

Radiation Synthesis of Poly(*N*-Vinylpyrrolidone-*co*-Methacrylic Acid) Hydrogels and Their Usability in Uranyl Ion Adsorption

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ABSTRACT: In this study, *N*-vinylpyrrolidone(VP)/methacrylic acid (MAA) mixtures have been prepared at three different mole percents which the methacrylic acid composition around 5, 10, and 15%. Poly(*N*-vinylpyrrolidone-*co*-methacrylic acid) P(VP/MAA) hydrogels irradiated at 3.4 kGy have been used for swelling and diffusion studies in water and uranyl ion solutions. The influence of dose, pH, relative amounts of monomers in MAA/VP monomer mixtures on the swelling properties have been investigated. P(VP/MAA) hydrogels were swollen in distilled water at pH 7.0. P(VP/MAA)1 hydrogel containing

36% (mole percent) methacrylic acid showed the maximum percent swelling in water. Adsorption isotherms were constructed for uranyl ions and P(VP/MAA) hydrogel systems. It has been found that P(VP/MAA) hydrogels have very high uptake of the uranyl ions successfully in water containing uranyl ions. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 543–550, 2009

Key words: uranyl ions; adsorption; poly(*N*-vinylpyrrolidone-*co*-methacrylic acid) hydrogels; gamma-irradiation

INTRODUCTION

Hydrogels are water-swollen networks (crosslinked structure) of hydrophilic homopolymers or copolymers. They acquire a great interest due to the facility of the incorporation of different chelating groups into the polymeric networks. Such polymeric hydrogels are promising materials in the field of hydrometallurgical applications and water purification due to their chemical stability especially hydrolytic and thermal stability.¹

Polymeric hydrogels are used in field of veterinary, food engineering, petrochemical industries, photographic technology, and in immobilized enzyme kinetics in bio-engineering, as a carrier of water, pesticides, fertilizer in agriculture,² and as an adsorbent for removal of some agent in environmental application. Some authors have reported on some cross-linked copolymer of the diethyl ester of vinyl phosphonic acid and acrylic acid, and crosslinked copolymers of some natural polymers and some monomers have been used for the adsorption of some heavy metal ions.³ However, the amidoxime derivatives of copolymeric hydrogels prepared from acrylonitrile and divinylbenzene have been used successfully in the recovery of uranium from sea-

water.^{4,5} Acrylamide/maleic acid hydrogels were used in adsorptions of some heavy metal ions in aqueous solutions⁶ and these hydrogels and acrylamide/itaconic acid hydrogels were used in adsorption of some basic dyes in aqueous solution.⁷

The most studied interpolymer complexes of poly-methacrylic acid (PMAA) are those formed either with polyethyleneoxide (PEO) or with poly(*N*-vinylpyrrolidone) (PVP), recently, properties of solid complexes of PMAA with PEO and PVP, respectively, have been studied by Usaitis and et al. The precipitation of the complexes was observed to be dependent on the concentration and pH of the solutions.⁸

In this work, poly(*N*-vinylpyrrolidone-*co*-methacrylic acid) P(VP/MAA) copolymer hydrogels were prepared by means of γ -rays induced homo and copolymerization as a clean and environment friendly source of initiation. The factors effect on the preparation and properties of the hydrogels were investigated and the adsorbing ability of the prepared hydrogels of uranyl ions was examined.^{9–13}

EXPERIMENTAL

Materials

The monomers used in this study *N*-vinylpyrrolidone (VP) and methacrylic acid (MAA) were obtained from Merck. *N,N* methylene bis acrylamide was used as crosslinking agent and it was obtained

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from Aldrich. Hydrochloric acid and sodium hydroxide used to adjust pH of the medium were obtained from Merck. The pH of the adsorption medium was changed between 4.0 and 9.0 by using different buffer systems (0.1 M CH₃COONa—CH₃COOH for pH 4.0–6.0, 0.1 M K₂HPO₄—KH₂PO₄ for pH 7.0 and 0.1 M NH₄OH—NH₄Cl for pH 9.0). Deionized water was used for preparation of hydrogels and in swelling and adsorption studies. Uranyl nitrate (UN), uranyl acetate (UA), potassium hexacyanoferrate(II) were supplied from Merck (Darmstadt, Germany).

Preparation of hydrogels

The solutions of monomers of MAA and VP were prepared in three different compositions (MAA/VP mole ratios: 5/95, 10/90, 15/85). These solutions were placed in polyvinylchloride straws of 3 mm diameter and irradiated in air at ambient temperature in a Gammacell 220 type γ irradiator. Doses of 0.4–20.0 kGy were applied at a fixed dose rate of 0.14 kGy h⁻¹. The hydrogels obtained in long cylindrical shapes were cut. Then these polymer pieces were washed in distilled water to remove the unreacted monomers (if any) and dried in air and in vacuum and stored for later evaluations. The percent gelation was determined gravimetrically. Approximately 80% gelation was performed for all mixtures at 3.4 kGy dose.

