

Development of Novel Adsorbent Materials for Recovery and Enrichment of Uranium from Aqueous Media

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ABSTRACT: A new polymeric adsorbent bearing both hydrophilic groups providing swelling in water and amidoxime groups for chelating with uranyl ions (UO_2^{2+}), has been developed and its adsorptive ability for recovering uranium from aqueous media has been investigated. The polymers obtained by irradiating the solution of polyethylene glycol (PEG) in acrylonitrile (AN) are defined as interpenetrating polymer networks (IPNs) and the adsorbent has been obtained by applying the amidoximation reaction to the IPNs with a conversion ratio of $\sim 60\%$. Kinetics of the conversion reaction of the cyano (CN) group to the amidoxime (HONCNH_2) group has been studied by reacting with hydroxylamine (NH_2OH) solution at a molar ratio of $\text{NH}_2\text{OH}/\text{CN} = 1.25$ in aqueous media at three different temperatures, 30, 40, and 50°C , for 3–4 days. The degree of amidoximation ratio was determined by UO_2^{2+} ion adsorption and FTIR spectrometry and the UO_2^{2+} ion adsorption values were found by both UV and gamma spectrometry and also by gravimetry. It was found that the polymeric adsorbent has a very high adsorption ability for uranium and quite a good stability in aqueous media. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2475–2480, 1997

Key words: IPN; uranium adsorption; gamma radiation; acrylonitrile; polyethylene glycol; FTIR

INTRODUCTION

In view of the anticipated exhaustion of terrestrial uranium reserves in the near future, further research has been directed to recovering uranium from nonconventional sources such as coal and natural waters ($0.1\text{--}10\text{ mg U/m}^3$), especially from seawater ($2.8\text{--}3.3\text{ mg U/m}^3$) during the last three decades. The recovery of uranium from contaminated water of flooded mines ($0.1\text{--}15\text{ mg U/m}^3$) also presents a very important environ-

mental problem to be solved. 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, and so on. Among many types of adsorbents, an amidoxime-group-containing adsorbent has widely been studied.^{1–6} This is mainly due to its large adsorption of uranium, and a high stability to chemical reagents like acids used for desorption when compared with such inorganic adsorbents as hydrous titanium oxide.⁷ Adsorbents containing both amidoxime groups and hydrophilic groups have a much higher uranium uptake than an adsorbent containing only amidoxime groups, because the amidoxime group is less hydrophilic among amide, carboxyl, and hydroxyl groups.^{4,8} The water uptake, and so the uranium uptake, increases in pro-

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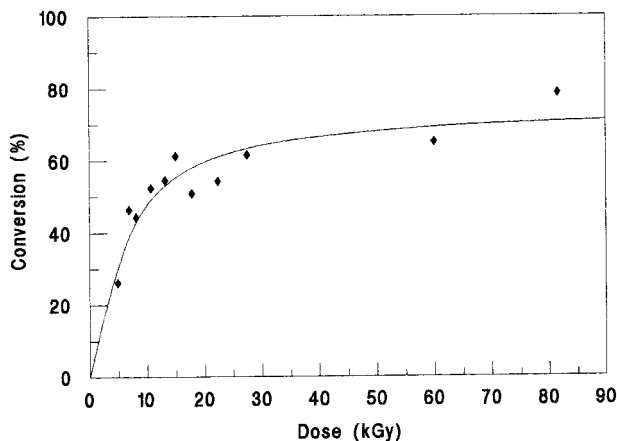


Figure 1 Conversion (%) of IPNs irradiated to various doses.

portion to the kind and the amount of hydrophilic groups because the diffusion of aqueous solution in more hydrophilic polymers will be faster than in less hydrophilic polymers, which is a rate-determining step for adsorption.⁹ From this point of view in this article a new polymeric adsorbent bearing both hydrophilic groups and amidoxime groups has been synthesized as interpenetrating polymer networks (IPNs) based on polyethylene glycol (PEG) and acrylonitrile (AN), and its adsorptive ability for uranium from aqueous media has been investigated.

