Use of Amidoximated Acrylonitrile/*N*-Vinyl 2-Pyrrolidone Interpenetrating Polymer Networks for Uranyl Ion Adsorption from Aqueous Systems

NURSEL PEKEL, NURETTIN ŞAHINER, OLGUN GÜVEN

Department of Chemistry, Hacettepe University, 06532 Beytepe, Ankara, Turkey

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ABSTRACT: Poly(*N*-vinyl 2-pyrrolidone) (PVP)/acrylonitrile (AN) interpenetrating polymer networks (IPNs) were synthesized and amidoximated for the purpose of uranyl ion adsorption. The adsorption of amidoximated IPNs was studied from different uranyl ion solutions (850, 1000, 1200, 1400, and 1600 ppm). The result of all our adsorption studies showed that the bonding between UO_2^{2+}-amidoxime groups complied with the Langmuir-type isotherm. The adsorption capacity was found as 0.75 g UO_2^{2+}/g dry amidoximated IPN. In order to increase the UO_2^{2+} ion adsorption capacity the amidoximated IPN was treated with alkali, but no significant increase could be observed. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2324–2329, 2001

Key words: acrylonitrile; interpenetrating polymer networks; uranyl ion; adsorption; amidoxime

INTRODUCTION

There were many studies on the removal of heavy metal ions from wastewater and seawater, especially for the selective recovery and enrichment of uranyl ions.[1–5] Seawater, in addition to a large amount of dissolved alkali and rare earth alkali metal ions, contains a smaller amount of heavy metal and uranyl ions. Therefore, the adsorbents to be used for uranium recovery purposes should be highly selective and of high capacity. Various organic adsorbents containing different functional groups that are more or less selective toward uranyl ions were synthesized and used for this purpose. Polyamine resins comprise one such family.[6] Polyethyleneimine and polyallylamine resins, after being suitably changed, were used for the recovery and preconcentration of uranium from seawater.[7] Chelating resins, which were used as one of the ion exchange systems for the recovery of uranium from waste- and seawaters, has become increasingly more important in recent years. The polymers containing amidoxime groups are one of the most used systems. Amidoxime groups have a selective behavior toward uranyl ions, forming a chelate with uranyl ions. Recently a number of studies were published on the adsorption of uranyl ions by polymers and copolymers containing amidoxime functional groups.[8–14] In above-mentioned studies the amidoxime groups were introduced by the conversion of nitrile groups with hydroxylamine hydrochloride in acrylonitrile (AN) polymers. The polymers and copolymers used for this purpose were all hydrophobic in nature. In this study the aim was to use more hydrophilic amidoxime copolymers for the adsorption of uranyl ions from aqueous solutions for recovery and enrichment purposes. Interpenetrating networks consisting of poly(*N*-vinyl 2-pyrrolidone) (PVP) and polyacrylonitrile

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Correspondence to: N. Pekel (nursel@hacettepe.edu.tr).

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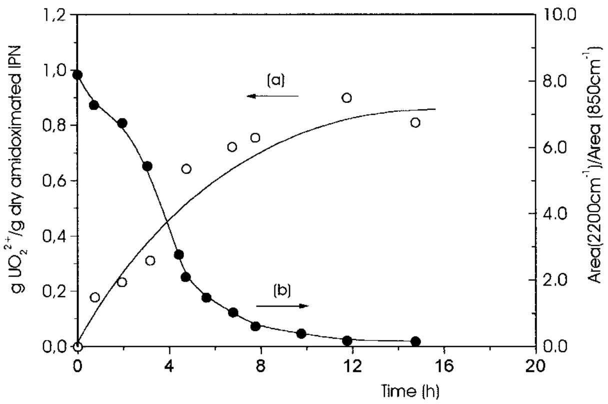


Figure 1 (a) The change of UO_2^{2+} adsorption with the amidoximation reaction time. (b) The conversion of acrylonitrile into amidoxime as followed by FTIR.

(PAN) moieties were prepared and characterized in our previous work.[15] The adsorption capacity of these interpenetrating polymer networks (IPNs) functionalized with amidoxime groups was investigated in the present work.