Composition of hydrogels

The irradiated monomer mixtures were dried in vacuum oven until a constant weight and subjected to extraction with deionized water as solvent. Uncrosslinked polymer and residual monomer were removed from the gel structure. The amount of uncrosslinked MAA was determined by titration of extract against NaOH (0.05 M) to phenolphthalein end point.

Swelling studies

Dried P(VP/MAA) hydrogels (2 mm thickness, 3 mm diameter) were weighed and they were left to swell in deionized water and dye solution of desired pH (4,7,9) at ambient temperature. Periodically, the P(VP/MAA) hydrogels were withdrawn from the solution and weighed after removing the excess surface water. The measurements were continued until the weight of P(VP/MAA) hydrogels reached a constant value. The percent swelling of each P(VP/MAA) hydrogel was calculated from the following relation:

$$\% \text{Swelling} = [(m_t - m_0) / m_0] \times 100 \quad (1)$$

where m_t is the mass of swollen P(VP/MAA) at time t , and m_0 is the initial mass of dry P(VP/MAA). Some

parameters (diffusion characters, equilibrium water content, etc.) were calculated by using swelling data.

Spectroscopic analysis

Fourier Transform Infrared (FTIR) spectra of P(VP/MAA) hydrogels, P(VP/MAA) hydrogels which contain uranyl ions were recorded between 4000 and 400 cm⁻¹ on a Nicolet 520 FTIR spectrometer as KBr pellets. The P(VP/MAA) hydrogels and P(VP/MAA)-uranyl ion systems were characterized by comparing the FTIR spectra of P(VP/MAA) hydrogels and P(VP/MAA)-uranyl ion systems.

Adsorption studies

Adsorption of the uranyl ions from aqueous solutions was investigated in continuous adsorption equilibrium studies. Effect of the initial concentration, pH, effect of MAA content in hydrogel, and mass of hydrogel on the adsorption capacity were studied. For adsorption studies, optimum mass of hydrogel was determined. The aqueous solution of uranyl ions were prepared in the concentration range of 50–1500 ppm (mgUO₂²⁺L⁻¹). Approximately 0.1 g of P(VP/MAA) hydrogels were transferred into 25 mL of uranyl solutions at pH 7.0. The adsorption of hydrogel was allowed to equilibrium for 3 days at 25°C. The P(VP/MAA) hydrogels were removed from the adsorption medium after the adsorption completed. A 1 mL solution of potassium hexacyanoferrate(II) (1 gL⁻¹) was added to 10 mL of the uranyl solutions and the mixture was held for 30 min. The adsorption experiments were carried out spectrophotometrically. Potassium hexacyanoferrate(II) was used as a complexing agent, giving an absorption maximum at 526 nm. Amount of adsorbed uranyl ions per gram of the hydrogels were also determined. The amount of adsorption per unit mass of the P(VP/MAA) hydrogels were evaluated by using the following equation.

$$q_e = [(C_0 - C_e) \times V] / W \quad (2)$$

where, q_e is the amount of uranyl ions adsorbed onto unit dry mass of the P(VP/MAA) hydrogels (mgg⁻¹), C_0 and C_e are the concentrations of the dye in the initial solution and the aqueous phase after treatment for a certain period of time, respectively (mgL⁻¹), V is the volume of the aqueous phase (L), and W is the amount of dry P(VP/MAA) hydrogels used (g).

RESULTS AND DISCUSSION

Swelling and diffusion studies

Because the gelation reached maximum extent at 3.4 kGy irradiation dose, so, the hydrogels irradiated at

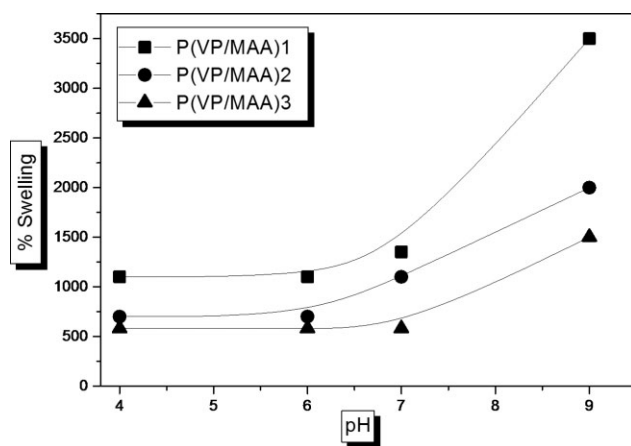


Figure 1 Effect of pH on swelling behaviour of P(VP/MAA) copolymer hydrogels at 25°C, I : 0.1 M, total dose given: 3.4 kGy.

