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POLAROGRAPHIC DETERMINATION OF URANYL ION ADSORPTION ON POLY-(2-HYDROXYETHYL METHACRYLATE/ITACONIC ACID) HYDROGELS

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ABSTRACT

Copolymeric hydrogel adsorbents containing hydrophilic groups both providing swelling in water and chelating with uranyl ions were prepared by using γ-rays and their adsorptive ability for recovering uranium from aqueous media was investigated. Uranyl adsorption capacities of the hydrogels were determined by polarographic techniques to be 4.9–6.0 (mg UO_2^{+2}/g dry gel) at pH 3.87 and 4.2–5.6 (mg UO_2^{+2}/g dry gel) at pH 5.4 from 15 ppm uranyl nitrate solution, depending on the mole content of IA in the hydrogel. The adsorption studies show that the temperature and the ionic strength of the solution influence uranyl ion adsorption by P(HEMA/IA) hydrogels.

Key Words: Hydrogel; Poly(2-hydroxyethyl methacrylate/itaconic acid); Polarographic determination; Uranyl adsorption.

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INTRODUCTION

The removal and recovery of metal ions has a potentially vast range of applications in conserving environment and using resources. In this regard, the chelate–forming polymeric and copolymeric ligands have been extensively studied and many reviews are available in the field (1–5). These polymeric and copolymeric materials have been used for the preconcentration and separation of trace elements from seawaters, in particular, the inclusion of diprotic acid units copolymeric matrices as the complexation centers results in promising materials for the separation of heavy metal ions from aqueous solution (6).

Because of the anticipated exhaustion of terrestrial uranium reserves in the near future, during the last three decades, further research has been directed to recovering uranium from non-conventional sources, such as coal and natural waters (0.1–10 mg U/m^3), and especially from seawater (2.8–3.3 mg U/m^3). The recovery of uranium from the contaminated water found in flooded mines (0.1–15 mg U/m^3) also presents a very important environmental problem to be solved. The process of using adsorbents is thought to be the most effective method for recovering uranium because of the high selectivity for uranium, the ease of handling, environmental safety (7).

The water uptake, as well as the metal ions uptake, increases in proportion to the kind and the amount of hydrophilic groups because the diffusion of aqueous solutions in more hydrophilic polymers is faster than in less hydrophilic polymers, which is a rate-determining step for adsorption (8).

Differential pulse polarography has been used for trace element analysis with priority because of its highly sensitive and inexpensive instrumentation (9). Other accessible techniques capable of heavy metal ion determination, such as atomic absorption spectroscopy, UV spectrometry and Gamma spectrometry, often do not offer sufficient sensitivity and selectivity for accurate determination at the trace concentration. These are all time-consuming procedures and the loss of these metals is also possible.

We now report the synthesis of the diprotic acid containing 2-hydroxy ethyl methacrylate/itaconic acid copolymers and the examination of their adsorption abilities toward the uranyl ions. For the determination of adsorbed uranyl ion, polarographic technique was used in this study. The effect of external stimuli, such as pH temperature and ionic strength on the uranyl ions adsorption capacity of these hydrogels has also been investigated.

EXPERIMENTAL

Chemicals

The two monomers used in this study, HEMA and IA, were obtained from Merck and BDH, respectively. The glacial acetic acid, phosphoric acid, and boric acid used to prepare Britton–Roinson (B-R) buffers were obtained from Merck. The uranyl nitrate (UN) used for the adsorption studies was purchased from Fisher.

Preparation of Hydrogels

Three components were used in the preparation of HEMA/IA hydrogels: HEMA, IA, and water. Aqueous solutions of monomers were prepared in 1 mL of pure water in different compositions (HEMA/IA mole ratios, 97.3/2.7, 96.0/4.0, 94.7/5.3, 89.9/10.1). These monomer solutions were placed in the PVC straws of 4 mm diameter and irradiated by 2.8 kGy in air at ambient temperature in PX-γ-30 Isslodovateji irradiator at a fixed dose rate of 3.36 kGy h^{-1}.

