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Uranyl ion adsorptivity of *N*-vinyl 2-pyrrolidone/acrylonitrile copolymeric hydrogels containing amidoxime groups

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Summary

N-vinyl 2-pyrrolidone (VP) / Acrylonitrile (AN) copolymeric hydrogels were synthesized by using γ-radiation and amidoximated for the purpose of uranyl ion adsorption. Optimum amidoximation time was determined by following the uranyl ion, UO_2^{2+}, adsorption capacity. The adsorption of amidoximated copolymers was studied from different uranyl ion solutions (1000-1850 ppm). The results of all adsorption studies showed that the interaction between UO_2^{2+} and amidoxime groups comply with Langmuir type isotherm. The adsorption capacity was found as 0.54 g UO_2^{2+} /g dry amidoximated copolymeric hydrogels. From the stoichiometric calculations, it was found that the bonding between UO_2^{2+} and amidoxime groups is ***1*** to ***4***.

Introduction

To recover uranium from different media, numerous resins with various chelating groups are used (1-5). The most preferred of these adsorbents are those containing amidoxime groups, which show high selectivity towards uranyl ion. Sekiguchi et. al.(6) and Kubota (7) have prepared amidoxime group containing resins and showed the recovery of uranyl ion from seawater with high adsorption yield. Moreover, amidoxime group containing polymers are used in pre-concentration of rare earth elements, in treatment of wastewater for the extraction of ions such as Cd^{2+}, Hg^{2+}, Cu^{2+}, Co^{2+}, Pb^{2+} etc (8).

There are relatively fewer studies related with hydrogels designed and synthesized for the uranyl ion adsorption from aqueous solutions (9, 10). For the separation, in the use of chelating functional group containing hydrogels, some features of adsorbent such as durability, reuseability and practical applicability are very important. In this aspect, hydrogels have some advantages over other systems. Recently, we (11, 12) prepared amidoxime containing interpenetrating polymer networks based on poly (N-vinyl 2-pyrrolidone/acrylonitrile) with γ-rays, and found a high adsorption capacity as 0.75 g UO_2^{2+}/g dry resins from aqueous uranyl ion solutions. In addition, we also synthesized

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amidoxime containing hydrogel prepared from N-vinylimidazole/acrylonitrile copolymers for the adsorption of uranyl ion from aqueous solutions (13, 14).

Herein, we studied the uranyl ion adsorption of amidoximated poly (AN/VP) hydrogels. Adsorption isotherms were obtained and the binding mechanism of UO_2^{2+} with amidoxime groups was explained. The mechanism between UO_2^{2+} ion and amidoximated copolymer was tried to explain by using FT-IR technique.

Experimental

Preparation of Hydrogels

Detailed information on the radiation synthesis and characterization of both original and amidoximated poly (AN/VP) hydrogels have already been communicated in an earlier publication (15).

Amidoximation Conversion

For each hydrogel compositions (0.67:1.00, 1.00:1.00, 1.50:1.00, and 2.00:1.00 mole ratios of poly (AN/VP) hydrogels), amidoximation reactions were conducted at 30, 40 and 50°C to determine optimum polymer conversion conditions for uranyl ion adsorption. Samples, taken from the reaction media during the amidoximation reaction, placed into distilled water for two days and then dried in both air and vacuum oven at 40°C. Hydrogels with various compositions, after amidoximation reaction, were put into uranyl ion solutions at different concentrations (1000-1850 ppm) in a continuously shaked thermostatically controlled water bath. Adsorption capacities of gels were plotted against amidoximation time, the most convenient temperature and reaction time were determined. All the adsorption studies were done with the hydrogels exposed to optimum reaction time and temperature.

