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INFLUENCE OF CROSSLINKING AND POROSITY ON THE URANIUM ADSORPTION OF MACRORETICULAR CHELATING RESIN CONTAINING AMIDOXIME GROUPS

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ABSTRACT

Macroreticular chelating resins (RNH) containing amidoxime groups with various degrees of crosslinking were synthesized by using various amounts of divinylbenzene (DVB) or/and poly(ethylene glycol) dimethacrylate [ethylene glycol dimethacrylate (1G), diethylene glycol dimethacrylate (2G), triethylene glycol dimethacrylate (3G), tetraethylene glycol dimethacrylate (4G), and nanoethylene glycol dimethacrylate (9G)] as crosslinking reagent. The effects of crosslinking reagents on the pore structure, ion-exchange capacity, swelling ratio, and adsorption ability for uranium of RNH were investigated. The adsorption ability of RNH for uranium was tested by use of natural seawater or U-spiked seawater. RNH-1G samples prepared by using 1G were shown to have macroreticular structures by measuring the specific surface area. RNH-1G had high adsorption ability and good physical stability. Though RNH-4G samples obtained by using 4G had little macroreticular structure (macropore), these resins showed high adsorption ability for uranium on treatment with 0.1 *M* NaOH at 30°C for 15 h. RNH-4G was found to have low physical and chemical stability. For the preparation of RNH with effective pore structure for the recovery of uranium, as well as chemical and physical stability, the simultaneous use of DVB and 1G or 4G as crosslinking reagent was examined (abbreviated as RNH-DVB-1G and RNH-DVB-4G). The RNH-DVB-1G showed high adsorption ability for uranium. Repeated use did not cause deterioration of either RNH-DVB-1G or RNH-DVB-4G. RNH-DVB-1G samples with various degrees of crosslinking were prepared, and the uranium recovery of the resins was also investigated by a column method. Although the RNH-DVB-1G samples with the same degree of crosslinking had almost the same content of amidoxime groups, the uranium recovery of each RNH-DVB-1G sample was considerably different and increased by treatment with alkali solution. These results indicate that the adsorption ability of RNH-DVB-1G for uranium in seawater was not only affected by the macropores but also by the micropores formed by swelling of the resins.

INTRODUCTION

We have studied selective adsorption resins for metal ions based on the formation of macromolecule-metal complexes. From the point of view of energy resources in the future, atomic power is expected to play an important role. Thus an industrial system for uranium recovery from seawater must be established in the near future. Recently we found that macroreticular chelating resins containing amidoxime groups are most effective for recovery of uranium from seawater and reported that the pore structure of the resins greatly affected the adsorption ability for uranium [1-7].

In the present work, macroreticular chelating resins containing amidoxime groups with various pore structures have been prepared by using several crosslinking reagents, and the influence of crosslinking and porosity on the uranium adsorption was investigated.

EXPERIMENTAL

Macroreticular acrylonitrile-polyethylene glycol dimethacrylate or DVB copolymer beads (RN) were synthesized by suspension polymerization in the presence of toluene as diluent. A solution of purified acrylonitrile, crosslinking reagents, toluene (80 vol%/monomer), and benzoyl peroxide (2 mmol/50 cm^3 monomer) was combined in an autoclave with a solution of Na_2SO_4 (30 g), gelatin (0.3 g), and $CaCO_3$ (5 g) in 500 cm^3 water. Polyethylene glycol dimethacrylates used as crosslinking reagents were ethylene glycol dimethacrylate (1G), diethylene glycol dimethacrylate (2G), triethylene glycol dimethacrylate (3G), tetraethylene glycol dimethacrylate (4G), and nanoethylene glycol dimethacrylate (9G). The DVB used was technical grade (containing 55% DVB). The mixture was stirred until the monomers were dispersed as fine droplets. The suspension was heated to 60°C. Polymerization was carried out at 60-70°C for 4 h. Then the suspension was heated to 90°C and kept at this temperature for 1 h. The product was filtered off and washed with 1 *M* HCl, hot water, and methanol. After drying, copolymer beads with the desired diameter were selected (32-60 mesh).

A solution of sodium hydroxide in methanol was added dropwise to a solution of hydroxylamine hydrochloride in methanol. After the mixture had been stirred sufficiently, sodium chloride precipitated and was filtered off. The concentration of free hydroxylamine in it was determined by titration with 0.5 *M* hydrochloric acid after 1 cm^3 of the filtrate was diluted with 49 cm^3 water. Amidoxime groups were introduced to the RN by means of the reaction of RN (8 g) in pressure bottles with a solution (80 cm^3) of 3% hydroxylamine in methanol for 2 h at 80°C. The product (RNH) was filtered off, washed with pure water until no hydroxylamine was released, air dried, and dried *in vacuo* at 40°C for 2 h.

Treatment of the RNH with Sodium Hydroxide Solution (Alkali Treatment)

The RHN (1 g) was treated with 100 cm^3 of 0.1 *M* sodium hydroxide solution at 30°C for 15 h. The resulting resin was washed with deionized water until the wash water became neutral, air dried, and dried *in vacuo* at 40°C for 2 h.