EXPERIMENTAL

Preparation of IPNs

The IPNs were prepared by irradiating AN solutions of PVP in a ^{60}Co-γ irradiator at room temperature. The composition of the IPNs used in this study was 31/69% by weight for PVP/PAN. After the amidoximation procedure, the conversion of the nitrile groups in the PAN was found to be 99%. The details of the preparation, characterization, and amidoximation are published elsewhere.[15]

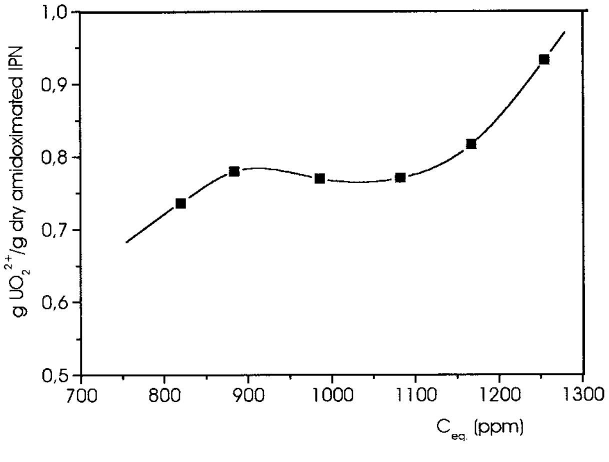


Figure 2 An adsorption isotherm of a UO_2^{2+} ion onto an amidoximatd IPN from a 1400-ppm UO_2^{2+} ion solution.

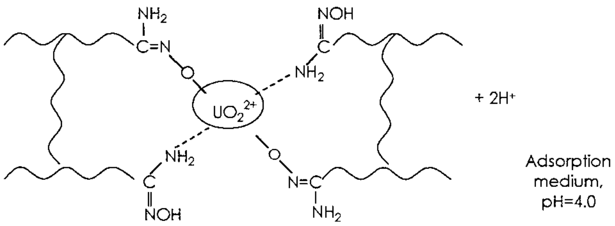


Figure 3 The bonding mechanism between the UO_2^{2+} ion and amidoxime group.

Adsorption of UO_2^{2+} Ion

Uranyl acetate [$UO_2(CH_3COO)_2$] from BDH Co. was used as the source of uranyl ions. The sodium salicylate that forms a complex with uranyl ions for UV spectrophotometry measurements was also supplied by BDH. In the studies of amidoximated IPN's there were UO_2^{2+} ion adsorption steps that were followed. Different UO_2^{2+} ion solutions were prepared (850–1600 ppm) using uranyl acetate. Amidoximated IPNs with a weight range of 0.025–0.150 g were added to 200 mL of UO_2^{2+} ion solutions. The solutions were shaken in closed flasks at 25 ± 1°C for 24 h (pH 4.0). During the shaking process, a 1-mL aliquot was taken and sodium salicylate was added to form a complex. Then their UV spectra were taken at 430 nm, and concentration changes were observed.

The amount of adsorbed UO_2^{2+} ions was calculated using the following equation:

$$A = (V/m) \times (C_0 - C)(1/1000)$$

where A is the amount of adsorbed UO_2^{2+} ions (g UO_2^{2+}/g dry amidoximated IPNs), V is the volume of the UO_2^{2+} ion solution (L), m is the dry weight of amidoximated IPN (g), C_0 is the initial concentration of UO_2^{2+} ions (ppm), and C is the equilibrium concentration of UO_2^{2+} ions (ppm).

Spectroscopic and Thermal Analysis

FTIR spectra of IPNs with and without UO_2^{2+} were taken with a Nicolet 520 FTIR spectrophotometer. The thermal behavior of the UO_2^{2+} ion adsorbed IPN was investigated using a Du Pont 951 thermogravimetric analyzer. The amount of uranium adsorbed to the amidoximated IPNs was determined by a γ spectrometer. The γ measure-