Adsorption Process

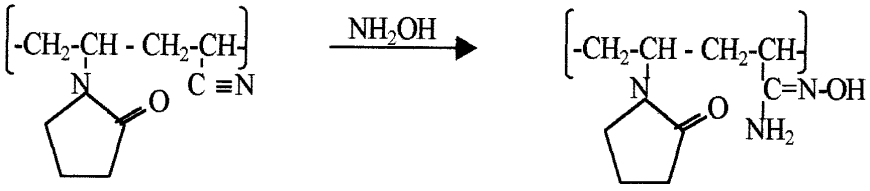
Uranyl acetate, $UO_2(CH_3COO)_2$ and sodium salicylate, the product of BDH were used. Approximately 0.2 g of dry amidoximated poly (AN/VP) hydrogels (4-5mm in length, cylindrical shaped) was placed into 100mL of uranyl ion containing solutions (pH=4.0 in distilled water) for sufficient time. After the uranyl ion adsorption, the amount of UO_2^{2+} ion concentration in solution was determined with Hitachi 100-60 model UV-vis spectrophotometer using sodium salicylate as complexing agent. The adsorption capacities were calculated using the following equation,

$$A = \frac{C_o - C}{w} V \frac{1}{1000}$$

where, *A*, the amount of adsorbed UO_2^{2+} ion (g) per dry gel (g), C_o and C, the initial and equilibrium concentrations of UO_2^{2+} ion solutions (mg/L), respectively, V, the volume of UO_2^{2+} ion solution (L), and w, the weight of dry gel (g).

Results and Discussion

The synthesis, swelling features, and amidoximation of poly (AN/VP) hydrogels have already been described in the previous paper (15). The aqueous solutions of hydroxylamine hydrochloride, ($NH_2OH.HCl$) neutralized with NaOH was used for the amidoximation reaction of 0.67:1.00, 1.00:1.00, 1.50:1.00, and 2.00:1.00 mole ratios of poly (AN/VP) hydrogels. Amidoximation reactions conducted at three different temperatures, 30, 40, 50°C, for all composition of hydrogels. The schematic representation of conversion of C≡N groups to amidoxime groups are shown below,



Samples, taken from reaction media during the amidoximation reaction in pre-determined time intervals, put into distilled water to remove unreacted species and then dried in air. To determine the equilibrium adsorption amount, approximately 0.2 g of dry hydrogels put into ca 1800 mg/L UO_2^{2+} ion containing solutions for certain periods. The amounts of adsorbed UO_2^{2+} at equilibrium versus amidoximation time plots were constructed to determine the optimum amidoximation time and temperature, Figure 1, 2. It can be seen from these figures that, the amidoximation conversion initially increases rapidly and then reach almost a constant value. Optimum amidoximation time was determined as 50hours. When temperatures are taken into account it is found that the amidoximation conversion is the fastest at 50°C for 0.67:1.00 and 2.00:1.00 mole ratios of poly (AN/VP) hydrogel. Curves, drawn for the other compositions, show very similar results. Moreover, similar experimental results were obtained by Okamoto et al. (16), with uranyl ion adsorption studies. They grafted acrylonitrile onto polypropylene, polyethylene as an adsorbent and converted the nitrile groups to amidoxime groups. They reported that the fastest and the highest amount of conversion could be obtained at 80°C.

