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Enhancement of Uranyl Ion Uptake by the Prestructuring of Poly(2-hydroxyethyl methacrylate itaconic acid) Hydrogels in the Presence of Lead and Cadmium Ions/Polarographic Determination

Cengiz Özyürek, Tuncer Çaykara, Recai İnam

Department of Chemistry, Faculty of Art and Science, Gazi University, 06500 Besevler, Ankara, Turkey

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ABSTRACT: Poly(2-hydroxyethyl methacrylate/itaconic acid) [P(HEMA/IA)] hydrogels were prepared by the γ -ray irradiation of aqueous solutions. In the presence of lead and cadmium ions, the UO_2^{2+} ion uptake on P(HEMA/IA) hydrogels was investigated with two types of hydrogel systems prepared by nonprestructuring and prestructuring methods. A differential pulse polarographic technique was used for the determination of trace quantities of uptake elements by the measurement of the reduction peak currents at -200 , -410 , and -580 mV for UO_2^{2+} , Pb(II), and Cd(II) ions, respectively. Hydrogels prestructured with UO_2^{2+} ions

took up approximately 45% more UO_2^{2+} ions than hydrogels prepared by the usual procedure. The UO_2^{2+} ion uptake capacity of the hydrogels increased with an increasing percentage of itaconic acid in the hydrogel systems and an increasing concentration of UO_2^{2+} ions in the presence of Pb(II) and Cd(II) ions. Uptake studies showed that other stimuli, such as the temperature and ionic strength of the solutions, also influenced the UO_2^{2+} ion uptake capacity of the P(HEMA/IA) hydrogels. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2385–2390, 2003

INTRODUCTION

The selective removal and recovery of metal ions has a potentially vast range of applications for the conservation of the environment and the use of natural resources. In this respect, polymeric and copolymeric hydrogels have been extensively studied, and many reviews are available in the field.^{1–5} These hydrogels have usually been used for the preconcentration and separation of trace elements from seawater. For increased and improved metal ion uptake capacity in hydrogels, either comonomers carrying some specific ligands are incorporated into their structures or the chemical structures of repeating units are chemically modified. Some typical examples include poly(*N*-vinyl-2-pyrrolidone-*g*-tartaric acid) and poly(*N*-vinyl-2-pyrrolidone-*g*-citric acid) systems.^{6,7}

During the last few years, prearrangement reactions have been developed for the enhancement of the adsorption of metal ions. For example, Efendiev and Kabanov⁸ and Nishide et al.⁹ developed prearrangement reactions to increase the capacity and selectivity of some systems for prechosen metal ions. The applied principle involves the use of the polymer composition

memory and the 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 the removal of the template ions from the crosslinked system.

In this study, poly(2-hydroxyethyl methacrylate/itaconic acid) [P(HEMA/IA)] hydrogels were prepared and tested for uranyl ion uptake in the presence of lead and cadmium ions for the purpose of removing these pollutants from an aqueous environment. The same hydrogel systems were later prepared in a prestructured manner to increase their capacities for the removal of uranyl ions. The effect of external stimuli, such as the pH and ionic strength, on the uranyl ion uptake capacity in the presence of lead and cadmium ions of these hydrogels was also investigated.

EXPERIMENTAL

Apparatus

A polarographic analyzer system (PAR 174 A), equipped with a mercury drop timer, was used. The drop time of the mercury electrode was approximately 2–3 s (2.75 mg/s). A Kalusek electrolytic cell with a reference saturated electrode, separated by a liquid junction, was used in a three-electrode configuration. The counter electrode was platinum wire. The polarograms were recorded with a Linseis LY 1600 X–Y

Correspondence to: T. Çaykara (tcaykara@hotmail.com).

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recorder. Pulse polarograms were recorded under the conditions of a drop life of 1 s, a scanning rate of 5 mV/s, a pulse duration of 50 ms, and a pulse amplitude of 50 mV.

