Enhancement of Uranyl Ion Uptake by Prestructuring of Acrylamide–Maleic Acid Hydrogels

PINAR AKKAS, OLGUN GÜVEN

Department of Chemistry, Hacettepe University, Beytepe 06532, Ankara, Turkey

ABSTRACT: Acrylamide–maleic acid (AAm–MA) hydrogels were prepared by gamma-irradiation of their aqueous solutions. UO_2^{+2} ion uptake on P(AAm–MA) hydrogels was investigated using two types of gel systems prepared by a simple irradiation method and a prestructured reaction. It has been observed that gels prestructured with UO_2^{+2} ions adsorbed approximately 15–20% more UO_2^{+2} ions than gels prepared in pure water (the usual method). It was also found that the uranyl ion adsorption capacity of hydrogels increased with an increasing amount of maleic acid in the gel system and an increasing concentration of uranyl ion in the solution. A possible interaction mechanism between the groups in the copolymeric gels and UO_2^{+2} ion has been proposed based on the stoichiometry and the spectroscopic evidence. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 284–289, 2000

Key words: uranyl ion uptake; hydrogels; prestructuring of gels; acrylamide–maleic acid hydrogels

INTRODUCTION

A hydrogel is defined as a crosslinked hydrophilic polymer or copolymer that is capable of imbibing a considerable quantity of water, up to swelling equilibrium. Hydrogels have widespread application in the bioengineering, biomedicine, pharmaceutical, veterinary, food industry, agriculture, photographic technology, and other fields. They are used as controlled-release systems for drugs, in the production of contact lenses and artificial organs in biomedicine, and as adsorbents for the removal of some agents in environmental applications. Many types of adsorbents have been tested for the removal of metal ions. In order to increase and improve the metal ion uptake capacity of hydrogels, either comonomers carrying some specific ligands are incorporated into their structures or the chemical structure of repeating units is chemically modified.

Typical examples of the former are acrylamide–itaconic acid and acrylamide–maleic acid systems.[1–4] Acrylonitrile-based polymers recently have been converted into amidoxime structures in order to improve their adsorption properties. Amidoxime groups containing polymeric adsorbents are notable because of their high loading of metal ions.[5–9] During the last few years prearrangement reactions have been developed for the enhancement of the adsorption of metal ions. For example, Kabanov[10] and Nishide[11] developed prearrangement reactions to increase the capacity and selectivity of some systems for prechosen metal ions. The principle applied involves the use of a polymer composition "memory" and conformational arrangement of the molecules of a noncrosslinked polymer into a position suitable for complex formation with a metal and the subsequent fixing of the conformations formed by intermolecular crosslinking with removal of the template ions from the crosslinked system. In this study acrylamide–maleic acid hydrogels were prepared and tested for uranyl ion uptake with the purpose of removing these pollutants from the

aqueous environment. The same hydrogel systems were later prepared in a prestructured manner to increase their capacities for the removal of uranyl ions.

EXPERIMENTAL

Materials

In this study acrylamide (AAm) and maleic acid (MA) monomers and uranyl acetate (UA) were obtained from BDH. Sodium salicylate, used in the determination of the uranyl ion concentration, was obtained from Fisher. All materials were used as received.

Preparation of Hydrogels

In the first part of this study, aqueous solutions of monomers of 1 g AAm and 20, 40, 60, and 80 mg MA were prepared in 1 mL of pure water at different compositions (AAm–MA mole ratios: 98.8: 1.2, 97.6:2.4, 96.5:3.5, 95.3:4.7). Hydrogels obtained from these systems are denoted as P(AAm–MA)- 1, 2, 3, and 4, respectively. These solutions were placed in PVC straws 3 mm in diameter and irradiated in a Gammacel 220–type irradiator at different doses between 0.45 and 18.00 kGy to find the dose required for maximum gel formation. After gelation, hydrogels, obtained in long cylindrical shapes, were cut into pieces 3–4 mm in length. These hydrogels were subjected to Soxhlet extraction, with water as a solvent, then dried in a vacuum oven at ambient temperature to a constant weight. Uncrosslinked polymer and/or residual monomers were removed from the gel structure by this extraction. Percentage gelation, that is, percentage conversion of monomers into an insoluble network, was based on the total weight of diprotic acid and monomer in the initial mixture. The amount of MA in the monomer, polymer, and/or copolymer form was determined by titration of extract against NaOH (0.05N) to a phenolphthalein end point, but no titrate was consumed for all AAm–MA hydrogels reaching 100% conversion, which was obtained for all mixtures after 15 kGy irradiation. The gels prepared, purified, and dried according to the above-mentioned procedures were stored in vials in the dark and at room temperature for further use in swelling and adsorption experiments. The reproducibility of the swelling behaviors of gels was checked by repeated swelling/deswelling