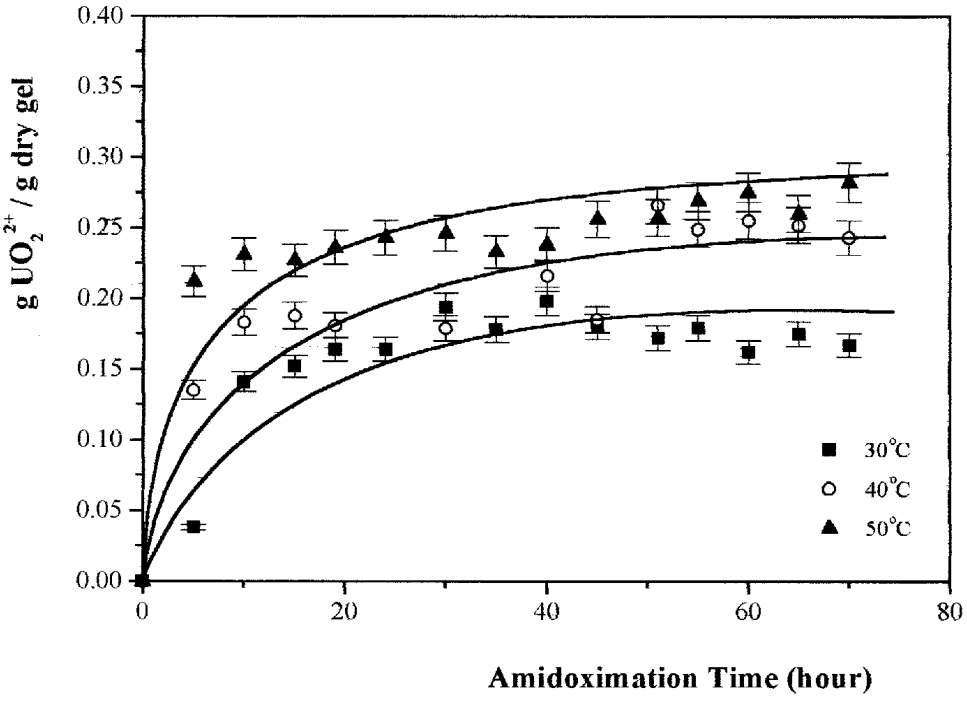


Figure 1. Changing of uranyl ion adsorption with amidoximation time for 0.67:1.00 mole ratio of poly (AN/VP) hydrogel.

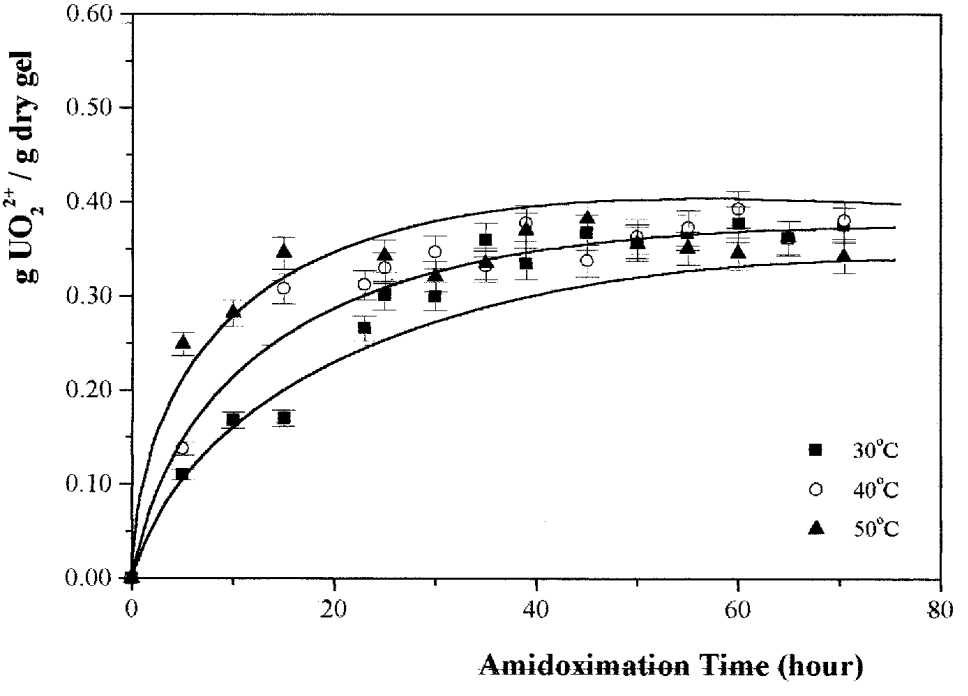


Figure 2. Changing of uranyl ion adsorption with amidoximation time for 2.00:1.00 mole ratio of poly (AN/VP) hydrogel.

After the determination of optimum conversion conditions, amidoximated hydrogels put into 1000, 1200, 1400, 1600, and 1850 mg/L uranyl ion containing solutions until the adsorption equilibrium was reached. Meanwhile, UO_2^{2+} ion adsorption was not observed for pure poly (N-vinyl 2-pyrrolidone) hydrogel. Adsorption isotherms were constructed by graphing the amount of adsorbed UO_2^{2+} ion at equilibrium versus UO_2^{2+} solution concentrations remaining in the solution at equilibrium. In addition, adsorption isotherms were obtained at 25±0.1°C constant temperature. Figure 3 shows the adsorption isotherms of hydrogels with different AN contents, which were amidoximated at 50°C.

