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Adsorptions of Some Heavy Metal Ions in Aqueous Solutions by Acrylamide/Maleic Acid Hydrogels

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ABSTRACT

In this study, acrylamide–maleic acid (AAm/MA) hydrogels in the form of rod have been prepared by γ-radiation. They have been used for adsorption of some heavy metal ions such as uranium, iron, and copper. For the hydrogel containing 40 mg of maleic acid and irradiated at 3.73 kGy, maximum and minimum swellings in the aqueous solutions of the heavy metal ions have been observed with water (1480%) and the aqueous solution of iron(III) nitrate (410%), respectively. Diffusions of water and heavy metal ions onto hydrogels have been found to be of the non-Fickian type of diffusion. In experiments of uranyl ions adsorption, Type II adsorption has been found. One gram of AAm/MA hydrogels sorbed 14–86 mg uranyl ions from solutions of uranyl acetate, 14–90 mg uranyl ions from solutions of uranyl nitrate, 16–39 mg iron ions from solutions of iron(IV) nitrate, and 28–81 mg copper ions from solutions of copper acetate, while acrylamide hydrogel did not sorb any heavy metals ions.

Key Words. Hydrogel; Poly(acrylamide/maleic acid); Adsorption; Uranyl ion; Heavy metal ions

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INTRODUCTION

Hydrogels has many applications and have been extensively studied because they combine glassy behavior (when in the dry state) with elastic behavior (when sufficient water is absorbed). The behavior of highly swollen hydrogels is a function of the network characteristic (such as degree of swelling, diffusion coefficient, crosslink density, mesh size, etc.), which in turn is connected with the chemical structures (1).

Hydrogels have found widespread applications in bioengineering, biomedicine, pharmaceutics, veterinary uses, food industry, agriculture, photographic technology, and other fields. They are used as controlled release systems of drugs, in the production of contact lenses and artificial organs in biomedicine, as adsorbents for the removal of some agents in environmental applications, in immobilized enzyme kinetics in bioengineering, and as carriers of water, pesticides, and fertilizer in agriculture (2). Polyacrylamide (PAAm) hydrogels can absorb water and are biocompatible with physiologic body fluids (3, 4). PAAm hydrogels and its derivatives are used for protein adsorption (5, 6). Many reports have been published on the polyelectrolytic behavior of alternating copolymers of maleic acid in aqueous solutions (7).

It has been reported that some crosslinked copolymers of the diethyl ester of vinyl phosphonic acid and acrylic acid, as well as crosslinked copolymers of some natural polymers and some monomers, have been used for the adsorption of some heavy metal ions (8–11). Amidoxime derivatives of copolymeric hydrogels prepared from acrylonitrile and divinylbenzene has been used successfully in the recovery of uranium from the seawater (12–14).

In this study, novel hydrogels prepared with acrylamide and maleic acid were used to increase the adsorption capacity of acrylamide for heavy metal ions.

EXPERIMENTAL

Materials

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

Methods

Preparation of Hydrogels

One gram acrylamide (AAm) was dissolved in 1 mL of aqueous solutions of 0, 20, 40, and 60 mg maleic acid (MA). These solutions were placed in

PVC straws of 3 mm diameter and irradiated 2.00, 2.60, 3.73, 4.65, 5.20, and 5.71 kGy in air at ambient temperature in a Gammacell 220 type γ-irradiator at a fixed dose rate of 0.72 $\text{kGy}\cdot\text{h}^{-1}$. The hydrogels, obtained as long cylindrical shapes, were washed and dried in air and vacuum.

Hydrogels containing 40 mg maleic acid and having been irradiated with 3.73 kGy were swollen in distilled water and in aqueous solutions of uranyl acetate, uranyl nitrate, iron(III) nitrate, and copper acetate at 25°C to find the parameters of diffusion and swelling. Swollen gels removed from the water bath at regular intervals were dried superficially with filter paper, weighted, and placed in the same bath.