3.4 kGy irradiation dose were used in this study. P(VP/MAA)1, P(VP/MAA)2, P(VP/MAA)3 have been used for three different compositions of P(VP/MAA) hydrogels which contain VP/MAA monomer mixtures at three different mole percents, which are 64/36, 78/22, 82/18, respectively.¹⁴

pH-sensitive copolymers can be prepared by using ionic monomer such as methacrylic acid. Charged groups attached to the polymeric network structure played an essential role in swelling and adsorption properties.¹⁵ It can be seen that the swelling behaviour of the copolymer is greatly influenced by its composition.¹⁴ The equilibrium swelling behaviour of P(VP/MAA) copolymer hydrogels were investigated as a function of pH. Figure 1 shows a typical behaviour of a pH-sensitive copolymer hydrogel. The pH sensitivity of such hydrogel is fully dependent on its composition. All of the investigated copolymer hydrogels possess change in the swelling degree at pH value around pH 6, which is the approximately pKa value of MAA (isobutyric acid repeating monomer unit, pKa = 4.83) ($K_a = 1.48 \times 10^{-5}$).^{16,17} At pH values lower than the pKa value, the carboxylic groups are completely undissociated and the swelling degree is very low. At pH values higher than the pKa value the swelling degree increased due to the dissociation of the carboxylic groups and broken the hydrogen bonding. The increase in the MAA content in the hydrogel leads to the increment in the carboxylate groups and consequently increases the electrostatic repulsion which results in the expansion of the network structure.

The swelling behaviours of P(VP/MAA) hydrogels in distilled water and solutions of uranyl ions are determined, and the results for P(VP/MAA)1 hydrogel are shown in Figure 2. As seen from this figure, the swelling capacities of P(VP/MAA)1

hydrogels are in the range of 35–800 % in the aqueous solution of uranyl ions at pH 7.0. The equilibrium swelling of P(VP/MAA)1 hydrogels is high (40–1353%) in water. Because poly(*N*-vinylpyrrolidone) is a non-ionic polymer, ionizable groups on the polymer were increased by adding MAA to *N*-vinyl pyrrolidone monomer. So, these hydrogels have many carboxyl groups that can increase the interactions between the uranyl ions and carboxyl groups of hydrogels. These figures show that the swelling behaviours of P(VP/MAA)1 hydrogels in water and aqueous solution of uranyl ions are similar to each other. The equilibrium swelling of P(VP/MAA)1 hydrogel whose MAA content is the highest is higher than those of the aqueous solution of uranyl ions. The uranyl ions interact with the carboxyl groups of MAA and carbonyl groups of VP, so the hydrophilic groups of the hydrogel are not bonded with water. For this reason, swelling of the hydrogel decreased in solutions of uranyl ions.

To study diffusion phenomena in P(VP/MAA)1 hydrogels, the swelling curves of P(VP/MAA)1 hydrogels were used to determine the nature of the diffusion of water and uranyl ions into hydrogels by the following equation.¹⁸

$$F = M_t/M_\infty = kt^n \quad (3)$$

where M_t and M_∞ denote the amount of solvent diffused into the gel at time t and infinite time (at equilibrium), respectively, k is a constant related to the structure of the network, and the exponential n is a number used to determine the type of diffusion. This equation was applied to the initial stages of swelling. Plots of $\ln(F)$ versus $\ln(t)$ are shown in Figure 3. The exponents (n) and k were calculated from the slope and intercept of the lines and the results

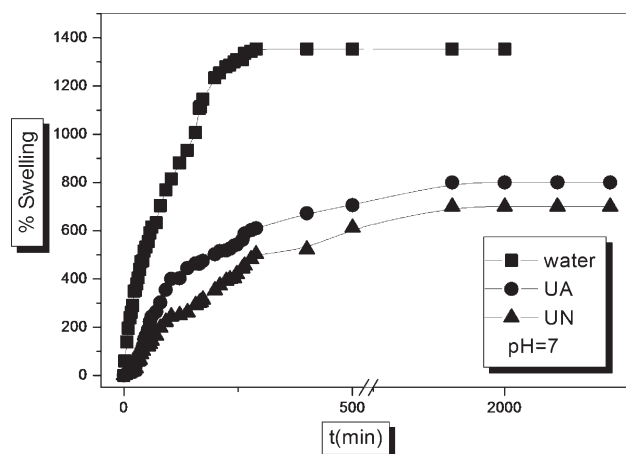


Figure 2 Swelling behaviour of P(VP/MAA)1 hydrogel in 100 mgL⁻¹ uranyl acetate and uranyl nitrate solutions at 25°C. I : 0.1M, total dose given: 3.4 kGy.

