

Recovery of Uranium from Seawater. X. Pore Structure and Uranium Adsorption of Macroreticular Chelating Resin Containing Amidoxime Groups

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SYNOPSIS

Eight types of amidoxime-type resin (RNH) were derived from macroreticular acrylonitrile-divinylbenzene copolymer beads, which were synthesized by varying the amount of polymerization initiator. Although these RNH are similar in chemical properties and physical pore structure, they exhibited different adsorption abilities for uranium. The porous structure of RNH in swollen state was analyzed by gel permeation chromatography in aqueous medium. The calibration curves yielded useful information on the pore structure of RNH in the swollen state and it was recognized that the pore structure in the swollen state is important for the improvement of the adsorption rate.

INTRODUCTION

In an earlier study,¹⁻³ we demonstrated that macroporous chelating resin (RNH-DVB), containing amidoxime groups, prepared from acrylonitrile (AN)-divinylbenzene (DVB) copolymer beads, possesses an effective physical pore structure (macropore) for recovery of uranium in natural seawater. In our recent study,⁴⁻⁶ RNH-DVB prepared by the simultaneous use of crosslinking reagent, such as ethylenglycol dimethacrylate, or containing acidic groups, such as hydroxamic acid and carboxylic acid groups, exhibited a high adsorption rate for uranium in seawater because of the macropore and pore structure formed by swelling (micropore). In this study, we synthesized a series of chelating resins, varying conditions of the polymerization to improve the adsorption rate of RNH-DVB, which is important for future industrial use. Also investigated was the effect of micropore and macropore structure on the adsorption ability for uranium.

EXPERIMENTAL

Preparation of RNH-DVB

Macroreticular AN-DVB (DVB, 10 mol %) copolymer beads (RN) were synthesized by suspension polymerization in the presence of toluene (100 vol % per monomer) as diluent, and benzoylperoxide (BPO) or azobisisobutyronitrile (AIBN), as polymerization initiator. The copolymer beads with desired diameter (32-60 and 80-100 mesh) were selected and amidoxime groups were introduced by means of a reaction with 3% hydroxylamine methanol solution for 2 h at 80°C. The characterization of these resins and the determination of uranium were carried out by the methods previously reported.⁴⁻⁶

Gel Permeation Chromatography

Chromatographic measurements were performed with a Waters Assoc., 6000 p.s.i. pump (Model 510) and a Shodex refractive index detector. The RNH (80-100 mesh) was packed into a glass column (25 cm × 4 mm I.D.) and distilled water or sodium chloride solution was passed through the column at a

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Table I Characteristics of RN

RN	Polymerization Initiator (mmol/dm ³ -monomer)	N Content (%)	Specific Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Dry Volume (cm ³ /g)
(1)	BPO 40	16.6	96.5	0.818	2.9
(2)	BPO 60	16.9	96.7	0.794	2.9
(3)	BPO 120	17.6	98.0	0.682	2.7
(4)	BPO 180	17.1	93.1	0.695	2.7
(5)	AIBN 40	17.7	89.6	0.599	2.6
(6)	AIBN 60	17.2	83.0	0.702	2.7
(7)	AIBN 120	17.7	71.0	0.648	2.6
(8)	AIBN 180	17.9	73.9	0.782	2.9

flow rate of 0.5 cm³/min. The calibration curves were obtained by plotting the average molecular weights (M_n) against the peak elution volumes of standard samples of the dextrans T10 (M_n , 5.7×10^3), T40 (M_n , 23.4×10^3), T70 (M_n , 36×10^3) and T2000 (M_n , 2×10^3) (Pharmacia Co.), maltotriose and maltoheptaose (Sigma Co.), and ribose (Kohjin Co.). The amount of sample injected was 2–20 μ g. The hold-up volume of a column was measured with heavy water (D₂O).

RESULTS AND DISCUSSION

Preparation and Characterization of RNH

The characteristics of RNs synthesized in this study are listed in Table I. All these RNs were prepared

by using 10 mol % of DVB as a crosslinking agent and 100 vol % of toluene per monomer as diluent. Eight types of RN (1)–(8) were defined by the amounts of BPO and AIBN used as a polymerization initiator. The polymerization yield of these RNs was above 90% and the content of nitrogen based on the nitrile group is approximately consistent with the theoretical value. Specific surface area, pore volume, and pore size distribution, as shown in Table I and Figure 1, indicate that each of the RNs has the physical pore structure, but could not reveal the influence of polymerization initiator on the formation of macropores. These RNs were treated with hydroxylamine methanol solution. Since amidoxime groups introduced to RN behave as the amphoteric groups, both the anion and cation exchange capacity were measured to evaluate the content of the ami-

