Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Karadağ, Erdener , Saraydin, Dursun and Güven, Olgun(1995) 'Behaviors of Acrylamide/Itaconic Acid Hydrogels in Uptake of Uranyl Ions from Aqueous Solutions', Separation Science and Technology, 30: 20, 3747 — 3760
To link to this Article: DOI: 10.1080/01496399508015140
URL: http://dx.doi.org/10.1080/01496399508015140

SEPARATION SCIENCE AND TECHNOLOGY, **30**(20), pp. 3747–3760, 1995

Behaviors of Acrylamide/Itaconic Acid Hydrogels in Uptake of Uranyl Ions from Aqueous Solutions

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ABSTRACT

In this study, adsorptions of uranyl ions from two different aqueous uranyl solutions by acrylamide–itaconic acid hydrogels were investigated by a spectroscopic method. The hydrogels were prepared by irradiating with γ-radiation. In the experiment of uranyl ions adsorption, Type II adsorption was found. One gram of acrylamide–itaconic acid hydrogels sorbed 178–219 mg uranyl ions from the solutions of uranyl acetate, 42–76 mg uranyl ions from the aqueous solutions of uranyl nitrate, while acrylamide hydrogel did not sorb any uranyl ion. For the hydrogel containing 40 mg of itaconic acid and irradiated to 3.73 kGy, swelling of the hydrogels was observed in water (1660%), in the aqueous solution of uranyl acetate (730%), and in the aqueous solution of uranyl nitrate (580%). Diffusions of water onto hydrogels were a non-Fickian type of diffusion, whereas diffusions of uranyl ions were a Fickian type of diffusion.

Key Words. Hydrogel; Poly(acrylamide/itaconic acid); Adsorption; Uranyl ion; Swelling

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INTRODUCTION

Hydrogels are water-swellable, three-dimensional polymeric networks. The capacity of hydrogels to absorb water is enormous and can be as much as 1000 times the mass of polymer. Hydrogels find considerable applications and have been extensively studied because they combine glassy behavior (when in the dry state) with elastic (when sufficient water is absorbed). The behavior of highly swollen hydrogels is, of course, a function of the network characteristic (such as degree of swelling, diffusion coefficient, crosslink density, mesh size, etc.) which in turn are connected with chemical structures (1).

Hydrogels have widespread applications in bioengineering, biomedicine, pharmaceutical, veterinary, food industry, agriculture, photographic technology, and other fields. They are used as controlled release systems of drugs, for the production of contact lenses and artificial organs in biomedicine, as adsorbents for the removal of some agent in environmental applications, for immobilized enzyme kinetics in bioengineering, and as carriers of water, pesticides, and fertilizer in the agriculture field (2). Polyacrylamide (PAAm) hydrogels have capability for water absorption and biocompatibility with physiologic body fluids (3, 4). PAAm hydrogels and their derivatives were used in work on protein adsorption, etc. (5, 6).

Some authors have reported on some crosslinked copolymers of the diethyl ester of vinyl phosphonic acid and acrylic acid, and crosslinked copolymers of some natural polymers and some monomers have been used for the adsorption of some heavy metal ions (7–10). On the other hand, the amidoxime derivatives of copolymeric hydrogels prepared from acrylonitrile and divinylbenzene has been used successfully in the recovery of uranium from seawater (11–14). In our previous study, acrylamide/maleic acid hydrogels were used in adsorptions of some heavy metal ions in aqueous solutions (15).

In this study, novel hydrogels prepared with acrylamide and itaconic acid were used to increase the adsorption capacity of acrylamide hydrogels for uranyl ions. These hydrogels were previously used in adsorptions of some basic dyes in aqueous solutions (16).

EXPERIMENTAL

Materials

Acrylamide and itaconic acid monomers were obtained from B.D.H. (Poole, UK). Uranyl nitrate (UN), uranyl acetate (UA), and potassium hexacyanoferrate(II) were purchased from Merck (Darmstad, Germany).

Methods

Preparation of Hydrogels

One gram of acrylamide (AAm) was dissolved in 1 mL of aqueous solutions of 0, 20, 40, and 60 mg itaconic acid (IA). These solutions were placed in PVC straws of 3 mm diameter and irradiated with 2.60, 3.73, 4.65, 5.20, and 5.71 kGy in air at ambient temperature in a Gamacell 220 Type γ irradiator at a fixed rate of 0.72 kGy·h^{-1}. Hydrogels obtained in long cylindrical shapes were washed and dried, first in air and then in a vacuum.