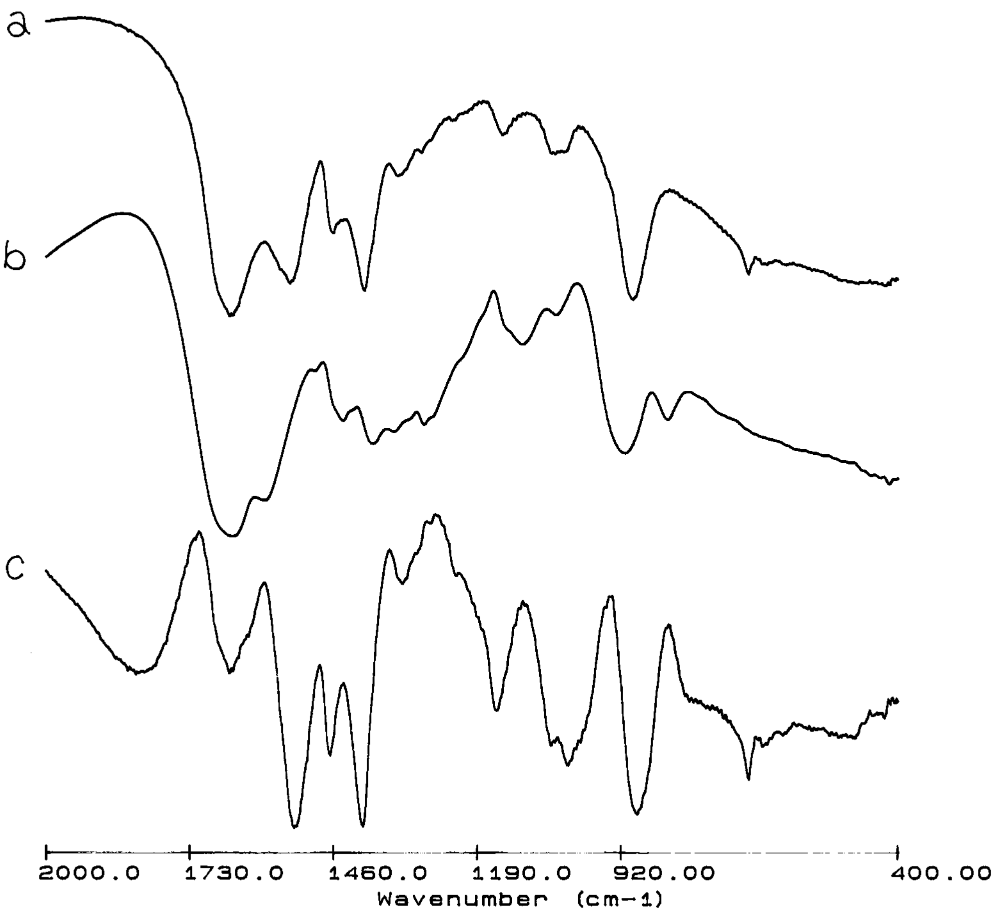


Figure 4 FTIR spectra of an amidoximated IPN and a UO_2^{2+} ion adsorbed amidoximated IPN: UO_2^{2+} ion adsorbed (curve a), UO_2^{2+} ion unadsorbed (curve b), and the spectral difference between (a) and (b) (curve c).

ments were obtained with an ORTEC-GWL-110220-S γ spectrometer system with a 110 cm^3 well-type HPGe detector.

RESULTS AND DISCUSSION

UO_2^{2+} Ion Adsorption

It is well known that some kinds of amidoxime-type chelating resins are useful for the adsorption of uranyl ions.[16,17] The chelating resins are synthesized through the reaction of acrylic resins and hydroxylamine. In order to improve both the stability of the swelling of the resins and the free movement of the functional groups, amidoxime group-containing fibrous sorbents[18,19] for metal ions were synthesized by high-energy radiation-induced grafting of AN followed by amidoximation of C≡N groups with hydroxylamine.

In this study PVP/PAN IPNs prepared with γ irradiation were used for uranyl adsorption from aqueous solutions after an amidoximation reaction. The synthesis, characterization, and amidoximation of the IPNs used in the adsorption studies were previously reported elsewhere.[15]

The presence of amidoxime groups plays a very important role in the adsorption of uranyl ions. The extent of conversion of C≡N groups to amidoxime was followed spectroscopically in our previous work.[15] In order to follow the course of this conversion to amidoximation, the UO_2^{2+} ion adsorption capacity of IPNs were determined occasionally in parallel with FTIR spectroscopy. As shown in plot a in Figure 1, the amount of adsorbed UO_2^{2+} ions first increased with the amidoximation time and then remained unchanged. It was observed that the functional groups changes on the IPNs were completed in approxi-

