

Polarographic Determination of the Competitive Adsorption of U(VI), Pb(II), and Cd(II) Ions on Poly(*N*-vinyl-2-pyrrolidone-*g*-citric acid) Hydrogels

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Received 19 July 2002; accepted 29 August 2002

ABSTRACT: Poly(*N*-vinyl-2-pyrrolidone-*g*-citric acid) [P(VP-*g*-CA)] hydrogels were prepared for the removal of U(VI), Pb(II), and Cd(II) from aqueous solutions containing different amounts of these ions (2.5–10 mg/L). Different pHs (1–13), temperatures (20–40°C), and ionic strengths (0.5M) were also tried for the adsorption behavior of these ions. The competitive adsorption values of U(VI), Pb(II), and Cd(II) ions on pure poly(*N*-vinyl-2-pyrrolidone) were low [0.71–2.03 mg of U(VI)/g of dry gel, 0.15–1.58 mg of Pb(II)/g of dry gel, and 0.10–0.68 mg of Cd(II)/g of dry gel]. The incorporation of citric acid significantly increased the adsorption of these ions [0.67–2.12 mg of U(VI)/g of dry gel, 0.44–1.88 mg of Pb(II)/g of dry gel, and 0.04–0.92 mg of Cd(II)/g of dry gel for P(VP-*g*-CA)-1; 0.71–2.36 mg of U(VI)/g of dry gel, 0.60–2.16 mg of Pb(II)/g of

dry gel, and 0.14–0.80 mg of Cd(II)/g of dry gel for P(VP-*g*-CA)-2; and 0.79–2.47 mg of U(VI)/g of dry gel, 0.70–2.30 mg of Pb(II)/g of dry gel, and 0.20–0.86 mg of Cd(II)/g of dry gel for P(VP-*g*-CA)-3]. The observed affinity order of adsorption was U(VI) > Pb(II) > Cd(II) for competitive conditions. The optimal pH range for the removal of these ions was 5–9. Competitive adsorption studies showed that other stimuli, such as the temperature and ionic strength of the solution, also influenced the U(VI), Pb(II), and Cd(II) adsorption capacity of P(VP-*g*-CA) hydrogels. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2019–2024, 2003

Key words: hydrogels; adsorption; radiation

INTRODUCTION

Polymeric and copolymeric substrates are constantly being developed and used for complexation with metal ions, either for ion exchange or selective adsorption. These polymeric and copolymeric ligands are tailor-synthesized to remove certain metal ions from aqueous media. The introduction of diprotic or triprotic acidic groups into hydrogels based on acrylamide and *N*-vinyl 2-pyrrolidone imparts chelating properties to these hydrogels.^{1–3} The complexation of these diprotic acidic groups with some heavy metal ions provides an efficient method of removal from aqueous systems by poly(2-hydroxyethyl methacrylate-maleic acid) hydrogels.⁴

The removal of heavy metals from environmental samples is especially important because their excess intake leads to pronounced toxic symptoms. For example, uranium is one of the most seriously threatening heavy metals because of its toxicity and some radioactivity. Excessive amounts of uranium have found their way into the environment through activities associated with the nuclear industry. Uranium contamination poses a threat in some surface and

ground waters.⁵ The toxic effect of lead involves several organs and is the result of a variety of biochemical defects. Nervous systems of infants and children are particularly sensitive to lead toxicity.⁶ The risks to health arising from cadmium are great, and the effect of less acute exposure to dietary or environmental sources usually reflects the toxic action of a high body burden on the kidney and possibly the skeleton. The toxicity of cadmium has been reviewed in detail.⁷