tests. During the second use of a dried gel, a slight increase in swelling was observed because of the more relaxed configuration attained by the polymer chains during the first swelling process.[1] It has been shown that similar gels produced for biomolecule adsorption purposes can be used up to eight times without any change in their swelling/deswelling ratios.[12]
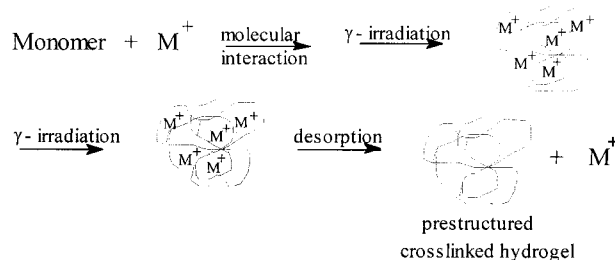
The second part of the study explored the uptake of UO_2^{+2} ions by hydrogels. To increase the capacity of UO_2^{+2} ion uptake while preparing the AAm–MA solutions, uranyl acetate (UA) solutions with UO_2^{+2} ions in three different concentrations (500, 1000, and 1500 mg/mL) were used instead of pure water. Thus, prestructured hydrogels were prepared by radiation processing of the monomers dissolved in an aqueous salt solution at 15 kGy. The hydrogels, obtained in long cylindrical shapes, were cut into pieces 3–4 mm long. The UO_2^{+2} ions held by the crosslinked hydrogels were desorbed into 0.5M HCl for 48 h, and these prestructured hydrogels were dried for further use. Although this may not be considered as a molecular printing process because of the formation of some favored structures during gelation, UO_2^{+2} ion uptake showed an increase.

UO_2^{+2} ion uptake of gels that were prepared with distilled water and prestructured with UA solution were followed kinetically for four MA amounts and three UO_2^{+2} ion concentrations. For this purpose, 0.3 g of both types of dry P(AAm–MA) hydrogels was transferred into a 100-mL solution of UA in three concentrations at 25°C and shaken continuously.

The number of UO_2^{+2} ions in the solution at time intervals was determined with Philips a 8715 UV–vis spectrophotometer. Sodium salicylate was used as a complexing agent, giving an absorption maximum at 430 nm. All results were given as an average of three measurements. The concentration of the UO_2^{+2} ions in the solution was determined with an accuracy of ±5% (95% confidence).

RESULTS AND DISCUSSION

In order to impart chelating properties to the base polymeric structure—polyacrylamide, in this case—we have tried to introduce a diprotic acid, namely, maleic acid, into the hydrogel structure. Maleic acid does not homopolymerize, as can be expected from its 1,2-disubstituted structure, when it is irradiated in an aqueous solution. A
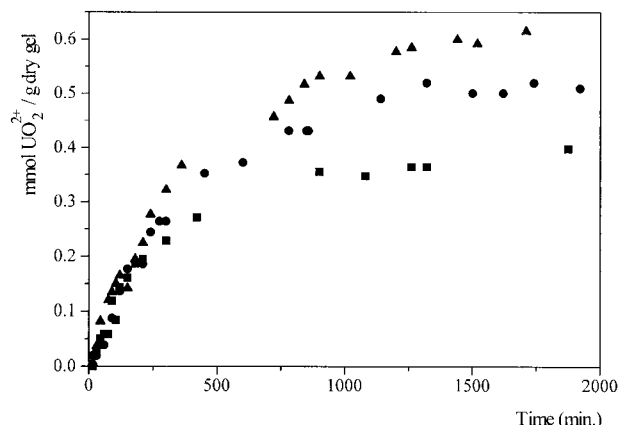
Figure 1 Prestructured scheme of polymer with metal ions.