Chemicals

The two monomers used in this study, 2-hydroxyethyl methacrylate (HEMA) and itaconic acid (IA), were obtained from Merck (Darmstadt, Germany) and BDH (Poole, UK), respectively. Glacial acetic acid, phosphoric acid, and boric acid used to prepare Britton–Robinson buffers were obtained from Merck. The uranyl nitrate, lead nitrate, and cadmium nitrate used for adsorption studies were purchased from Fisher (USA).

Preparation of the hydrogels

In the first part of this study, aqueous solutions of monomers were prepared in 1.0 mL of pure water in different compositions (the HEMA/IA molar ratios were 97.3/2.7, 96.0/4.0, 94.7/5.3, and 89.9/10.1). The prepared monomer solutions were placed in poly(vinyl chloride) straws 4 mm in diameter and irradiated by 2.8 kGy in air at the ambient temperature in a PX- γ -30 Isslodovateji irradiator at a fixed dose rate of

3.36 kGy h⁻¹. Hydrogels, obtained in long, cylindrical shapes, were cut into pieces 3–4 mm long. The pieces were dried in a vacuum oven at 315 K to a constant weight and subjected to Soxhlet extraction with water. The uncrosslinked polymer and unreacted IA were removed from the gels by this extraction. The extracted gel pieces were dried again in a vacuum oven at 315 K to a constant weight. The amount of unreacted IA in the aqueous extract was determined by titration with NaOH (0.05M) to a phenolphthalein end point, but no titrate was consumed for all P(HEMA/IA) hydrogels reaching 100% conversion, which was obtained for all mixtures after 2.8 kGy of irradiation. The gels prepared, purified, and dried according to the aforementioned procedures were stored in vials in the dark and at room temperature for further use in adsorption experiments.

The second part of this study explored the uptake of UO_2^{2+} ions by hydrogels. To increase the capacity of UO_2^{2+} ion uptake while preparing HEMA–IA solutions, we used 26.5 mM uranyl nitrate solutions instead of pure water. Therefore, prestructured hydrogels were prepared by radiation processing of the monomers dissolved in uranyl nitrate solutions at 2.8 kGy. Figure 1 shows schematically the prestructuring process. The hydrogels, obtained in long, cylindrical