For separation, in the use of hydrogels containing chelating functional group, some features of adsorbents, such as durability, reusability, and practical applicability, are very important. In this respect, hydrogels have advantages over other system.⁸ For uranyl ion adsorption from aqueous solutions, we synthesized, with a radiation technique, hydrogels based on *N*-vinyl 2-pyrrolidone and containing different functional groups.^{2,3} The radiation synthesis of poly(*N*-vinyl-2-pyrrolidone-*g*-citric acid) [P(VP-*g*-CA)] hydrogels and their network characterization effect of external stimuli on the equilibrium degree of swelling were very well demonstrated in our previous studies.³ In this article, we report the effect of external stimuli, such as the pH, temperature, and ionic strength, on the adsorption capacity of P(VP-*g*-CA) hydrogels. The adsorption of trace amounts of these ions was possible because of techniques, such as differential pulse polarography (DPP), used for the de-

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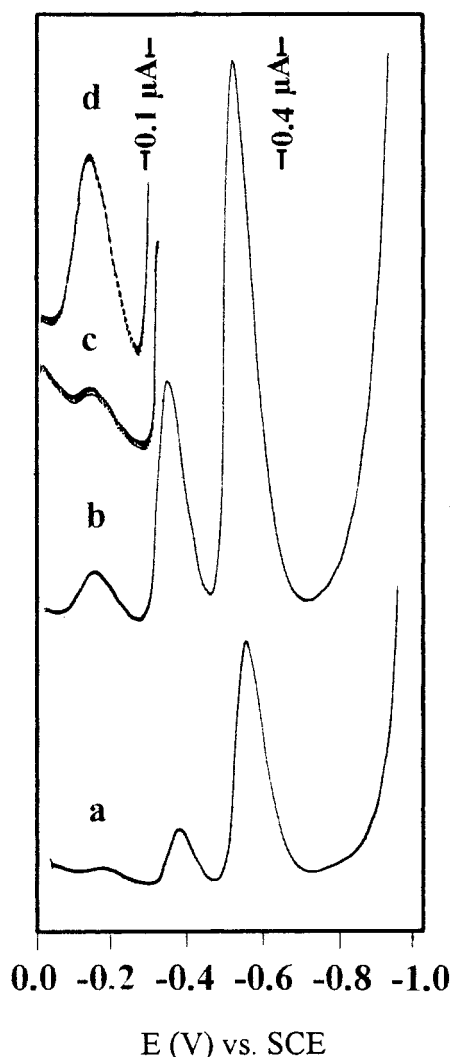


Figure 1 DPP polarograms used for the determination of adsorbed U(VI), Pb(II), and Cd(II) on P(VP-g-CA)-3 hydrogels from 5 mg/L solutions: (a) 10-mL extract solution and (b) 10-mL extract solution and the standard addition of 50 μL of 500 mg/L U(VI), Pb(II), and Cd(II). Parts c and d are magnified forms of parts a and b for the U(VI) peak.

termination of trace elements usually encountered in biological or environmental samples.

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 Kalousek electrolytic cell with a saturated calomel electrode as a reference, 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 recorder. Pulse polarograms were recorded under the conditions of a drop life of 1 s, a scan

rate of 5 mV/s, a pulse duration of 50 ms, and a pulse amplitude of 50 mV.

Chemicals

N-Vinyl-2-pyrrolidone (VP) and citric acid (CA) were obtained from Aldrich (Milwaukee, WI) and Carlo Erba (Milan, Italy), respectively. Glacial acetic acid, phosphoric acid, and boric acid were used to prepare Britton–Robinson buffers, and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, and $\text{Cd}(\text{NO}_3)_2$ were obtained from Merck (Darmstadt, Germany). The uranyl nitrate used for the adsorption studies was purchased from Fisher (USA).

Preparation of the hydrogels

Three components were used in the preparation of P(VP-g-CA) hydrogels: VP, CA, and distilled water. A 2-mL aqueous solution of VP and 60, 90, or 120 mg of CA were prepared in 1 mL of pure water (98.4/1.6, 97.6/2.4, or 96.8/3.2 VP/CA molar ratio). The solution was placed in a poly(vinyl chloride) straw 4 mm in diameter and irradiated to 25 kGy in air at the ambient temperature in an Isslodovateji PX- γ -30 γ -irradiator at a fixed dose rate of 3.87 kGy/h.