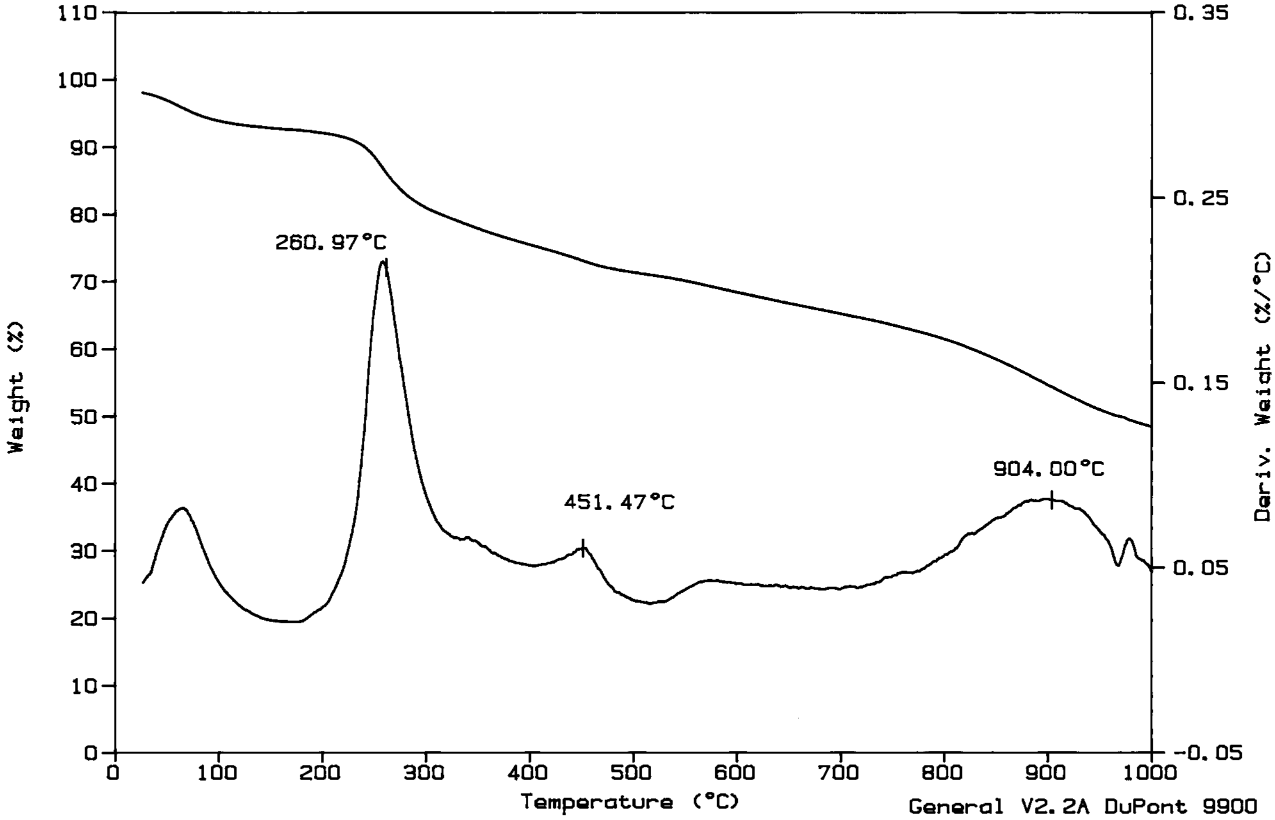


Figure 5 A TGA thermogram of a UO_2^{2+} ion adsorbed amidoximated IPN.

mately 14 h (Fig. 1, plot b). The plateau regions observed in Figure 1 correspond to the same reaction times.

After 14 h of amidoximation, IPN particles with approximately 1.180-mm (16-mesh) sizes were taken and placed in UO_2^{2+} ion containing solutions for studying the adsorption kinetics. Figure 2 shows the typical adsorption isotherm obtained from a 1400-ppm UO_2^{2+} ion solution. The other isotherms observed in solutions prepared with different concentrations (850, 1000, 1200, and 1600 ppm) were the same as this one. The common characteristic of all these isotherms was that at first adsorption they increased rapidly, then they reached a plateau region, and finally the adsorption increased again at lower adsorbent amounts. In other words, the UO_2^{2+} ion adsorption on the IPN was higher at lower adsorbent amounts, yielding Langmuir-type isotherms. The main characteristic of a Langmuir-type isotherm is that dissolved molecules have a high tendency to bond with the surface.[20] At the beginning of adsorption, all amidoxime groups, because they are not bound, have immediate electrostatic interaction with UO_2^{2+} ions. As the adsorption proceeds, the nonbonding amidoxime groups existing in the IPN structure decrease; therefore, the interactions with the UO_2^{2+} ions become difficult. As the concentration increases the isotherm types remain unchanged, and this indicates that the bonding between the UO_2^{2+} ions and amidoxime groups always has the same character. Meanwhile, before the amidoximation reaction, the IPN does not adsorb any UO_2^{2+} ions from the UO_2^{2+} ion solutions.

