

The Effect of Gel Composition on the Uranyl Ions Adsorption Capacity of Poly(*N*-vinyl 2-pyrrolidone-*g*-citric acid) Hydrogels Prepared by Gamma Rays

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ABSTRACT: Poly(*N*-vinyl 2-pyrrolidone-*g*-citric acid) (PVP-*g*-CA) hydrogels with varying compositions were prepared from ternary mixtures of *N*-vinyl 2-pyrrolidone–citric acid–water by using ⁶⁰Co γ -rays. The effect of gel composition on the uranyl ions adsorption capacity of PVP-*g*-CA hydrogels was investigated. Uranyl adsorption capacity of these hydrogels were found to be in the range of 18–144 mg [UO₂²⁺]/g dry gel from the aqueous solution of uranyl nitrate and 22–156 mg [UO₂²⁺]/g dry gel from the aqueous solution of uranyl acetate, depending on the content of citric acid in the hydrogel, while poly(*N*-vinyl 2-pyrrolidone) hydrogel did not sorb any uranyl ion. The swelling of PVP-*g*-CA hydrogel containing 2.7 mol % CA was observed in water (1620%), in uranyl acetate solution (1450%) and in uranyl nitrate solution (1360%), as compared to 700% swelling of pure PVP hydrogels. The diffusion coefficients were varied from 12.57 up to 4.04 $\cdot 10^{-8}$ m² s⁻¹. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1037–1043, 2000

Key words: hydrogel; poly(*N*-vinyl 2-pyrrolidone-*g*-citric acid); swelling; uranyl adsorption

INTRODUCTION

The removal of uranium from contaminated water is a major environmental problem because of the difficulty of treating such waters by conventional methods. The process using adsorbents is thought to be the most effective method for recovering uranium because of the high selectivity for uranium, the ease of handling the safety to the environment.

Some authors have reported on some crosslinked copolymers of the diethyl ester of vinyl

phosphoric acid and acrylic acid and crosslinked copolymers of some natural polymers have been used for the adsorption of some heavy metals ions.^{1–4} On the other hand, the amidoxime derivatives of copolymeric hydrogels prepared from acrylonitrile and divinyl benzene has been used successfully in the recovery of uranium from seawater.^{5–8} Hydrogels are crosslinked hydrophilic polymers that are used for the purpose of complexation with metal ions either for ion exchange or selective adsorption purposes. These polymeric ligands are tailor-synthesized to remove certain metal ions or groups from aqueous media. In the more recent years, a series of articles have been published by Saraydin, Karadag, and Güven who

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synthesized new hydrogels from the copolymers of acrylamide and diprotic itaconic acid and maleic acid.^{9–11} These authors also published that these hydrogels are potential adsorbents for biological agents and dyes and heavy metal ions from aqueous solution.^{12–15}

In this study, Poly(*N*-vinyl 2-pyrrolidone-*g*-citric acid) (PVP-*g*-CA) hydrogels triprotic acid moieties containing were prepared by grafting of citric acid during polymerization of *N*-vinyl 2-pyrrolidone with ⁶⁰Co γ -rays. The hydrogels thus prepared were characterized in view of their swelling properties, the nature of the water diffusion, and the application to the adsorption of uranyl ions from aqueous solution.

EXPERIMENTAL

Materials

The *N*-vinyl 2-pyrrolidone (VP) monomer was supplied by Aldrich, and the citric acid (CA) was supplied by Carlo Erba. The uranyl acetate and uranyl nitrate used for the adsorption studies and the sodium salicylate used for the complexing agent were purchased from Merck.

Preparation of Hydrogels

Aqueous solutions of VP and CA were prepared in 1 mL of pure water in different compositions (VP-to-CA mole ratios of 98.4/1.6, 97.6/2.4, and 96.8/3.2). Solutions thus prepared were placed in the PVC straws of 4 mm diameter and were irradiated to 25 kGy in air at an ambient temperature in a PX- γ -30 Isslodovateji irradiator at a fixed dose rate of 3.87 kGy h⁻¹.