Composition of the hydrogels

The hydrogels, obtained in long, cylindrical shapes, were cut into pieces 3–4 mm long and were stored for later evaluations. The irradiated mixtures were dried in a vacuum oven at 315 K to a constant weight and were subjected to Soxhlet extraction with water as a solvent. The ungrafted CA and residual monomer were removed with this extraction from the gel structure. The extracted gels were dried again in a vacuum oven at 315 K to a constant weight. The amount of unreacted CA was determined by the titration of the extract against NaOH (0.05M) to the phenolphthalein end point. The molar percentages of CA in P(VP-g-CA)-1, P(VP-g-CA)-2, and P(VP-g-CA)-3 were 1.1, 1.8, and 2.7, respectively.

Adsorption of U(VI), Pb(II), and Cd(II) ions onto poly(*N*-vinyl-2-pyrrolidone) (PVP) and P(VP-g-CA) hydrogels

P(VP-g-CA) hydrogels (~ 0.0300 g) were immersed in 15.0-mL solutions in a concentration range of 2.5–10 mg/L (pH ≈ 7) and were 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 U(VI), Pb(II), and Cd(II) in the solution were determined by DPP. 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

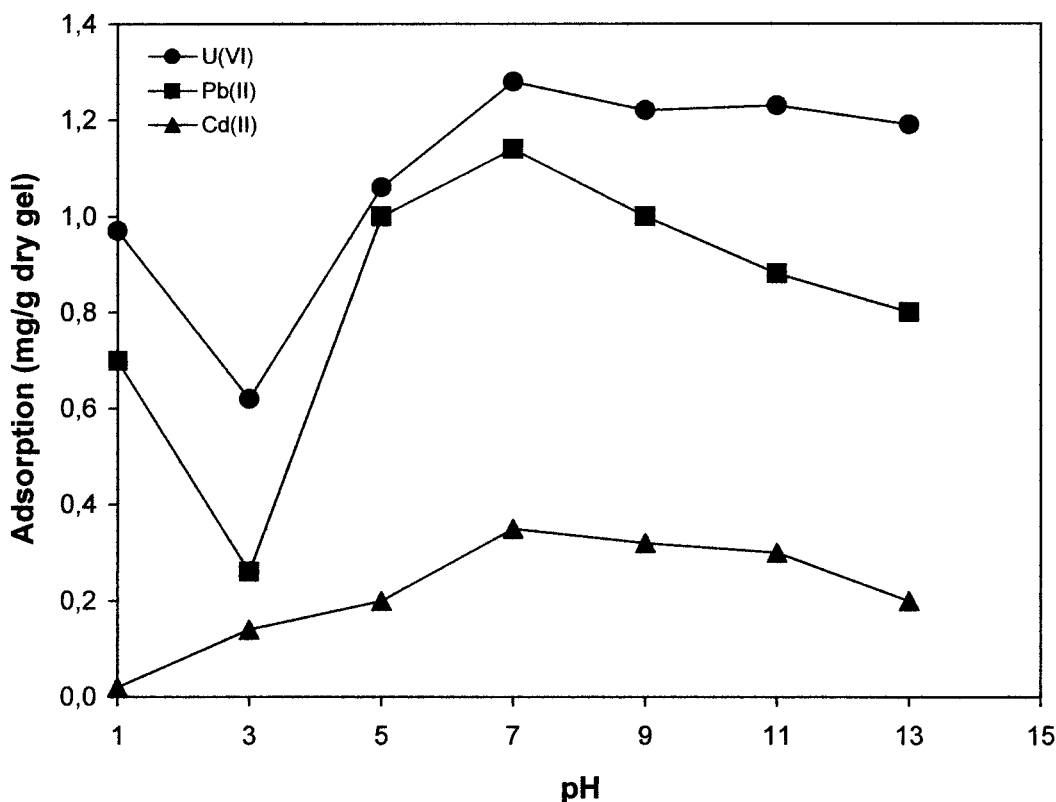


Figure 2 Effect of the pH of U(VI), Pb(II), and Cd(II) on the adsorption capacities of P(VP-g-CA)-1 hydrogels.