Hydrogels containing 40 mg IA and irradiated to 3.73 kGy were swollen in distilled water, aqueous solutions of uranyl acetate, and aqueous solutions of uranyl nitrate at 25°C to measure the diffusion and swelling parameters. Swollen gels removed from a water bath at regular intervals were dried superficially with filter paper, weighted, and placed in the same bath.

About 0.1 g acrylamide–itaconic acid (AAm/IA) hydrogels were transferred into 50 mL solutions of UA and UN in the concentration range 50–600 mg UO_2^{2+}·L^{-1} and allowed to equilibrate for 24 hours at 25°C. These aqueous solutions were separated by decantation from the hydrogels. A 1 mL solution of potassium hexacyanoferrate(II) with a concentration of 1 g·L^{-1} was added to 10 mL of the uranyl solutions and allowed to stand for 30 minutes. Spectrophotometric measurements were carried out using a Perkin-Elmer Coleman 295 model VIS spectrophotometer at ambient temperature. The absorbances of these uranyl-complex solutions at 525 nm wavelength were measured (17). Distilled water was chosen as the reference. The concentrations of uranyl ions were found by using suitable calibration curves.

For the investigation of the adsorption capability of swollen and dried AAm/IA hydrogels, dried AAm/IA hydrogels were used for the adsorption of uranyl ions.

Hydrogels separated from aqueous solutions of uranyl ions were left for 3 days in distilled water at 25°C to investigate the desorption.

RESULTS AND DISCUSSION

Thermal properties, spectroscopic properties, mechanical properties, swelling behavior, diffusional properties, and network properties of hydrogel systems were investigated in our previous study (18).

Swelling and Diffusion

Swelling behaviors of AAm/IA hydrogel containing 40 mg IA and irradiated at 3.73 kGy were followed gravimetrically. The percentage swelling of hydrogels is calculated from the following relation (19):

$$\%S = [(m_t - m_0)/m_0] \times 100 \tag{1}$$

where m_t is the mass of swollen gel at time t and m_0 is the initial mass of the swollen gel.

The dynamic swelling curves (5, 6) of AAm/IA hydrogel containing 40 mg IA and irradiated at 3.73 kGy in distilled water and solutions of uranyl ions are shown in Fig. 1.

Figure 1 shows that maximum and minimum swellings occur with water (1660%) and with an aqueous solution of uranyl nitrate (580%).

The following equation is used to determine the nature of the diffusion of water and uranyl ions into hydrogels (5, 6, 19):

$$F = kt^n \tag{2}$$

where F denotes the amount of solvent fraction at time t, k is a constant related to the structure of the network, and the exponential n is a number used to determine the type of diffusion.

This equation is applied to the initial stages of swelling. Plots of $\ln(F)$ versus $\ln(t)$ are shown in Fig. 2. The exponents are calculated from the slope of the lines.

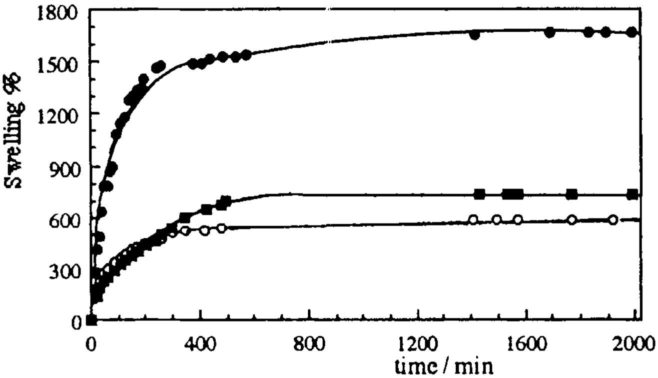


FIG. 1 Dynamic swelling curves of AAm/IA hydrogels containing 40 mg IA. Total doses: 3.73 kGy. (○) Uranyl nitrate, (■) uranyl acetate, (●) water.