In order to increase its adsorption capacity, the amidoximated IPN was reacted with NaOH at 50°C to hydrolyze the remaining $C{\equiv}N$ groups to carboxylic acid groups. Scheme 1 shows the reaction of NaOH with the $C{\equiv}N$ group in the IPNs. At the end of the reaction, the solid was filtrated, dried, and put in the UO_2^{2+} ion solution at a certain concentration. However, there was not any clear change in the extent of adsorption when we measured the final concentration. This result can be explained by the conversion of 99% of the $C{\equiv}N$ groups in the IPN into amidoxime groups.

In the studies to explain the quality of bonding between the UO_2^{2+} ion and amidoxime group from mathematical calculations on the plateau region

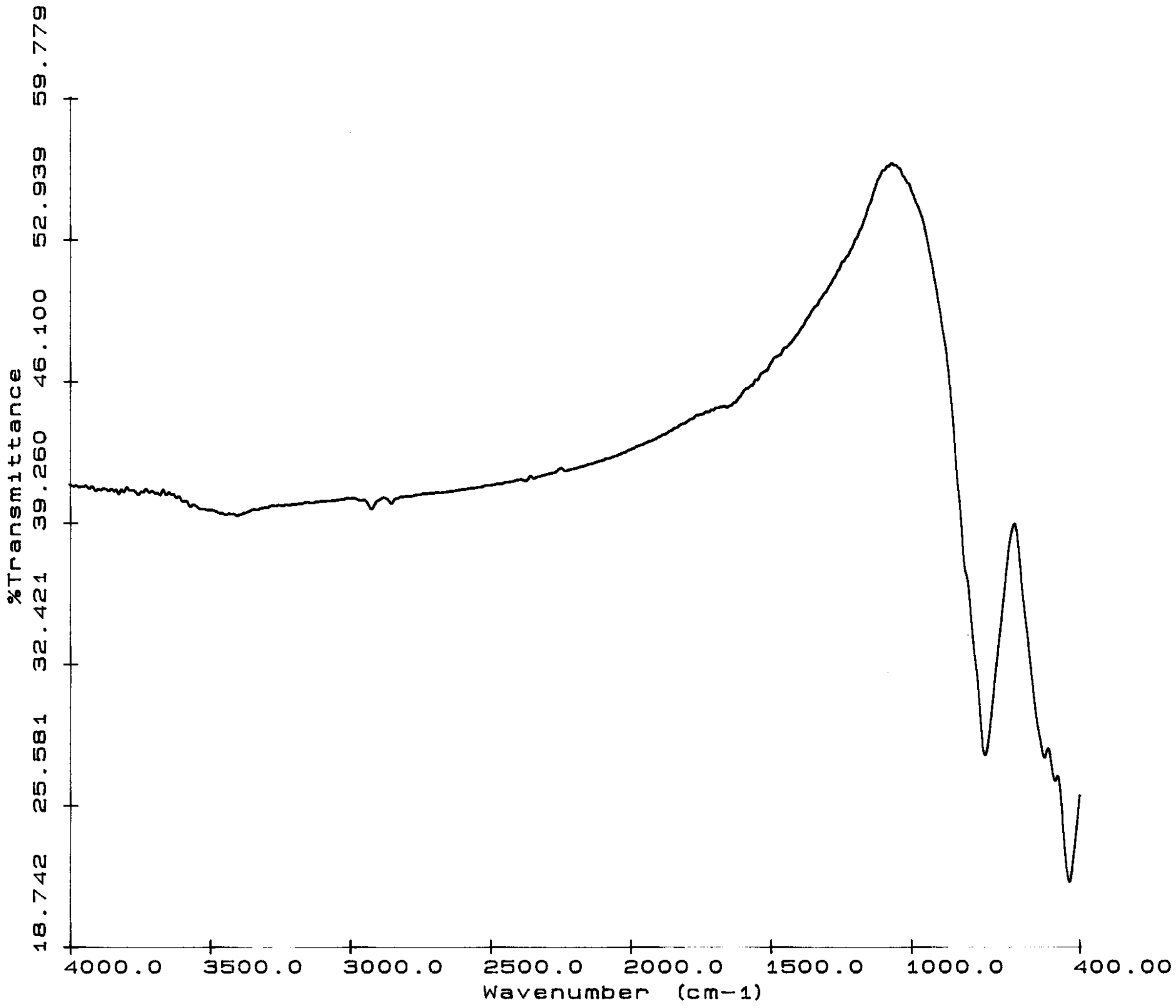
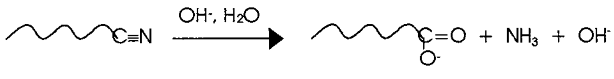