Figure 2 The adsorption curves of P(AAm/MA)-4 hydrogels in different concentrations of UO_2^{+2} ion solutions: (■) 500 ppm; (●) 1000 ppm; (▲) 1500 ppm.

parallel trial irradiating pure solid maleic acid or its aqueous solutions provided additional confirmation of this expectation. In the presence of a monomer with a high polymerization tendency such as acrylamide, however, it randomly incorporated into the main chain.[1] Similar behavior has been observed when maleic acid is irradiated in the presence of *N*-vinyl-2-pyrrolidone. Due to its low solubility in water, it was not possible to prepare copolymers with maleic acid contents higher than what is stated in the Experimental section. Within the concentration limits used in this study it is known that there is 1 MA unit for every 20–100 AAm repeating units in the gels prepared.

It has been found that for all P(AAm–MA) gel systems, the percentage of monomer–gel conversion increased with an increase in the irradiation dose. After irradiations doses of 15 kGy and higher it was determined that 100% gelation was achieved for every AAm–MA composition. A similar dose–conversion relation was observed with the attempt to obtain hydrogels in prestructured forms. Figure 1 shows schematically the prestructuring process for the prestructuring reaction: First a complex between a monomeric ligand and a metal ion (M^+) is formed and simultaneously crosslinked by γ radiation; then the metal ion M^+ is removed by treating with a dilute acid solution.[10,11] In this study UA solutions containing 500, 1000, and 1500 mg/mL UO_2^{+2} ion concentrations were used to carry out prestructuring reactions, and the uptake of UO_2^{+2} ions at these concentrations was later studied. At the end of the uptake process, UO_2^{+2} ion concentrations were calculated as mmol UO_2^{+2}/g dry gels, and time versus concentrations curves were plotted.

In order to see whether the base polymer used in the preparation of hydrogels—namely, poly(acrylamide)—has any adsorption capacity for UO_2^{+2} ions, first pure PAAm hydrogel was brought into contact with UO_2^{+2} solutions. No adsorption was observed. In the copolymeric hydrogels, however, the intake of UO_2^{+2} ions was evident from the yellowish color of the gels. Figure 2 shows the uranyl ion uptake from different concentrations of UO_2^{+2} ion solution. By increasing UO_2^{+2} ion concentration in UA solutions, the number of adsorbed UO_2^{+2} ions increased for a given amount of adsorbent. It has also been observed that increasing the MA content in the gel system caused an increase in the adsorbed UO_2^{+2} ions for a given initial solution concentration (Fig. 3). This increase shows that the increase of adjacent carboxyl groups in the hydrogels following an increase of MA content favored the electrostatic
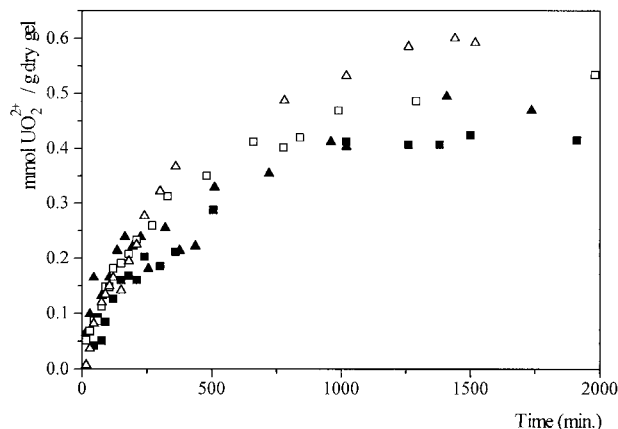
Figure 3 The adsorption curves of P(AAm/MA)- 4 hydrogels with different amounts of MA and prestructured with 1500 ppm UO_2^{+2} ion solution: (■) P(AAm/MA)-1; (▲) P(AAm/MA)-2; (□) P(AAm/MA)-3; (△) P(AAm/MA)-4.

Table I   Maximum Adsorption of UO_2^{+2} Ions by P(AAm/MA) Hydrogels from Different Solutions

Gel Name	UO_2^{+2} (500 ppm)		UO_2^{+2} (1000 ppm)		UO_2^{+2} (1500 ppm)	
	a	b	a	b	a	b
P(AAm/MA)-1	0.29	0.27	0.39	0.34	0.45	0.38
P(AAm/MA)-2	0.34	0.27	0.49	0.42	0.50	0.45
P(AAm/MA)-3	0.35	0.29	0.52	0.43	0.60	0.52
P(AAm/MA)-4	0.39	0.36	0.52	0.47	0.61	0.53

Values given as mmol UO_2^{+2}/g dry gel: (a) prestructured, (b) prepared with water.

interactions between the cationic UO_2^{+2} ions and the anionic and polar groups of the MA in the hydrogels. The number of adsorbed UO_2^{+2} ions as a function of the amount of MA and concentration of UO_2^{+2} ions are given in Table I. In order to see the specific effect of MA on enhancing UO_2^{+2} adsorption, a comparative test was made using AAm–acrylic acid hydrogels. Under similar experimental conditions it has been observed that a hydrogel of AAm–AA with a 1:2 mole ratio adsorbed only half the UO_2^{+2} ions adsorbed by the P(AAm/MA)-4 gel used in this work. This shows the importance of spatial distribution of the carboxylic acid groups to provide the best chelating configuration.