Compositions of Hydrogels

The hydrogels, obtained in long cylindrical shapes, were cut into pieces of 4–5 mm length and were dried in air and a vacuum oven. The uncrosslinked polymer and ungrafted CA were removed from the gels by extraction with distilled water. The amount of unreacted CA in the extract was determined by titration of extract against NaOH (0.05 mol/L) to the phenolphthalein endpoint. Mole percentages of CA in gel 1, gel 2, and gel 3 were found to be 1.1, 1.8, and 2.7, respectively.

Swelling

The dried hydrogels with the initial weights m_0 were swollen in distilled water, aqueous solutions

of uranyl acetate, and uranyl nitrate at 25°C. The swollen gels were removed from the water bath, dried with a filter paper, weighed and replaced in the same bath. The mass percentage swelling was calculated from the following equation:¹⁶

$$S\% = [(m_t - m_0)/m_0] \cdot 100 \quad (1)$$

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

Adsorption

For the adsorption of uranyl ions onto PVP-*g*-CA hydrogels, 0.1 g of the dry gel was placed in 50 mL of a solution of uranyl acetate and uranyl nitrate in the concentration range of 50–500 ppm and was allowed to equilibrate for 48 h at 25°C. These aqueous solutions were separated with decantation from the hydrogels. A 0.1 mL solution of sodium salicylate (10% m/m) was added to 3 mL of the uranyl solutions. Spectrophotometric measurements were carried out using a Jenway 5105 ultraviolet–visible (UV–vis) spectrophotometer at ambient temperature. The absorbances of uranyl–complex solutions at a 466 nm wavelength were measured. Distilled water was chosen as the reference. The concentrations of uranyl ions were found by using suitable calibration curves.

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

RESULTS AND DISCUSSION

Swelling and Diffusion

When VP monomer solutions are irradiated with γ -rays in the presence of citric acid, its graft polymers can be obtained during the polymerization of VP. In our recent study,¹⁷ we have discussed the structure and physical properties of the PVP-*g*-CA hydrogels produced in this work. The total dose required for the onset gelation for pure VP, the sensitizing effect of water, and the influence of CA on the gelation of VP monomer were also reported.¹⁷ After irradiation, the yield of pure PVP homopolymer was around 96 wt %.¹⁷

The swelling curves of PVP-*g*-CA hydrogel containing 2.7 mol% CA in water and solutions of uranyl ions are shown in Figure 1. As can be seen from Figure 1, maximum and minimum swelling occurred with water (1620%) and with an aqueous

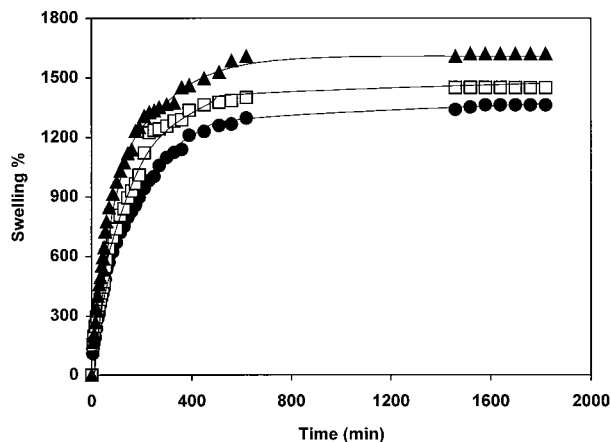


Figure 1 Swelling curves of PVP-g-CA hydrogel containing 2.7 mol % CA: (●) uranyl nitrate, (□) uranyl acetate, and (▲) water.

solution of uranyl nitrate (1360%). However, the swelling of pure PVP hydrogels in water was determined as 700%. The kinetics of swelling of PVP-g-CA hydrogels was used for the calculation of some characteristic parameters.

The study of diffusion phenomena in hydrogels and water is of importance as it clarifies polymer behavior.¹⁸ For the hydrogel characterization, the diffusion coefficient can be calculated by various

methods.^{19–20} The short-time approximation method is used for calculation of diffusion coefficients of hydrogels. The short-time approximation is valid for the first 60% of swelling.²¹ The diffusion coefficients of these cylindrical hydrogels are calculated by the following relation:

$$F = M_t/M_\infty = 4(Dt/\pi r^2)^{1/2} - \pi(Dt/\pi r^2) - \pi/3\pi(Dt/\pi r^2)^{3/2} + \quad (2)$$

