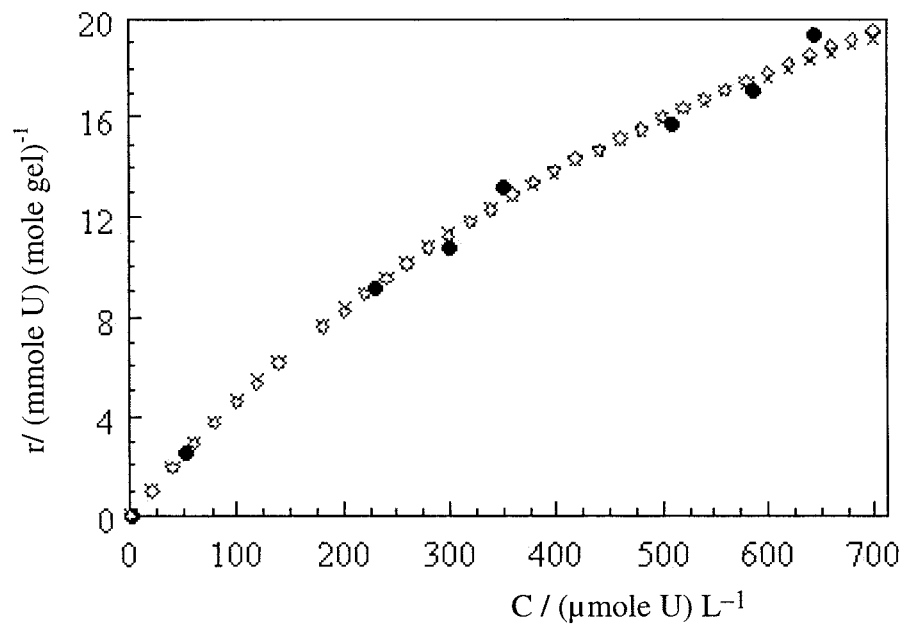
$$\text{Klotz equation; } \frac{1}{r} = \frac{1}{n} + \frac{1}{nK} \frac{1}{C} \quad (8)$$

$$\text{Scatchard equation; } \frac{r}{C} = Kn - Kr \quad (9)$$

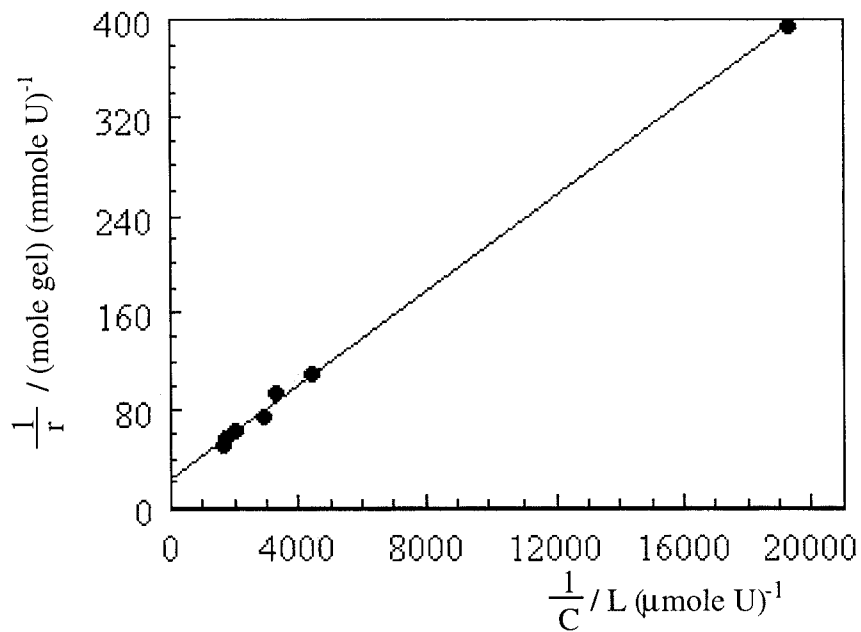
$$\text{Langmuir equation; } \frac{C}{r} = \frac{1}{nK} + \frac{1}{n} C \quad (10)$$

The plots of polymer-ion binding system using Klotz, Scatchard and Langmuir methods are shown in Figs. 11, 12 and 13, respectively. The binding parameters of uranyl ion/hydrogel binding system were calculated from the intercepts and slopes of the plots.