Treatment of the RNH with Hydrochloric Acid Solution (Acid Treatment)

RNH (1 g) was treated with 100 cm^3 of 1 *M* hydrochloric acid solution at 60°C for 5 h. The resulting resin was washed with deionized water until the wash water became neutral, air dried, and dried *in vacuo* at 40°C for 2 h.

Measurement of Macroreticular Structure (Macropores)

The macroporous nature was characterized by the specific surface area, pore volume, and average pore radius. Specific surface areas of RNH were measured on a Yuasa surface-area apparatus (BET method). Pore volume and average pore radius of RNH were determined on a Carlo-Erba mercury porosimeter (Model 1520).

Measurement of Apparent Anion-Exchange Capacity

RNH (0.5 g) and 100 cm^3 of 0.1 *M* hydrochloric acid solution were shaken in a glass-stoppered Erlenmeyer flask at 30°C for 15 h. The anion-exchange capacity was determined by titrating the Cl^- in the supernatant with $AgNO_3$ solution.

Measurement of Apparent Cation-Exchange Capacity

RNH used for the measurement of anion-exchange capacity was washed with deionized water until the wash water became neutral, air dried, and dried *in vacuo* at 40°C for 2 h. The RNH (0.25 g) and 50 cm^3 of 0.1 *M* sodium hydroxide solution were shaken in a glass-stoppered Erlenmeyer flask at 30°C for 15 h. After shaking, 5 cm^3 of supernatant was titrated with 0.1 *M* hydrochloric acid solution, and Cl^- released to the 5 cm^3 supernatant was separately titrated with 0.05 *M* $AgNO_3$ solution. The cation-exchange capacity was determined by the Cl^- released from the amount of sodium hydroxide exhausted. In the case of RNH after acid treatment, after the cation-exchange capacity was measured, the anion-exchange capacity was also measured.

Adsorption of Uranium from Spiked Seawater

RNH (0.1 g) and 25 cm^3 natural seawater spiked with $UO_2(NO_3)_2 \cdot 6H_2O$ · - (10 mg U/dm^3) were shaken at 30°C for 1 h. The resin was filtered off, and samples of the filtrate were taken for spectrophotometric determination of uranium with Arsenazo-III.

Recovery of Uranium from Seawater by the Column Method

RNH was treated with a 3% sodium chloride solution for 24 h at room temperature, and then 1.5 cm^3 of this RNH was packed in a glass column (a diameter of 1 cm). Natural seawater (20 L) was passed through this column at a space velocity (SV) of 300 h^{-1} at 25-30°C. The uranium adsorbed on the RNH was eluted by passing 10 bed volumes of a 0.5 *M* sulfuric acid solution through the column at SV 3 h^{-1}. Uranium in eluate was determined spectrophotometrically with Arsenazo-III. After this, the RNH was washed with water until the wash water became neutral and then the adsorption-elution procedure was repeated.

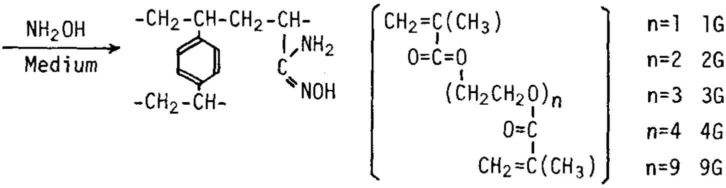
RESULTS AND DISCUSSION

Scheme 1 shows the route for the preparation of the chelating resins containing amidoxime groups. The macroreticular chelating resins were prepared by using acrylonitrile and DVB for crosslinking by suspension polymerization in the presence of toluene as diluent, and followed by treating with hydroxylamine in methanol. These copolymer beads and resins containing amidoxime groups are abbreviated as RN and RNH-DVB, respectively.

Table 1 shows the effect of divinylbenzene and toluene on the pore structure of the macroreticular copolymer beads. The copolymer beads were prepared by using a constant amount of DVB and various volumes of toluene or by using a constant volume of toluene and various amounts of DVB.

The pore structure of the resins was affected considerably by the amount of DVB and toluene used as diluent. The copolymer beads prepared in the presence of 20-40 vol% of toluene and by using 5.3 mol% of DVB have a low specific surface area. The copolymer beads prepared in the presence of 20 vol% of toluene had a rather low specific surface area and pore volume.

Figure 1 shows the adsorption ability for uranium in seawater and the anion-exchange capacity of the RNH-DVB prepared by use of various volumes of toluene and 16.2 mol% of DVB. The adsorption ability of the resins for uranium was tested by use of natural seawater. The content of amidoxime



SCHEME 1. Preparation of chelating resins containing amidoxime groups.

TABLE 1. Effect of Divinylbenzene and Toluene on the Pore Structure of Macroreticular Copolymer Beads (RN)

Composition of monomer[a]			Properties of copolymer		
DVB, mol%	AN, mol%	Toluene, vol%[b]	Specific surface area, m^2/g	Average pore radius, Å	Pore volume, mL/g
16.2	72.3	20	5.0	122	0.038
16.2	72.3	40	22.7	148	0.119
16.2	72.3	60	68.1	150	0.260
16.2	72.3	80	121.0	168	0.491
16.2	72.3	100	128.0	197	0.729
16.2	72.3	120	105.0	247	1.034
5.3	91.0	80	43.4	268	1.165
10.7	81.7	80	126.0	188	0.726
16.2	72.3	80	121.0	168	0.491
21.9	62.6	80	120.0	142	0.353
27.6	52.8	80	93.4	131	0.190

[a] DVB = divinylbenzene, AN = acrylonitrile.
[b] (Toluene/monomer) X 100%.