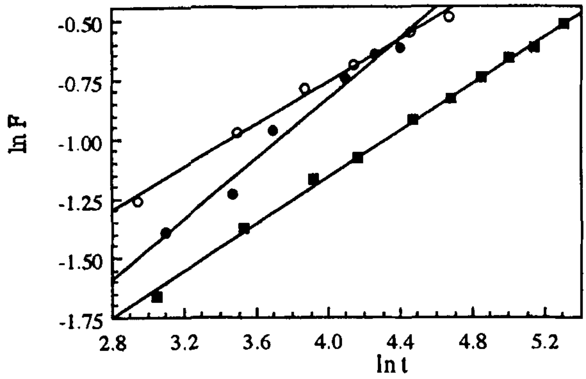


FIG. 2 Swelling kinetics curves of AAm/IA hydrogels containing 40 mg IA. Total doses: 3.73 kGy. (○) Uranyl nitrate, (■) uranyl acetate, (●) water.

Diffusion coefficients are calculated from the following relation (20):

$$D = 0.049/(t/4l^2)_{1/2} \qquad (3)$$

where D is in $\mathrm{cm}^2 \cdot \mathrm{s}^{-1}$, t is the time at which the swelling is one-half the equilibrium value ($V/V_0 = 1/2$), and l is the radius of the swollen cylindrical sample. The intrinsic diffusion coefficient may be expressed as

$$\mathcal{D} = D(1 - V)^{-3} \qquad (4)$$

where V is the volume fraction of solvent penetrating the polymer by time t as defined above (20).

Values of the equilibrium percentage swelling (S_{eq}, %), parameters of diffusion, and diffusion coefficients of the hydrogels are listed in Table 1.

The percentage equilibrium swelling of the hydrogel is low (580 and 730%) in solutions of the uranyl ions but high (1660%) in water. The uranyl ions interacted with the carboxyl groups of itaconic acid in the hydrogel, so the hydrophilic groups of the hydrogel are not bonded with water. Thus, swelling of the hydrogel decreased in solutions of uranyl ions.

When relaxation is much faster than diffusion, the cumulative swelling follows Fickian diffusion. When diffusion is much faster than relaxation, cumulative swelling also follows Fickian diffusion but at a much slower rate. In the intermediate case, swelling takes the anomalous or *non-Fickian* form where $1/2 < n \leq 1$ (21). In *non-Fickian* diffusion, diffusion and relaxation are isochronal effective (21, 22). In the experiments, the number used to determine the type of diffusion (n) was found to be 0.63 for the

TABLE 1
Swelling and Diffusion Parameters of AAm/IA Hydrogel Containing 40 mg IA. Total Dose Given: 3.73 kGy

Solution	$\%S_{eq}$	$k \times 10^2$	n	$D \times 10^5$ cm^2·s^{-1}	$\mathcal{D} \times 10^5$ cm^2·s^{-1}
Water	1660	3.4	0.64	11.03	15.45
Uranyl acetate	730	4.4	0.49	5.58	6.13
Uranyl nitrate	580	7.9	0.45	5.08	5.80

diffusion of water and 0.45 and 0.49 for the diffusions of uranyl nitrate and uranyl acetate, respectively. The diffusion of uranyl ions into the hydrogels was taken to be *Fickian* whereas the diffusion of water was taken to be *non-Fickian.*

The values given in Table 1 show that the diffusion coefficients of water are larger than the others, so diffusion of uranyl ions into gel pores is difficult. Table 1 also shows that the values of the intrinsic diffusion coefficient of hydrogels in water and the solution of uranyl ions are larger than their diffusion coefficient values because Eq. (3) measures not only the diffusion but also the mass flow of the whole system. Equation (4) gives the intrinsic diffusion coefficient for cases where no mass action effects occur (20).

The acetate and nitrate anions of the uranyl salts affect swelling. The uranyl acetate dissolves as molecules in the aqueous solution while the uranyl nitrate dissolves as ions in the aqueous solution (17). Thus, the cations of the salt containing nitrate anion interact with the carboxylic group of IA in the hydrogels, so the swelling of these hydrogels in the aqueous solution of the nitrate salt is low because of the swelling of these hydrogels in the aqueous solution of the acetate salt. These interactions can be electrostatic, such as ionic or ion–dipole (23).

Uranyl Ions Uptake

The second stage of our investigation was of the uptake of uranyl ions onto the AAm/IA hydrogels and of their usability as sorbents for uranyl ions.

In aqueous solutions, several characteristic properties of IA can be observed: the two-step dissociation process of dicarboxylate groups, the binding of counterions, etc. These properties of IA copolymers are attributed to two factors: 1) hydrophobic interaction of nonpolar side chains, and 2) short-range electrostatic interaction of a pair of carboxylate groups.