The derived values of the binding parameters  $K$ ,  $K_i$  and  $n$  are listed in Table 2 for the uranyl ion/hydrogel binding system. The final column



**Figure 11.** The binding isotherm of uranyl ions-AAm/HPMA/MA hydrogel binding system. ●; experimental, × × ×; Klotz curve, ...; Scatchard curve, ◇ ◇ ◇; Langmuir curve.



**Figure 12.** Klotz plot of uranyl ions-AAm/HPMA/MA hydrogel binding system.



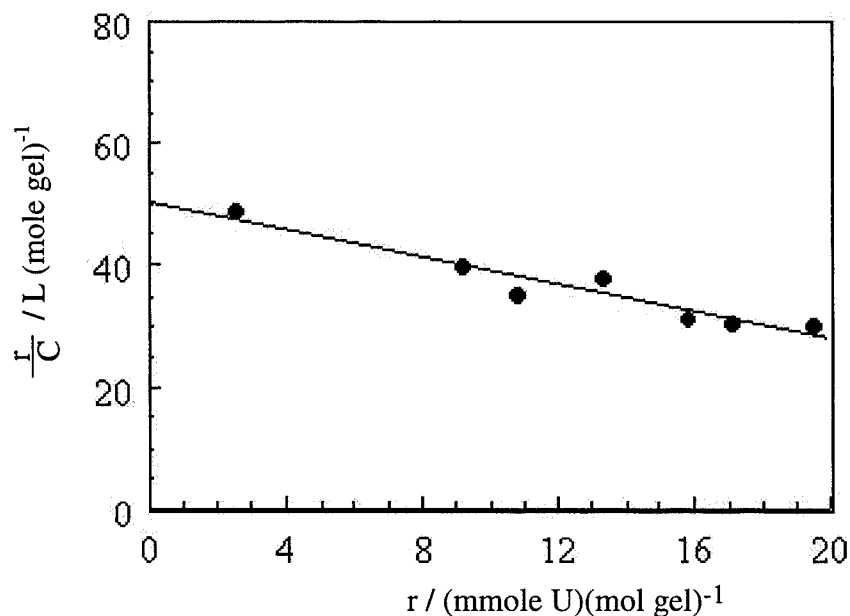


Figure 13. Scatchard plot of uranyl ions-AAm/HPMA/MA hydrogel binding system.

contains the derived values of the  $\hat{\theta}$ , the maximum fractional occupancy attained experimentally, calculated from the definition of fractional occupancy:

$$\hat{\theta} = \frac{r}{n} \quad (11)$$

using the value of  $r$  at the maximum experimental free  $U$  concentration.

Average value of  $K_i$  is  $51.0 \text{ L mole}^{-1}$ . The value shows that the interaction is strongly between uranyl ions and AAm/HPMA/MA. Average equilibrium constant is  $1.2 \times 10^3 \text{ L mol}^{-1}$ . This value of  $K$ , that is higher than unity, is indicated that uranyl ion has been sorbed very well by AAm/HPMA/MA. Average value of monolayer capacity of AAm/HPMA/MA is  $44 (\text{mmol U}) (\text{mol gel})^{-1}$ . The site size of uranyl ions is 23 base mole of AAm/HPMA/MA per one mol uranium i.e., 23 moles of constitutional repeating units of AAm/HPMA/MA hydrogel were binded one mole uranyl ion. On the other hand, the value of fractional occupancy equals to 0.44. The value shows that AAm/HPMA/MA is exactly unsaturated by uranyl ions in this experimental conditions. It is said that the half of monolayer coverage of AAm/HPMA/MA is saturated by uranyl ions.

To determine the thermodynamic parameters of the uranyl ion/hydrogel binding system, adsorption experiments are repeated at the constant

concentration ( $100 \text{ mg L}^{-1}$ ), and at 25 and 35°C. Adsorption heat ( $\Delta H$ ), adsorption free energy ( $\Delta G$ ) and adsorption entropy ( $\Delta S$ ) of the uranyl ion/hydrogel binding system were calculated following equations;

$$\ln \frac{C_2}{C_1} = -\frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (12)$$

$$\Delta G = -RT \ln K \quad (13)$$

$$\Delta G = \Delta H - T\Delta S \quad (14)$$

where  $C_1$  and  $C_2$  are the free uranyl ion concentration at the absolute temperature  $T_1$  and  $T_2$ , respectively.  $R$  is the universal gas constant.

The thermodynamic parameters of the uranyl ion/hydrogel binding system were calculated at 25°C and, are tabulated in Table 3.