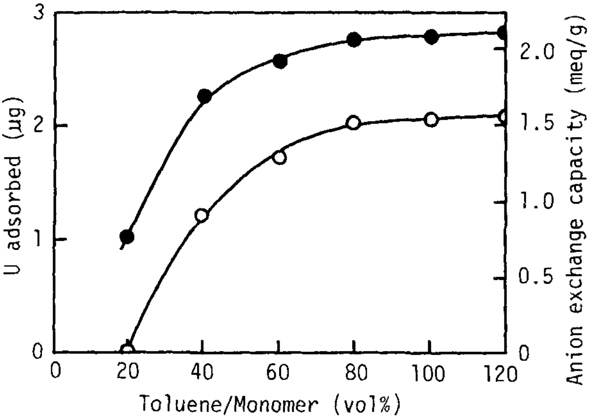


FIG. 1. Effect of toluene during the preparation of chelating resin on the adsorption of uranium. DVB: 16.2 mol%. Reaction conditions: 3% NH_2OH-CH_3OH, 80°C, 2 h. (○) U adsorbed. (●) Anion-exchange capacity.

groups in the resins can be evaluated from the anion-exchange capacity. The RNH-DVB prepared by use of 20 vol% of toluene showed no adsorption ability for uranium, irrespective of its anion-exchange capacity.

Figure 2 shows the adsorption ability for uranium in seawater and the anion-exchange capacity of RNH-DVB samples prepared by using various amounts of DVB and 80 vol% of toluene. The anion-exchange capacity of the resins decreased with increasing degree of crosslinking. However, the RNH-DVB prepared with 10-15 mol% of DVB showed a maximum adsorption ability for uranium.

These results show that the adsorption ability for uranium is not only affected by the chemical structure but also by the physical structure of the resins.

In order to investigate the influence of crosslinking and porosity on the uranium adsorption of macroreticular chelating resins containing amidoxime groups, chelating resins containing amidoxime groups with various kinds and amounts of crosslinking reagent were prepared and the adsorption ability and pore structure of the resins were measured.

First as a hydrophilic crosslinking reagent, poly(ethylene glycol) dimethacrylate was used instead of DVB, followed by treatment with hydroxylamine in methanol, as mentioned before. These resins are abbreviated as RNH-nG.

Figure 3 shows the adsorption ability of RNH-nG for uranium as tested

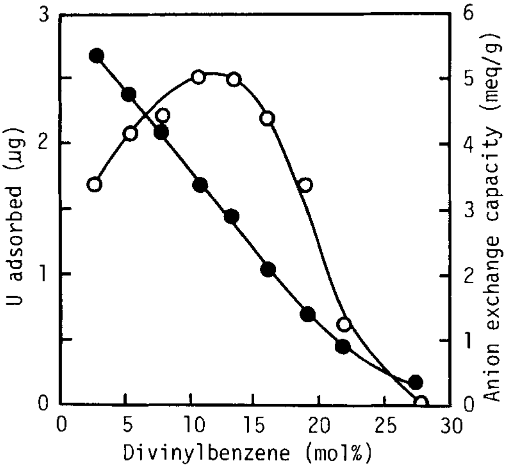


FIG. 2. Effect of crosslinking on the ion-exchange capacity and the adsorption of uranium from seawater. (●) Anion-exchange capacity. Batch method: Resin 0.5 g, 100 cm^3 0.1 *M* HCl, 30°C, 15 h. (○) Adsorption of uranium. Batch method: Resin 0.1 g, seawater 1 dm^3, room temperature, 96 h.

by use of U-spiked seawater. The adsorption ability of the resins was affected by the kind and amount of poly(ethylene glycol) dimethacrylates used for crosslinking, tending to decrease with increasing length of the ethylene glycol units. Of these resins, RNH prepared with 30 mol% of 1G gave the highest adsorption ability. The adsorption ability of these resins was increased by treating with 0.1 *M* NaOH at 30°C for 15 h ("alkali treatment"). The increase of the adsorption ability after alkali treatment increased in the order RNH-1G < -2G < -3G < -4G < -9G. In order to clarify these phenomena, the properties of the RNH-nG were measured.

Table 2 shows the characteristics of pore structure and swelling ratio of RNH-nG with various degrees of crosslinking. RNH-1G, -2G, and -3G had large specific surface areas and average pore radii. This means that these resins have macropores. On the other hand, RNH-4G with a high degree of crosslinking and RNH-9G had no macropores. The specific surface area of RNH-1G is rather large and increased with increasing degree of crosslinking, though the average pore radius decreased with increasing degree of crosslinking. RNH-4G and -9G had large swelling ratios after alkali treatment. The reason for this will be mentioned later.