where D is the diffusion coefficient, t is the time, and r is the radius of the cylindrical polymer sample. A graphical comparison of equations (1) and (2) shows the semiempirical Equation (2) with $n = 0.5$ and $k = 4(Dt/r^2)^{1/2}$. The diffusion coefficients of the hydrogels were calculated from the slope of the lines of F versus $t^{1/2}$ (Fig. 2). The results are listed in Table I. Values of the equilibrium percentage swelling (S_{eq} , %), parameters of diffusion and diffusion coefficients of the hydrogels are given in the same table. The percentage equilibrium swelling of the hydrogel is lower in uranyl solutions than in water. This decrease was attributed to the adsorption of uranyl ions in the gel system and the exclusion of water molecules at the expense of adsorbed ions and an increase of the ionic strength of the swelling solution. It has

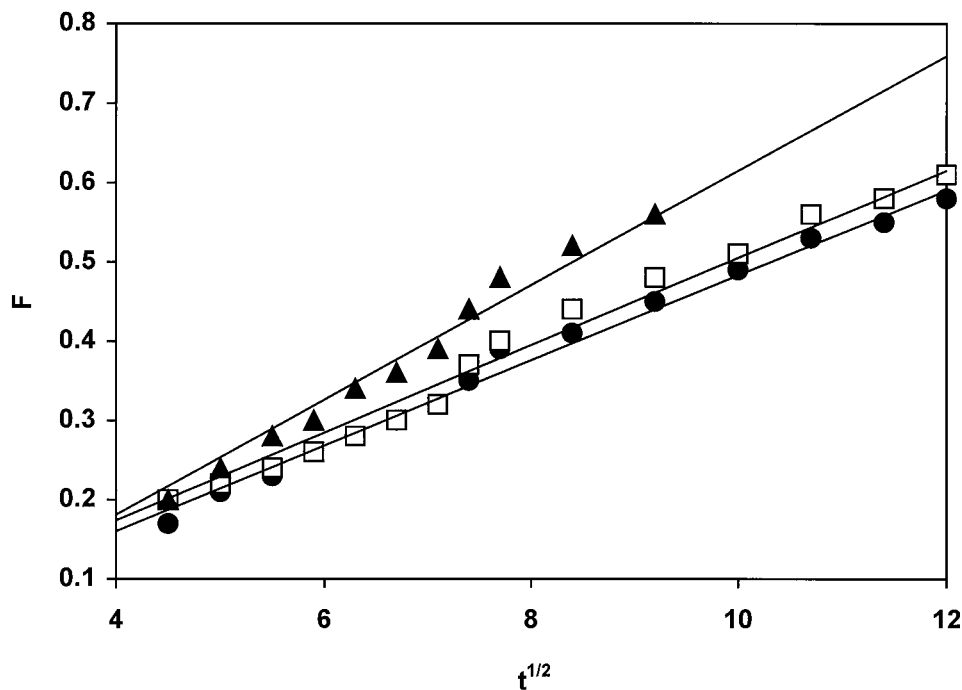


Figure 2 Plot F versus $t^{1/2}$ for PVP-g-CA hydrogel containing 2.7 mol % CA: (●) uranyl nitrate, (□) uranyl acetate, and (▲) water.

Table I Swelling and Diffusion Parameters of PVP-g-CA Hydrogel Containing 2.7 mol % CA

Solution	S_{eq} (%)	$k \cdot 10^2$	$D \cdot 10^8 \text{ m}^2 \text{ s}^{-1}$
Water	1620	7.23	12.57
Uranyl acetate	1450	5.52	5.38
Uranyl nitrate	1360	5.32	4.04

been determined that the equilibrium swelling value of PVP-g-CA hydrogels is very sensitive to the ionic strength of the swelling solution.¹⁷ The values given in the Table I are that the diffusion coefficients of water are larger than the others, so diffusion of uranyl ions into gel pores is relatively difficult.