Compositions of Hydrogels

Hydrogels obtained in long cylindrical shapes were cut into 3–4 mm pieces. The pieces were dried in a vacuum oven at 315 K to constant weight and subjected to Soxhlet extraction with water. The uncross-linked polymer and unreacted IAs were removed from the gels by this extraction. The extracted gel pieces were dried again in vacuum oven at 315 K to constant weight. The amount of unreacted IA in the aqueous extract was determined by titration with NaOH (0.05 M) to a phenolphthalein end point. Mole percentages of IA in the Gel 1, Gel 2, Gel 3, and Gel 4 were found to be 2.7, 4.0, 5.3, and 10.1, respectively.

Swelling Studies

Dried hydrogels were left to swell in a solution of desired pH (1–8) at ambient temperature until equilibrium (maximum swelling) was attained. The swollen gels were removed from the swollen media, quickly bottled with a dry filter paper, and weighed. The equilibrium-swelling ratio of hydrogels was determined gravimetrically, assuming the additivity of volume through the following equation:

$$Q = 1 + (w_2/w_1 - 1)\, \rho_{\mathrm{polymer}}/\rho_{\mathrm{solvent}} \tag{1}$$

where Q is the swelling ratio of hydrogels by volume, w_1 is weight of the hydrogel before swelling, w_2 is the weight of the hydrogel at equilibrium swelling $\rho_{\mathrm{polymer},}$ and ρ_{solvent} are densities of polymer and solvent, respectively.

Adsorption of UO_2^{+2} on Hydrogels

A certain amount of P(HEMA/IA) hydrogel (~0.05 g) was put into 20 mL $UO_2(NO_3)_2 \cdot 6H_2O$ solution (pH = 1–7) in concentration range 5–50 ppm and allowed to equilibrate for 96 hours at ambient temperature. Then the adsorbent was taken away by decantation from the solution. The equilibrium concentration of UO_2^{+2} ion in the solution was determined by Differential Pulse Polarographic technique (DPP). Ten mL of uranyl nitrate (UN) (5–50 ppm) in the polarographic cell was deaerated by passing pure nitrogen gas for about 5 min. Polarograms were taken by scanning the potential from 0.00 mV to about –1300 mV, at the initial time and 96 h later. The UO_2^{+2} ion showed two peaks at –200 mV and –950 mV in 0.1 M HCl during the potential scan. Both peaks decreased due to the adsorption of UO_2^{+2} ions on gels (see Fig. 1). From the differences between the peak cur-