About 0.1 g acrylamide–maleic acid (AAm/MA) hydrogels were transferred into 50 mL solutions of UA and UN in the concentration range 50–600 mg UO_2^{2+} L^{-1}, solutions of copper acetate (2 g Cu^{2+} L^{-1}), and solutions of iron(III) nitrate (500 mg Fe^{3+} L^{-1}), and allowed the equilibrate for 24 hours at 25°C. These aqueous solutions were separated from the hydrogels by decantation. A 1 mL solution of potassium hexacyano ferrat(II) (concentration 1 $g\cdot L^{-1}$) was added to 10 mL of the uranyl solutions, and 1 mL of ammonium hydroxide (concentration 3 $mol\cdot L^{-1}$) was added to 10 mL of the copper solutions, and the mixture were held 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, the absorbances of iron solutions at 400 nm wavelength and the absorbances of copper-complex solutions at 620 nm wavelength were measured (15). Distilled water was used as a reference. The concentrations of heavy metal ions were found by using suitable calibration curves.

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

RESULTS AND DISCUSSION

Thermal, spectroscopic, mechanical, diffusional, and network properties of hydrogel systems as well as their swelling behaviors were investigated in our previous study (16).

Swelling and Diffusion

Swelling behaviors of AAm/MA hydrogel containing 40 mg MA and irradiated at 3.73 kGy were followed gravimetrically. Percentage swelling of hydrogels was calculated from the following relation (17):

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

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

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

Figure 1 shows that maximum and minimum swellings occur with water (1480%) and with an aqueous solution of iron(III) nitrate (410%).

The following equation is used to determine the nature of the diffusion of water and heavy metal ions into hydrogels (5, 6, 17).

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

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 were calculated from the slope of the lines.

Diffusion coefficients were calculated from the following relation (18):

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

where D is in $cm^2 \cdot s^{-1}$, 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 cylindrical sample. The intrinsic diffusion coefficient may be expressed as

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

where V is the volume fraction of solvent penetrating the polymer by time t as defined above (18).

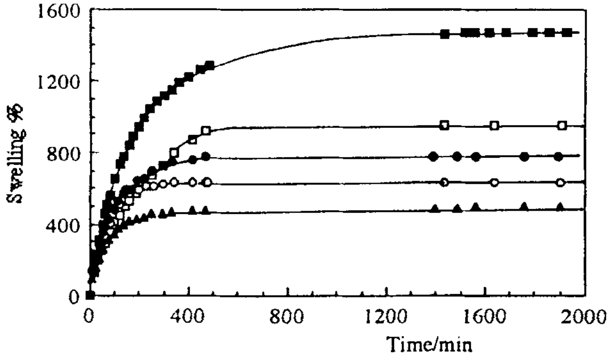


FIG. 1 The swelling curves of AAm/MA hydrogel containing 40 mg MA and irradiated at 3.73 kGy in water and solutions of heavy metal ions: (□) uranyl acetate, (●) uranyl nitrate, (○) copper acetate, (▲) iron(III) nitrate, (■) distilled water.

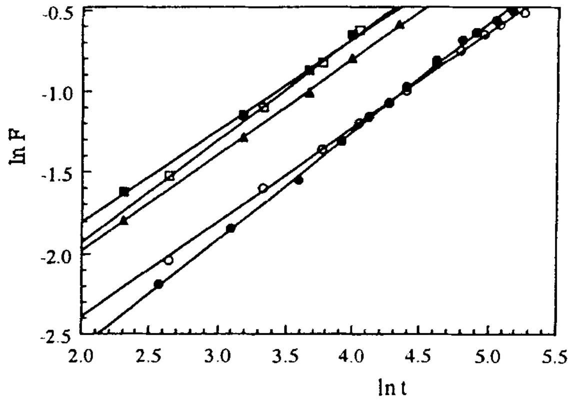


FIG. 2 The curves of swelling kinetics of hydrogels prepared from AAm/MA containing 40 mg MA. Total doses given, 3.73 kGy. (□) Uranyl acetate, (●) uranyl nitrate, (○) copper acetate, (▲) iron(III) nitrate, (■) distilled water.

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

Table 1 shows that the percentage equilibrium swelling values of the hydrogel are low (410–960%) in solutions of heavy metal ions and high (1480%) in water. The heavy metal ions interact with the carboxyl groups of maleic 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 heavy metal ions.