Adsorption of Uranyl Ions

To observe the adsorption of uranyl ions, PVP-g-CA hydrogels were placed in aqueous solution of uranyl nitrate and uranyl acetate and allowed to equilibrate for 2 days. At the end of this time, the PVP-g-CA hydrogels in solution of uranyl nitrate and uranyl acetate were darkened as compared to the colors of the original solutions, while PVP hydrogels did not sorb any uranyl ions from the

solution. The mass of uptake of uranyl ions per unit mass of adsorbent was calculated from the following relation:

$$\text{Adsorbed } \text{UO}_2^{2+} \text{ (mg/g dry gel)} = \frac{C_i - C}{m} V_t \quad (3)$$

where C_i and C are the initial and equilibrium concentrations of solution of adsorbate, V_t is the total volume of solution of adsorbate, and m is the mass of dry adsorbent

Graphs of adsorbed $[\text{UO}_2^{2+}]$ against the equilibrium concentrations of uranyl ions C are plotted in Figures 3 and 4.

Adsorption of uranyl ions from solution of uranyl nitrate and uranyl acetate onto PVP-g-CA hydrogels corresponds to Type II isotherms.²² In the vast majority of cases, physical adsorption gives rise to a Type II isotherm. The model is controlled by the forces between the adsorbent and the adsorbate molecules, the vertical interactions, and neglects the forces between; and the adsorbate molecule and its neighbors in the same layer are controlled by the horizontal interactions. From the nature of the intermolecular forces, it is certain that the adsorbate-adsorbate interactions must be far from negligible when a layer is approaching completion; and the average separation of molecules are therefore small in relation to their size.²²

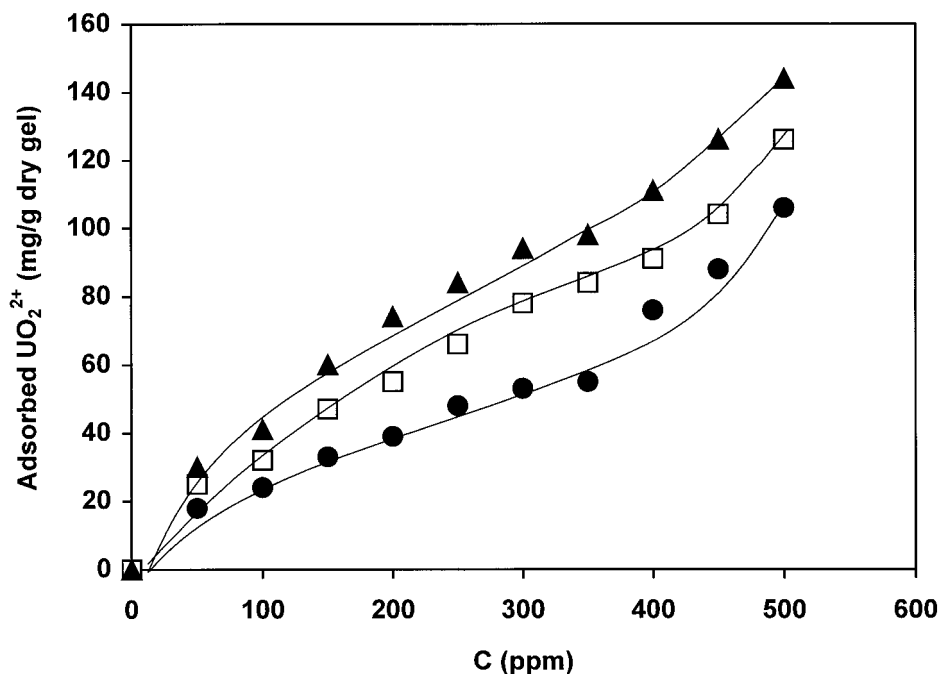


Figure 3 The isotherms of adsorptions of uranyl ions from uranyl nitrate solutions onto PVP-g-CA hydrogels: (●) gel 1, (□) gel 2, and (▲) gel 3.