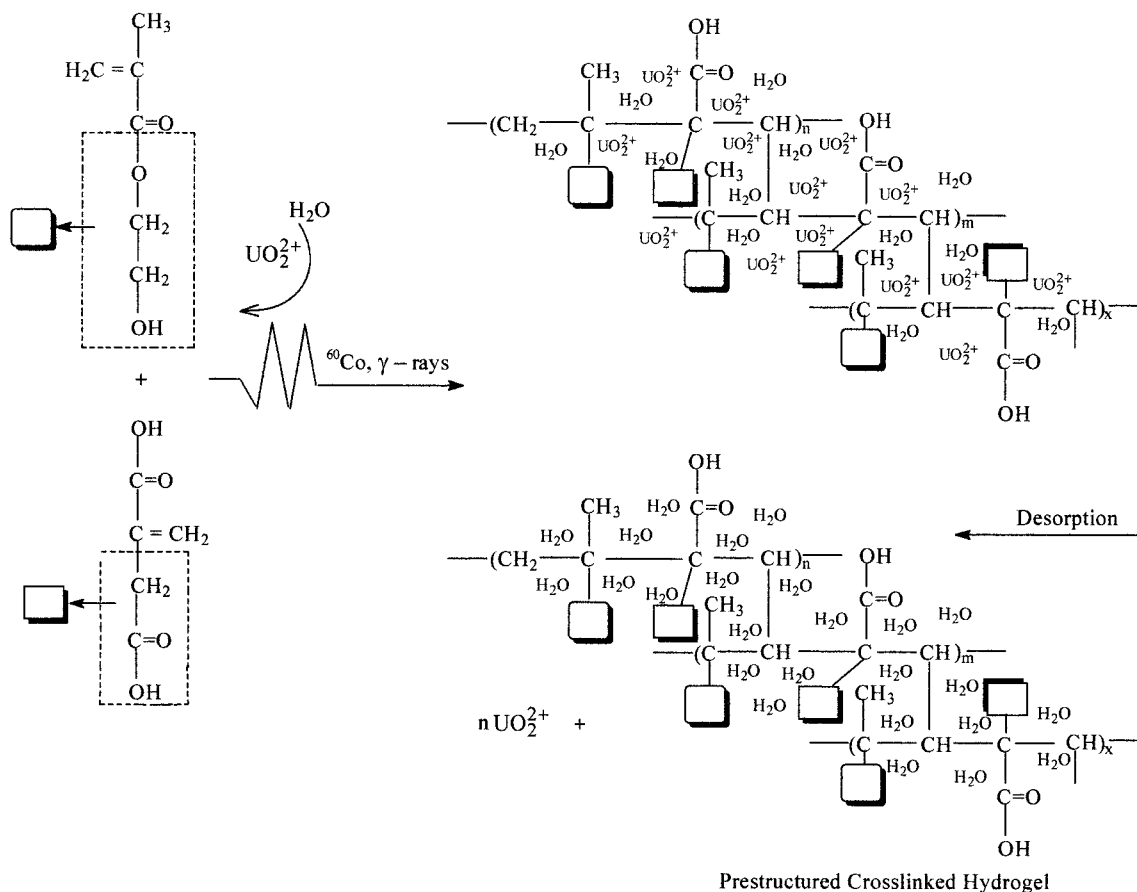


Figure 1 Prestructured scheme of a polymer with UO_2^{2+} ions.

shapes, were cut into pieces 3–4 mm long. The UO_2^{2+} ions held by the crosslinked hydrogels were desorbed into 0.1M NaOH for 30 days (until approximately 100% of the uranyl ions desorbed), and these prestructured hydrogels were dried for further use. Although this may not be considered a molecular printing process because of the formation of some favored structures during gelation, the UO_2^{2+} ion uptake showed an increase.

Polarographic determination of the uranyl uptake in the presence of lead and cadmium ions

The UO_2^{2+} ion uptake of hydrogels prepared in distilled water and prestructured with uranyl nitrate solutions were investigated in the presence of lead and cadmium ions. For this purpose, approximately 0.04 g of each type of dry P(HEMA/IA) hydrogel was immersed in a 20.0-mL solution in the concentration range of 1.85–18.50 μM ($\text{pH} \approx 5.54$) and allowed to stand for 4 days. At the end of this time, the adsorbent was taken away by decantation from the solution. The equilibrium concentrations of UO_2^{2+} , Pb(II) , and Cd(II) in the solution was determined with a differential pulse polarographic technique. Ten milliliters of the solution in the polarographic cell was deaerated by the passage of pure nitrogen gas (99.99%) for about 5 min. The polarograms were recorded by the scanning of the potential from -100 to about -1100 mV. The UO_2^{2+} , Pb(II) , and Cd(II) ions showed peaks at -200 , -410 , and -580 mV, respectively, in the acidic solution ($\text{pH } 1$; Fig. 2). After standard additions of 100- μL mixtures containing 18.5 μM UO_2^{2+} , 24.2 μM Pb(II) , and 44.6 μM Cd(II) , the peak currents increased proportionally, and nonuptake ions were detected.

RESULTS AND DISCUSSION

Effects of pH

The nature of adsorption depends on several parameters, such as the ionic charge, ionic strength, pH, temperature, ability to be hydrolyzed, and formation of polynuclear species.^{10,11} The uptake characteristics of 18.50 μM UO_2^{2+} ions in the presence of Pb(II) and Cd(II) ions were investigated in buffer solutions over a pH range of 1.0–7.0 at a fixed temperature (20°C). Figure 3(a–d) shows the changes in the uptake of UO_2^{2+} and Pb(II) on P(HEMA/IA) hydrogels prepared with the nonprestructuring and prestructuring methods at several pH values. No uptake was observed for Cd(II) at any hydrogel composition or pH. The difference in the uptake values can be explained by the different affinities of the heavy metal ions for donor groups (i.e., carboxyl group) in the metal-chelating ligand IA. As shown in Figure 3, consistent with polyelectrolyte systems, the uptake of UO_2^{2+} and Pb(II)