Figure 6 A FTIR spectrum by TGA of the residue of a burned UO_2^{2+} ion adsorbed amidoximated IPN.

values of the adsorption isotherm, the amidoxime group/UO_2^{2+} ion ratio was found to be 4/1. The bonding mechanism can be as shown in Figure 3. As can be seen in Figure 3, the UO_2^{2+} ion is proposed to be coordinated by four amidoxime groups. A similar situation was found in amidoxime modified poly(vinyl alcohol)'s Cu^{2+} adsorption. Because amidoxime groups are bidentate, two amidoxime groups interact with one Cu^{2+} ion, and the other two amidoxime groups take place in coordination.[21] In order to be able to explain the bindings between the UO_2^{2+} ions and amidoxime groups, the most UO_2^{2+} ion adsorbed IPN's spectrum was taken with FTIR.



Scheme 1

As a result of the interaction between the UO_2^{2+} ion and amidoxime groups some band strengthening and a certain shift took place in the FTIR spectra. We show the spectrum difference of 99% converted IPN[15] and UO_2^{2+} ion adsorbed IPN in Figure 4. We observed a 50 cm^{-1} shift in the spectrum of UO_2^{2+} ion adsorbed IPN (Fig. 4, spectrum a) due to the interactions with UO_2^{2+} ions in the C═N band at 1600 cm^{-1} in the amidoximated IPN (Fig. 4, spectrum b). Furthermore, the N—O stretching vibration band observed at 915 cm^{-1} not only increased in its band intensity but also shifted because of the interactions resulting from UO_2^{2+} bindings. In the spectrum difference (Fig. 4, spectrum c), the shifts in N—O at 915 cm^{-1} and

C═N stretching vibration at 1600 cm^{-1} showed that the binding was caused by the oxygen atoms on the newly formed H_2N—C═NOH groups with UO_2^{2+} ions. To compare the amount of IPN's UO_2^{2+} ion adsorption, we studied amidoximated PAN's UO_2^{2+} ion adsorption with the maximum uranium gained system. The adsorption amount was found to be 0.54 g UO_2^{2+}/g dry PAN in a 1400-ppm UO_2^{2+} ion solution. Yet, when the same system was taken into account, the adsorption amount observed for the amidoximated IPN was found to be 0.75 g UO_2^{2+}/g dry IPN. Hence, we could say that the PVP existing in the IPN structure had an increasing effect for adsorption capacity. The existence of PVP in the structure determines the IPN's swelling properties. As the IPN swells more, the amount of conversion of C≡N groups in the core increases. Because of this, the amount of UO_2^{2+} ion adsorption of the amidoximated IPN could be found to be more than the amidoximated PAN's observed adsorption amount.

After the experimental studies, to determine whether or not we could regain uranium and shed light on the character of the adsorbed UO_2^{2+} ion on the IPN's structure, we took the TGA thermogram of the UO_2^{2+} ion adsorbed IPNs in an O_2 atmosphere. TGA evaluations of IPN before and after the amidoximation reaction were reported in our previous work.[15] Figure 5 shows the dynamic thermogram and its derivative for the UO_2^{2+} adsorbed amidoximated IPN. The weight loss of the IPN was around 50% in the heating process of up to 1000°C. Due to the interaction between the amidoxime group and UO_2^{2+} ion, the decomposition temperature observed at 261°C corresponded to the amidoxime groups and at 451°C corresponded to the PVP groups in the amidoximated IPN. Moreover, a new decomposition peak at 904°C represented newly formed U_3O_8. When the FTIR spectrum of the UO_2^{2+} ion adsorbed amidoximated IPN burned in the thermal analyzer was taken, the structure was found as U_3O_8 compared to the literature[22] (Fig. 6). Additionally, a 365 mg ^{238}U/g waste ratio was obtained from the counting of the TGA waste in the γ counter. We illustrated that uranium as U_3O_8 can be mostly regained by burning a UO_2^{2+} ion adsorbed IPN.

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