Preparation of Macroreticular Chelating Resins Containing Dihydroxyphosphino and/or Phosphono Groups and Their Adsorption Ability for Uranium

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Synopsis

The macroreticular chelating resins (RSP, RSPO, RCSP, and RCSPO) containing dihydroxy-phosphino and/or phosphono groups were prepared and their adsorption capacity for UO_2^{2+} and the recovery of uranium from sea water were investigated. RSP and RCSP were prepared by phosphorylation of macroreticular styrene–divinylbenzene copolymer beads and the chloromethylated copolymer beads, respectively. RSPO and RCSPO were prepared by oxidation of RSP and RCSP, respectively. The order of recovery of uranium from sea water with these four resins is as follows: $RCSPO \simeq RCSP > RSPO > RSP$. The adsorption of uranium in sea water was not only affected by the chemical structure, but also by physical structure of the resins. Uranium adsorbed on the resins was eluted with $0.25 \sim 1 \ mol \cdot dm^{-3} \ Na_2CO_3$ or $NaHCO_3$ solution by batch and column methods. The average recovery ratios of uranium from sea water with Na-form and H-form RCSP on 10 recycles were 84.9% and 90.5%, respectively, when 20 dm^3 of sea water was passed through the column (resin 4 cm^3, 10 mm $\phi \times 50$ mm) at the space velocity of 60 h^{-1}. RCSP has a high physical stability and resistance against acid and alkali solution.

INTRODUCTION

Phosphorylated organic compounds are well known as extraction solvents for the recovery and purification of uranium. Some phosphorylated polymers, prepared by Kennedy et al.,[1-3] exhibited considerable selectivity for UO_2^{2+}. The macroreticular chelating resins are more practical than gel type resins for the removal and recovery of heavy metal ions from industrial waste solution because of their physical stability and high adsorption rate.[4] However, the macroreticular chelating resins containing dihydroxyphosphino and/or phosphono groups have never been investigated. On the other hand, recently major interest has been directed to the recovery of uranium in sea water from the viewpoint of the anticipated exhaustion of terrestrial uranium reserves in the near future.[5]

In previous papers,[6-8] we reported that the macroreticular chelating resins containing amidoxime groups have a high selective adsorption ability for uranium in sea water and the resins are highly effective for recovery of uranium from sea water.

In this article, the macroreticular chelating resins containing dihydroxyphosphino and/or phosphono groups were prepared, and the influence of chemical and physical structure of the resins on the absorption of uranium in sea water was investigated.

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EXPERIMENTAL

Preparation of Macroreticular Chelating Resins. The macroreticular styrene–divinylbenzene (DVB) copolymer beads were synthesized by suspension polymerization in the presence of 2,2,4-trimethylpentane as diluent. Copolymer beads with the desired diameter were selected (32–60 mesh). The styrene–DVB copolymer beads (RS) (5 g) were chloromethylated with chloromethylether (31.4 mL) at 0–5°C for 3 h in the presence of tetrachloroethane (3.1 mL) as swelling agent and aluminum chloride (6.7 g) as catalyst.

RS or its chloromethylated derivative (RCS) (5 g) was slowly stirred in a mixture of phosphorus trichloride (50 mL) and aluminum chloride (22.5 g) for several minutes and then refluxed for 6 h. The phosphorylated resins (RSP and RCSP) were filtered off and placed in ice water. After the vigorous reaction subsided, the phosphorylated resins were washed with water and left overnight in 2 mol·dm^{-3} NaOH solution. Subsequently, the phosphorylated resins were washed with water and then with 1 mol·dm^{-3} HCl solution and left overnight in the HCl solution to convert them to H-form. Finally, the resins were washed with water until the wash water was chloride-free and then dried. RSP and RCSP were oxidized with concentrated nitric acid at room temperature for 24 h to obtain resins (RSPO and RCSPO) which contained only phosphono groups. The resins were washed with water until the wash water was neutral.