of the potential from -100 to about -1200 mV. The U(VI), Pb(II), and Cd(II) ions showed peaks at -200 , -410 , and -580 mV, respectively, in an acidic solution (pH 1; Fig. 1). After standard additions of $50 \mu\text{L}$ of a 500 ppm mixture of U(VI), Pb(II), and Cd(II), the peak currents increased proportionally, and nonadsorbed ions were detected. Because the initial amounts of the ions were known, the difference was obviously the amount of adsorbed ions.

RESULTS AND DISCUSSION

Effects of pH

The complexation of heavy metal ions by a chelating ligand is usually a strong function of the pH.^{2,4} The adsorption characteristics of the adsorbent toward U(VI), Pb(II), and Cd(II) ions were investigated in buffer solutions containing 5 mg/L ions over the pH range of 1.0 – 13.0 at a fixed temperature (20°C). Figure 2 shows the changes in the adsorbed ions of the P(VP-g-CA)-1 hydrogel with changing pH values. The complexation behavior of these ions was especially sensitive to pH changes at lower pH regions. Several authors have observed the inhibition of metal chelation due to a decrease in pH in different adsorbents.^{9,10} Therefore, it has been proposed that protons and metal ions compete for the same binding sites. As shown in Figure 2, the adsorption capacities increased

with increasing pH, reaching maximum values around $\text{pH} \cong 7$, and then slightly decreased. A similar behavior was also observed for pure PVP and P(VP-g-CA) hydrogel systems. The maximum adsorption of the metal ions onto the hydrogels may be ionic in nature because the acidic groups of these hydrogels in metal-ion solutions were completely dissociated at neutral or basic pHs. The amounts of adsorbed ions on pure PVP at $\text{pH} \cong 7$, at which point the maximum adsorption was observed, were 1.30 mg of U(VI)/g of dry gel, 1.20 mg of Pb(II)/g of dry gel, and 0.30 mg of Cd(II)/g of dry gel. The maximum adsorption values of the P(VP-g-CA) hydrogels at the same pH were 1.85 – 2.20 mg of U(VI)/g of dry gel, 1.58 – 2.10 mg of Pb(II)/g of dry gel, and 0.47 – 0.64 mg of Cd(II)/g of dry gel, depending on the CA contents in the hydrogels. The difference in the adsorption 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 CA.

Competitive adsorption

The U(VI), Pb(II), and Cd(II) ion adsorption from aqueous solutions by pure PVP and P(VP-g-CA) hydrogels was investigated as described in the Experimental section. The results for competitive conditions (the adsorption from solutions containing all metal