Figure 4 shows the adsorption of uranyl ions from UO_2^{+2} ion solutions with P(AAm/MA) hydrogels prepared by using the usual and the prestructuring methods. At the beginning of the process the adsorption is rather fast. After some time, however, equilibrium was reached for both types of gels. It was observed that gels prestruc-

tured by uranyl ions adsorbed approximately 15–20% more UO_2^{+2} ions than gels prepared by the usual procedure. A similar result was observed previously by Efendiev and Kabanov.[10] They prepared a complex forming polymeric sorbents. Diethyl esters of vinyl phosphoric acid and acrylic acid were chosen as initial monomers to prepare these polymer sorbents. These adsorbents were prepared in the presence of an adsorbing substance that provided the prestructured reaction. An investigation of the copper ion uptake by the crosslinked sorbents showed that the prearrangement of macromolecules for this ion uptake made it possible to increase the sorption capacity and to significantly improve their characteristics in composition with the same copolymer crosslinked by the usual method without such prearrangement.[8]

Nishide et al. crosslinked poly(4-vinyl pyridine) with 1,4-dibromobutane with some template metal ions, and the adsorption behaviour of copper, cobalt, zinc, and cadmium ions on these resins was studied. The resin prepared with a metal ion as template preferentially adsorbed the metal ion used as a template.[11,13]

Both these reports and our work indicate that, as described in Figure 1, the presence of a specific ion during the preparation of gel structures provides a geometric arrangement that improves further adsorption of the same ion from the solution. A somewhat similar ordering of acrylic acid monomers along prepolymerized poly(acrylic acid) chains has been reported in the works of Chapiro et al.[14,15] The term *prestructuring,* used here to describe the process of the ordering of chain segments around uranyl ions, does not imply a very well-controlled molecular imprinting. It is suggested that the separation performance of gels is enhanced by an improved control of mesh size or microporosity of gels through interactions pro-
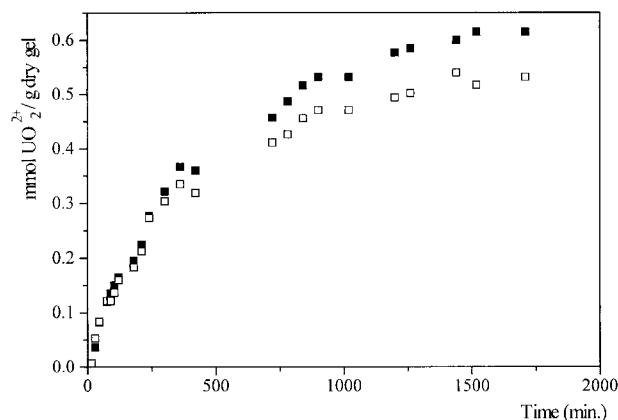
Figure 4   The adsorption curves of P(AAm/MA)-4 hydrogels in 1500 ppm UO_2^{+2} ion solutions: (■) pre-structured with 1500 ppm UO_2^{+2} ion solutions; (□) prepared with distilled water.

Table II   Stoichiometric Ratios Calculated from Maximum Adsorption of P(AAm/MA) Hydrogels

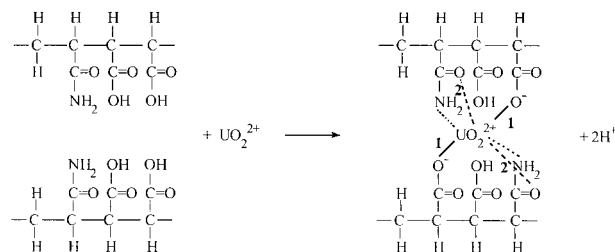| Gel Name	UO_2^{+2} (500 ppm)			UO_2^{+2} (1000 ppm)			UO_2^{+2} (1500 ppm)		
	a	b	c	a	b	c	a	b	c
P(AAm/MA)-1	1.72	1.71	0.70	2.30	2.28	0.94	2.66	2.64	1.08
P(AAm/MA)-2	1.03	1.02	0.42	1.47	1.46	0.60	1.50	1.49	0.61
P(AAm/MA)-3	0.71	0.70	0.29	1.07	1.06	0.44	1.23	1.22	0.50
P(AAm/MA)-4	0.61	0.60	0.25	0.81	0.80	0.33	0.96	0.95	0.39

Values calculated by using ionization constant MA and SA. (a) experimental (b) according to MA (c) according to SA.

vided by the specific ions used as templates during their preparation.

