Recovery of Uranium from Seawater. VI. Uranium Adsorption Ability and Stability of Macroporous Chelating Resin Containing Amidoxime Groups Prepared by the Simultaneous Use of Divinylbenzene and Ethyleneglycol Dimethacrylate as Crosslinking Reagent

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Synopsis

Macroporous chelating resins (RNH-DVB-1G) containing amidoxime groups with various degrees of crosslinking were synthesized by varying the amount of divinylbenzene (DVB) and ethyleneglycol dimethacrylate (1G). It was confirmed that the content of amidoxime group decreased with an increase in the degree of crosslinking. On the other hand, the amount of amidoxime group hydrolyzed by acid treatment showed a tendency to decrease with an increase in degree of crosslinking. From the measurement of specific surface area and pore size distribution, it was found that the macropore of RNH-DVB-1G with the same degree of crosslinking was remarkably affected by the composition of crosslinking reagent (DVB and 1G). The RNH-DVB-1G prepared in the present work were applied to the recovery of uranium from seawater. It was found that the uranium adsorption ability of RNH-DVB-1G with the same degree of crosslinking was remarkably affected by the proportion of DVB and 1G, although each RNH-DVB-1G had the same content of amidoxime group. In the case of RNH-DVB-1G prepared with 25 mol% of crosslinking reagent, the resin prepared with 10 mol% of DVB and 15 mol% of 1G showed the high adsorption ability for uranium in seawater. These results indicate that the simultaneous use of DVB and 1G contributes to the formation of effective macropore and micropore for recovery of uranium from seawater and the increase of chemical and physical stability.

INTRODUCTION

In earlier research,[1-3] we demonstrated that macroporous chelating resin (RNH-DVB) containing amidoxime groups prepared by using divinylbenzene (DVB) as crosslinking reagent has an effective physical pore structure (macropore) for recovery of uranium from seawater and high physical stability. However, RNH-DVB with a high degree of crosslinking showed a low adsorption ability for uranium in seawater because of the decrease of hydrophilicity. On the other hand, the resins prepared with the hydrophilic crosslinking reagent such as ethyleneglycol dimethacrylate (1G) or tetraethyleneglycol dimethacrylate (4G), exhibited the high adsorption ability for uranium because of the favorable pore structure (micropore) based on the large swelling

caused by alkali treatment. But these resins showed a low chemical and physical stability.[4] In our recent study,[5] it has been also ascertained that RNH-DVB containing amidoxime group and other functional groups such as hydroxamic acid and carboxylic groups exhibited the high adsorption ability for uranium in seawater by the formation of macropore and micropore. In this article, macroporous chelating resins (RNH-DVB-1G) with the high degree of crosslinking were synthesized by using simultaneously DVB as hydrophobic crosslinking reagent and ethyleneglycol dimethacrylate (1G) as hydrophilic crosslinking reagent. The effect of pore structure on the adsorption ability of each RNH-DVB-1G for uranium in seawater and the stability of RNH-DVB-1G were investigated in detail.

EXPERIMENTAL

Preparation of RNH-DVB and RNH-DVB-1G

Macroporous acrylonitrile (AN)-DVB and AN-DVB-1G copolymer beads (RN) were synthesized by the suspension polymerization and the RN was treated with hydroxylamine methanol solution by the same method described previously.[2-4] The resin (1 g) was treated with 100 cm^3 of 0.1 mol dm^{-3} sodium hydroxide solution at 30°C for 15 h (alkali treatment) or with a 100 cm^3 of 1 mol dm^{-3} hydrochloric acid solution at 60°C for 5 h (acid treatment). An apparent anion and cation exchange capacity of the above resins was measured by the method reported previously.