Measurement of Porosity and Swelling Ratios of Resins. Resins were dried in a vacuum at 50°C for 8 h. The surface areas of the resins were measured on a Yuasa surface area apparatus (BET method). Pore volumes and average pore radius of the resins were determined on a Carlo-Erba mercury porosimeter (Model 1520). Swelling ratio was calculated by using the following equation.

$$\text{swelling ratio} = \frac{\text{volume of wet resins (cm}^3)}{\text{volume of dry resins (cm}^3)} \tag{1}$$

Measurement of Total Ion Exchange Capacity. The phosphorylated resin (0.25 g) was placed in a glass-stoppered Erlenmeyer flask. Then 50 cm^3 of a 0.1 mol·dm^{-3} NaOH–1 mol·dm^{-3} NaCl solution was poured into the flask. The mixture was allowed to stand at 25°C for 48 h with occasional shaking. The cation exchange capacity was determined by titrating the concentration of NaOH in the supernatant liquid with a 0.1 mol·dm^{-3} HCl solution.

Measurement of Salt Splitting Capacity. The resin (H-form) (0.25 g) was placed in a 100 cm^3 Erlenmeyer flask and 50 cm^3 of a 2 mol·dm^{-3} NaCl solution was poured into the flask, and the mixture was shaken at 30°C for 1 h. The supernatant layer was decanted into a 250-cm^3 measuring flask. The above procedure was repeated until the total volume of the supernatant amounted to 250 cm^3. Salt splitting capacity was determined by titrating 50 cm^3 aliquots of the supernatants with a 0.1 mol·dm^{-3} HCl solution.

Measurement of Adsorption Capacity for Metal Ions. In a glass-stoppered Erlenmeyer flask, 0.1 g of the resins and 50 cm^3 of a 0.1 mol·dm^{-3} metal ion solution were placed and the mixture was shaken at 30°C for 15 h. The amount of metal ion adsorbed on the resins was calculated by chelatometric or colorimetric determination of metal ion concentration in the supernatant. Metal ion solution was prepared from metal nitrates of reagent grade. The pH dependence of adsorption capacity was also investigated. The adsorption capacity for metal

ions was measured over the pH range 0.5–6 (HNO$_3$ and acetate buffer) and 7–13 (NaOH and acetate buffer).

Recovery of Uranium from Sea Water. The recovery of uranium from sea water with the resins (Na-form or H-form) was carried out by column method. Five thousand bed volumes of sea water were passed through the column at a space velocity of 60 h^{-1}. The uranium adsorbed on the resins was eluted by passing 10 bed vol of a 0.25 mol·dm^{-3} Na$_2$CO$_3$ solution through the column at various space velocities and the resins were washed with water. When we use H-form resins, the H-form resins were conditioned as follows: After elution, the resins were converted to the H-form by passing 10 bed vol of a 1 mol·dm^{-3} HCl solution through the column, followed by washing with water. This adsorption–elution procedure was repeated several times. The trace amount of uranium was determined by colorimetry with 2,7-bis(2-arsenophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid or 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol.

RESULTS AND DISCUSSION

Effect of Porosity on the Ion Exchange Capacity and on the Adsorption Capacity for Metal Ions. In the previous paper,[7] we reported that the adsorption capacity for uranium of macroreticular chelating resins containing amidoxime groups was greatly affected by the porosity of the resins. In this study, the effect of the porosity on the properties of RSP was investigated. RS with various porosities was prepared by varying the amount of 2,2,4-trimethylpentane which was used as diluent in the suspension polymerization. The macroreticular chelating resins containing dihydroxyphosphino and/or phosphono groups were prepared by the route in Scheme 1.