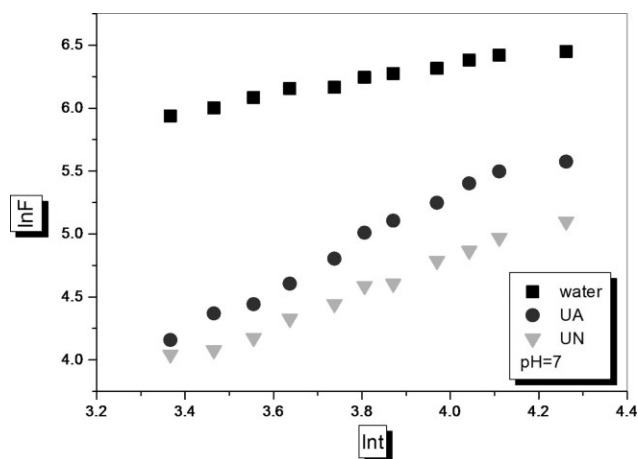


Figure 3 Plots of $\ln(F)$ versus $\ln(t)$ of P(VP/MAA)1 hydrogels in water and 100 mgL^{-1} uranyl acetate and uranyl nitrate solutions at pH 7 and 25°C . I: 0.1 M , total dose given: 3.4 kGy .

were given in Table I. Diffusion coefficients were calculated from the relation¹⁹

$$D = 0.049/(t/4r^2)^{1/2} \quad (4)$$

where D is in $\text{cm}^2\text{min}^{-1}$, t is the time at which the swelling is one-half the equilibrium value ($V/V_0 = 1/2$), and r is the radius of the swollen cylindrical sample. Diffusion coefficients are also listed in Table I.

Table I shows the diffusion coefficients (D) and the index (n), for P(VP/MAA)1 hydrogels at pH 7.0. Diffusion coefficients of P(VP/MAA)1 hydrogels varied from 4.75×10^{-4} to $3.29 \times 10^{-4} \text{ cm}^2\text{min}^{-1}$. These diffusion coefficients lead to the higher water uptake rate than those of the uranyl ions. The exponents n of the hydrogels with the different hydrogel equilibrium water content, which was defined as the weight percentage of water sorbed to that of hydrogels, exhibit greater departure from 0.5 which is characteristics of non-Fickian transport. The information from Table I reveals that the coupling between molecular transport and stress relaxation during hydrogels swelling become more pronounced for samples at higher equilibrium water absorption.²⁰ The acetate and nitrate anions of the heavy metal salts affect swelling. Acetate salts dissolve as molecularly in the aqueous solution whereas nitrate salts dissolve as ions.¹³

Spectroscopic analysis of P(VP/MAA) and P(VP/MAA)-uranyl ion systems

The FTIR spectrum of P(VP/MAA) hydrogel shows some bands revealing the presence of PMAA and PVP. The spectrum of P(VP/MAA) (Fig. 4) shows

1700 , 1485 , 1396 cm^{-1} bands, typical of the $\nu(\text{C}=\text{O})$ of the cyclic groups and 1200 , 1100 cm^{-1} bands, (CH_3) related to C and carboxylic group in PMAA. The band at $1700\text{--}1725 \text{ cm}^{-1}$ $\nu(\text{C}=\text{O})$ of the carboxylic group and at 1436 cm^{-1} $\nu(\text{C}-\text{C})$ stretching band of pyrrolidone ring, in addition to these bands we can see the C-N absorption band at 1180 cm^{-1} in PVP in Figure 4. In the FTIR spectrum of P(VP/MAA)1 hydrogel, the bands that belong to both components can be seen. These results indicate that the MAA monomer copolymerized with VP monomer.

The FTIR spectrum of P(VP/MAA) hydrogels at different compositions are shown in Figure 5. The most important peak appeared at 1690 cm^{-1} . This peak at 1690 cm^{-1} $\nu(\text{C}=\text{O})$ of the carboxylic group increased gradually with increasing MAA percent in the hydrogels.

To determine the nature of the interaction between the uranyl ions and P(VP/MAA)1 hydrogel, FTIR spectra of P(VP/MAA)1, uranyl ions and P(VP/MAA)1-uranyl ion systems are given in Figure 6. The peaks observed in P(VP/MAA)1 in the range of $3600\text{--}3300 \text{ cm}^{-1}$ are O-H bands. The peaks at 2900 cm^{-1} are C-H stretching vibrations in all structure. Figure 6 shows also the FTIR spectra of P(VP/MAA)1 hydrogels 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.²¹