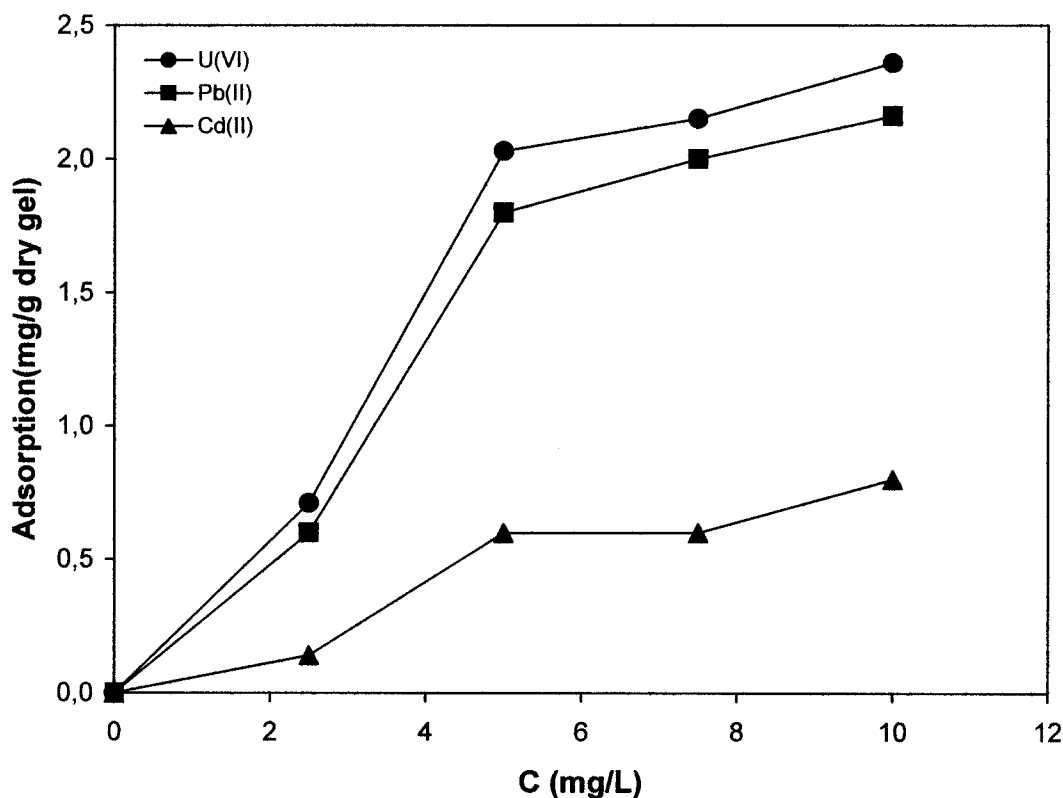


Figure 3 Effect of the concentration (C) of U(VI), Pb(II), and Cd(II) on the adsorption capacities of P(VP-g-CA)-2 hydrogels.

ions) for U(VI), Pb(II), and Cd(II) ion adsorption from aqueous solutions in the concentration range of 2.5–10 mg/L at $\text{pH} \cong 7.0$ are presented in Figure 3 and Table I. The metal-ion adsorption values on pure PVP for U(VI), Pb(II), and Cd(II) were determined in the range of 0.71–2.03 mg/g of dry gel, 0.15–1.58 mg/g of dry gel, and 0.10–0.68 mg/g of dry gel, respectively. The metal ions can be adsorbed nonspecifically by physical adsorption, associated with the weak forces of physical attraction such as van der Waals forces, or by chemical adsorption, associated with the exchange of electrons and the formation of a chemical bond between the metal ions and the PVP surfaces (especially with the carbonyl groups of the PVP chain). However, CA incorporation significantly increased the adsorption of these ions. The amounts of the adsorbed ions on P(VP-g-CA)-1, P(VP-g-CA)-2, and P(VP-g-CA)-3 were 0.67–2.12, 0.71–2.36, and 0.79–2.47 mg/g of dry gel for U(VI), 0.44–1.88, 0.60–2.16, and 0.70–2.30

mg/g of dry gel for Pb(II), and 0.04–0.92, 0.14–0.80, and 0.20–0.86 mg/g of dry gel for Cd(II), respectively (Table I). The observed affinity order was $\text{U(VI)} > \text{Pb(II)} > \text{Cd(II)}$. Because P(VP-g-CA) had better swelling properties in aqueous solutions,¹¹ the metal ions could diffuse and absorb (or entrap) within the mesh sizes of these hydrogels. The specificity of the metal-chelating ligand (i.e., carboxylic groups) might also have contributed to this high adsorption capacity.