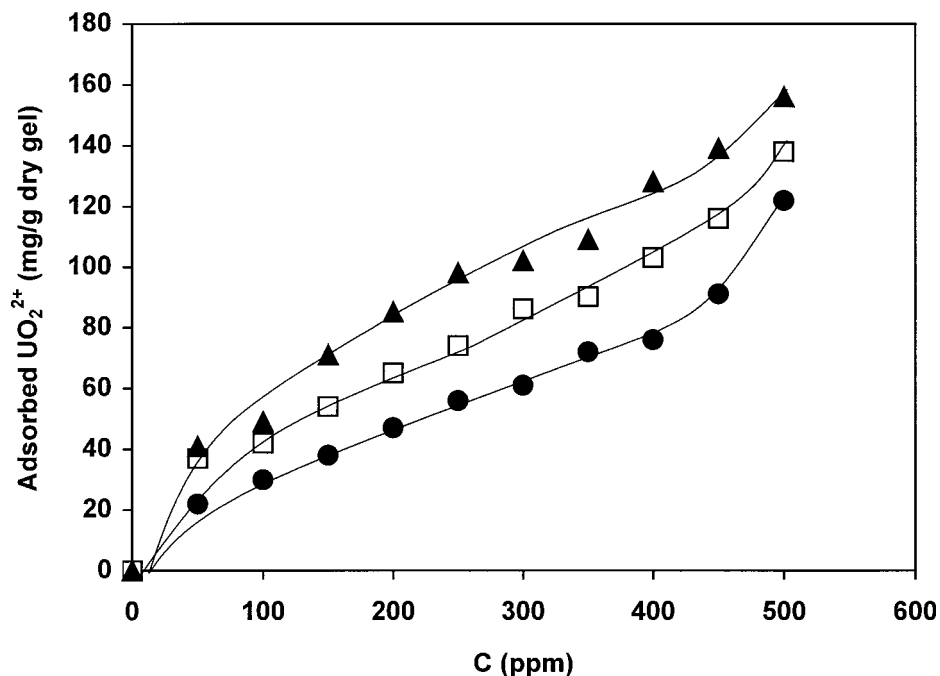


Figure 4 The isotherms of adsorptions of uranyl ions from uranyl acetate solutions onto PVP-g-CA hydrogels: (●) gel 1, (□) gel 2, and (▲) gel 3.

The adsorption of uranyl ions from solutions of uranyl acetate is higher than from solutions of uranyl nitrate. Some interactions that are af-

ected by the swelling properties of the hydrogels are effective for the adsorptions of uranyl nitrate and uranyl acetate onto the PVP-g-CA hydrogels.

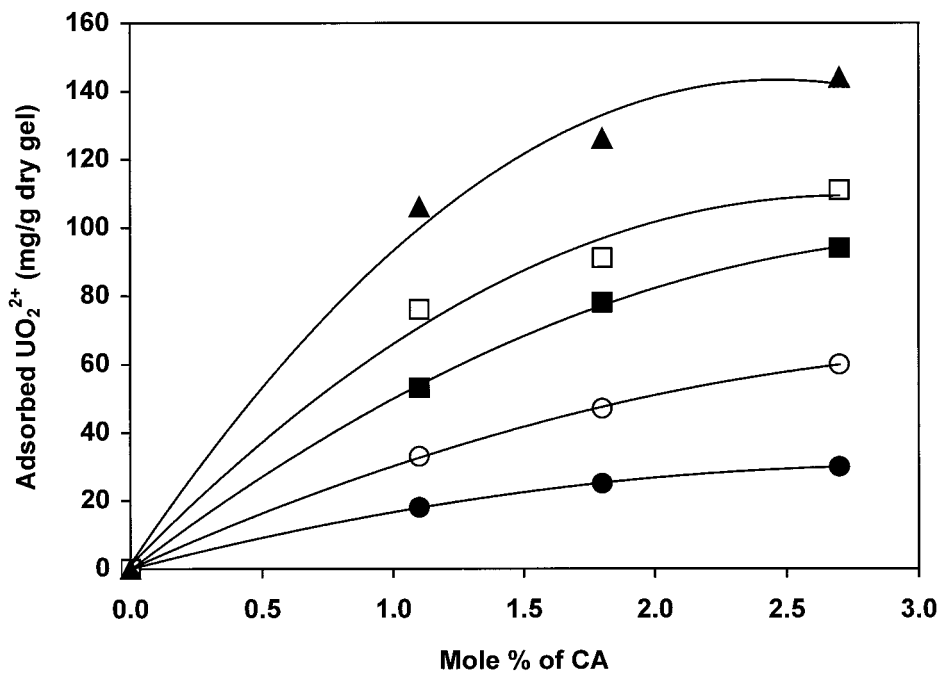


Figure 5 The effect of mol % of CA in the gel system on uranyl ions adsorption from uranyl nitrate solutions: (●) 50, (○) 150, (■) 300, (□) 400, and (▲) 500 ppm.