To observe the adsorption of uranyl ions, AAm and AAm/IA hydrogels were placed in aqueous solutions of heavy metals (uranyl acetate, uranyl nitrate, cobalt nitrate, nickel chloride, chrome nitrate) and allowed to equilibrate for 2 days. At the end of this time the AAm/IA hydrogels in solutions of uranyl acetate and uranyl nitrate were dark compared to the colors of the original solutions, while AAm hydrogels had not sorbed any uranyl ions from the solutions. Since PAAm is a nonionic polymer (24), ionizable groups on the polymer were increased by adding IA to AAm monomer. Therefore, these hydrogels have many carboxyl groups that can increase the interaction between the uranyl ions and the carboxyl groups in the hydrogels. The solutions of uranyl ions were used in the adsorption experiments. Uranyl salts from two different uranyl ions sources (such as uranyl nitrate and uranyl acetate) were selected for an investigation of the effects of anionic groups of uranyl salts. The possible interactions between uranyl ion and AAm and AAm/IA hydrogels are shown in Schemes 1 and 2, respectively.

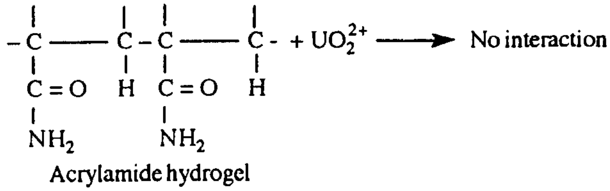
The uptake of uranyl ions onto new hydrogel systems, including AAm/IA, was investigated. The mass of uptake of uranyl ions per unit mass of adsorbent, q_e, can be calculated from the following relation:

$$q_e = \frac{C_i - C}{m} V_t \tag{5}$$

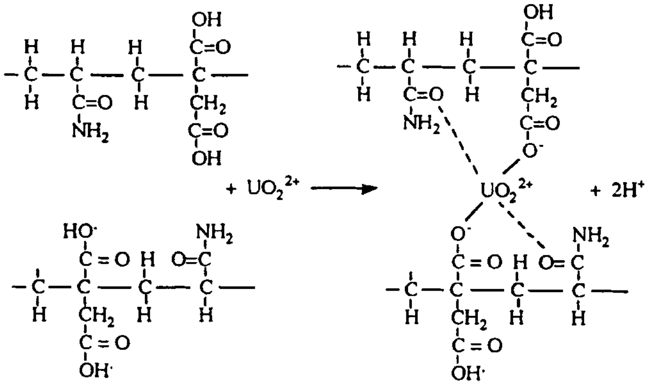
where q_e is in mg uranyl ion per gram dry adsorbent, C_i and C are the initial and equilibrium concentrations of solution of adsorbate in mg·L^{-1}, V_t is the total volume of solution of adsorbate in liters, and m is the mass of dry adsorbent in grams.

Graphs of q_e against the equilibrium concentrations of uranyl ions, C, are plotted in Figs. 3 and 4.

Adsorption of uranyl ions from solutions of UA and UN onto AAm/IA hydrogels corresponds to Type II isotherms (25). Physical adsorption gives rise to a Type II isotherm in the vast majority of cases. The model



SCHEME 1 The possible interaction between uranyl ion and AAm hydrogel.



SCHEME 2 The possible interaction between uranyl ion and AAm/IA hydrogel.

restricts attention to the forces between the adsorbent and the adsorbate molecules—the *vertical* interactions—and neglects the forces between an adsorbate molecule and its neighbors in the same layer—the *horizontal* interactions. From the nature of intermolecular forces it is certain that these adsorbate–adsorbate interactions must be far from negligible when a layer is approaching completion and the average separation of molecules is therefore small in relation to their sizes (25).

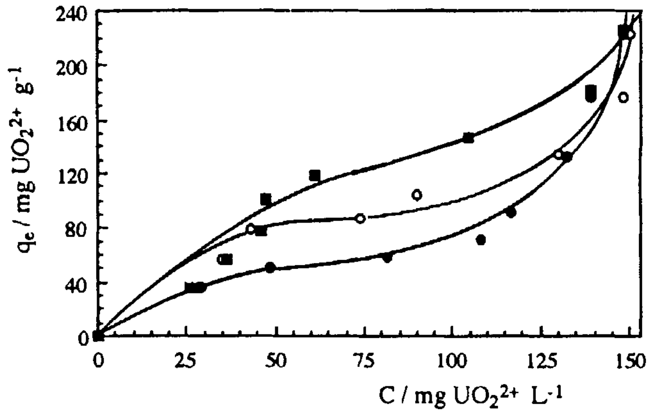


FIG. 3 The isotherms of adsorptions of uranyl ions from aqueous solutions of uranyl acetate onto AAm/IA hydrogels. Total doses: 5.20 kGy. (●) 20 mg IA, (○) 40 mg IA, (■) 60 mg IA.