Different polymeric adsorbents with a wide range of adsorption capacities for heavy metal ions have been reported. Roozmond et al.¹² showed 40 mg of Cd(II)/g and 32 mg of Cu(II)/g with pyrazole-containing poly(styrene-divinylbenzene) adsorbents. Denizli et al.¹³ used Alkali Blue 6B-attached poly(ethylene glycol dimethacrylate-2-hydroxyethyl methacrylate) [P(EGDMA-HEMA)] adsorbents, for which the maximum adsorption capacities were 2.3 mg of Cu(II)/g, 5.52 mg of Cd(II)/g, and 128 mg of Pb(II)/g.

TABLE I
Effect of the Concentration (C) on the Adsorption of U(VI), Pb(II), and Cd(II) Ions for PVP and P(VP-g-CA) Hydrogels

C (mg/L)	PVP			P(VP-g-CA)-1			P(VP-g-CA)-2			P(VP-g-CA)-3		
	U(VI)	Pb(II)	Cd(II)	U(VI)	Pb(II)	Cd(II)	U(VI)	Pb(II)	Cd(II)	U(VI)	Pb(II)	Cd(II)
2.5	0.71	0.15	0.10	0.67	0.44	0.04	0.71	0.60	0.14	0.79	0.70	0.20
5.0	1.48	0.18	0.46	1.58	1.24	0.46	2.03	1.60	0.48	2.27	1.52	0.48
7.5	1.97	1.39	0.60	1.97	1.80	0.70	2.15	2.00	0.60	2.29	2.10	0.54
10.0	2.03	1.58	0.68	2.12	1.88	0.92	2.36	2.16	0.80	2.47	2.30	0.86

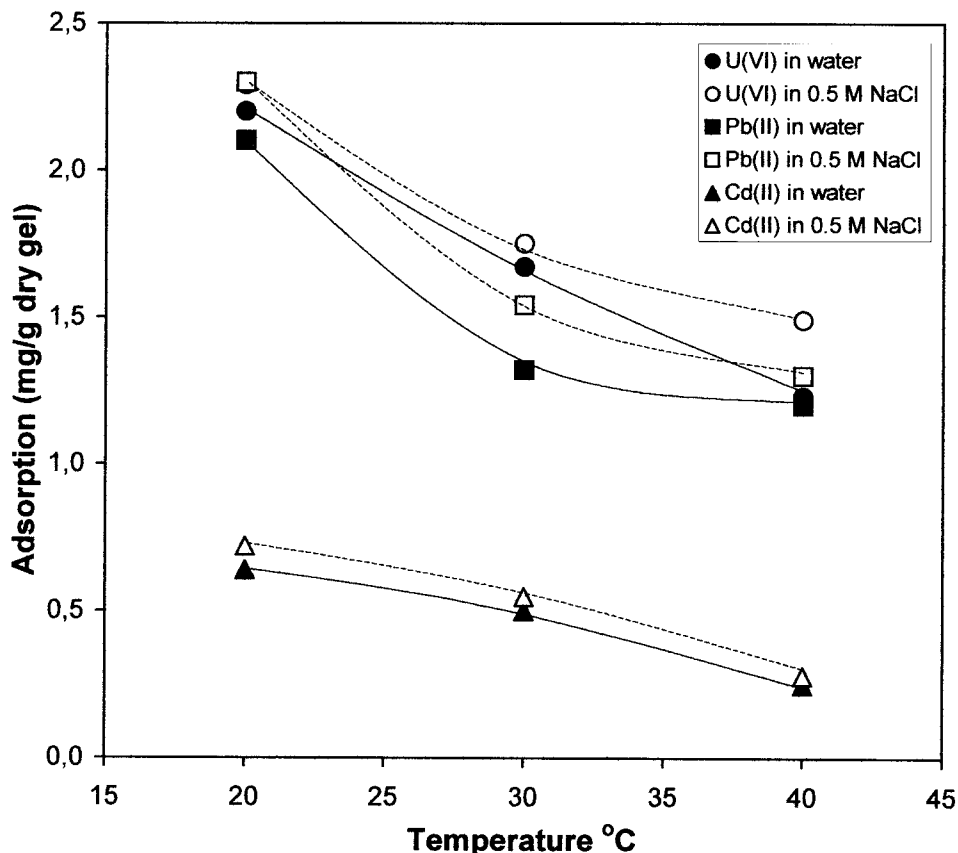


Figure 4 Variation of the adsorbed of U(VI), Pb(II), and Cd(II) ions from water and a 0.5M NaCl solution with the temperature.