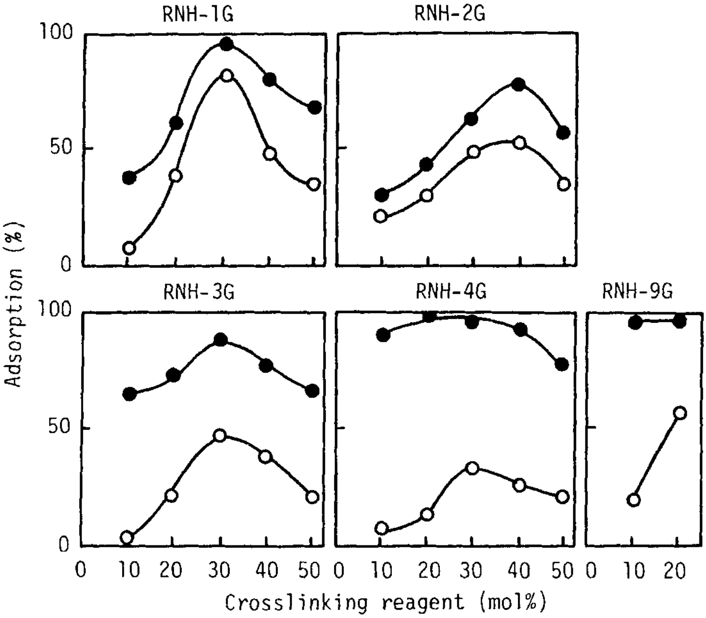


FIG. 3. Effect of crosslinking reagent on the adsorption of uranium. Resin 0.1 g, seawater 25 cm^3 (250 μg of uranium added), shaking at 30°C for 1 h. (○) Nontreated resin. (●) Alkali-treated resin.

Figure 4 shows the ion-exchange capacities of the RNH-nG. The anion-exchange capacity of all these resins decreased with increasing degree of crosslinking, as did the cation-exchange capacity. The anion-exchange capacity of RNH was decreased by alkali treatment, whereas the cation-exchange capacity was increased by alkali treatment. The change in the cation-exchange capacity increased in the order of RNH-1G < -2G < -3G < -4G < -9G. RNH-4G and -9G showed especially large increases of cation-exchange capacity on alkali treatment. This indicates that carboxyl groups were formed by the hydrolysis of amidoxime, nitrile, and ester groups of the resins. In fact, carboxyl groups were observed by IR spectra of the resins.

The large swelling of the RNH-4G and -9G mentioned before is attributed to an increase of the hydrophilicity due to carboxyl groups formed by the hydrolytic cleavage of crosslinking reagent. It is considered that the carboxyl groups formed by alkali treatment contribute not only to the high swelling but also to the complexation of uranium in seawater. However, it has been reported that macroreticular resins containing carboxyl groups are not effective for recovery of uranium from seawater [3].

TABLE 2. Pore Structure and Swelling Ratio of RNH-1G, -2G, -3G, -4G, and -9G

Crosslinking reagent, mol%		Specific surface area, m^2/g	Average pore radius, Å	Pore volume, cm^3/g	Swelling ratio[a]	
					V_2/V_1	V_3/V_1
1G	10	1.4	2977	0.85	1.4	1.8
	20	17.3	473	0.46	1.3	1.3
	30	54.8	211	0.56	1.2	1.1
	40	102.0	129	0.40	1.3	1.2
	50	140.0	143	0.44	1.2	1.1
2G	10	1.8	2927	0.82	1.6	3.0
	20	9.1	1023	0.50	1.4	1.8
	30	12.6	584	0.48	1.3	1.3
	40	16.9	368	0.43	1.4	1.4
	50	13.7	260	0.24	1.4	1.3
3G	10	12.6	756	0.58	1.2	4.6
	20	12.2	583	0.33	1.3	2.9
	30	11.7	511	0.22	1.2	1.9
	40	9.9	217	0.12	1.3	1.4
	50	12.1	186	0.09	1.3	1.5
4G	10	7.6	461	0.17	1.6	12.4
	20	0.8	307	0.04	1.6	6.2
	30	0.4	318	0.04	1.6	3.6
	40	0.0	–	–	1.9	3.4
	50	0.0	–	–	1.8	2.5
9G	10	0.0	–	–	2.3	29.3
	20	0.0	–	–	2.4	14.1

[a] V_1 = dry volume of RNH, V_2 = wet volume of RNH, V_3 = wet volume of RNH after alkali treatment.