The number (n) to determine the type of diffusion was found to be over 0.50 in the experiments. Hence the diffusion of water and heavy metal ions into the hydrogel has a *non-Fickian* character (19). In this kind of diffusion, diffusion and relaxation are isochronal effective. The values

TABLE 1
The parameters of Swelling and Diffusion of AAm/MA Hydrogel Containing 40 mg MA. 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	1480	2.0	0.66	8.83	11.33
Uranyl acetate solution	960	4.2	0.58	5.33	6.33
Uranyl nitrate solution	630	7.9	0.63	6.33	7.00
Copper acetate solution	480	5.3	0.59	7.17	8.00
Iron(III) nitrate solution	410	4.2	0.57	6.00	6.33

given in the Table 1 show that the diffusion coefficients of water are larger than the other values so diffusion of heavy metal ions into gel pores is difficult. Table 1 also shows that the values of the intrinsic diffusion coefficient of hydrogels in water and solutions of heavy metal ions are larger than their diffusion coefficient values. Equation (3) gives a measure of the mass flow of the whole system as well as of the diffusion. Equation (4) gives the intrinsic diffusion coefficient for cases where there are no mass action effects (18).

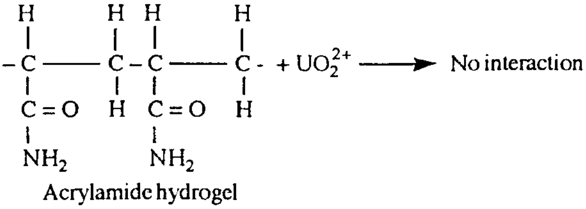
The acetate and nitrate anions of the heavy metal salts affect swelling. Acetate salts dissolve as molecules in the aqueous solution while nitrate salts dissolve as ions (15). Thus, cations of salts containing nitrate anions interact with the carboxylic group of MA in the hydrogels, so the swelling of these hydrogels in a solution of nitrate salts are small compared to the swelling of these hydrogels in a solution of acetate salts. These interactions can be electrostatic interaction such as ionic or ion–dipole interactions (7).

Adsorption

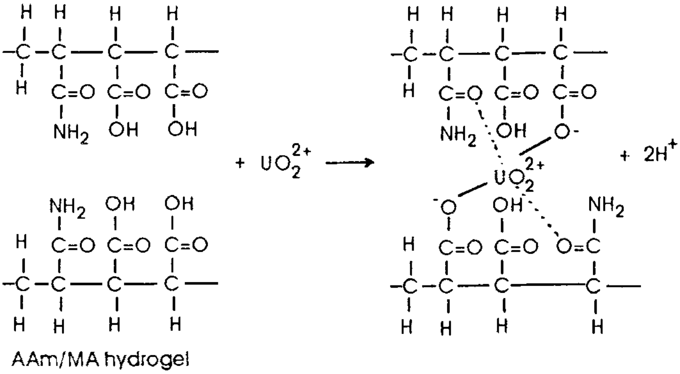
We investigated the adsorption of some heavy metal ions onto the AAm/MA hydrogels.

Many studies have been published on the polyelectrolyte behaviors of alternating copolymers of maleic acid in aqueous solutions. Several characteristic properties has been observed: conformational transition, a two-step dissociation process of dicarboxylate groups, binding of counterions, etc. These properties of maleic acid copolymers are attributed to two factors: 1) hydrophobic interaction of nonpolar side chains, and 2) short-range electrostatic interaction of a pair of adjacent nearest-neighbor carboxylate groups (7).

In order to observe the adsorption of some heavy metal ions, AAm and AAm/MA hydrogels were transferred into aquatic solutions of uranyl acetate, uranyl nitrate, copper acetate, iron(III) nitrate, cobalt nitrate, nickel chloride, and chrome nitrate, and allowed to stand for 2 days. At the end of this time, AAm/MA hydrogels in solutions of UN, UA, iron(III) nitrate and copper acetate showed dark colorations of the solutions, while AAm had not sorbed any heavy metal ions from their solutions. Since poly(acrylamide) is a nonionic polymer (20), ionizable groups on the polymer were increased by the addition of maleic acid to acrylamide monomer. Therefore, these hydrogels have many carboxyl groups which can be cause an increase of interaction between heavy metal ions such as uranyl, iron, and copper ions, and the carboxyl groups in the hydrogels. These heavy metal ion solutions were used in the experiments of adsorption. On the other hand, selected uranyl salts from two different uranyl ion sources, uranyl nitrate and uranyl acetate, were used for the investigation of the effects of anionic groups of uranyl salts. The possible interactions between uranyl ion and AAm and AAm/MA hydrogels are shown in Schemes 1 and 2.