Table I shows the porosity, i.e., specific surface area, average pore radius, and pore volume of RSP prepared. The total ion exchange capacity and salt splitting capacity of RSP increased with an increase (Fig. 1) in the amount of 2,2,4-trimethylpentane used in the synthesis of RS. The respective capacity approached each constant value at the concentrations above 80 vol % of 2,2,4-trimethylpentane. Figure 2 shows the adsorption capacities for Ca^{2+}, Fe^{3+}, and UO$_2^{2+}$ of RSP having various porosities. The amount of Ca^{2+} adsorbed on the resins is proportional to the total ion exchange capacity of RSP (Fig. 2), whereas the amount of Fe^{3+} and UO$_2^{2+}$ adsorbed was maximum in the case of RSP which was
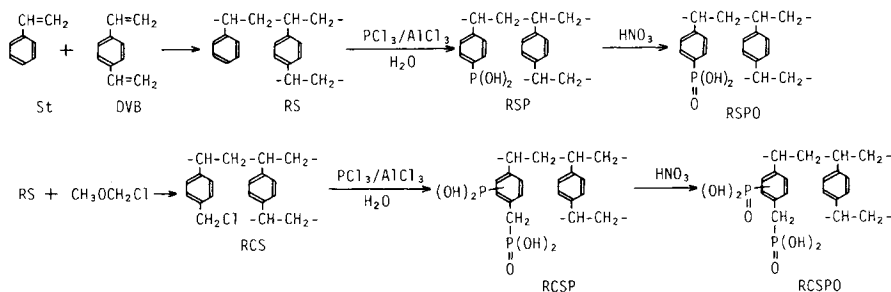
Scheme 1. Preparation of resin.

TABLE I
Porosity of RSP

2,2,4-Trimethyl-pentane (vol %)[a]	Specific surface area (m²/g)	Average pore radius (Å)	Pore volume (cm³/g)
0	—	—	—
30	—	—	0.01
60	0.18	140	0.02
80	3.58	210	0.09
100	40.0	256	0.50
120	35.3	548	0.90
140	13.7	3600	1.62

[a] This value represents vol % (per monomer) of 2,2,4-trimethylpentane used in the synthesis of RS (DVB: 10 mol %).

prepared from RS synthesized by using 100 vol % of 2,2,4-trimethylpentane.

Effect of Crosslinking on the Ion Exchange Capacity and the Adsorption of Metal Ions. RS with various degrees of crosslinking was synthesized by using various amounts of DVB in the presence of a constant volume (100 vol % per monomer) of 2,2,4-trimethylpentane. RCSP was prepared from RS by the route described in Scheme 1. Table II shows the porosity and swelling ratio of these RCSP: The specific surface area increased with an increase in the degree of crosslinking, whereas average pore radius was largest in the case of RCSP which was prepared by using 15 mol % of DVB. It also shows that the swelling ratio decreased with an increase in the degree of crosslinking. The swelling ratio of RCSP, which was prepared by using 3–5 mol % of DVB, was much larger than that of other RCSP. It follows that RCSP, which was prepared by using 3–5 mol % of DVB, does not have a macroporous structure. The effect of crosslinking of these RCSP on the ion-exchange capacity and the adsorption capacity for metal ions was investigated. The results are shown in Figures 3 and 4. The ion exchange capacity decreased with an increase in the amount of DVB. The amount of Ca^{2+} adsorbed on RCSP is proportional to the ion exchange capacity.
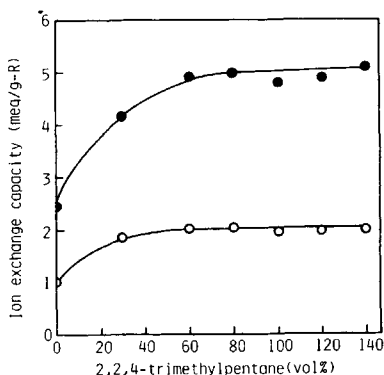