The relation between the nature of the copolymer P(VP/MAA)1 and their uranyl ions complexation behaviour is generally complicated by many possible interactions. Oxygen in the carbonyl group of VP and MAA are responsible for the interaction of the uranyl ions with the hydrogel. Because the mobile π -electrons are pulled strongly towards oxygen. Carbonyl carbon is electron deficient and carbonyl oxygen is electron rich, the uranyl ions act as electron acceptors and taken up by coordination to the donor oxygen of the carbonyl group. We can say that in FTIR spectra of P(VP/MAA)1-uranyl ion systems, the interaction between P(VP/MAA)1 and uranyl ions occurred on oxygen atom in MAA carbonyl group. It can be concluded that there is an ion-ion

TABLE I
The Variation of the Swelling and Diffusion Parameters of P(VP/MAA)1 Hydrogels in Water and Uranyl Solutions with pH 7.0 at 25°C . I: 0.1 M , Total Dose Given: 3.4 kGy

Solution	Seq %	$k \times 10^2$	n	$D \times 10^4 (\text{cm}^2\text{s}^{-1})$
Water	1353	1.9	0.65	4.75
Uranyl acetate	800	1.12	0.60	3.85
Uranyl nitrate	700	0.80	0.58	3.29

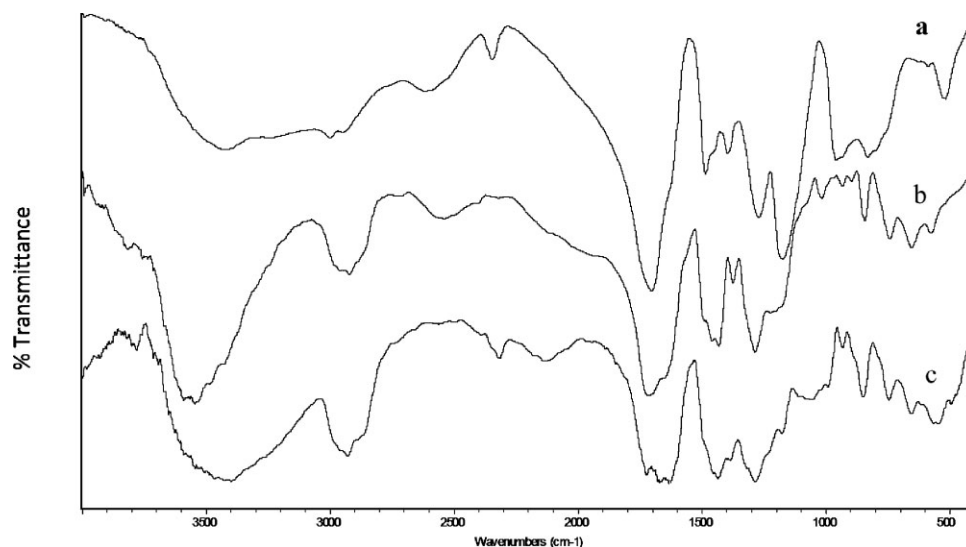


Figure 4 FTIR spectra of (a) PMAA, (b) P(VP/MAA)1, (c) PVP.

interaction between cationic groups of uranyl ions and carboxyl groups of hydrogels. These may occur between negative charge of carboxyl group on the hydrogels and positive charge on the uranyl ions.

Because poly(*N*-vinylpyrrolidone) is a non-ionic polymer, ionizable groups on the polymer were increased by adding MAA to *N*-vinylpyrrolidone monomer. So, these hydrogels have many carboxyl groups that can increase the interactions between the cationic groups and carboxyl groups of hydrogels. These groups can interact with small molecules or ions and, these species bind to *N*-vinylpyrrolidone copolymers with non-covalent or covalent bonds. In the uranyl ion/hydrogel system, uranyl ion has a cationic character and, can interact by electrostatic forces with the anionic carboxyl groups of methacrylic acid in the VP/MAA hydrogel (Fig. 7).

Therefore, the cationic character of ions may be important factor for binding to *N*-vinylpyrrolidone hydrogels containing monoprotic moieties.

Adsorption studies of P(VP/MAA) hydrogels in aqueous solution of uranyl ions

It is known that the uncharged polymer, poly(*N*-vinylpyrrolidone) has ability to bind reversibly to various molecules (dyes, metals, and some polymers) by forming association complexes.²² Macromolecules in solution form association complexes with species of low molecular weight or with macromolecules. Association between two macromolecules involves binding between the specific functional groups present in the two chains and in addition, the effect due to the macromolecules themselves