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



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

The adsorptions of uranyl ions onto the hydrogel system containing AAm/MA were investigated. The mass of adsorbate 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 adsorbate per gram dry adsorbent, C_i and C are the initial and equilibrium concentrations of the solution of adsorbate in $mg \cdot L^{-1}$, V_t is the total volume of solution of adsorbate in liters, and m is the mass of dry adsorbent in grams.

The graphs of q_e against the equilibrium concentrations of uranyl ions, C, are plotted in Fig. 3, which shows that adsorption of uranyl ions from of UA and UN solutions onto AAm/MA hydrogels corresponds to isotherms of Type II (21). In the vast majority of cases, physical adsorption gives rise to a Type II isotherm. The model is restricted 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 the 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 size (21).

The adsorption of uranyl ions from UA solutions is higher than from UN solutions (Fig. 2). Some interactions that are affected by the swelling properties of hydrogels are effective for UN and UA adsorptions onto AAm/MA hydrogels.

Type II isotherms obtained experimentally display a rather long straight portion of yields following an inflection point. 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 (21).

The monolayer capacities of AAm/MA for uranyl ions in the aqueous solutions of uranyl acetate and uranyl nitrate were found by the Point B

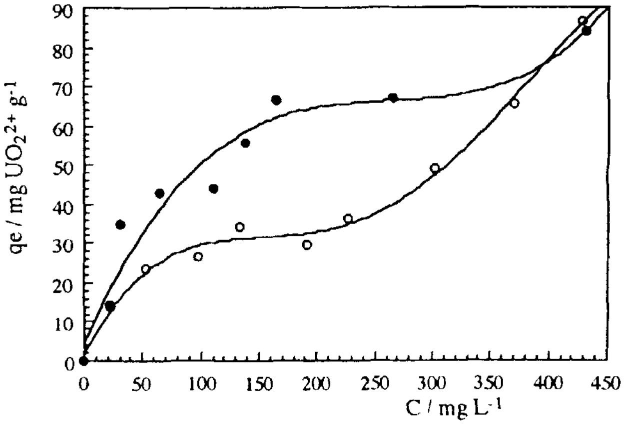


FIG. 3 The isotherms of adsorptions of uranyl ions onto AAm/MA hydrogel: (○) uranyl nitrate, (●) uranyl acetate.

method from Fig. 3 to be 66 and 32 mg·g^{-1}, respectively. These results are parallel to the adsorption results.

Hydrogels taken out the solutions of uranyl ion were held for 3 days in distilled water, and desorptions of uranyl ions were showed by the light yellowish coloration of the water; the hydrogels returned to their original colors. Therefore, this adsorption of uranyl ions is physical adsorption.

The variation of adsorptions of uranyl ions from a UN solution with a concentration of 200 mg UO_2^{2+} L^{-1} and from a UA solution with a concentration of 250 mg UO_2^{2+} L^{-1} with the content of MA in the hydrogels and the irradiation dose was investigated. These uranyl ion concentrations were selected from the linear portion of the adsorption isotherms in Fig. 3. The mass of adsorbed uranyl per gram of hydrogel versus the MA content of the hydrogel and the irradiation dose are plotted in Figs. 4 and 5, respectively.

Figure 4 shows that the adsorption of uranyl ions on AAm/MA hydrogels increases with an increase with the MA content in the hydrogels. The increase of carboxyl groups in the hydrogels with an increase of MA content is caused by electrostatic interactions between the cationic uranyl ions and the anionic groups of maleic acid in the hydrogels.

Figure 5 shows that the adsorption of uranyl ions increases with an increase of irradiation dose at low doses, while the adsorption are approximately constant at high doses. The hydrogel crosslinks increase with increasing irradiation dose and cause the pores to become smaller. It is therefore difficult for the large uranyl ions to enter the small pores and to be held there.