Fig. 1. Effect of porosity on the ion exchange capacity; resin, RSP (DVB 10 mol %): (O) salt splitting capacity; (●) cation exchange capacity.
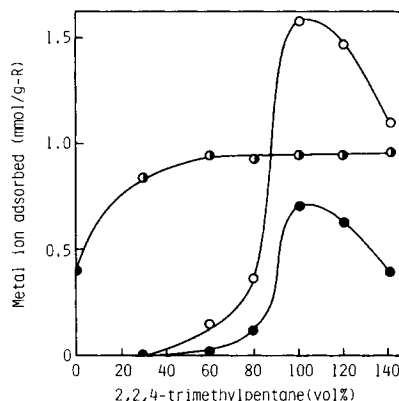
Fig. 2. Effect of porosity on the adsorption of various metal ions; resin, RSP (DVB 10 mol %): (O) UO_2^{2+} (pH 3.3); (●) Fe^{3+} (pH 2.4); (◐) Ca^{2+} (pH 5.6); pH, initial pH of solution.

RCSP, which was prepared by using 10 mol % of DVB, had the highest adsorption capacity for Fe^{3+} and UO^{2+}, although the ion exchange capacity of the RCSP was lower than that of RCSP with lower degree of crosslinking. The adsorption of metal ions was not only affected by the chemical structure (amount of chelating groups), but also by the physical structure (porosity) of the resins (Figs. 1–4 and Tables I and II). Hence, the favorable size of macropore and micropore of the wet resins was necessary for the adsorption of UO_2^{2+} with RSP and RCSP. However, the pore size of macropore and micropore of the wet resins could not be determined.

Properties of the Chelating Resins Containing Dihydroxyphosphino and/or Phosphono Groups. The chelating resins, which were prepared from RS synthesized by using 10 mol % of DVB in the presence of 100 vol % of 2,2,4-trimethylpentane, have the highest adsorption capacity for metal ions. For this reason, RSP, RSPO, RCSP, and RCSPO were prepared under the above conditions and their properties were compared. These resins were identified as RSP-10, RSPO-10, RCSP-10, and RCSPO-10, respectively.

TABLE II
Porosity and Swelling Ratio of RCSP[a]

Divinyl-benzene (mol %)	Specific surface area (m²/g)	Average pore radius (Å)	Pore volume (cm³/g)	Swelling ratio	
				H form	Na form
3	—	—	0.02	1.77	3.08
5	3.70	145	0.06	1.54	2.54
10	39.3	226	0.44	1.38	1.80
15	45.1	318	0.73	1.34	1.57
20	52.9	275	0.68	1.31	1.55
30	85.3	230	0.75	1.23	1.39
40	123.6	175	0.79	1.24	1.39

[a] These polymers were synthesized in the presence of 100 vol % (per monomer) of 2,2,4-trimethylpentane.
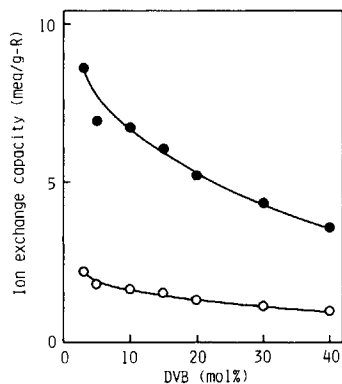
Fig. 3. Effect of crosslinking on the ion exchange capacity; resin, RCSP: (○) salt splitting capacity; (●) cation exchange capacity.

Table III shows the total ion-exchange capacity, salt-splitting capacity, apparent acid dissociation constant obtained from the titration curves, and phosphorus content of these resins. The total ion exchange capacity of RSPO-10 (Table III) was about twice that of RSP-10, and the total ion exchange capacity of RCSPO-10 was slightly larger than that of RCSP-10. Therefore, the amount of dihydroxyphosphino groups of RCSP-10 is very small.