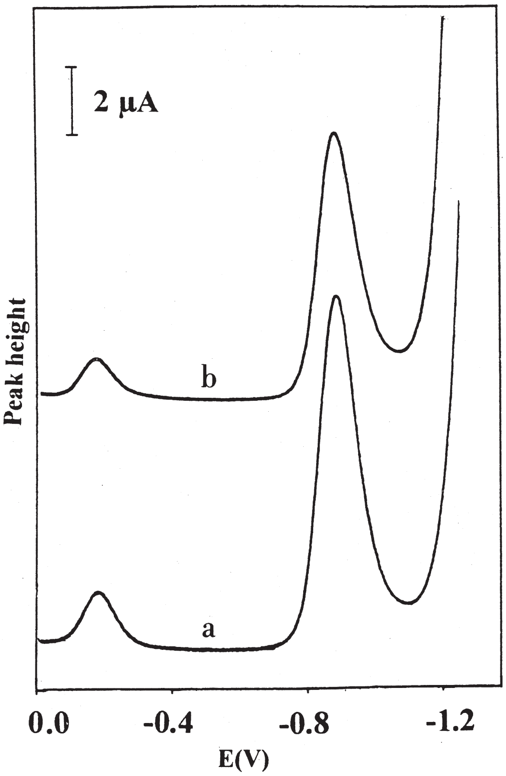


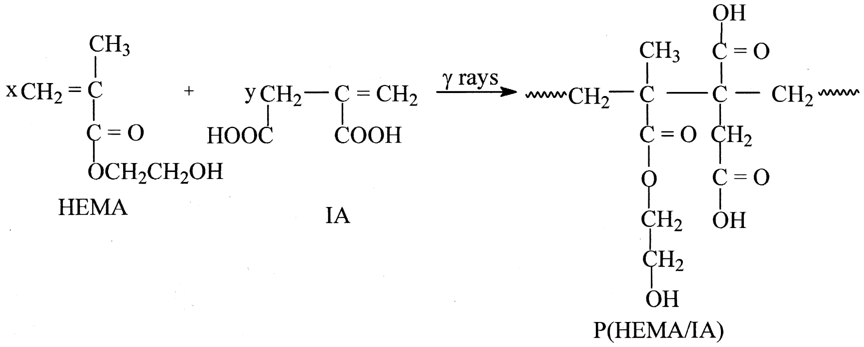
Figure 1. Differential pulse polarograms of UO_2^{+2} ion (30 ppm). (**a**) Polarogram of 30 ppm UO_2^{+2} before adsorption. (**b**) Polarogram of 30 ppm UO_2^{+2} after adsorption (96 h).

rents, the amount of adsorbed UO_2^{+2} ions was calculated. The conditions were drop time 1 s, current range 0.2 mA, pulse amplitude 50 mV, and scan rate 5 mV s^{-1}.

RESULTS AND DISCUSSION

Synthesis of Hydrogels

When HEMA/IA/water is irradiated with γ-rays, free radicals are generated in the aqueous solution. Random reactions of these radicals with the monomers lead to the formation of copolymers of HEMA/IA. When the irradiation dose is increased beyond the certain value, the polymer chains cross-link and gel is then obtained. γ-Rays induced copolymerization of HEMA and IA is a free radical process, and can be designated as follows:



Percentage gelation, i.e., percentage conversion of monomers into insoluble network, was based on the total weight of diprotic acid and monomer in the initial mixture. One hundred percent gelation was observed for HEMA/IA mixtures after 2.8 kGy irradation.

Swelling Behavior of Hydrogels

The equilibrium swelling behaviors of P(HEMA/IA) hydrogels were investigated as a function of pH at fixed ionic strength ($I = 0.1$) and temperature ($T = 25°C$). Figure 2 shows the swelling behaviors of these hydrogels containing various mole ratios of IA at various pH media. Swelling of hydrogels was found to increase with pH. In all compositions, the maximum extent of swelling reacted at pH 7 and above, due to the complete dissociation of acid groups of IA

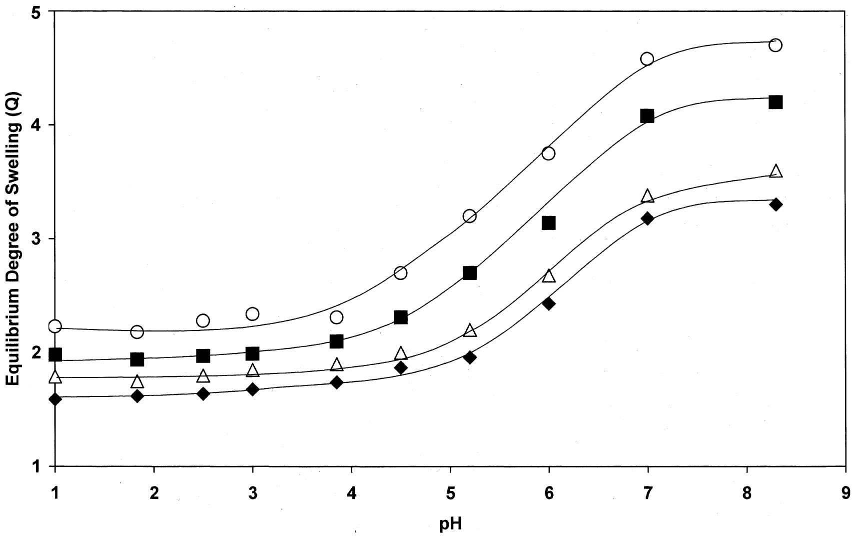
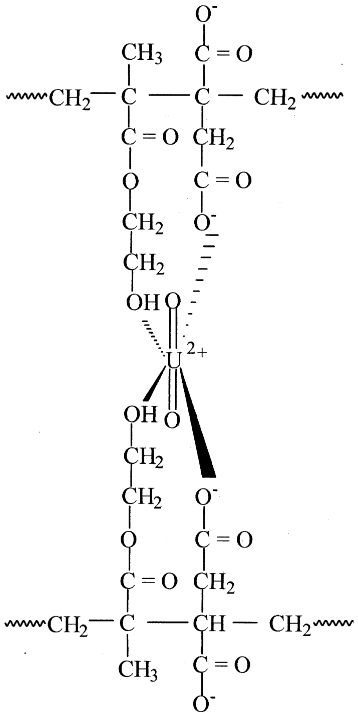