EXPERIMENTAL

Synthesis of IPNs

IPNs were obtained by dissolving polyethylene glycol (PEG, 35,000) in acrylonitrile (AN) and then irradiating this solution with gamma rays to various doses. Irradiation of the solutions was carried out by a ⁶⁰Co-gamma irradiator with 5.0 kGy h⁻¹ dose rate at room temperature. Certain amounts of these IPNs [(*m*_{IPN})₀] were immersed into dimethyl formamide (DMF) for 48 h and then into deionized water for 24 h, and finally they were dried at 40°C to constant mass [(*m*_{IPN})_f]. Conversion ratio (CR) of the IPNs was defined as CR = (*m*_{IPN})_f/*m*_{IPN})₀. IPNs used in the following experiments were prepared by irradiating the solution at a dose of 14.1 kGy that is the approximate value reached at the beginning of the CR(%)–dose graph plateau (Fig. 1). The IPNs were cut in a cylindrical shape (~ 3 mm diameter, ~ 3 mm height) and used in this geometry.

Amidoximation of Cyano Groups

The cyano (CN) group of the IPNs was changed into an amidoxime (HONCNH₂) group by reacting with hydroxylamine (NH₂OH) solution at a molar ratio of NH₂OH/CN = 1.25 in aqueous media at three different temperatures, 30, 40, and 50°C, for 3–4 days. The IPNs were immersed into deionized water for 48 h before the amidoximation reaction. Hydroxylamine solution was prepared by neutralizing the aqueous hydroxylamine hydrochloride solution with solid sodium hydroxide. The amidoximated IPNs taken from the reaction vessel at certain time intervals were put into deionized water for 24 h and then dried at 40°C to constant mass. The degree of amidoximation ratio was determined by UO₂²⁺ ion adsorption measurements and by a Nicolet 520 Model FTIR spectrometer.

Water Content and Mass Loss of Amidoximated IPNs

Certain amounts of IPNs [(*m*_{IPN})₀] amidoximated at different time intervals were immersed into deionized water for 48 h and were weighed [(*m*_{IPN})_w] after removal of only the water adhering to outer surfaces of them. Then the wetted IPNs were dried at 40°C to constant mass and the mass was determined [(*m*_{IPN})_d]. The water content and the mass loss of amidoximated IPNs were defined as [(*m*_{IPN})_w - (*m*_{IPN})₀]/(*m*_{IPN})₀ (g H₂O/g IPN) and [(*m*_{IPN})₀ - (*m*_{IPN})_d]/(*m*_{IPN})₀ × 100 (%), respectively.¹⁰

Adsorption of UO₂²⁺ Ion on Amidoximated IPNs

Certain amounts of IPNs (~ 0.025 g) amidoximated at different time intervals were put into 20 cm³ of 0.01M UO₂(NO₃)₂·6H₂O solution for 48 h (pH = 4). Then the adsorbent was taken away from the solution, rinsed with deionized water, and dried at 40°C to constant mass. The equilibrium concentration of UO₂²⁺ ion in the solution was determined by UV spectrometry. Sodium salicylate was used as a complexing agent with the absorption maximum at 450 nm and the absorption measurements were done by a Hitachi Model 200-20 double beam UV visible spectrophotometer at 450 nm against blank solution (deionized water). The amount of uranium adsorbed to the IPNs was determined by gamma spectrometry and also by gravimetric measurements. Gamma measurements were obtained by ORTEC-GWL-