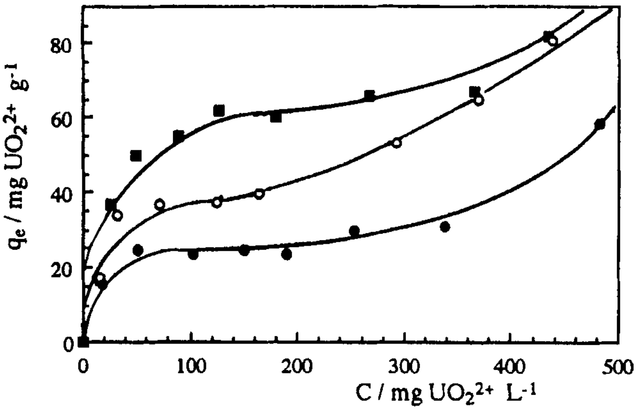


FIG. 4 The isotherms of adsorptions of uranyl ions from aqueous solutions of uranyl nitrate onto AAm/IA hydrogels. Total doses: 5.20 kGy. (●) 20 mg IA, (○) 40 mg IA, (■) 60 mg IA.

The adsorption of uranyl ions from solutions of UA is higher than from solutions of UN. Some interactions that are affected by the swelling properties of the hydrogels are effective for the adsorptions of UN and UA onto the AAm/IA hydrogels.

The Type II isotherms obtained experimentally display a rather long straight portion of yield up to the point of inflection. The point at which this linear portion begins was termed "Point B" and was taken to indicate the completion of the monolayer, so that the adsorption at Point B, say n_B, should be equal to the monolayer capacity (25).

The monolayer capacities of AAm/IA hydrogels for uranyl ions in aqueous solutions of uranyl acetate and uranyl nitrate were found by the Point B method from Figs. 3 and 4, and plots of the monolayer capacities versus IA content of AAm/IA hydrogels are presented in Fig. 5. The results in Fig. 5 parallel the adsorption results.

The uptakes of uranyl ions onto the swollen hydrogels were investigated. For this, 40 mg IA containing 5.20 kGy irradiated AAm/IA hydrogels were used for adsorption. Adsorption isotherms of the swollen and the initially dry hydrogels are given in Fig. 6.

Figure 6 shows that the uptakes of uranyl ions onto dry hydrogels are higher than the uptakes of uranyl ions onto swollen hydrogels. Hydrophilic groups in the swollen hydrogel can interact with water, and uptakes of uranyl ions can be prevented by these carboxylic groups, so uptakes of

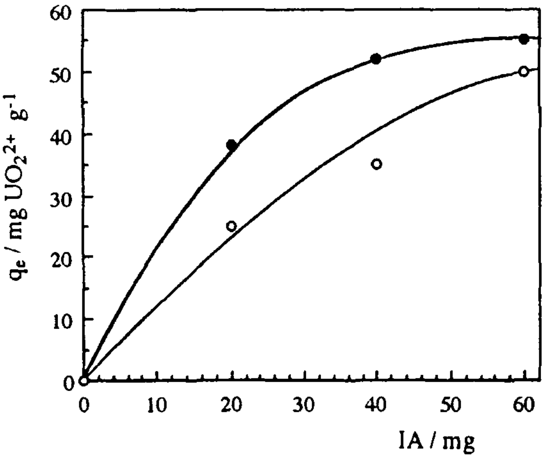


FIG. 5 The variation of monolayer capacity of uranyl ions from aqueous solutions onto AAm/IA hydrogels. Total doses: 5.20 kGy. (●) Uranyl acetate, (○) uranyl nitrate.

uranyl ions can be decreased in the swollen gels with respect to the initially dry gel.

Monolayer capacities of the swollen and dry gels were found by the Point B method. These values of the swollen and dry gels are 47 and 52 mg UO_2^{2+}/g, respectively. These results are parallel to the adsorption results of swollen and dry gels.