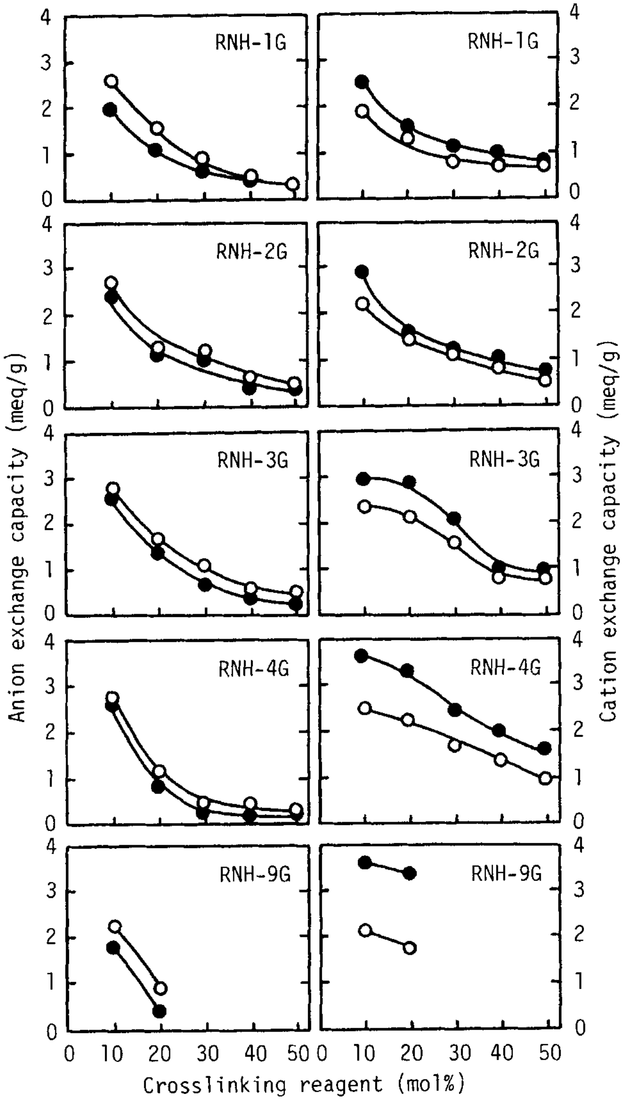


FIG. 4. Effect of crosslinking reagent on the ion-exchange capacity: (○) nontreated resin, (●) alkali-treated resin.

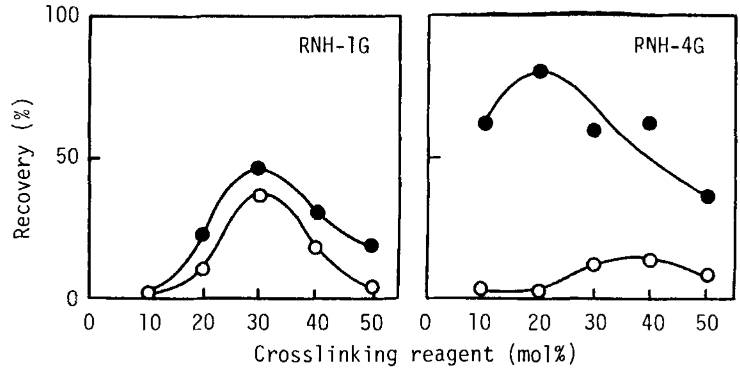


FIG. 5. Effect of crosslinking reagent on the recovery of uranium by the column method. Resin 1.5 cm^3, seawater 20 L (downward flow), SV 300 h^{-1}, 25-30°C, elution 0.5 *M* H_2SO_4, 10 L/L resin, SV 3 h^{-1}. (○) Nontreated resin, (●) alkali-treated resin.

These results indicate that the rapid adsorption onto RNH-1G is based on the macropores of the resins, and the large increase of adsorption ability of RNH-4G on alkali treatment, which had no macropores before the treatment, is attributed to the formation of a favorable pore structure due to the high swelling of RNH caused by alkali treatment.

The recovery of uranium from natural seawater was investigated by a column method (Fig. 5). In order to recover trace amounts of uranium from seawater, it is very important that large volumes of seawater are contracted with adsorbents that have a high adsorption rate. In this experiment, seawater was passed through a column at a high flow rate of space velocity (300 h^{-1}) for better evaluation of adsorption ability. RNH-1G and RNH-4G, after alkali treatment, showed high adsorption for uranium in seawater, particularly the latter.

For the industrial recovery of uranium from seawater, an adsorbent of high chemical and physical stability is desirable because of long-term recycling procedures. In order to test the durability of RNH-4G, the adsorption-elution procedure was repeated 10 times. The elution of uranium adsorbed on the resins could easily be carried out with 10 bed volumes of 0.5 *M* H_2SO_4 solution. RNH prepared with 20 mol% of 4G gave 75% recovery in the first cycle, but showed a gradual decrease of recovery during the recycles.

For the preparation of RNH resins of chemical and physical stability and effective macropores and micropores for the recovery of uranium, DVB and

TABLE 3. Specific Surface Area of RNH-DVB-1G, -4G, or -9G

DVB, mol%	1G, 4G, or 9G, mol%	Specific surface area, m^2/g RNH-DVB-1G	RNH-DVB-4G	RNH-DVB-9G
10	0	39.0	43.1	–
10	1	–	48.9	34.8
10	2	39.4	47.8	40.3
10	3	–	46.5	47.5
10	4	40.7	–	–
10	5	47.2	53.2	0.3
10	6	60.7	–	–
10	8	69.3	–	–
10	10	81.3	9.8	–
10	15	114.0	0.0	–

polyethylene glycol dimethacrylate were used as simultaneous hydrophobic and hydrophilic crosslinking reagent, respectively.