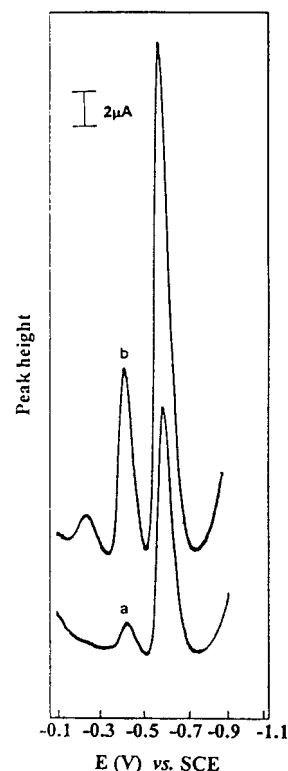


Figure 2 Differential pulse polarograms used for the determination of the uptake of metal ions on P(HEMA/IA) hydrogels from 18.5 μM UO_2^{2+} , 24.2 μM Pb(II) , and 44.6 μM Cd(II) : (a) 10-mL extract solution and (b) standard addition of 18.5 μM UO_2^{2+} , 24.2 μM Pb(II) , and 44.6 μM Cd(II) .

ions in the gel systems strongly depended on pH. The first and second dissociation constants of IA were $\text{p}K_{a1} = 3.85$ and $\text{p}K_{a2} = 5.4$. Two maximum peaks were observed at pH 3.8 and pH 5.4. The maximum uptake of UO_2^{2+} and Pb(II) ions onto the hydrogels may be ionic in nature because the acidic groups of these hydrogels in metal ion solutions were completely dissociated at $\text{p}K_{a1}$ and $\text{p}K_{a2}$. The hydrogels prestructured by uranyl ions took up approximately 45% more UO_2^{2+} and 40% more Pb(II) than hydrogels prepared by the usual procedure for all gel compositions. A similar result was observed previously by Nishide et al.⁹ They prepared complex-forming polymeric sorbents [poly(4-vinyl pyridine) with 1,4-dibromobutane with some template metal ions] and studied the adsorption behavior of copper, cobalt, zinc, and cadmium ions on these resins. A resin prepared with a metal ion as a template preferentially adsorbed the metal ion used as a template. Their work and this work indicate that, as described in Figure 1, the presence of a specific ion during the preparation of a gel structure provides a geometric arrangement that improves further adsorption of the same ion from solution. 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