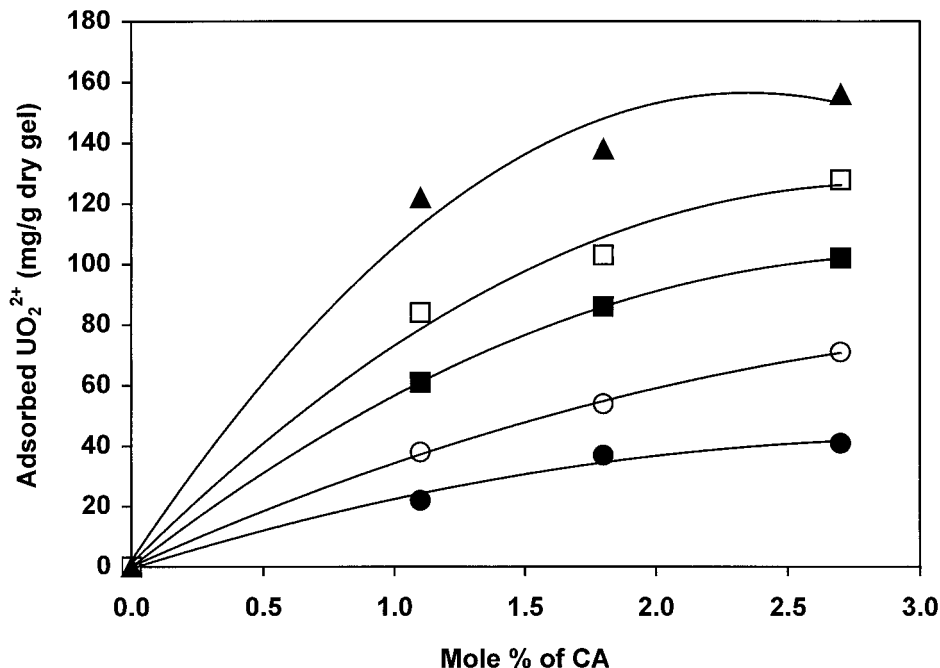


Figure 6 The effect of mol % of CA in the gel system on uranyl ions adsorption from uranyl acetate solutions: (●) 50, (○) 150, (■) 300, (□) 400, and (▲) 500 ppm.

The amount of adsorbed uranyl ions depends on the concentration of uranyl solutions and the mole percentage of CA in the gel system, as shown in Figures 5 and 6. As can be seen from these figures, the uranyl adsorption capacity of these hydrogels were found in the range of 18–144 mg $[\text{UO}_2^{2+}]/\text{g}$ dry gel for the uranyl nitrate solution and in the range of 22–156 mg $[\text{UO}_2^{2+}]/\text{g}$ dry gel for the uranyl acetate solution. Increasing the amount of CA in hydrogel from 1.1 to 2.7 mol % causes a significant increase in the amount of adsorbed uranyl ions. The reason of this increase can be thought of an increase in specific interactions between positively charged uranyl ions and ionized CA in the hydrogel as well as an increase in the free volume of gel available for diffusion. The pH of pure water containing PVP-*g*-CA gels, uranyl acetate, and uranyl nitrate solutions are 4.81, 5.37, and 4.14, respectively. The first, second, and third dissociation constants of CA are $pK_{a1} = 2.94$, $pK_{a2} = 4.14$, and $pK_{a3} = 5.82$. The adsorption of uranyl ions onto PVP-*g*-CA hydrogels may be ionic in nature since the acidic groups of PVP-*g*-CA hydrogels in uranyl solutions completely dissociated at these pH.

Desorption was demonstrated when hydrogels were taken from the solutions of uranyl ions and allowed to stand for 3 days in distilled water.

However, the complete desorption of uranyl ions from PVP-*g*-CA hydrogels was observed at pH 1.

CONCLUSION

In this study, we have tried to see the effect of gel composition on the uranyl ions adsorption capacity of PVP-*g*-CA hydrogels. The CA content in the gel system, as it is clearly shown in this work, in both solutions of uranyl nitrate and uranyl acetate, plays an important role on the adsorption behaviors of PVP-*g*-CA hydrogels. These hydrogels are potential sorbents to be used for the removal of uranyl ions from wastewater and aqueous effluents.

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