Table 3 shows the specific surface area of RNH-DVB-1G, RNH-DVB-4G, and RNH-DVB-9G with various amounts of hydrophilic crosslinking reagents. The specific surface area of RNH-DVB-1G increased with increasing amount of 1G. On the other hand, the specific surface area of RNH-DVB-4G prepared with from 1 to 5 mol% of 4G was about 50 m^2/g, but that of RNH-DVB-4G and RNH-DVB-9G prepared with more than 6 mol% of 4G or 9G decreased considerably. This decrease of the specific surface area resulted in a decrease in the adsorption of uranium.

In order to compare RNH-DVB-1G with RNH-DVB in detail, the chemical stability of RNH-DVB and RNH-DVB-1G against acidic solution was assessed from the change of anion-exchange capacity after acid treatment. The results are shown in Fig. 6(A). Although the anion-exchange capacity of both RNH-DVB and RNH-DVB-1G was decreased by acid treatment, the RNH-DVB and RNH-DVB-1G with the high crosslinking have higher chemical stability than those with lower crosslinking as shown by the decreased ratio of anion-exchange capacity calculated by

$$\text{Decrease ratio} = \frac{C_0 - C_a}{C_0} \times 100\ (\%),$$

where C_0 and C_a are the anion-exchange capacity before and after acid treatment, respectively.

The chemical stability of RNH-DVB was higher than that of RNH-DVB-1G with the same crosslinking degree. On the other hand, the uranium recovery of these resins was also investigated by the column method with natural seawater (Fig. 6B). Seawater (20 L) was passed through a glass column (10 mm diameter) packed with 1.5 cm^3 of each resin at a high flow rate (SV of 30 h^{-1}, downward flow). In the case of RNH-DVB, the recovery of uranium decreased noticeably with an increase in the crosslinking degree. The RHN-DVB with the higher crosslinking did not show an increase of recovery by alkali treatment. In the case of RNH-DVB-1G, no decrease of uranium recovery by

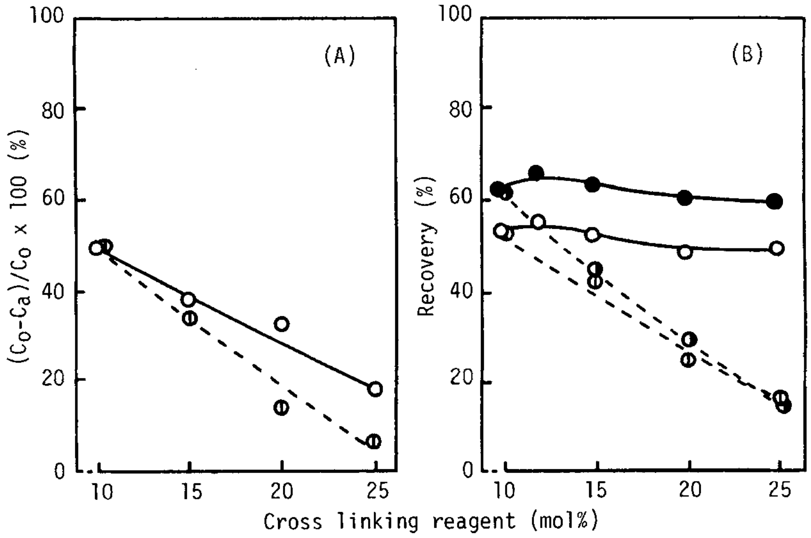


FIG. 6. The stability and the recovery of uranium by the column method. (A) C_0: Anion-exchange capacity before acid treatment; C_a: anion-exchange capacity after acid treatment. (◑) RNH-DTB, (○) RNH-DTB-1G. (B) Column method: Adsorption (resin 1.5 cm^3, seawater 20 L, SV 300 h^{-1}, 28°C). Elution (0.5 M H_2SO_4 10 L/L resin, SV 3 h^{-1}. (○, ○) RNH-DVB; (○, ●) RNH-DVB-1G (DVB 10 mol%); (○, ◑) untreated resin; (●, ◑) alkali-treated resin.