Figure 2. Effect of pH on the equilibrium degree of swelling values of P(HEMA/IA) Hydrogels: (◆) Gel 1, (Δ) Gel 2, (■) Gel 3, (○) Gel 4.

at this pH value and above. The first and second dissociation constants of IA were $pK_{a1} = 3.85$ and $pK_{a2} = 5.44$. Since the first and second dissociation constants for IA were rather close, the consecutive swellings near these pH values overlap and double–step swelling versus pH curves can be observed in Fig. 2. Charged groups attached to the polymeric network structure played an essential role in swelling properties. Previous studies have shown that swelling behaviors of charged hydrogels are a function of the ionic composition of the swelling agent (10).

Adsorption of UO_2^{+2} on Hydrogels

To determine the adsorption of UO_2^{+2} ions, P(HEMA/IA) hydrogels were placed in aqueous solutions of uranyl nitrate and allowed to equilibrate for 4 days. After this time, the colors of UO_2^{+2} ion–adsorbed P(HEMA/IA) were observed to change from light yellow to dark brown. P(HEMA/IA) hydrogels have many carboxylic acid groups that can increase the interaction between uranyl ions and acidic groups in the hydrogels. Possible interactions between uranyl ion and acidic groups can be designated as follows:



The amount of adsorbed UO_2^{+2} ions depends on the concentration of uranyl solutions and the mole percentage of IA in the gel system as shown in Fig. 3. As can be seen from the figure, the uranyl adsorption capacity of these hydrogels was found to be in the range of 2.9–12.9 mg UO_2^{+2}/g dry gel. Increasing the amount of IA in hydrogel from 2.7 to 10.1 mole % caused significant increases in the amount of adsorbed UO_2^{+2} ions. This increase is caused by an increase in specific interactions between positively charged UO_2^{+2} ions and ionized IA in the hydrogel, as well as an increase of free volume of gel available for diffusion.

The Effect of pH on the UO_2^{+2} Adsorption

In order to investigate the effect of pH on the UO_2^{+2} adsorption capacities of hydrogels, adsorption experiments were followed at varying pH and a fixed temperature (25°C). Figure 4 shows the change in the adsorbed UO_2^{+2} ions of P(HEMA/IA) hydrogels containing various mole ratio of IA with changing pH values. Consistent with poly-electrolyte systems, adsorption of UO_2^{+2} ions in the