Measurement of Macropore and Swelling Ratio

Specific surface area of resins was measured on a Yuasa surface area apparatus (BET method). Pore volume and radius of resins were determined on a Carlo-Erba mercury porosimeter (Model 1520). An apparent volume (V1) of dry resin was measured with a graduated filter (100 cm^3). The volume (V2) of wet resin was measured with the graduated glass filter after allowing to stand in pure water at room temperature for 24 h with occasional shaking. On the other hand, the volume (V3) of wet resin after alkali treatment was also measured. Swelling ratio was calculated by the following equation.

$$\text{Swelling ratio} = \frac{\text{volume of wet resin}}{\text{volume of dry resin}}$$

Recovery of Uranium from Seawater by Column Method

The recovery of uranium from seawater was carried out by column method. The wet resin (1.5 cm^3) treated with 3% NaCl solution for 24 h at room temperature was packed in a glass column (1.0 cm diameter). Natural seawater (20 dm^3) was passed through the column at a space velocity (SV) of 300 h^{-1} (down-flow) at 28–30°C. The uranium adsorbed on the resins was eluted by passing 10 bed volume of a 0.5 mol dm^{-3} sulfuric acid solution through the column at a SV of 3 h^{-1}. The uranium in eluate was determined spectrophotometrically with arsenazo III.

RESULTS AND DISCUSSION

First, the macroporous copolymer beads (RN-DVB and RN-DVB-1G) with various degrees of crosslinking were synthesized by using various amounts of DVB, or DVB and 1G. Macroporous chelating resins containing amidoxime groups were prepared by the reaction of the above RN-DVB or RN-DVB-1G with a hydroxylamine methanol solution (abbreviated as RNH-DVB and RNH-DVB-1G, respectively). The anion exchange capacity of all RNH-DVB or RNH-DVB-1G is shown in Figure 1. RNH-DVB was prepared with 10–25 mol% of DVB. RN-DVB-1G was prepared by the simultaneous use of 10 mol% of DVB and various amounts of 1G, and the total amount of crosslinking reagent used was 10–25 mol%. In general, it is known that the amount of functional group introduced to copolymer beads decreases, and physical stability increases with an increase in the degree of crosslinking. In the case of RNH-DVB or RNH-DVB-1G, the content of amidoxime group was evaluated from the anion exchange capacity. It was confirmed that the content of amidoxime group decreased with an increase in the degree of crosslinking. The chemical stability was assessed from the change of anion exchange capacity after it was immersed in hydrochloric acid solution at 60°C for 5 h (abbreviate as acid treatment). As shown in Figure 1, the content of amidoxime group of RNH-DVB or RNH-DVB-1G decreased with acid treatment. This chemical change means that the amidoxime group is hydrolyzed to change the acidic groups such as hydroxamic acid or carboxylic groups.[5] The decrease ratio of anion exchange capacity was calculated by the following equation:

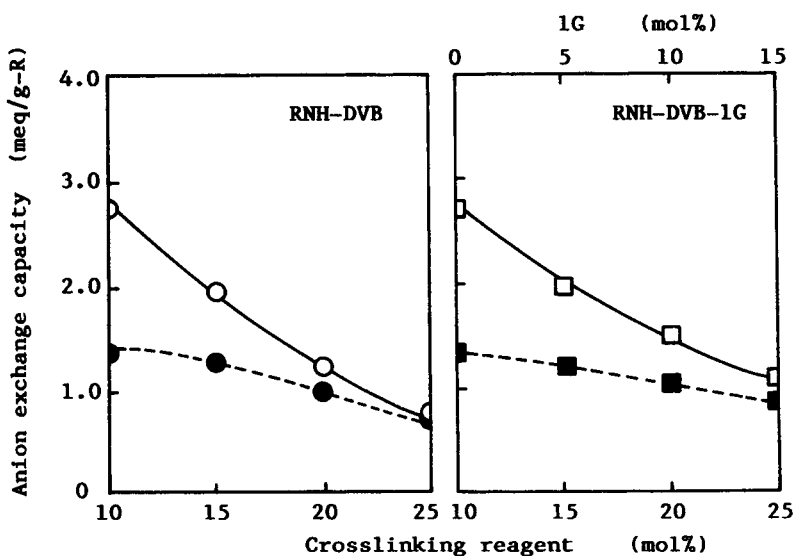$$\text{Conversion} = \left(\frac{C_0 - C_a}{C_0} \right) \times 100 \ (\%)$$