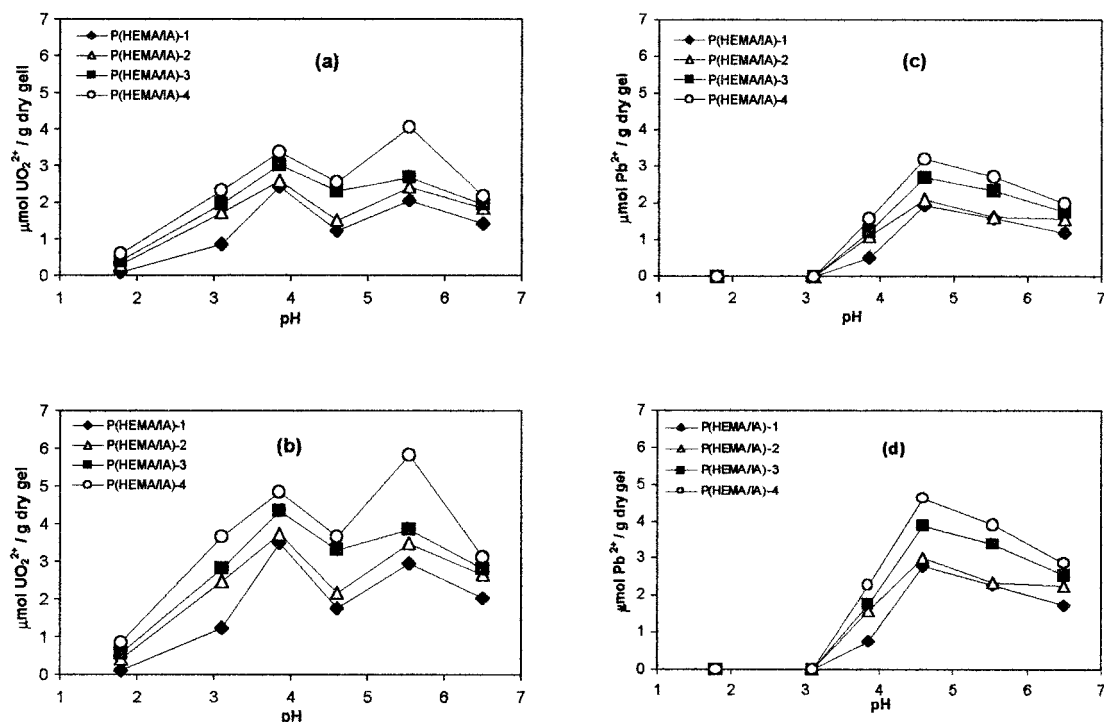


Figure 3 Effect of pH on the UO_2^{2+} and Pb(II) uptake capacities for P(HEMA/IA) hydrogels: (a) nonprestructured for UO_2^{2+} , (b) prestructured for UO_2^{2+} , (c) nonprestructured for Pb(II) , and (d) prestructured for Pb(II) .

molecular imprinting. It is suggested that the separation performance of gels is enhanced by improved control of the mesh size or microporosity of gels through interactions provided by specific ions used as templates during their preparation.

Effect of the concentration

To compare the effects of the uranyl concentration in the presence of Pb(II) (2.41–24.1 μM) and Cd(II) (4.46–44.6 μM) ions on hydrogels prepared with both nonprestructuring and prestructuring methods, we carried out the process at uranyl concentrations between 1.85 and 18.50 μM at $\text{pH} \approx 5.5$. The results for competitive conditions (uptake from solutions containing all the metal ions) are presented in Figure 4. The amounts of the ion uptake for P(HEMA/IA)-1, P(HEMA/IA)-2, P(HEMA/IA)-3, and P(HEMA/IA)-4 hydrogels prepared by the nonprestructuring method were found to be 0.24–2.52, 0.28–2.77, 0.32–2.92, and 0.33–3.15 $\mu\text{mol/g}$ of dry gel for UO_2^{2+} and 0.25–2.9, 0.29–2.51, 0.30–2.55, and 0.23–2.61 $\mu\text{mol/g}$ of dry gel for Pb(II) [Fig. 4(a,c)]. The hydrogels prepared by the prestructuring method took up approximately 45% more UO_2^{2+} ions and 40% more Pb(II) than hydrogels prepared by the nonprestructuring method, depending on the IA content [Fig. 4(b,d)]. This behavior shows the importance of the spatial distribution of the carboxylic acid groups for providing the best chelating configuration. Consequently, P(HEMA/IA) has better

swelling properties in aqueous solutions, and metal ions may diffuse and absorb (or entrap) within the mesh sizes of these hydrogels. The specificity of the metal-chelating ligand (i.e., carboxylic groups) may also contribute to this high adsorption capacity.

The adsorption of 42–76 mg of $\text{UO}_2^{2+}/\text{g}$ of dry gel from 50–600 ppm aqueous solutions on poly(acrylamide/itaconic acid) hydrogels was reported by Karadağ et al.¹² Because analytical tools used in many works usually include spectrophotometric techniques, the concentration of a synthetic solution containing the mentioned ions may be higher than in this work. With a polarographic technique, trace quantities of heavy metals could be determined directly without preconcentration and interference effects.