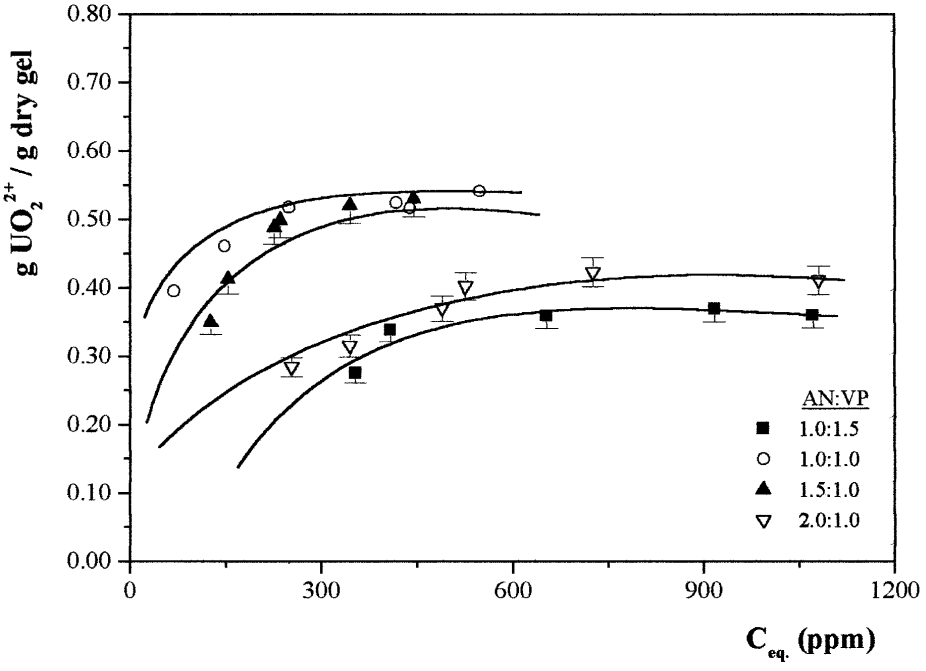


Figure 3. Adsorption isotherms of different composition of poly (AN/VP) hydrogels

These isotherms comply with Langmuir type for all compositions. The maximum amount of uranyl ion adsorption was found as 0.54 g of uranyl ion per g of dry amidoximated hydrogel for the composition of 1.00:1.00 of poly (AN/VP) hydrogels. This value is higher than any other values reported in the literature (0.3-0.4 g UO_2^{2+}/g dry resin) (17, 18) except recently reported results from this laboratory (12, 14). Although the adsorption time of hydrogels is relatively longer due to the three dimensional network forms, these hydrogels are found very efficient to be used in the separation processes.

Table 1 shows the maximum amount of adsorbed uranyl ions per g dry amidoximated hydrogels for different mole ratios of hydrogels. It can be seen from this table, the least amount UO_2^{2+} is adsorbed by 0.67:1.00 composition of poly (AN/VP) hydrogels. Since the AN content of this hydrogel is less than any other composition, the amount of amidoxime groups obtained by conversion of nitrile groups are also relatively small compared to the other compositions. For 2.00:1.00 composition of poly (AN/VP) hydrogels, although the initial acrylonitrile composition of this gel is the highest, the adsorbed amount of UO_2^{2+}, ion is lower than both 1.00:1.00 and 1.50:1.00 composition of hydrogels. Because the amidoximation conversion decreases with the increase of the AN content of hydrogels. In this copolymeric system, VP improves the swelling properties of hydrogel. Since the amidoximation reaction was conducted in aqueous medium, NH_2OH diffuses toward the gel with water during the swelling. The hydrophobicity of hydrogels increases depend on increasing AN amount, so that the amount of conversion of C≡N group becomes relatively small because of the diffusion of NH_2OH into the structure becomes more difficult. In case of 0.67:1.00 of poly (AN/VP) hydrogels, the total amount of C≡N groups are so low that even all C≡N groups were converted the amidoxime group, the amount of adsorbed UO_2^{2+} ion would be small. Because initial AN content of hydrogel is very low. These results are in accordance with the swelling studies (15).