The adsorption of 42–76 mg of U(VI)/g of dry gel from 50–600 mg/L aqueous solutions on poly(acrylamide/itaconic acid) hydrogels was reported by Karadağ et al.¹ Because the analytical tools used in many works usually included spectrophotometric techniques, the concentrations of synthetic solutions containing the mentioned ions were higher than those reported in this work. With a polarographic technique, trace quantities of heavy metals could be determined in real samples without preconcentration.

Effect of the ionic strength and temperature

The effect of the temperature and ionic strength on the adsorption capacities of hydrogels at 20, 30, and 40°C

(with thermostatic control) in water and 0.5M NaCl solutions at pH ≈ 7.0 were investigated, and the results obtained for U(VI), Pb(II), and Cd(II) ions are shown in Figure 4 and Tables II and III. As can be seen from Tables II and III, an increase in the CA content in the hydrogels caused an increase in the amount of adsorbed U(VI), Pb(II), and Cd(II) ions in both media at the same temperature. This increase could be attributed to the increments of carboxyl groups in the hydrogels because of an increase in the CA content, which resulted in electrostatic interactions between the cationic ions and the anionic groups. However, from a comparison of adsorbed U(VI), Pb(II), and Cd(II) ions, it was observed that the ionic strength of NaCl ions had a more pronounced effect on the ad-

TABLE II
Effect of the Temperature on the Adsorption of U(VI), Pb(II), and Cd(II) Ions for PVP and P(VP-g-CA) Hydrogels (in Water)

Hydrogel	20°C			30°C			40°C		
	U(VI)	Pb(II)	Cd(II)	U(VI)	Pb(II)	Cd(II)	U(VI)	Pb(II)	Cd(II)
PVP	1.30	1.20	0.30	1.06	0.70	0.17	0.41	0.10	0.04
P(VP-g-CA)-1	1.85	1.58	0.47	1.49	0.80	0.20	0.59	0.20	0.08
P(VP-g-CA)-2	2.00	1.80	0.60	1.59	1.20	0.30	1.15	0.56	0.15
P(VP-g-CA)-3	2.20	2.10	0.64	1.67	1.32	0.50	1.23	1.20	0.25

TABLE III
Effect of the Temperature and Ionic Strength on the Adsorption of U(VI), Pb(II), and Cd(II) Ions for PVP and P(VP-g-CA) Hydrogels (in 0.5M NaCl)

Hydrogel	20°C			30°C			40°C		
	U(VI)	Pb(II)	Cd(II)	U(VI)	Pb(II)	Cd(II)	U(VI)	Pb(II)	Cd(II)
PVP	1.47	1.23	0.48	1.10	0.88	0.10	0.71	0.44	0.03
P(VP-g-CA)-1	1.94	1.70	0.60	1.15	1.00	0.40	0.88	0.60	0.05
P(VP-g-CA)-2	2.12	1.98	0.70	1.59	1.41	0.42	1.41	0.73	0.05
P(VP-g-CA)-3	2.29	2.30	0.72	1.59	1.54	0.45	1.49	1.30	0.04

sorption properties of 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 interactions of U(VI), Pb(II), and Cd(II) ions and polymer chains increased. An increase in the temperature from 20 to 40°C caused a decrease in the amount of adsorbed U(VI), Pb(II), and Cd(II) ions. Because the adsorption decreased with temperature, temperature-dependence studies also revealed that the observed phenomenon was adsorptive in nature.

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