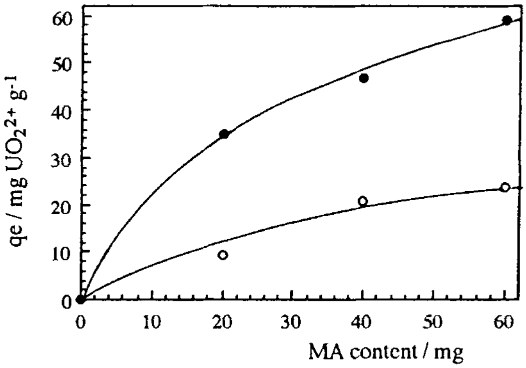


FIG. 4 The variation of adsorption of uranyl ions onto AAm/MA hydrogels with MA content. Total doses given, 2.60 kGy. (○) Uranyl nitrate, (●) uranyl acetate.

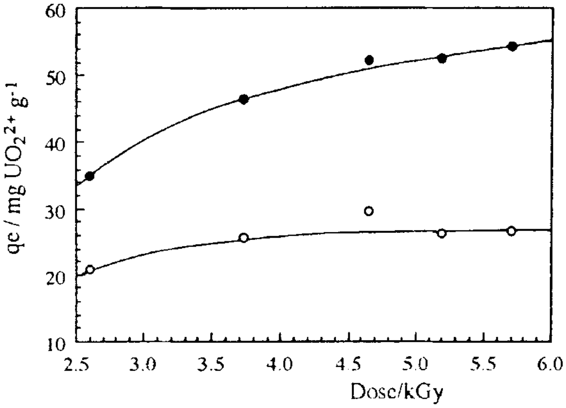


FIG. 5 The variation of adsorptions of uranyl ions onto AAm/MA hydrogels containing 40 mg of MA with the irradiation doses: (○) uranyl nitrate, (●) uranyl acetate.

As our final experiment, the adsorption of iron and copper ions onto the hydrogels was investigated. Plots of q_e versus MA content in the hydrogels are shown in Fig. 6. It shows that the adsorptions of iron and copper ions onto the hydrogels increases with an increase of MA content in the hydrogels. The increase of carboxyl groups in the hydrogels with the increase of MA content is caused by electrostatic interactions between the cationic ions of iron and copper and the anionic groups of maleic acid in the hydrogels.

The adsorption of iron and copper ions onto the hydrogels with an increase in irradiation dose did not show significant differences.

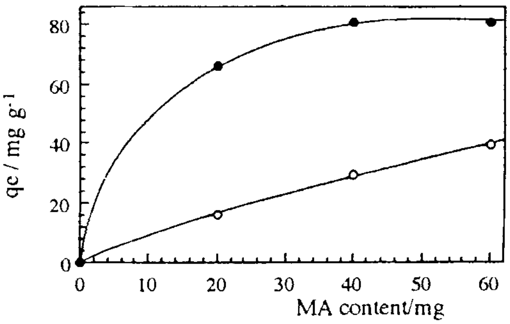


FIG. 6 The variation of adsorptions of iron and copper ions onto the hydrogels with MA content. Total doses given, 2.60 kGy. (○) Iron(III) nitrate, (●) copper acetate.

Hydrogels removed from solutions of iron and copper ions were held for 3 days in distilled water. The desorption of copper ions was shown by the light bluish coloration of water; the hydrogels also returned to their original colors. Therefore, the adsorption of copper ion is physical adsorption. However, the reddish AAm/MA hydrogel of adsorbed iron ion did not show any desorption. Therefore, the adsorption of iron ions is possibly chemical adsorption.

CONCLUSION

This study showed that AAm/MA hydrogels adsorb heavy metal ions such as uranyl, iron, and copper ions, while AAm hydrogels do not absorb any heavy metal ions.

Swellings experiments showed that the percentage equilibrium swelling of hydrogels is low (410–960%) in solutions of heavy metal ions, while the value is high (1480%) in water. The diffusion of water and heavy metal ions into AAm/MA hydrogels is of a non-Fickian character.

Type II adsorption was found in experiments of the adsorptions of uranyl ions. A Type II isotherm is characteristic of multilayer adsorption. The adsorption of heavy metal ions increased with the MA content in the hydrogels.

AAm/MA hydrogels can be used as sorbents for heavy metal ion water pollutants. Immobilization of some inorganic contaminants in hydrogels can clean wastewater, which is an important problem of environmental chemistry.

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