Effect of the ionic strength and temperature

The influence of the temperature and ionic strength on the uptake capacities of hydrogels at 15, 28, and 42°C (with thermostatic control) in water and a 0.1M NaCl solution was investigated, and the results obtained for UO_2^{2+} and Pb(II) ions are shown in Figure 5(a–d). When the uptakes of both hydrogels prepared by the prestructuring and nonprestructuring methods were compared, we found that the prestructured hydrogels had 45% more UO_2^{2+} and 40% more Pb(II) taken up than hydrogels prepared by the nonprestructuring method. As shown in Figure 5, an increase in the IA content in the hydrogels caused an increase in the

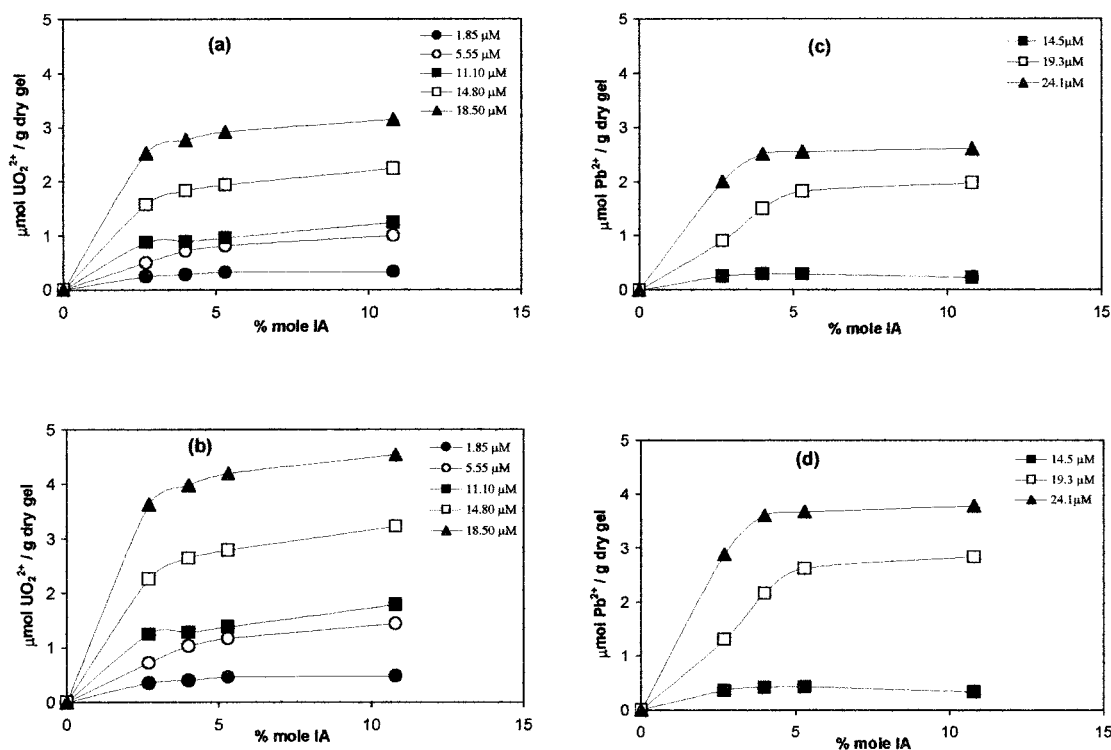


Figure 4 Effect of the concentration on the UO_2^{2+} and Pb(II) uptake capacities for P(HEMA/IA) hydrogels: (a) nonprestructured for UO_2^{2+} , (b) prestructured for UO_2^{2+} , (c) nonprestructured for Pb(II) , and (d) prestructured for Pb(II) .

amount of UO_2^{2+} and Pb(II) ions taken up in both media at the same temperature. This increase may be attributed to the increments of the carboxyl groups in

the hydrogels due to an increase in the IA content, which resulted in electrostatic interactions between the cationic ions and the anionic groups. However,