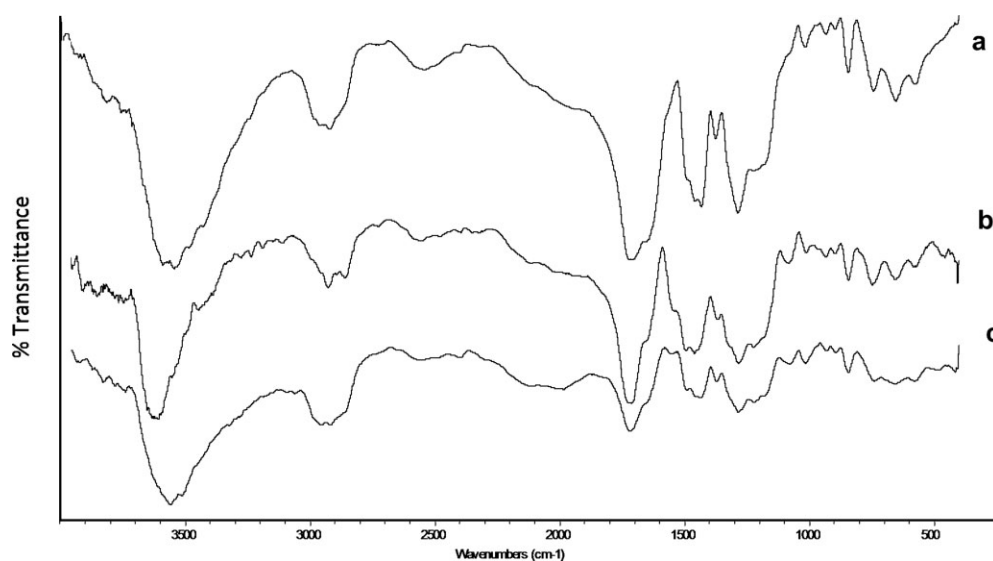


Figure 5 FTIR spectra of (a) P(VP/MAA)1, (b) P(VP/MAA)2, (c) P(VP/MAA)3.

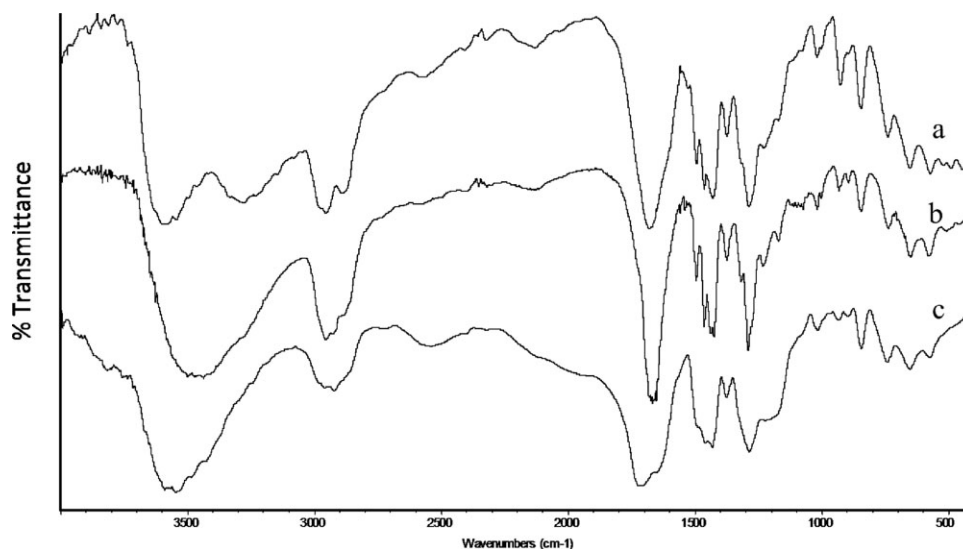


Figure 6 FTIR spectra of a) P(VP/MAA)1-UA system, b) P(VP/MAA)1-UN system, c) P(VP/MAA)1.

often termed as cooperative effect, the cooperative phenomena enhance the stability of the complex.

It is possible to combine the two properties in a single hydrogel to adsorb some ions into these hydrogels. In this study, we tried to combine the properties of two monomers in a P(VP/MAA) hydrogel. The adsorption of aqueous solutions of uranyl ions into P(VP/MAA) hydrogels was investigated.

The effect of uranyl ions on adsorption capacity of P(VP/MAA) hydrogels was investigated. The aqueous solutions of uranyl ions were prepared in the desired concentrations, and 0.1 g of P(VP/MAA) hydrogels irradiated 3.4 kGy were transferred into

25 mL of the synthetic aqueous solutions of uranyl ions at pH 7 and 25°C. In the experiments of adsorption at pH 7.0, two different uranyl salts, namely, uranyl nitrate and uranyl acetate were used for the investigation of the effects of the anionic groups of uranyl salts. The adsorption curves of the hydrogel in the aqueous solutions of uranyl ions are shown in Figures 8 and 9. These Figures show that the adsorption behaviours of P(VP/MAA) hydrogels for uranyl ions from aqueous solutions of uranyl acetate and uranyl nitrate are similar to each other. When the UO_2^{2+} ion concentration in UA and UN solutions increased, the mass of adsorbate per unit mass of