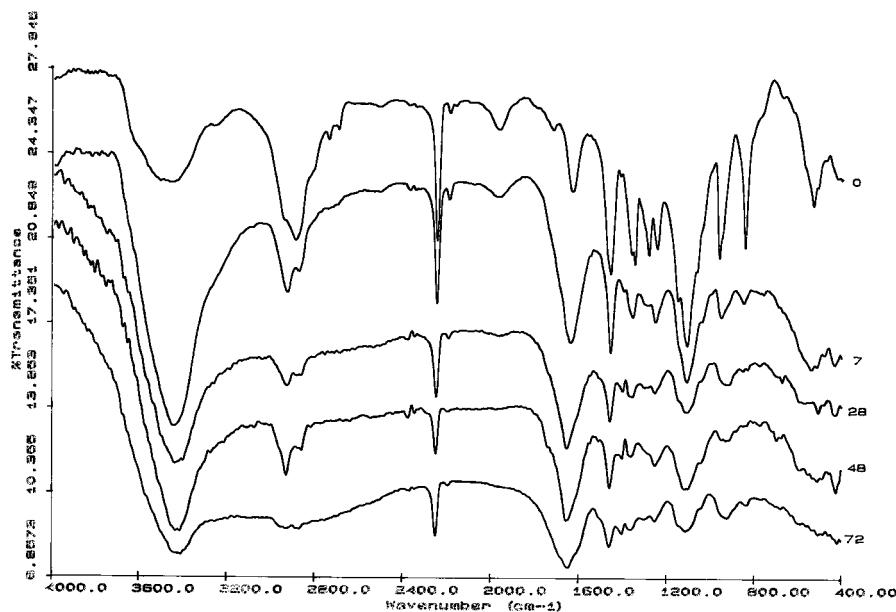


Figure 2 FTIR spectra of the IPNs amidoximated for 7, 28, 48, and 72 h at 30°C and the unreacted IPN.

110220-S Model gamma spectrometer system with a 110 cm³ well-type HPGe detector. The peak areas were determined for 63.283 and 92.5 keV energies of uranium.

RESULTS AND DISCUSSION

Synthesis of IPNs

The irradiated IPNs were in a white-colored, homogeneous structure and their hardness was increased with increasing doses. The change of the conversion ratio of the IPNs with dose was given in Figure 1. The resultant IPNs were prepared by irradiating the PEG-AN solution at a dose of 14.1 kGy that is the value reached at the beginning of the CR (%) / dose curve plato to avoid more cross-linking, which decreases the swelling and therefore the uranium uptake after amidoximation (Fig. 1).

Amidoximation of Cyano Groups

The FTIR spectra of the IPNs amidoximated for 7, 28, 48, and 72 hours at 30°C and the unreacted IPN are given in Figure 2. It was seen from the spectra that as the amidoximation reaction time has been increasing up to 72 h, the characteristic stretching band of nitrile (C≡N) group at 2242 cm⁻¹ has been decreasing steadily but has not completely disappeared, but the characteristic

stretching band of C=N group at 1652 cm⁻¹ has been increasing and broadening steadily. The bands at 3360 and 3390 cm⁻¹ are assigned to an antisymmetric and a symmetric stretching mode of NH₂ groups, respectively. The peak at 930 cm⁻¹ broadening steadily is assigned to the N—O stretching mode. These results clearly show that the conversion degree of the original nitrile groups to amidoxime groups through the treatment with hydroxylamine were increased with the reaction time, but after a 72h reaction period the conversion has not been completed.

Water Content and Mass Loss of Amidoximated IPNs

The change of the water content and the mass loss of the IPNs with the amidoximation time, amidoximated at three different temperatures, are given in Figures 3 and 4. The water content increased in proportion to the increase in time and concentration of amidoxime groups for the amidoximation reaction carried on at 30°C, but for the reactions carried on at 40 and 50°C it was found that initially increasing water content with increase in the concentration of amidoxime groups began to decrease again at ~ 30 and 15 h of reaction periods, respectively (Fig. 3). This showed that the uncrosslinked PEG chains might have been extracted in water therefore the hydro-

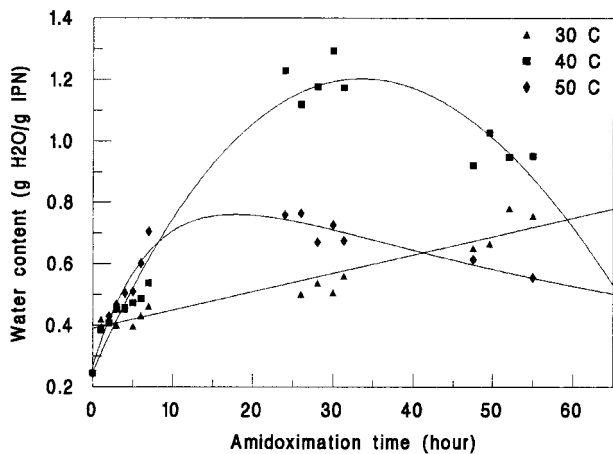


Figure 3 Water content of IPNs amidoximated at 30, 40, and 50°C.

philicity was decreased due to the more pronounced effect of PEG chains to hydrophilicity than the amidoxime groups. Probably the mass loss is increased accordingly (Fig. 4). The rate of change of the structure of IPNs from a more hydrophilic to a less hydrophilic character was approximately doubled with 10° temperature increase (Fig. 3). The rate of change of the mass loss also increases with temperature, probably in proportion to the increase in the amount of extracted PEG chains with increasing temperature (Fig. 4).