Figure 5 shows the potentiometric titration curves of these four resins. In the case of RSP, only one equivalence point could be observed, whereas, in the case of other resins, two equivalence points could be observed. These results suggest that RSP is a monobasic acid and other resins are dibasic acids, and that certain weak acid groups resulted from the oxidation of RSP. However, the formation of carboxyl groups could not be recognized from the infrared spectrum of RSPO. The phosphorus content of RSP was about twice that estimated from the total ion exchange capacity, considering the resins as dibasic acid, whereas the phosphorus content of RSPO agreed with that estimated in the same manner. Dihydroxyphosphino groups of RSP behave as monobasic acid groups and phosphono groups of RCSP behave as dibasic acid groups.
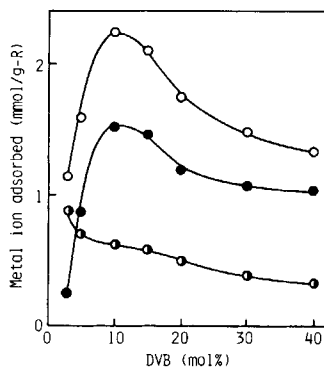

Fig. 4. Effect of crosslinking on the adsorption of various metal ions; resin, RCSP: (○) UO_2^{2+} (pH 3.3); (●) Fe^{3+} (pH 2.4); (◑) Ca^{2+} (pH 5.6); pH, initial pH of solution.

TABLE III
Ion Exchange Capacity, Apparent Acid Dissociation Constant, and Phosphorus Content of the Resins

Resin	Ct^a	Cn^b	$pKa_1{}^c$	$pKa_2{}^c$	P content (%)	
					Observed	Estimated[d]
RSP-10[e]	4.69	1.97	3.2	—	14.6	7.0
RSPO-10	8.54	2.32	2.9	8.5	13.3	13.2
RCSP-10	6.85	1.70	2.9	8.4	12.1	10.4
RCSPO-10	7.50	1.92	3.0	8.3	11.8	11.7

[a] Total cation exchange capacity.

[b] Salt splitting capacity.

[c] These values were obtained from the titration curves.

[d] These values were estimated from the total cation exchange capacity, considering the resins as dibasic acid.

[e] This value represents mol % of DVB used in the synthesis of RS.

The adsorption of UO_2^{2+}, Fe^{3+}, and Ca^{2+} with these four resins was investigated (Figures 6–8). The adsorption capacities of these resins for metal ions were approximately proportional to the total ion exchange capacity and the adsorption capacity for UO_2^{2+} was higher than that for Fe^{3+} and Ca^{2+}.

Elution of Uranium Adsorbed on the Resins. In order to repeatedly use these resins for recovery of uranium, it is necessary for uranium adsorbed to be eluted easily. The elution of uranium adsorbed on RSP-10, RSPO-10, and RCSP-10 was investigated by the batch method. Table IV shows the elution of uranium with various eluents. Uranium adsorbed on the resins was slightly eluted with 6 mol·dm^{-3} HCl or H_2SO_4 solution, whereas it was almost completely eluted with 0.25–1 mol·dm^{-3} Na_2CO_3 or $NaHCO_3$ solution. Figure 9 shows the elution curves of uranium with 0.25 mol·dm^{-3} Na_2CO_3 solution. The elution of uranium adsorbed on the resins was almost completed by passing seven bed volumes of 0.25 mol·dm^{-3} Na_2CO_3 solution through the column at the space velocity of 3–12 h^{-1}.

Recovery of Uranium from Sea Water. In order to recover uranium from sea water by a column method, the resin must have a high adsorption rate. The adsorption of UO_2^{2+} with RCSP having various degrees of crosslinking was in-
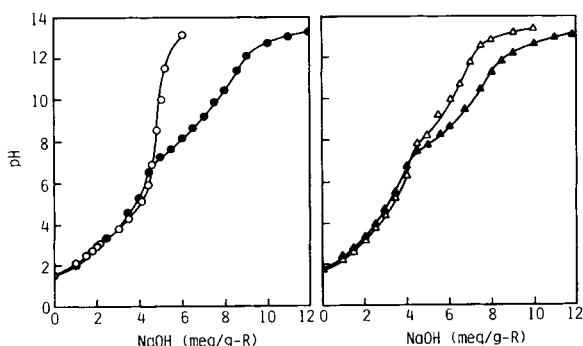