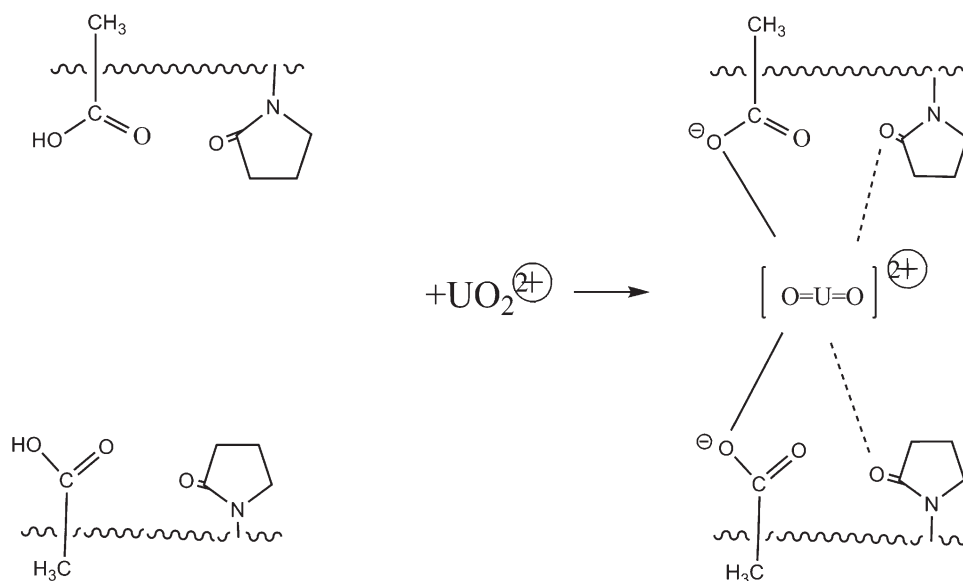


Figure 7 Possible electrostatic interaction between uranyl ions and VP/MAA hydrogel.

adsorbent, q_e increased and the adsorption rate of UO_2^{2+} ions from uranyl acetate solution to P(VP/MAA) hydrogels are the higher than those of uranyl nitrate solution.

To determine the effect of concentration of uranyl ion solutions on adsorption plots of q_e (q_e , $\text{mgUO}_2^{2+} \text{g}^{-1}$ hydrogel) against the free concentrations of the uranyl ions in the solutions (C , $\text{mgUO}_2^{2+} \text{L}^{-1}$) are shown in Figures 8 and 9 for UA and UN at pH 7.0 and 25°C , respectively. Figures 8 and 9 show that adsorption of uranyl ions into P(VP/MAA) hydrogels corresponds to Type S adsorption isotherms in the Giles classification system for adsorption of a solute from its solution.²³ In this type of adsorption isotherm, the initial curvature shows that when more sites in the substrate are filled it becomes increasingly difficult for a bombarding solute molecule to find a vacant site available. One gram of dry P(VP/MAA) hydrogels sorbed 40–400 mg uranyl ions from solutions of uranyl nitrate and 35–480 mg uranyl ions from solutions of uranyl acetate.

From these adsorption studies, it is seen that P(VP/MAA) hydrogels may be used as an adsorbent for removal of uranyl ions from water.

CONCLUSIONS

Spectroscopic analysis of homopolymer and copolymers were done to explain the interactions between the copolymer/homopolymer and uranyl ions. P(VP/MAA) hydrogel containing the highest MAA, showed maximum % swelling in distilled water and aqueous solution of uranyl ions at pH 7.0. Swelling increased the order of water > UA > UN at pH 7.0. Diffusion of water and the aqueous solution of ura-

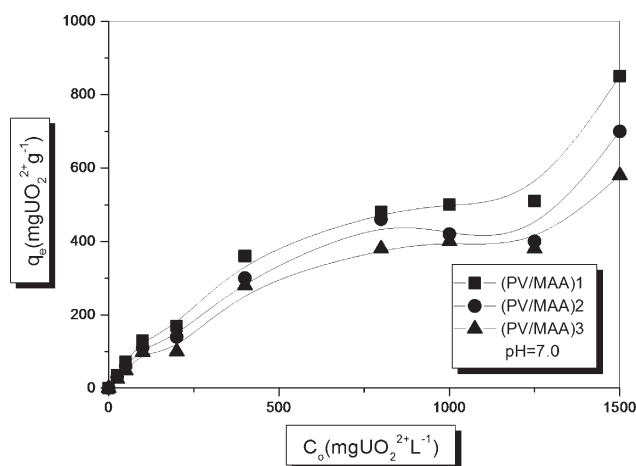


Figure 8 The adsorption isotherms of uranyl ions from aqueous solutions of uranyl acetate onto variations P(VP/MAA) hydrogels at pH 7.0 and 25°C . I : 0.1 M, total dose given: 3.4 kGy.