Fig. 1. Anion exchange capacity of RNH-DVB and RNH-DVB-1G before and after acid treatment: (○) RNH-DVB before acid treatment; (●) RNH-DVB after acid treatment; (□) RNH-DVB-1G before acid treatment; (■) RNH-DVB-1G after acid treatment.
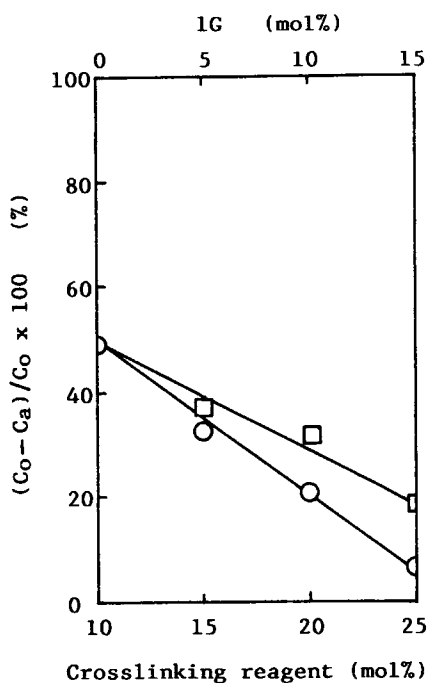
Fig. 2.   Stability of RNH-DVB and RNH-DVB-1G against acidic solution: Co; anion exchange capacity before acid treatment, Ca; anion exchange capacity after acid treatment, (○) RNH-DVB; (□) RNH-DVB-1G.

where C_0 and C_a are the anion exchange capacity before and after acid treatment, respectively. As shown in Figure 2, it was found that the conversion of amidoxime group decreased with an increase in the degree of crosslinking and the resin with the higher degree of crosslinking had higher chemical stability than that with the low degree of crosslinking. It was also found that the chemical stability of RNH-DVB was slightly higher than that of RNH-DVB-1G.

The effect of crosslinking on the adsorption ability for the uranium in natural seawater was investigated by column method. Seawater (20 dm^3) was passed through a glass column (10 mmϕ) packed with 1.5 cm^3 of each resin at the high flow rate (SV of 300 h^{-1}, down-flow). The recovery of uranium by using these resins is shown in Figure 3. In the case of RNH-DVB, the recovery of uranium decreased remarkably with an increase in the degree of crosslinking. The RNH-DVB with 25 mol% of DVB did not show the increase of recovery by alkali treatment. In the case of RNH-DVB-1G, the recovery of uranium was hardly decreased with an increase in the degree of crosslinking. And the all RNH-DVB-1G showed increased recovery by alkali treatment. These experimental results suggest that the simultaneous use of DVB and 1G contributed to the formation of effective pore structure for the recovery of uranium from seawater, especially in the case of RNH-DVB-1G with the high degree of crosslinking.