Fig. 5. The pH titration curves; resin: (O) RSP; (●) RSPO; (△) RCSP; (▲) RCSPO.
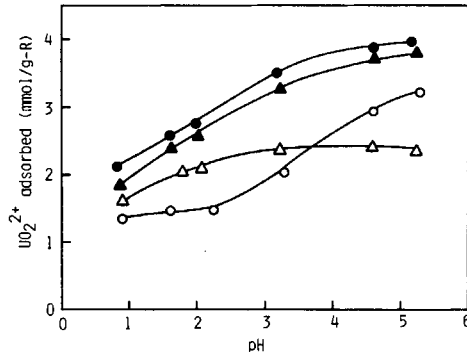
Fig. 6. Effect of pH on the adsorption of UO_2^{2+}; resin: (O) RSP-10; (●) RSPO-10; (△) RCSP-10; (▲) RCSPO-10.
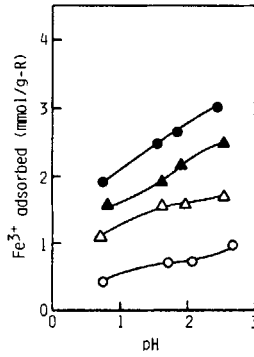

Fig. 7. Effect of pH on the adsorption of Fe^{3+}; resin: (O) RSP-10; (●) RSPO-10; (△) RCSP-10; (▲) RCSPO-10.
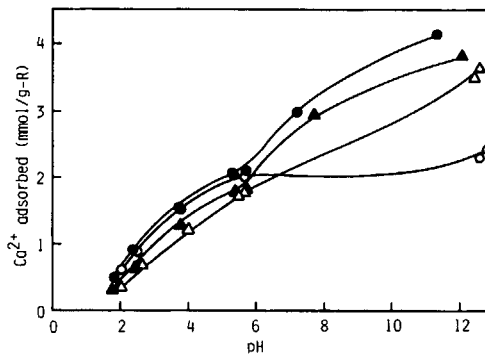

Fig. 8. Effect of pH on the adsorption of Ca^{2+}; resin: (O) RSP-10; (●) RSPO-10; (△) RCSP-10; (▲) RCSPO-10.

TABLE IV
Elution of Uranium Adsorbed on Resin

		Elution (%)[a]		
	Eluent	RSP-10	RSPO-10	RCSP-10
$0.5M$[b]	Na_2CO_3	100	100	100
$0.25M$	Na_2CO_3	100	100	99
$0.1M$	Na_2CO_3	100	64	94
$0.75M$	$NaHCO_3$	100	100	92
$0.5M$	$NaHCO_3$	99	68	85
$0.25M$	$NaHCO_3$	63	24	35
$6M$	HCl	3	17	45
$3M$	H_2SO_4	13	21	60

[a] Batch method: 0.25 g of resin on which 1000 μg of uranium was adsorbed, 25 cm^3 of eluent, shaking at 30°C for 1 h.

[b] mol·dm^{-3}.

vestigated (Fig. 10). Except for RCSP-5, which hardly has a macroporous structure, RCSP-10 and RCSP-15 showed a high adsorption rate. Since these macroreticular chelating resins containing dihydroxyphosphino and phosphono groups were found to have a high adsorption rate for UO_2^{2+}, the recovery of uranium from sea water with RSP-10, RSPO-10, and RCSPO-10 was investigated by the column method. The results of recycles with RSP-10, RSPO-10, and RCSP-10 are shown in Table V. The first recovery of uranium with RCSPO-10 was 87.5%, and it was only slightly higher than that with RCSP-10. For this reason, no further recycles with RCSPO-10 were carried out. RSP-10 and RSPO-10 exhibited lower recovery for uranium from sea water than RCSP-10. The reason why RSP-10 exhibited the lowest recovery is due to the fact that RSP has only one low pKa. On the other hand, RCSP-10 exhibited a higher recovery than RSP-10 due to the fact that RCSP has phosphono groups bound to methylene groups which easily form chelate with UO_2^{2+} because of their high flexibility. With RCSP-10, both the H-form and Na-form resin were used to recover UO_2^{2+} from sea water, and the adsorption–elution procedure was repeated 10 times.