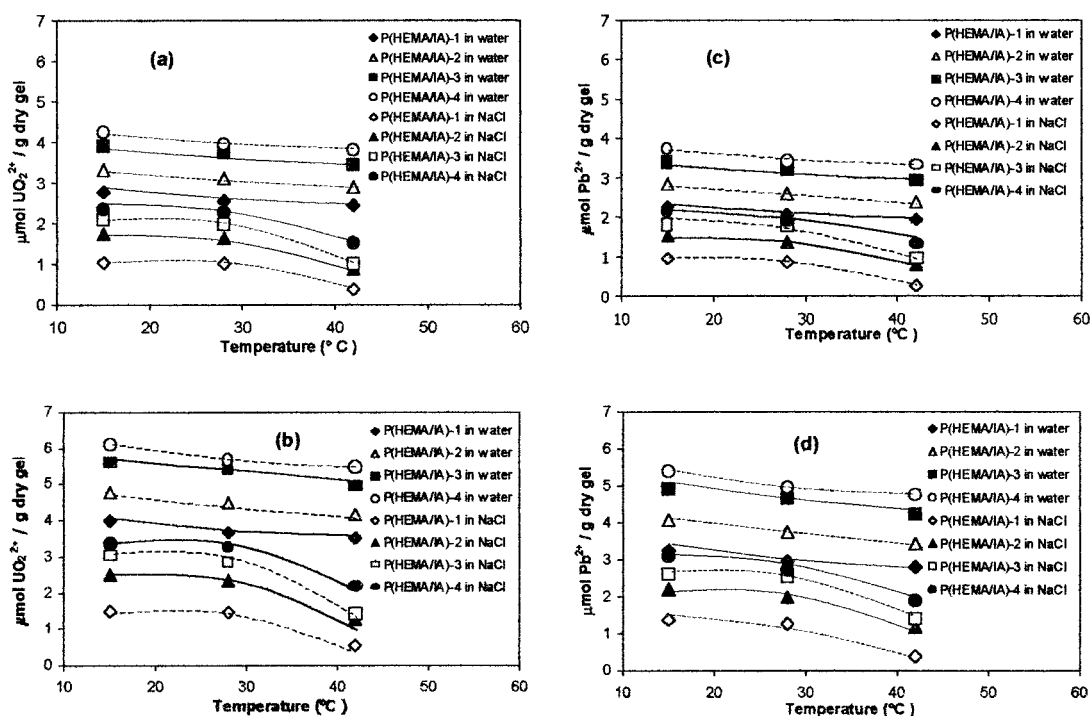


Figure 5 Effect of the ionic strength and temperature on the UO_2^{2+} and Pb(II) uptake capacities for P(HEMA/IA) hydrogels: (a) nonprestructured for UO_2^{2+} , (b) prestructured for UO_2^{2+} , (c) nonprestructured for Pb(II) , and (d) prestructured for Pb(II) .

comparing the UO_2^{2+} and Pb(II) ion uptakes, we observed that the ionic strength of NaCl solutions had a more pronounced effect on the uptake properties of the hydrogels. An increase in the ionic strength generally reduced the swelling because the difference in the concentrations of mobile ions between the gel and solution was reduced with a decrease in the osmotic swelling pressure of the ions inside the gels. Because of decreasing swelling and collapsing of the chains in the gel system, the possible interaction between UO_2^{2+} and Pb(II) ions and the polymer chain increased. However, increasing the ionic strength reduced the swelling degree because the low-molecular-weight ions (Na^+ and Cl^-) surrounded the charged groups and suppressed the polyelectrolyte effect at the same time that the ionic atmosphere of the counterions restricted the approach of metal ions to ligand groups. Moreover, the collapse of the gel at a high ionic strength could also change the size of the prestructured pores. An increase in temperature from 15 to 42°C caused a decrease in the amount of adsorbed UO_2^{2+} and Pb(II) ions. Because the adsorption de-

creased with temperature, temperature dependence studies also revealed that the observed phenomenon was adsorption.

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