In order to investigate the effect of pore structure on the properties of RNH-DVB-1G in detail, several kinds of RNH-DVB-1G with matched de-
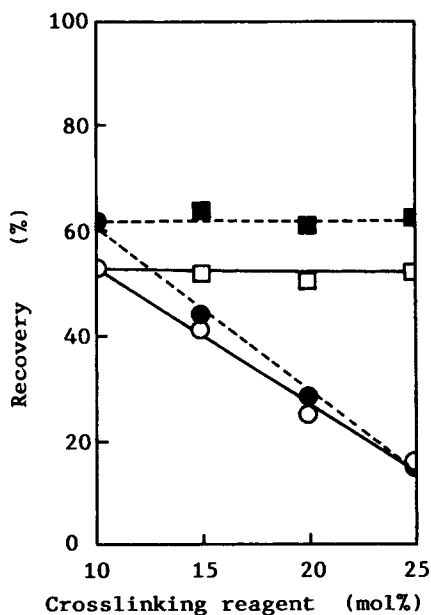
Fig. 3. Recovery of uranium from seawater by column method: loading, seawater 20 dm^3, SV 300 h^{-1}, temp. 30°C; elution: 0.5 mol dm^{-3} H$_2$SO$_4$ 10 dm^3/dm^3-R (SV 3 h^{-1}); resin 1.5 cm^3; (○, ●) RNH-DVB; (□,■) RNH-DVB-1G; (—) nontreated resin; (---) alkali-treated resin.
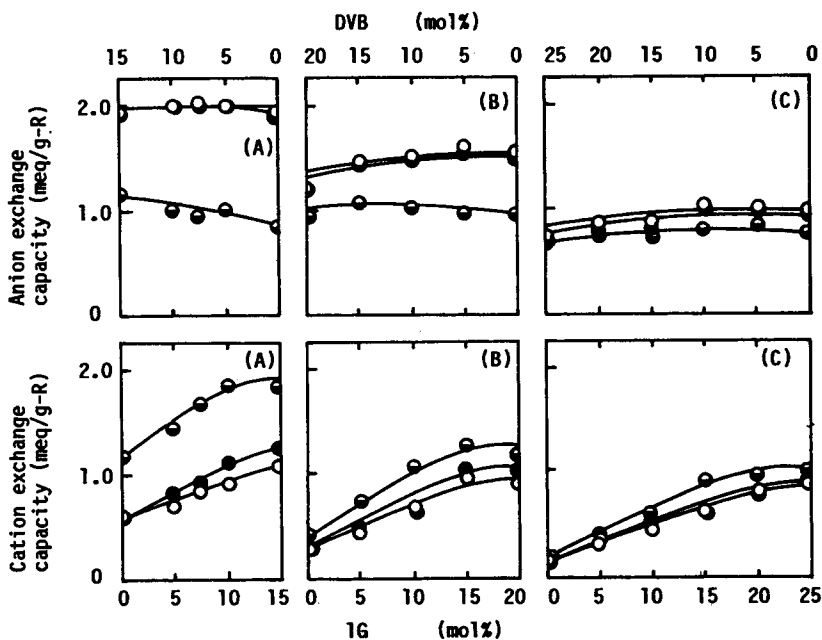

Fig. 4. Ion exchange capacity of non-, alkali-, and acid-treated resin: total amount of crosslinking reagents, (A) 15 mol%; (B) 20 mol%; (C) 25 mol%; (○) nontreated resin; (●) alkali-treated resin; (◐) acid-treated resin.

grees of crosslinking were synthesized by varying the proportion of DVB and
1G. The ion exchange capacity of RNH-DVB-1G prepared is shown in Figure
4. Since the RNH-DVB-1G with the same degree of crosslinking gave ap-
proximately the same anion exchange capacity, it was ascertained that the
amount of amidoxime group was hardly changed by the difference in the
composition of crosslinking reagent. On the other hand, the cation exchange
capacity of these resins with the same degree of crosslinking showed a
tendency to increase with an increase in the amount of 1G used. This increase
of cation exchange capacity indicates that acidic groups such as hydroxamic
acid and carboxylic groups have been formed by the reaction of ester groups
with hydroxylamine.[4] The changes of ion exchange capacity after alkali and
acid treatment are also shown in Figure 4. Since the anion exchange capacity
was not changed by alkali treatment, the amidoxime group was found to be
hardly hydrolyzed by a dilute alkaline solution such as 0.1 mol dm^{-3} NaOH.
By acid treatment, the anion exchange capacity decreased and the cation
exchange capacity increased. The amount of amidoxime group hydrolyzed
showed a tendency to decrease with an increase in the degree of crosslinking.
It was confirmed that the RNH-DVB-1G prepared with 25 mol% of crosslink-
ing reagent had higher chemical stability than that prepared with 15 mol% of
crosslinking reagent.

Specific surface area (SSA), dry volume (V1), wet volume (V2), wet volume
(V3) after alkali treatment, and swelling ratio (V2/V1 and V3/V2) of all
RNH-DVB-1G were measured. As shown in Table I, there was no difference in