Consequently, this study sought the possible interaction mechanism between groups that are sensitive in the copolymeric gels for UO_2^{+2} ion. For this purpose stoichiometric and experimental data obtained from FTIR spectra were used. First the data given in Table I were generated and mmol UO_2^{+2} ion/mmol MA ratios were determined. The data on stoichiometry of complexation are given in Table II.

P(AAm/MA)-1, which contains the lowest amount of MA, and 1500 ppm UO_2^{+2} solution, which corresponds to the most concentrated solution, were selected in order to investigate UO_2^{+2} ion adsorption stoichiometry onto MA. To propose a stoichiometry and adsorption mechanism, analytical calculations were done for both MA and succinic acid (SA), which is the saturated form of maleic acid (the polymerization mechanism is thought to proceed from a double bond on the MA).

The pH of the uranyl acetate solutions prepared in this work was stable at pH 4.5. The ionization degree of the first hydrogen of MA and SA were calculated as 99% and 40%, respectively, at pH 4.5. Since the ionization degree of the second hydrogen of MA was less than 1% at this pH, the ionization of the second hydrogen was neglected. Experimental results show that, for the

P(AAm/MA)-1/1500ppm UO_2^{+2} ion system, UO_2^{+2} ion uptake followed the ratio 2 UO_2^{+2} ion/1 MA. The theoretical calculations, which are based on MA structure, and the experimental results are in very good accordance. But for the SA structure this ratio found as 1 UO_2^{+2} ion/1 MA. Based on these findings, a mechanism for the binding of UO_2^{+2} to MA is proposed. This is shown in Figure 5. In order to propose a possible binding mechanism, FTIR spectra were analyzed. Figure 6 shows the FTIR spectra of P(AAm/MA)-3 gels before and after UO_2^{+2} ion adsorption. As can be seen from Figure 6, after UO_2^{+2} adsorption a new peak appeared at 935 cm^{-1}. This peak corresponds to interactions between the metal ions and ionizable groups.[16] According to these experimental results, the best possible interaction mechanism between P(AAm/MA) and UO_2^{+2} ions is proposed according to step 1, indicated on the mechanism shown in Figure 5.

CONCLUSION

In some previous studies made on the adsorption and removal of UO_2^{+2} ions from aqueous solutions, it had been determined that hydrogels pre-

Figure 5   Possible interaction mechanisms between P(AAm/MA) hydrogels and UO_2^{+2} ions.
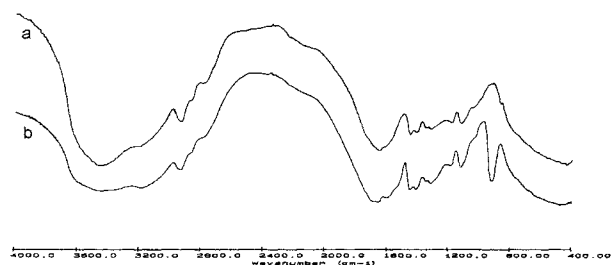
Figure 6   FTIR spectra of P(AAm/MA)-3 hydrogels a) before UO_2^{+2} ion adsorption and b) after UO_2^{+2} ion adsorption.

pared from acrylamide and maleic acid were effective for such a separation process.[3] In this work the same type of hydrogel was prepared in a prestructured form by synthesis in the presence of a particular adsorbent. It was shown that such a prestructuring, by using UO_2^{+2} as a template ion, improved the UO_2^{+2} ion uptake capacity of similar hydrogels by 15–20%, as compared to conventionally prepared systems. The importance of using diprotic acids in enhancing the adsorption capacity through efficient chelating ability was observed. A mechanism of interaction between UO_2^{+2} ions and polymer chains is proposed based on the information obtained on spectroscopic evidence and adsorption stoichiometry.

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