Adsorption of UO_2^{2+} Ion on Amidoximated IPNs

The colors of UO_2^{2+} ion-adsorbed IPNs were observed to change from light yellow to dark brown

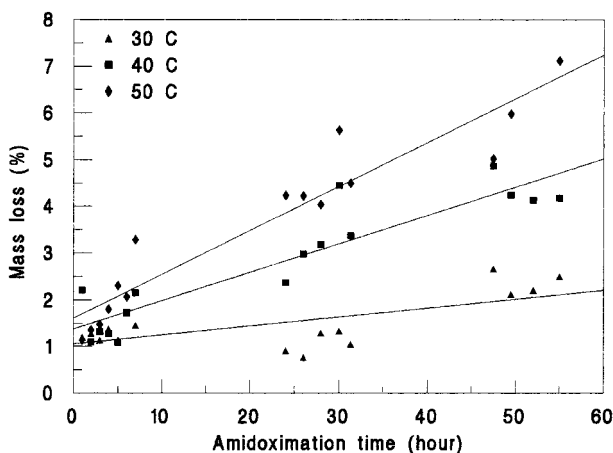


Figure 4 Mass loss of IPNs in water amidoximated at 30, 40, and 50°C.

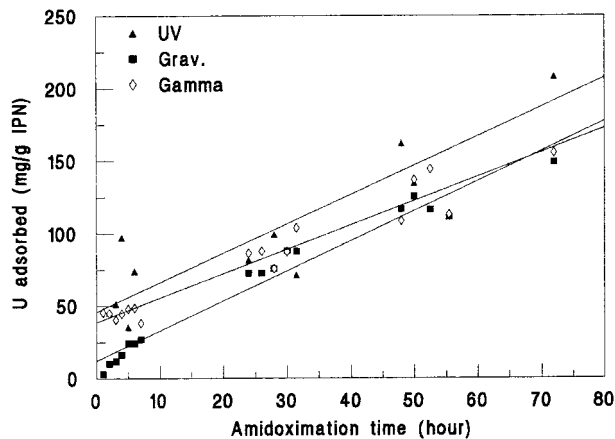


Figure 5 Uranium adsorption on IPNs amidoximated at 30°C obtained by gravimetry, UV, and gamma spectrometry.

in proportion to the increase in amidoximation time. Change in the amount of uranium adsorbed per gram of IPNs with the amidoximation time obtained by gravimetry, UV, and gamma spectrometry at 30°C is given in Figure 5. The amount of adsorbed uranium increased proportionally with the concentration of amidoxime groups of IPNs, which increased with the amidoximation time.

The results of Figure 5 show that the behavior of the curves were similar to each other for all methods, and similar behaviors were also observed for 40 and 50°C. Gravimetric and gamma spectrometric measurements were done from the solid IPNs directly. Gravimetric results gave the less scattered and the most reliable data for this study since the UO_2^{2+} ion is the only cation present in the aqueous medium. In the case of adsorption of the UO_2^{2+} ion from natural media (such as sea water, natural waters, mine water, etc.) gravimetric results could not be used because of the adsorption of some other cations existing in these media (such as Na, K, Mg, Ca, Fe, Ni, Cu, Zn, Pb, Mn, Al, Cr, Cd, As, Au, Ag, Ra, Th, Mo, V, etc.) together with the UO_2^{2+} ion. Having a high selectivity for uranium and no matrix effect, gamma spectrometric results would be the most reliable data for the adsorption of the UO_2^{2+} ion from natural media. Gamma spectrometric results can be considered to be more reliable at high uranium concentrations because of the low counting errors at high counting rates of the sample.