TABLE I
Specific Surface Area and Swelling Ratio of RNH-DVB-1G

Crosslinking reagent		Specific surface area (m^2/g)	V1[a]	V2[b]	V3[c]	Swelling ratio	
DVB (mol%)	1G (mol %)		(cm^3/g)			V2/V1	V3/V2
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] Dry volume of resin.
[b] Wet volume of resin.
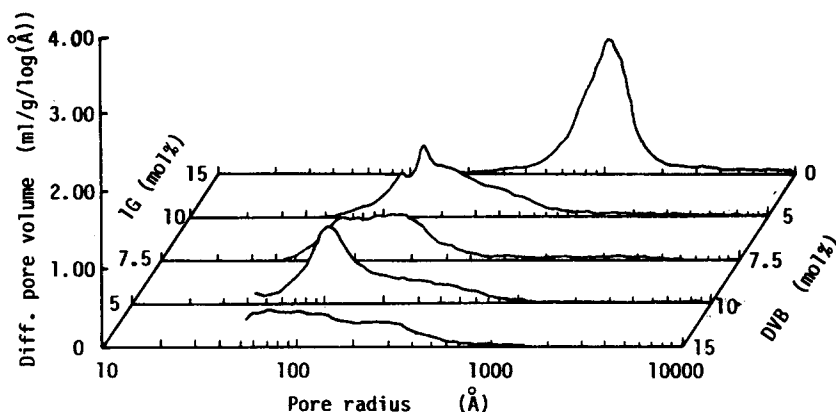[c] Wet volume of resin after alkali treatment.

Fig. 5.   Differential pore size distribution curves of RNH-DVB-1G: DVB + 1G = 15 mol%.

swelling ratio of RNH-DVB-1G. In particular, V3/V2 was about 1.0. This indicates that wet volume does not change by alkali treatment and the RNH-DVB-1G has high physical stability. In the series of RNH-DVB-1G with the same degree of crosslinking, the specific surface area showed a tendency to decrease remarkably with an increase in the proportion of 1G.

In order to characterize the macropore of RNH-DVB-1G, pore size distribution was measured by using mercury porosimeter. The differential pore size distribution curves are shown in Figures 5–7. The average pore radius of RNH-DVB-1G with the same degree of crosslinking shifted to large one with decrease in the proportion of 1G used as crosslinking reagent. The RNH-DVB-1G prepared with only 1G, which gave the low specific surface area, had the largest average pore radius. From these measurements of macropore, it was found that the composition of crosslinking reagent affected strongly the formation of macropore.

In order to investigate the effect of pore structure on the adsorption ability for uranium in seawater, the RNH-DVB-1G as described above was applied to the recovery of uranium from seawater. Although the RNH-DVB-1G with the same degree of crosslinking had the same content of amidoxime group, the
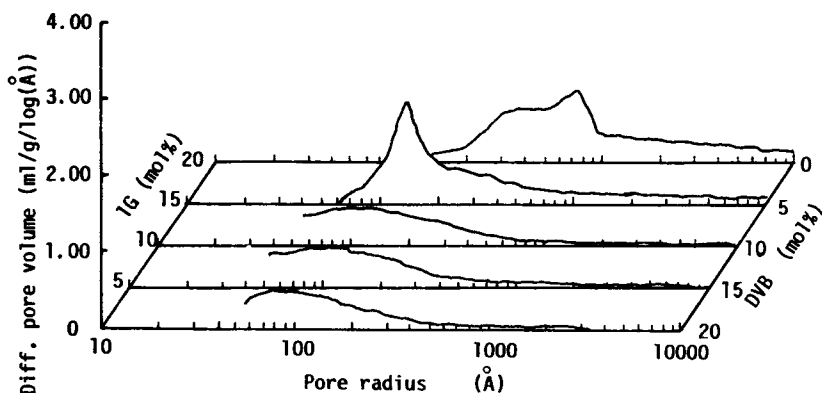

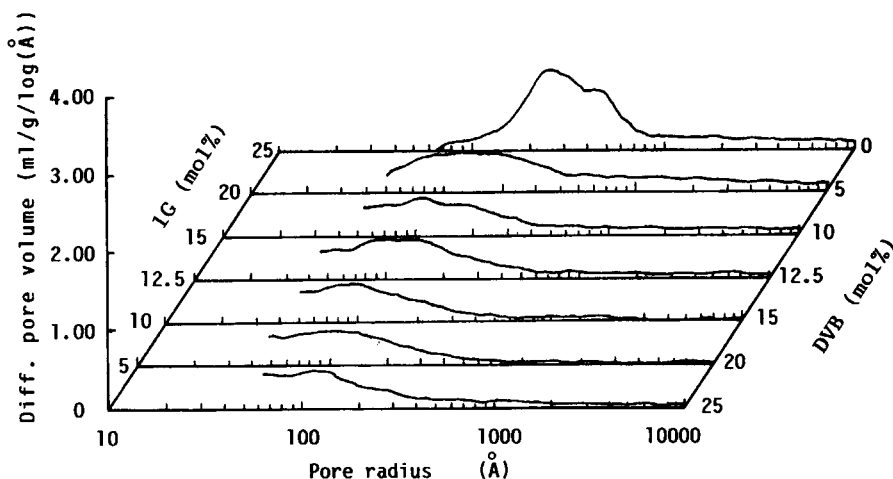Fig. 6.   Differential pore size distribution curves of RNH-DVB-1G: DVB + 1G = 20 mol%.