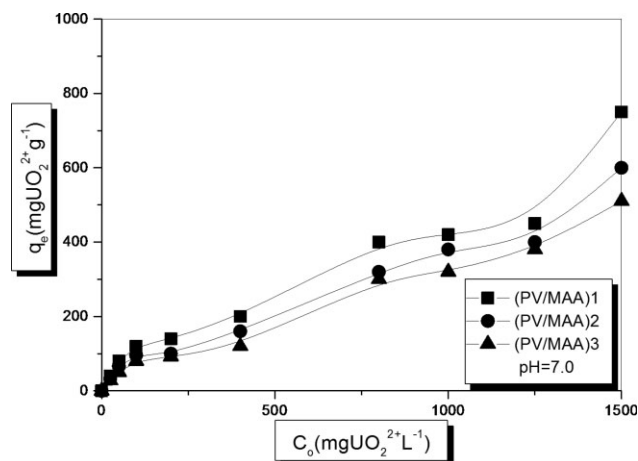


Figure 9 The adsorption isotherms of uranyl ions from aqueous solutions of uranyl nitrate onto variations P(VP/MAA) hydrogels at pH 7.0 and 25°C . I : 0.1 M, total dose given: 3.4 kGy.

nyl ions within hydrogels was found to be of a non-Fickian character. Diffusion coefficients were calculated for P(VP/MAA)1 hydrogel in water and aqueous solution of uranyl ions. Adsorption capacities of P(VP/MAA) hydrogels were changed with the concentration of aqueous solution of uranyl ions. The adsorption of uranyl ions was found to fit into Type S adsorption. Adsorption capacity of P(VP/MAA) hydrogels were changed the order of UA > UN. P(VP/MAA) hydrogels can be used easily be regenerated with HCl. This character of the possibility for reusing the reactive polymer several times makes it economically suitable for use.

References

- Rosiak, J. M. A Report on Radiation Synthesis of Hydrogels and Their Biotechnological Applications Report of the Consultant's Meeting on Radiation Synthesis of Hydrogels and Membranes for Separation Purposes, Takasaki, Japan, 1999.17–20, May.
- Andreoupolos, A. G. *Eur Polym J* 1989, 25, 977.
- Efendiev, A.; Kabanov, A. *Pure Appl Chem* 1982, 54, 2077.
- Hirotsu, T.; Katoh, S.; Sugasaka, K.; Seno, M.; Hagaki, T. *Sep Sci Technol* 1986, 21, 1101.
- Kabay, N.; Egawa, H. *Sep Sci Technol* 1993, 28, 1985.
- Saraydin, D.; Karadağ, E.; Güven, O. *Sep Sci Technol* 1996, 31, 423.
- Saraydin, D.; Karadağ, E.; Güven, O. *Sep Sci Technol* 1996, 31, 2359.
- Usaitis, A.; Mannu, S. L.; Tenhe, H. *Eur Polym J* 1997, 33, 219.
- Egawa, H.; Harada, H. *Nippon Kagaku Kaishi* 1979, 9, 58.
- Egawa, H.; Kabay, N.; Jyo, A. *Ind Eng Chem Res* 1994, 33, 657.
- Garg, B. S.; Sharma, R. K.; Bhojak, N.; Mittal, S. *Microchem J* 1999, 61, 94.
- Saraydin, D.; Şolpan, D.; Işikver, Y.; Ekici, S.; Güven, O. *J Macromol Sci Pure Appl Chem* 2002, 39, 969.

13. Şolpan, D.; Güven, O. J Macromol Sci Pure Appl Chem 2005, 42, 485.
14. Şolpan, D.; Kölge., Z.; Torun, M. J Macromol Sci Pure Appl Chem 2005, 42, 705.
15. Vazquez, B.; Gurruchaga, M.; Goni, F.; Roman, S. J Biomater 1997, 18, 521.
16. Marinsky, J. A.; Anspach, M. J Phys Chem 1975, 79, 439.
17. Travers, C.; Marinsky, J. A. J Polym Sci 1974, 47, 285.
18. Buckley, J. D.; Berger, M. J.; Poller, D. J Polym Sci 1962, 56, 163.
19. Li, Y.; Tanaka, T. J Chem Phys 1990, 92, 1365.
20. Shiaw-Guang, D.; Jium-Nan Chou, K. Polymer 1996, 37, 1019.
21. Okamoto, J.; Sugo, T.; Katakai, A.; Omichi, H. J Appl Polym Sci 1985, 30, 2967.
22. Subramanian, R.; Natarajan, P. J Polym Sci Polym Chem Ed 1984, 22, 437.
23. Giles, C. H.; Macewan, T. H.; Nakhwa, S. N.; Smith, D. J Chem Soc 1960, 74, 3973.