UV measurements were done from the solution indirectly and the amount of adsorbed uranium was found from the decrease in the concentration

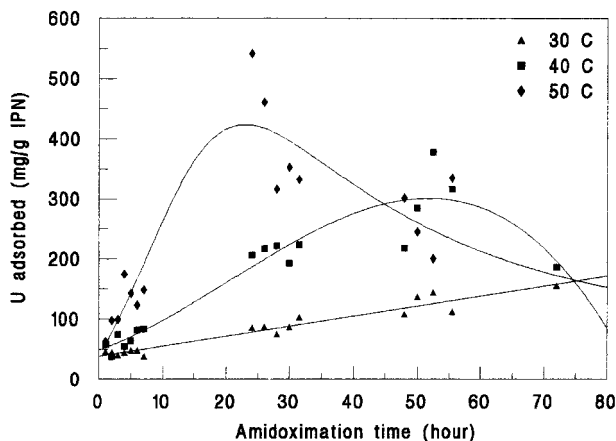


Figure 6 Uranium adsorption on IPNs amidoximated at 30, 40, and 50°C obtained by gamma spectrometry.

of UO_2^{2+} ions in the solution. A difference of 0.001 unit in absorbance measurements causes a change of 0.645 mg uranium in the equilibrium solution concentration, and this leads to a change of ~ 30 mg uranium per gram of IPN depending on the amount of IPNs used for the uranyl ion adsorption. The mean error of UV spectrometric results at 30°C is $\sim 40\%$, so UV results gave the most scattered and the least reliable data of the three methods. Although the UV spectrometry is quantitatively the least reliable method, it gives an approximate amount of adsorbed uranium values and a general idea about the adsorbent. Because of the great matrix effects, UV could not be the most suitable method for the determination of adsorbed uranium from natural media.

Change in the amount of uranium adsorbed per gram of IPNs with the amidoximation time obtained by gamma spectrometry at 30, 40 and 50°C is given in Figure 6. The results of Figure 6 show that initially the rate of uranium adsorption increased in proportion to the temperature, but the points were scattered after ~ 40 h of reaction time at 40°C and 20 h reaction time at 50°C due to the

disintegration of IPNs. No such effect has been observed for the samples prepared at 30°C. Similar results were obtained with the gravimetric and UV spectrometric data.

CONCLUSIONS

Maximal amounts of adsorbed uranium per gram of IPNs obtained by the methods used in this study are given in Table I.

The optimal experimental conditions to obtain an amidoximated IPN with the maximum uranium uptake having a certain geometrical shape and physical structure were determined as 50°C of amidoximation temperature and ~ 20 h of amidoximation time (Fig. 6). The maximum adsorption capacity of the IPNs obtained at these optimal conditions by gamma spectrometry is $\sim \geq 540$ mg U/g IPN/day. A new amidoxime polymer synthesized with acrylonitrile and hydroxamic acid, commercially named as "GoPur 3000," has been reported to have specific loads of 600 mg U/g adsorbent in mine water (pH = 5.5) and has a specific adsorption capacity of 880 mg U/g adsorbent for UO_2^{2+} ions.¹¹ The results obtained in the present work and those reported by the users of GoPur showed again that the amidoxime polymers are highly effective for recovery of uranium from aqueous media. Since amidoxime polymers display a significant affinity for a variety of metal ions present in the waters, more research should be conducted to assess these co-products along with uranium from aqueous media.

Further investigation is in progress in order to improve the mechanical strength and the adsorption capacity of IPNs for uranium by changing the molecular weight of PEG, geometrical shape of the IPNs, amidoximation reaction temperature and time, and also by applying alkaline treatment to hydrolyze the remaining nitrile groups to car-

Table I Maximal Amounts of Adsorbed Uranium per Gram of IPNs

Amidoximation Temperature (°C)	Uranium Adsorbed (mg/g IPN)		
	by Gravimetry	by UV-Spectrometry	by Gamma Spectrometry
30	149	208	156
40	340	190	379
50	353	398	542
Unreacted IPN	Mass loss	75	22

boxylic acid groups. The effects of pH and the concentrations of existing cations and anions in the aqueous media to the adsorption of uranium on IPNs will also be studied for spiked mine waters.

The quantitative measurements of uranium adsorption done by UV spectrometry, which is frequently used in the literature, was found to be the least reliable method as compared to gamma spectrometry and gravimetry. Gamma spectrometry was found to be the most reliable method for the adsorption of uranium from natural media.

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