Fig. 7. Differential pore size distribution curves of RNH-DVB-1G: DVB + 1G = 25 mol%.

recovery of uranium from seawater was remarkably different, as shown in Figure 8. These differences in the recovery of uranium suggest that the adsorption ability for uranium was greatly affected by the macropore and micropore of RNH-DVB-1G. The RNH-DVB-1G prepared by the use of satisfactory proportion of DVB and 1G had the high recovery of uranium from seawater. Also, these resins exhibited increased uranium recovery based
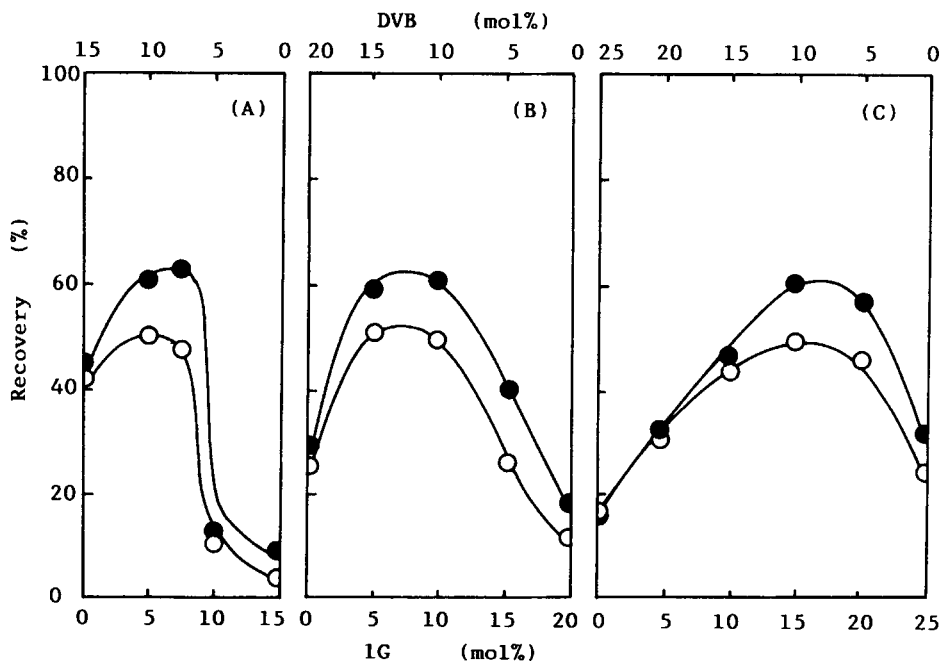

Fig. 8. Recovery of uranium from seawater by column method: loading, seawater 20 dm^3, SV 300 h^{-1}, temp. 25°C; elution: 0.5 mol dm^{-3} H$_2$SO$_4$ 10 dm^3/dm^3-R (SV 3 h^{-1}); resin 1.5 cm^3; ($\bigcirc$) nontreated resin; ($\bullet$) alkali-treated resin; (A) DVB + 1G = 15 mol%; (B) DVB + 1G = 20 mol%; (C) DVB + 1G = 25 mol%.

on the formation of micropore by alkali treatment. These facts indicate that the resins have the effective macropore and micropore for the recovery of uranium.

In conclusion, the results presented suggest that the chelating resin-containing amidoxime groups with high adsorption ability for uranium in seawater, physical and chemical stability, can be synthesized by the simultaneous use of DVB and 1G. The practical application of this RNH-DVB-1G as an adsorbent for recovery of uranium from seawater is under investigation.

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