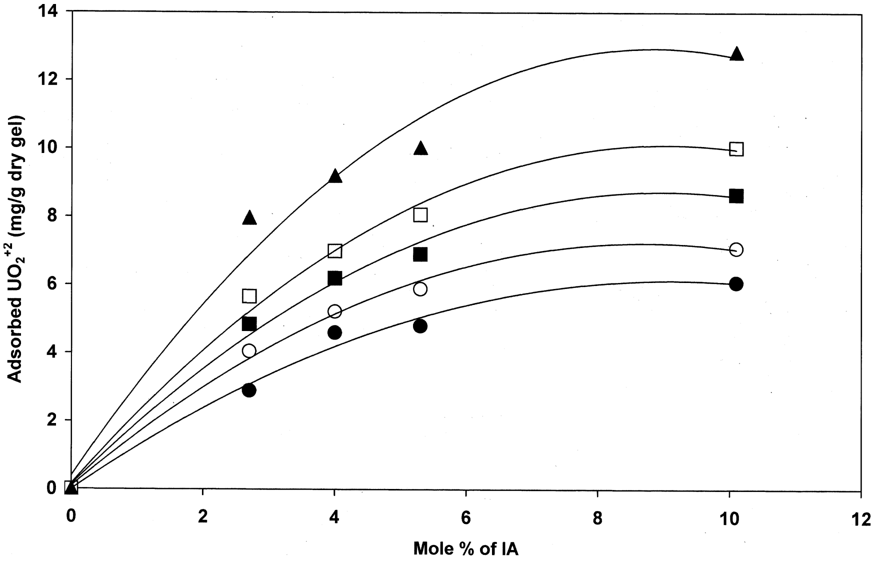


Figure 3. Effect of the mole % of IA in the gel system on the uranyl ion adsorption from uranyl nitrate solutions: (●) 5 ppm, (○) 15 ppm, (■) 30 ppm, (□) 40 ppm, (▲) 50 ppm.

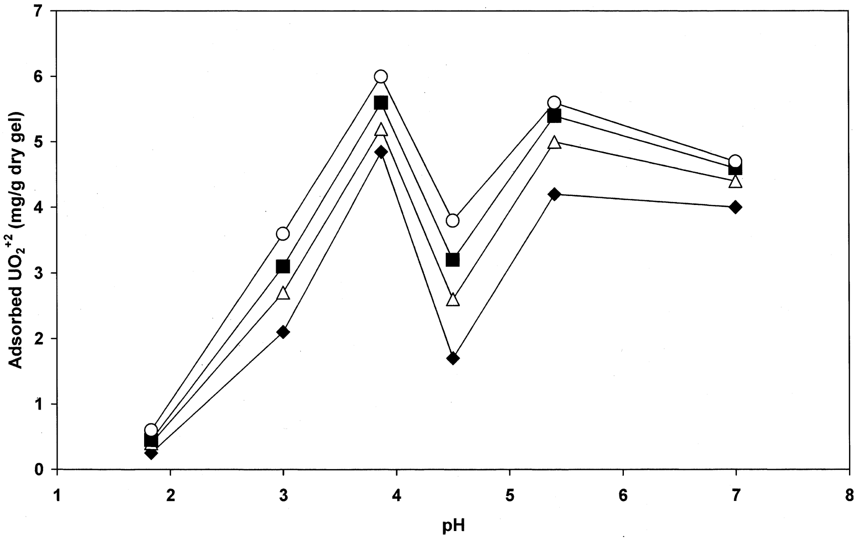


Figure 4. Effect of mole % of IA in the gel system on uranyl ions adsorption at various pH: (◆) Gel 1, (Δ) Gel 2, (■) Gel 3, (○) Gel 4.

gels systems strongly depended on pH. The pH of pure water containing P(HEMA/IA) gels and UN solution were 3.9 and 4.14 respectively. The first and second dissociation constants of IA were $pK_{a1} = 3.85$ and $pK_{a2} = 5.44$. Two maximum adsorption peaks were observed at pH 3.8 and 5.4, depending on IA content in the gel. If the amount of UO_2^{+2} ions adsorbed to the hydrogels were to be measured under the condition of seawater or contaminated water, pH would be adjusted about 4, excluding the carbonate effect. The adsorption of UO_2^{+2} ions onto P(HEMA/IA) hydrogels may be ionic nature, since the acidic groups of P(HEMA/IA) hydrogels in uranyl solutions are completely dissociated at these pH. The increments of adsorption capacity of P(HEMA/IA) hydrogels were approximately 20% and 25% at pH 3.8 and 5.4, respectively, depending on IA content. The results of this shrinking and reduction in the proximity of chains were provided an increase in intermolecular contacts. Similar effect on the adsorption of Ca^{2+} and Na^{+} ions for poly(acrylic acid) based hydrogels were observed by Khara and Peppas (11).