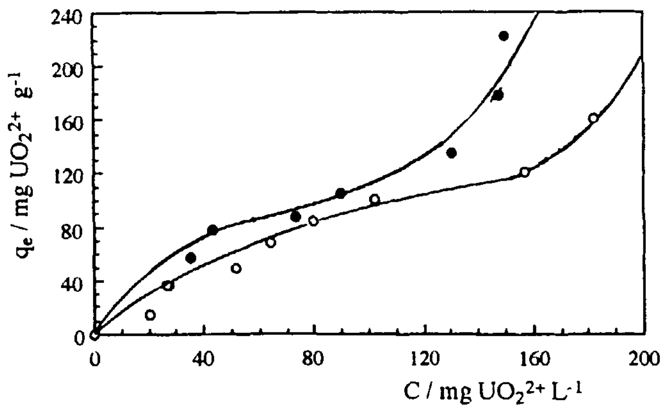


FIG. 6 The isotherms of adsorptions of uranyl ions from aqueous solutions of uranyl acetate onto AAm/IA hydrogels containing 40 mg IA. Total doses: 5.20 kGy. (●) Dry gel, (○) swollen gel.

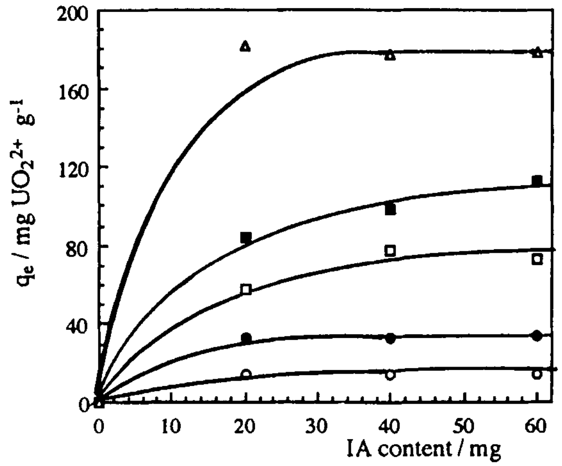


FIG. 7 The variation of adsorptions of uranyl ions from aqueous solutions of uranyl acetate in different initial concentrations onto AAm/IA hydrogels with IA content. Total doses: 2.60 kGy. (○) 50 mg $UO_2^{2+} \cdot L^{-1}$, (●) 100 mg $UO_2^{2+} \cdot L^{-1}$, (□) 200 mg $UO_2^{2+} \cdot L^{-1}$, (■) 300 mg $UO_2^{2+} \cdot L^{-1}$, (△) 500 mg $UO_2^{2+} \cdot L^{-1}$.

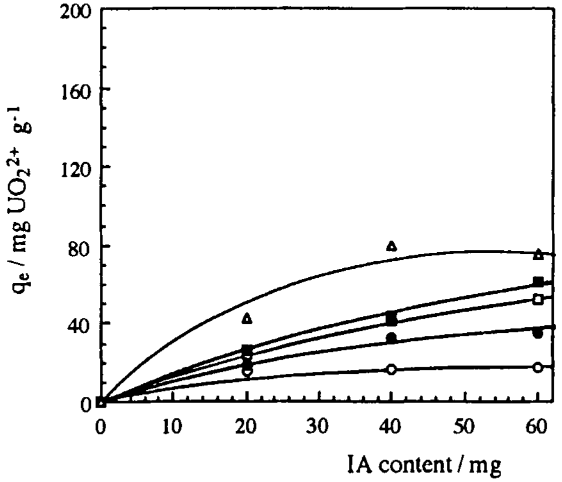


FIG. 8 The variation of adsorptions of uranyl ions from aqueous solutions of uranyl nitrate in different initial concentrations onto AAm/IA hydrogels with IA content. Total doses: 2.60 kGy. (○) 50 mg $UO_2^{2+} \cdot L^{-1}$, (●) 100 mg $UO_2^{2+} \cdot L^{-1}$, (□) 200 mg $UO_2^{2+} \cdot L^{-1}$, (■) 300 mg $UO_2^{2+} \cdot L^{-1}$, (△) 500 mg $UO_2^{2+} \cdot L^{-1}$.

The variation of the adsorptions of uranyl ions from UN and UA solutions with the IA content in the hydrogels and the irradiation dose was investigated. The mass of adsorbed uranyl per gram of the hydrogel versus the IA content of the hydrogel and the irradiation dose are plotted in Figs. 7, 8, 9, and 10, respectively.