As shown in Table 3, the sorption process is associated with zero enthalpy, negative free energy and positive entropy. Hence both energetic and hydrophobic forces involve in the sorption process. Hydrogen bonding from the oxygens of uranyl ions is likely candidate for the energetic forces. The intermolecular attraction between the substrate molecules after sorption and the hydrophobic interaction, if any, between uranyl ions and AAm/HPMA/MA hydrogel consequent changes in the water layer around the binding sites may be the contributing processes to the observed positive entropy changed. Binding of uranyl ions to the hydrogel is spontaneously due to the negative  $\Delta G$ . On the other hand, The adsorption of uranyl ions onto AAm/HPMA/MA hydrogel is a physical adsorption, because adsorption enthalpy is less than  $20 \text{ kJ mole}^{-1}$  (Table 3).

If Tables 2 and 3 are investigated together, it is shown that there are little differences between three linearization methods for calculating of binding and thermodynamic parameters of uranyl ion/hydrogel binding system. These linearization methods (Klotz, Scatchard and Langmuir methods) can be used in the hyperbolic binding systems for solute – polymer binding processes.

**Table 3.** Thermodynamic Parameters of AAm/HPMA/MA Hydrogel-Uranyl Ion Binding System

Method	$\Delta G/\text{kJ mol}^{-1}$	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{eu}$
Klotz	-17.69	0	59.4
Scatchard	-17.40	0	58.4
Langmuir	-17.36	0	58.3
Mean $\pm$ SD	$-17.48 \pm 0.18$	$0 \pm 0$	$58.7 \pm 0.6$

The variation of the adsorptions of the uranyl ions with the content of MA in the hydrogels and irradiation dose was investigated. The binding ratios of the uranyl ion/hydrogel binding system vs. MA content and irradiation dose were plotted, as presented in Figs. 14 and 15 respectively.

Figure 14 shows that the uptakes of uranyl ions onto AAm/HPMA/MA hydrogels increased with the increase of the content of MA in the hydrogels. The increase of carboxyl groups in the hydrogels with the increase of MA contents caused by the electrostatic interactions between the cationic uranyl ions and the anionic groups of maleic acid in the hydrogels.

Figure 15 shows that the adsorption of uranyl ions is increased with the increase of irradiation dose. The crosslinks of hydrogels have increased with irradiation dose. It can become too small of pores. In this way it is difficult for the big uranyl ions to get into small pores and to be held on there.

Hydrogels taken out the solutions of uranyl ion were waited for three days, in 50 mL distilled water, and desorption of uranyl ions was showed by the light yellowish coloration of water and hydrogels also have returned original colors. So, it can be said that uranyl ions were easily eluted from the hydrogels with distilled water.