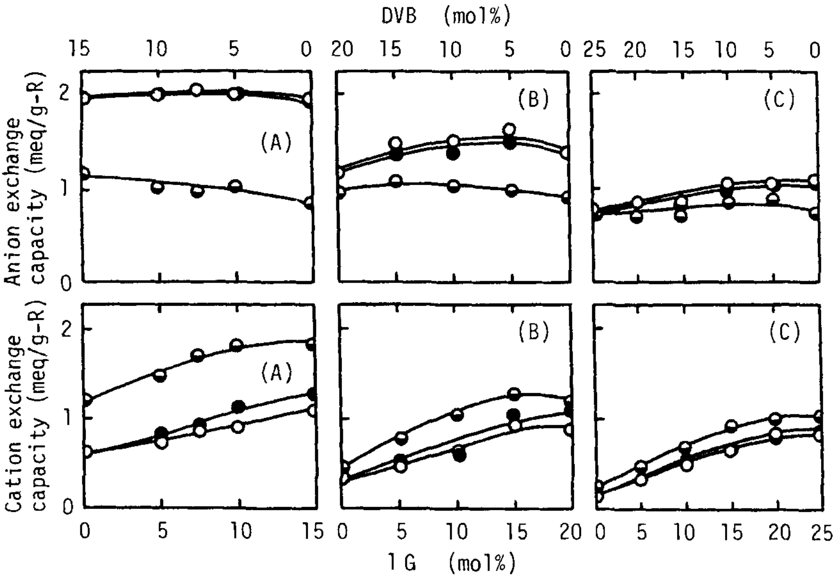


FIG. 7. Ion-exchange capacity of un-, alkali-, and acid-treated resin. Total amount of crosslinking reagents: (A) 15 mol%; (B) 20 mol%; (C) 25 mol%. (○) Untreated resin, (●) alkali-treated resin, (◒) acid-treated resin.

increasing the crosslinking was observed. Each RNH-DVB-1G sample indicated an increase of recovery by alkali treatment. These results suggest that the simultaneous use of DVB and 1G contributed to the formation of an effective pore structure for the recovery of uranium from seawater, especially in the case of RNH-DVB-1G with the higher crosslinking.

In order to characterize the RNH-DVB-1G in detail, the RNH-DVB-1G with the desired extent of crosslinking was synthesized by regulating the proportions of 1G and DVB, and the porosities of the resins were investigated. Total amounts of DVB and 1G were 15, 20, and 25 mol%. The results are shown in Fig. 7. The anion-exchange capacity of these resins with the same crosslinking was approximately constant, which confirmed that the amount of amidoxime groups introduced was not changed by the differences in the composition of the crosslinking reagent. The cation-exchange capacity of these resins with the same degree of crosslinking showed a tendency to increase with increasing amount of 1G used. Anion- and cation-exchange capacities of these resins after alkali treatment hardly changed. On the other hand, the anion-exchange capa-

TABLE 4. Specific Surface Area and Degree of Swelling of RNH-DVB-1G[a]

Crosslinking reagent		Specific surface				Swelling ratio	
DVB, mol%	1G, mol%	area, m^2/g	V_1, cm^3/g	V_2, cm^3/g	V_3, cm^3/g	V_2/V_1	V_3/V_2
15	0	76.6	1.9	2.6	2.6	1.4	1.0
10	5	55.8	1.8	2.5	2.5	1.4	1.0
7.5	7.5	45.1	2.1	2.6	2.6	1.2	1.0
5	10	33.7	2.0	2.6	2.6	1.3	1.0
0	15	10.0	2.0	2.5	2.7	1.3	1.1
20	0	158.0	2.0	2.8	2.8	1.4	1.0
15	5	112.0	2.1	2.7	2.6	1.3	1.0
10	10	83.6	1.9	2.7	2.7	1.4	1.0
5	15	50.7	2.0	2.6	2.6	1.3	1.0
0	20	17.3	1.9	2.5	2.6	1.3	1.0
25	0	242.0	2.1	2.8	2.8	1.3	1.0
20	5	203.0	2.0	2.8	2.8	1.4	1.0
15	10	143.0	2.0	2.7	2.7	1.4	1.0
10	15	103.0	2.0	2.7	2.7	1.4	1.0
5	20	74.5	1.9	2.6	2.6	1.4	1.0
0	25	36.7	2.0	2.7	2.7	1.4	1.0

[a] V_1 = dry volume of resin, V_2 = wet volume of resin, V_3 = wet volume of resin after alkali treatment.

city decreased and cation-exchange capacity increased on treatment with 1 *M* HCl at 60°C for 5 h. These changes of ion-exchange capacity indicate that amidoxime groups are hydrolyzed to acidic groups. This effect tended to increase with increasing proportion of 1G, and to decrease with increasing degree of crosslinking. It was confirmed that the RNH-DVB-1G resin prepared with 25 mol% of 1G and DVB had higher chemical stability than those prepared with 15 and 20 mol% of 1G and DVB.

Specific surface area and swelling ratio of all RNH-DVB-1G resins are shown in Table 4. Hardly any difference in swelling was observed. The fact that the V_3/V_2 ratio was near 1.0 indicates that wet volume was not changed by alkali treatment and that the RNH-DVB-1G resin has high physical stability. On the other hand, in the series of RHN-DVB-1G with the same crosslinking, the specific surface area showed an appreciable tendency to decrease with increasing proportion of 1G.

Figure 8 shows the pore distributions of these RNH-DVB-1G resins. The RNH which was crosslinked with only 1G had macropores characterized by a large average pore radius. The average pore radius had a tendency to decrease with increasing crosslinking. The macropores were characterized by small average pore radius which increased with an increasing proportion of DVB. These results confirm that the amount and proportion of crosslinking reagents influence the distribution of macropores.

The recovery of uranium by the column method was investigated by using RNH-DVB-1G (Fig. 9). Although the RNH-DVB-1G resin with the same degree of crosslinking had almost the same content of amidoxime groups, the recovery of uranium with each resin was quite different and the adsorption ability of the resins was increased by treating with alkali. These results indicate that the difference in the macropores strongly influenced the adsorption rate of uranium and that the micropores formed by swelling also increased the recovery of uranium. These results show that the adsorption ability of RNH for the recovery of uranium from seawater was not only affected by the chemical structure but also by the macropores and micropores formed by swelling the resins.