Figures 7 and 8 show that the uptakes of uranyl ions onto AAm/IA hydrogels increase with an increase of the IA content in the hydrogels. The increase of carboxyl groups in the hydrogels with an increase of IA content is caused by electrostatic interactions between the cationic uranyl ions and the anionic groups of IA in the hydrogels.

Figures 9 and 10 show that the adsorption of uranyl ions is approximately constant at all doses. The crosslinks of hydrogels increase with irradiation dose, resulting in smaller pores. It is difficult for the big uranyl ions to get into small pores and be held there.

Hydrogels taken out of the solutions of uranyl ion were allowed to stand for 3 days in distilled water, and the desorptions of uranyl ions were shown by the light yellowish coloration of the water and the return of hydrogels to their original colors. It can be said that this adsorption of uranyl ions is physical adsorption.

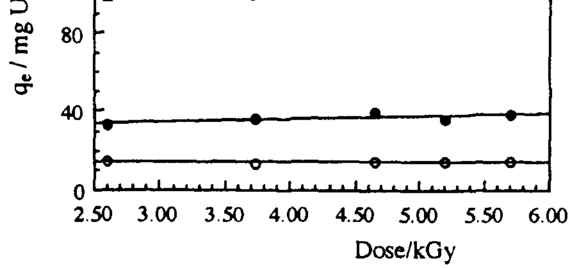


FIG. 9 The variation of adsorptions of uranyl ions from aqueous solutions of uranyl acetate in different initial concentrations onto AAm/IA hydrogels containing 40 mg of IA with the irradiation doses. (○) 50 mg $UO_2^{2+} \cdot L^{-1}$, (●) 100 mg $UO_2^{2+} \cdot L^{-1}$, (□) 300 mg $UO_2^{2+} \cdot L^{-1}$, (■) 500 mg $UO_2^{2+} \cdot L^{-1}$.

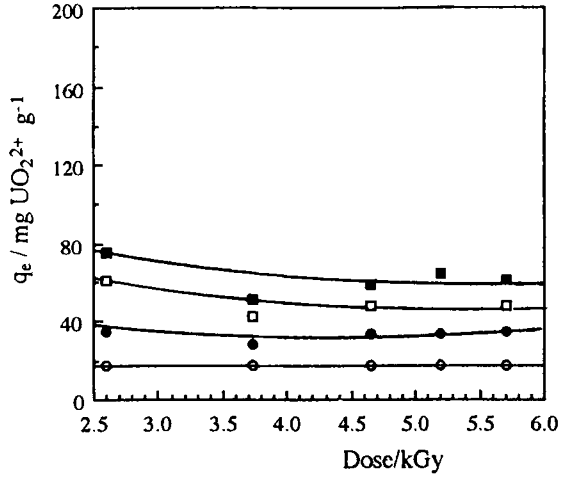


FIG. 10 The variation of adsorptions of uranyl ions from aqueous solutions of uranyl nitrate in different initial concentrations onto AAm/IA hydrogels containing 40 mg of IA with the irradiation doses. (○) 50 mg $UO_2^{2+}\cdot L^{-1}$, (●) 100 mg $UO_2^{2+}\cdot L^{-1}$, (□) 300 mg $UO_2^{2+}\cdot L^{-1}$, (■) 500 mg $UO_2^{2+}\cdot L^{-1}$.

CONCLUSION

Swellings experiments have shown that the values of percentage equilibrium swelling of hydrogels are low (580 and 730%) in solutions of the uranyl ions and high (1660%) in water. On the other hand, the diffusion of water has a non-Fickian character and the diffusion of uranyl ions into AAm/IA hydrogels has a Fickian character.

This study has also shown that AAm/IA hydrogels adsorb uranyl ions while AAm hydrogels do not.

Type II adsorption isotherms, characteristic of multilayer adsorption, were found. The adsorption of uranyl ions increased with the IA content in the hydrogels.

It was shown that AAm/IA hydrogels can be used as sorbents for water pollutants such as uranyl ions. Immobilization of some inorganic contaminants in hydrogels can be used to clean wastewater, which is one of the most important problems of environmental chemistry.

ACKNOWLEDGMENT

We are grateful to the Polymer Group of the Chemistry Department of Hacettepe University for preparation of the hydrogels.

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Received by editor April 28, 1995