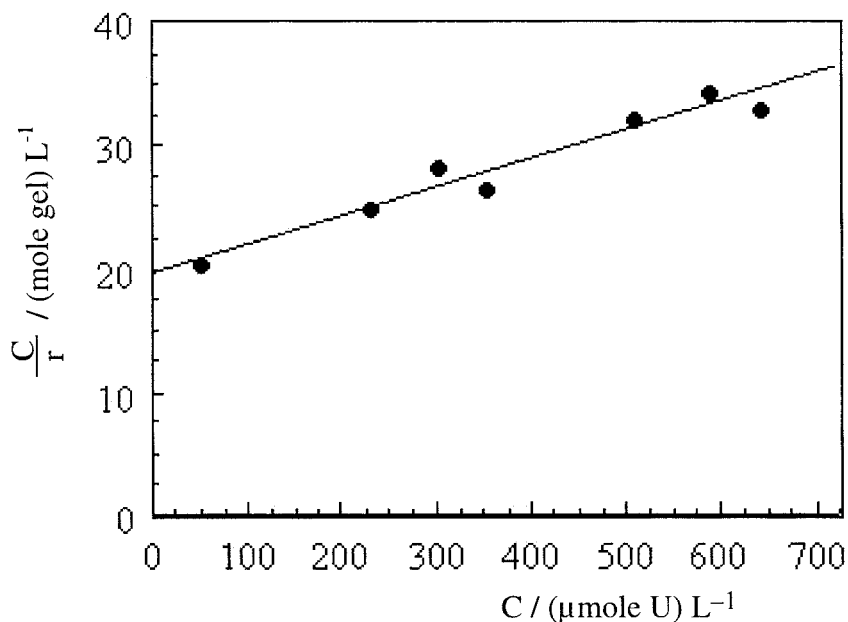
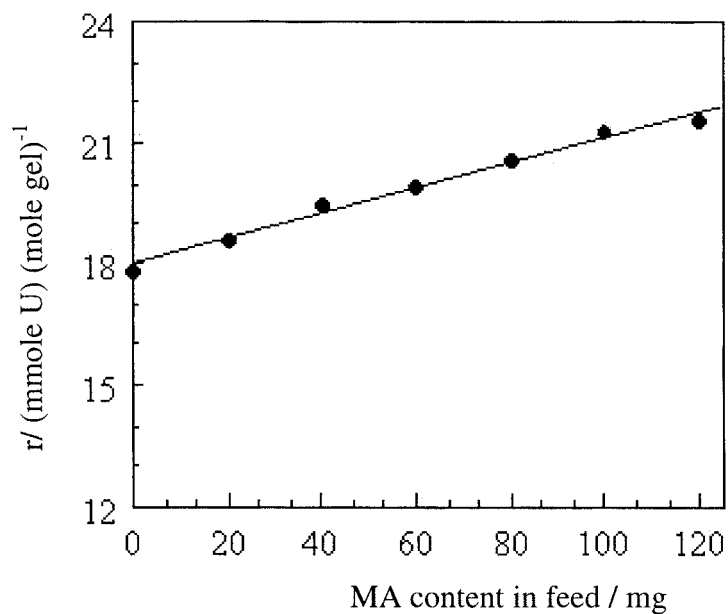
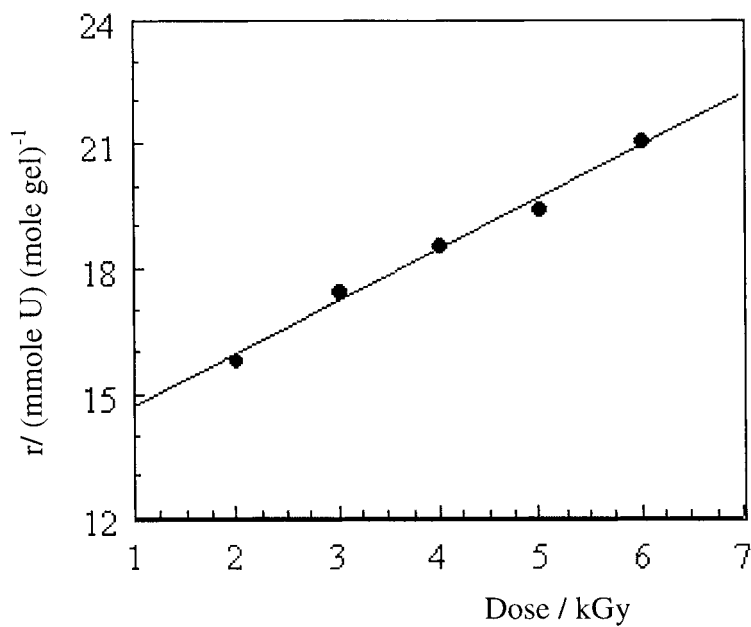


Figure 14. Langmuir plot of uranyl ions-AAm/HPMA/MA hydrogel binding system.



**Figure 15.** The effect of Ma content on the binding of uranyl ions onto AAm/HPMA/MA hydrogel.



**Figure 16.** The effect of irradiation dose on the binding of uranyl ions onto AAm/HPMA/MA hydrogel.

## CONCLUSION

The terpolymeric AAm/HPMA/MA hydrogels were synthesized using gamma radiation. To impart the uranyl ion adsorptivity, MA incorporated into the AAm/HPMA hydrogel. From the swelling studies of the hydrogels, it was found that monomer type and hydrophilicity are effective on the swelling behavior. From the values of equilibrium swelling in water, AAm/HPMA hydrogels swelled low, while AAm hydrogel swelled higher. As a result, the structure and the hydrophilicity of the monomers have great effect on the swelling of polymers.

Concentration of uranyl ions, irradiation dose and MA content of the hydrogel were found to be effective, while temperature was not very effective for the uranyl ion binding process. Uranyl ion adsorption studies showed L Type adsorption isotherms in the Giles adsorption classification.

Consequently, it can be concluded that AAm/HPMA/MA hydrogels can be used as an efficient sorbent for removal of water pollutant such as uranyl ions. These types of adsorbents are very promising because of their high adsorption capacity, reusability and the easiness of handling with the safety to environment.

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