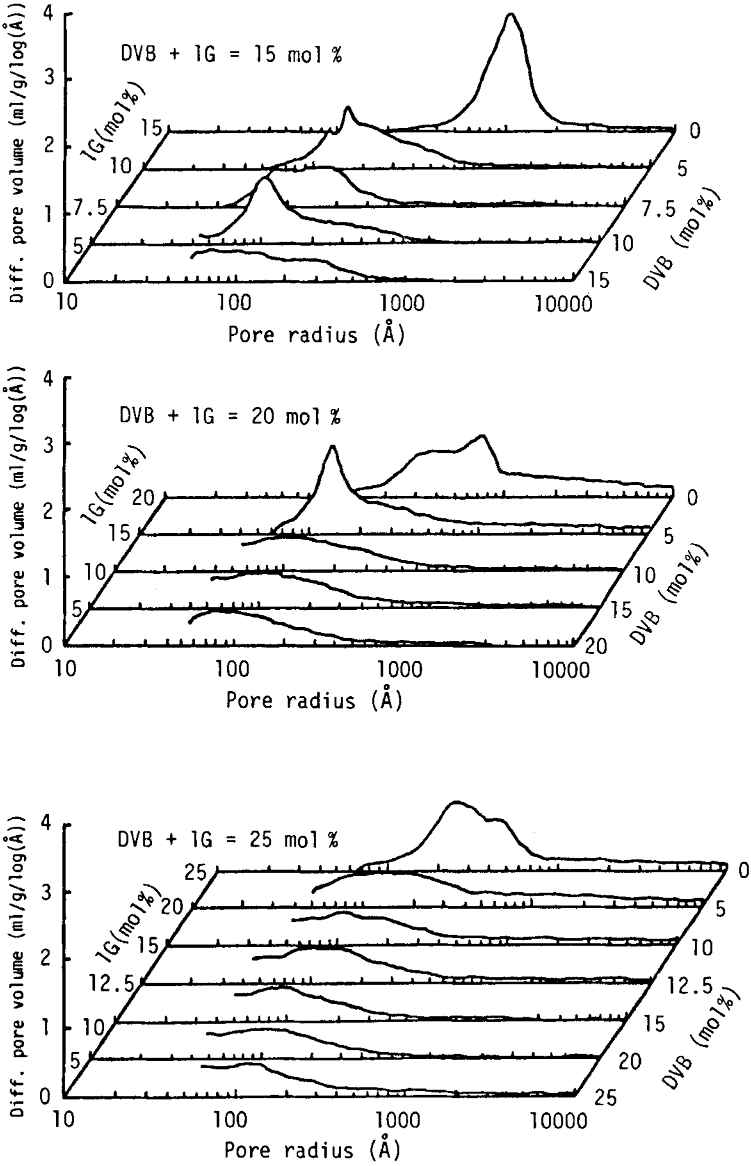


FIG. 8. Differential pore size distribution curves of RNH-DVB-1G.

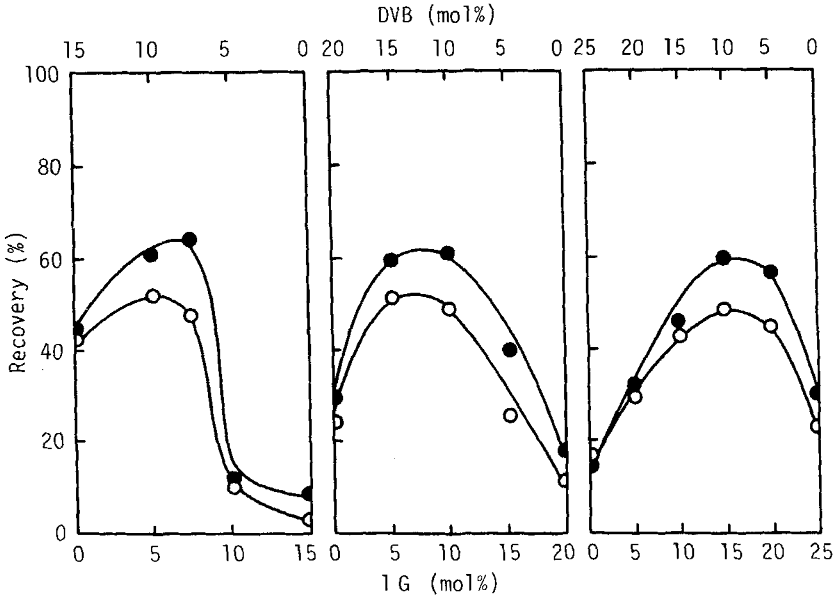


FIG. 9. Recovery of uranium from seawater by the column method. Loading: seawater 20 L, SV 300 h^{-1}, 25°C. Elution: 0.5 *M* H_2SO_4 10 L/L resin (SV 3 h^{-1}). Resin: 1.5 cm^3. (○) Untreated resin, (●) alkali-treated resin.

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