Effect of Ionic Strength and Temperature on UO_2^{+2} Adsorption

The effect of temperature and ionic strength on the UO_2^{+2} adsorption capacities of P(HEMA/IA) hydrogels were investigated at 15, 28, and 42°C in

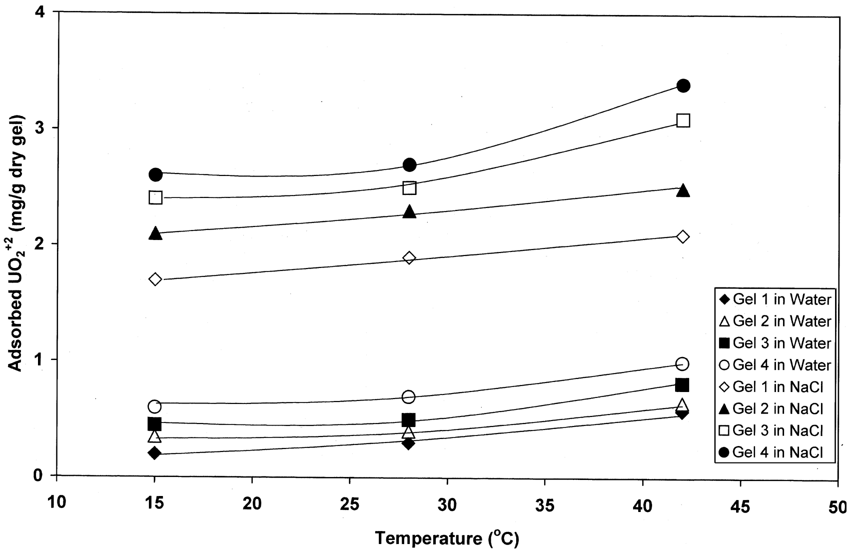


Figure 5. Variation of adsorbed uranyl ions from water and NaCl solution with temperature.

water and 0.1 M NaCl solutions. Variations of adsorbed UO_2^{+2} ions in pure water and NaCl solution with IA content for the above temperatures are presented in Fig. 5. As can be seen from this figure, an increase of the IA content in the hydogel caused an increase in the amount of adsorbed UO_2^{+2} ions in both media. When the adsorbed UO_2^{+2} ions in pure water with NaCl solution were compared, it was observed that the ionic strength of NaCl had a less pronounced effect on the adsorption properties of hydrogels (Fig. 5). An increase in ionic strength generally decreased the swelling, because the difference in concentration of mobile ions between the hydrogel and solution reduced the osmotic swelling pressure of these ions inside the hydrogel. Due to the decrease in swelling and collapsing of chains in the hydrogel, the possible interaction between the UO_2^{+2} ions and polymer chain increased. Fig. 5 also shows the effect of temperature on the UO_2^{+2} adsorption. An increase in the temperature from 15°C to 42°C caused an increase in the amount of adsorbed UO_2^{+2} ions. This increase was again attributed to the shrinking of the hydrogels with increasing temperature.

CONCLUSION

In this study, we have tried to see the effects of hydrogel composition, pH, ionic strength, and temperature on the UO_2^{+2} ions adsorption capacity of P(HEMA/IA) hydrogels. For the determination of adsorbed uranyl ion, polarographic technique was used. As this work shows, not only hydrogel composition but also external stimuli—pH, ionic strength, and temperature—play an important role in the adsorption behaviors of P(HEMA/IA) hydrogels. These hydrogel are potential sorbents to be used for the removal of UO_2^{+2} ions from wastewater and aqueous effluents.

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