Table 1. The amount of UO_2^{2+} ion (g) per g dry amidoximated hydrogel for different compositions

AN:VP ratio	g UO_2^{2+} / g dry gel
0.67:1.00	0.36
1.00:1.00	0.54
1.50:1.00	0.53
2.00:1.00	0.40

Figure 4 shows the FT-IR spectra of amidoximated and uranyl ion adsorbed amidoximated 1.00:1.00 mole ratio of poly (AN/VP) hydrogels. The structural changes with amidoximation reactions were given in the previous paper (15). When FT-IR spectra of uranyl ion adsorbed and unadsorbed hydrogels are compared, the C=N band at around 1600cm^{-1} shifts to 1540cm^{-1}, and the N-O band at 915cm^{-1} shifts to 900cm^{-1} by means of interactions of corresponding groups with uranyl ion. As can be seen from the difference FT-IR spectrum (Figure 4c) and known the literature, the band at 900cm^{-1} assigned to O-U-O stretching vibration. Similar results were obtained by Rivas et. al. (18).

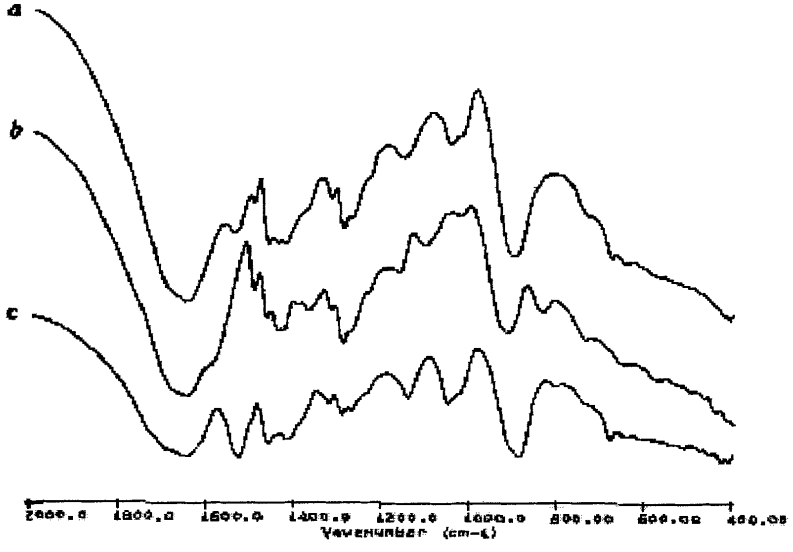
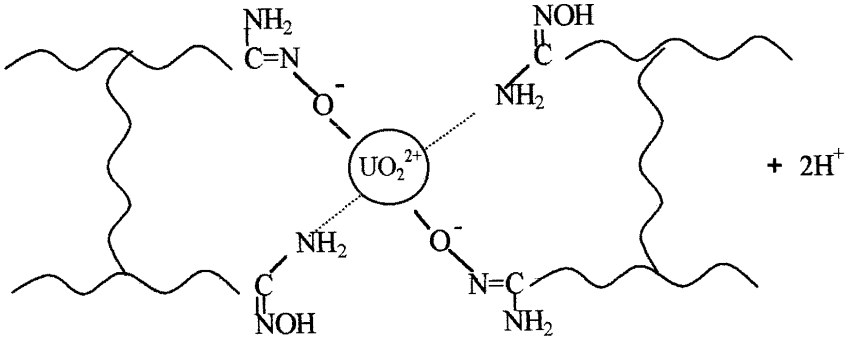


Figure 4. FT-IR spectra of (a) UO_2^{2+} adsorbed, (b) UO_2^{2+} free hydrogel, and (c) difference spectrum (a) and (b)

From the literature (17), the binding mechanism between UO_2^{2+} and amidoxime groups known as 4 amidoxime groups are used for 1 UO_2^{2+} ion. In the light of similar studies (12, 14), we suggested a binding mechanism between UO_2^{2+} ion and amidoxime group using gravimetrical calculations. The possible suggested mechanism shown below:



There are many studies for the adsorption of uranyl ion with amidoxime functional group containing polymers and/or copolymers, yet this study is interesting in the aspect of first time used modified hydrogel to recover uranyl ion from aqueous systems. Moreover, the recovery and the enrichment of UO_2^{2+} ion from wastewaters can be realized very efficiently by using these amidoximated hydrogel, sorbents.

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