The average recovery ratios of uranium with H-form and Na-form RCSP-10 were 90.5% and 84.9%, respectively. H-form RCSP exhibited higher recovery
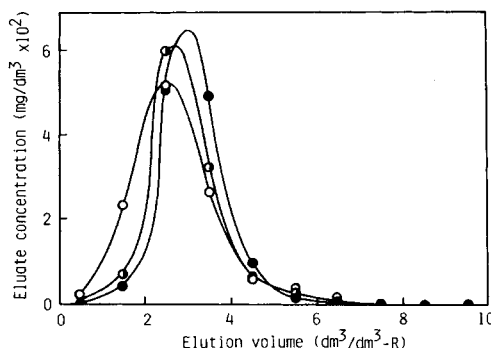

Fig. 9. Effect of flow rate on the elution of uranium from RCSP; resin, Na-form 4 cm^3; eluent, 0.25 mol·dm^{-3} Na_2CO_3 solution; flow rate (SV·h^{-1}); (O) 3; (◑) 6; (●) 12.
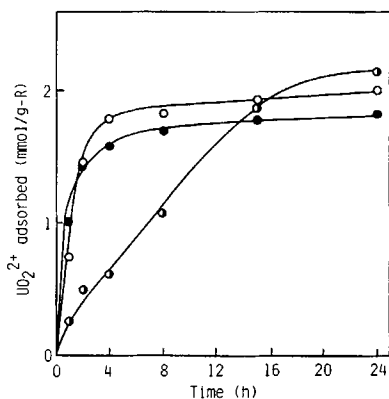
Fig. 10. Effect of crosslinking on the rate of adsorption of UO_2^{2+}; resin: (◐) RCSP-5; (○) RCSP-10; (●) RCSP-15.

of uranium from sea water. However, the Na-form RCSP was more favorable for the recovery of uranium than the H-form RCSP, because it could be reused immediately by washing the resins with water or sea water, after the adsorbed uranium was eluted with Na_2CO_3 solution. The recovery ratios of uranium from sea water with the Na-form RCSP were 84.9%, 58.7%, and 46.7% at the space velocity of 60 h^{-1}, 180 h^{-1}, and 300 h^{-1}, respectively. Furthermore, the adsorption capacity of the resins for UO_2^{2+} did not decrease even after treatment with 1 $mol \cdot dm^{-3}$ NaOH and HCl solution at 60°C for 24 h. Thus, the resins have high resistance against acid and alkali solution.

As described above, since RCSP exhibits high adsorption capacity, high adsorption rate for uranium in sea water, and high chemical and physical stability, it should be an excellent resin for recovery of uranium from sea water.

TABLE V
Recovery of Uranium from Sea Water by Column Method

| | Recovery of uranium (%) | | | |
Cycle no.	RSP-10 Na-form	RSPO-10 Na-form	RCSP-10 H-form	RCSP-10 Na-form
1	20.9	41.7	98.7	86.7
2	17.7	52.1	93.7	79.6
3	23.4	42.6	86.1	88.4
4	18.3	39.0	95.2	85.3
5	17.8	44.4	92.8	93.3
6	—	52.0	89.4	82.3
7	—	—	85.3	86.4
8	—	—	91.0	79.6
9	—	—	86.3	81.2
10	—	—	86.4	86.3
Average	19.6	45.3	90.5	84.9

ª Resin: RSP-10, RSPO-10, and RCSP-10; sea water: 20 dm^3, 25 ± 2°C, flow rate: SV 60 h^{-1}.

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