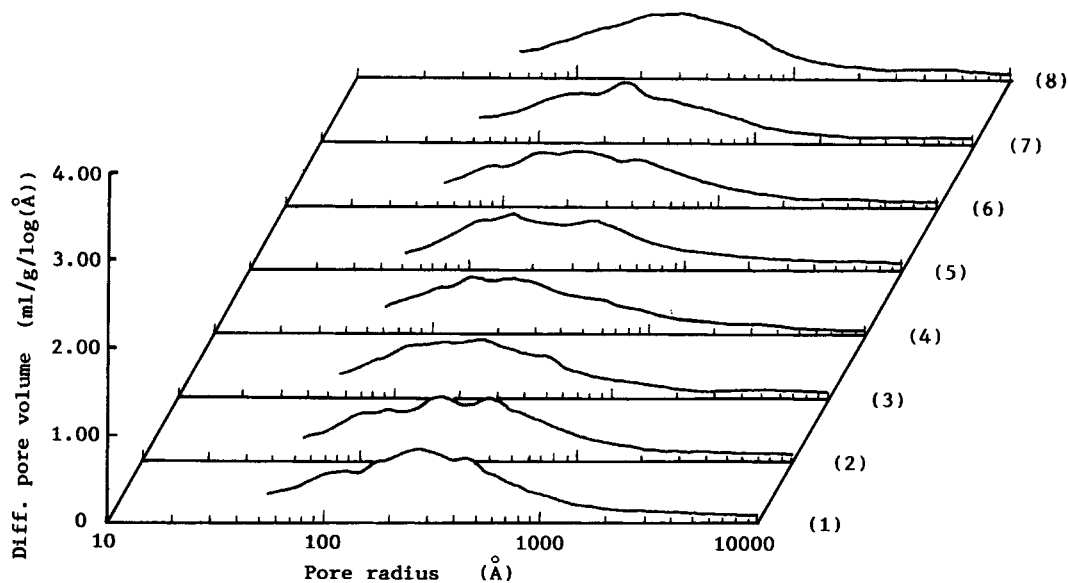


Figure 1 Pore size distribution curves of RN.

doxime group or acidic groups introduced to each RN. As shown in Table II, the anion exchange capacities of these RNHs are nearly equal. These results indicate that almost the same degree of amidoxime groups was introduced to each RN. Although it is difficult to verify the concentration of the amidoxime groups on the RNH by means of infrared spectroscopy, each RNH gave the same infrared spectrum, which exhibited the characteristic absorption of amidoximes.⁷ The adsorption capacity of these RNHs for uranyl ion is also shown in Table II. The amidoxime groups of each RNH functioned effectively for the adsorption of the uranyl ion and all types of RNHs had the high capacity of 0.6–0.7 mmol g⁻¹.

Adsorption Ability for Uranium

It is necessary that the adsorbents utilized for the recovery of uranium in seawater have a high adsorption rate for uranium. The adsorption of uranium from spiked seawater is shown in Figure 2. The adsorption of uranium on RNH (1) and (2) was remarkably low, as compared with that of the other RNHs. This difference was attributed to the adsorption rate of uranium. In fact, this difference disappeared by the long term contact of the RNH with the spiked seawater. The adsorption rate of uranium greatly influences the recovery of uranium, which is known to be present as tricarbonate uranyl complex anion in natural seawater. In order to evaluate the adsorption rate of each RNH for uranium, natural seawater (20 dm³) was passed through a column packed with 1.5 cm³ of RNH (1)–(8) at a high flow rate (SV 300 h⁻¹). As shown in Figure 3, the tendency of recovery was in agreement with that of adsorption for uranium in spiked seawater, but

Table II Chemical Properties of RNH

RNH	Anion Exchange Capacity (meq/g)	Cation Exchange Capacity (meq/g)	UO ₂ ²⁺ Adsorbed ^a (mmol/g)
(1)	2.7	1.1	0.64
(2)	2.8	1.4	0.71
(3)	2.7	1.4	0.62
(4)	2.8	1.4	0.71
(5)	2.8	1.5	0.67
(6)	2.8	1.3	0.71
(7)	2.8	1.4	0.71
(8)	2.8	1.2	0.71

^a Batch method (0.01 mol dm⁻³ UO₂²⁺, 30°C, 24 h).

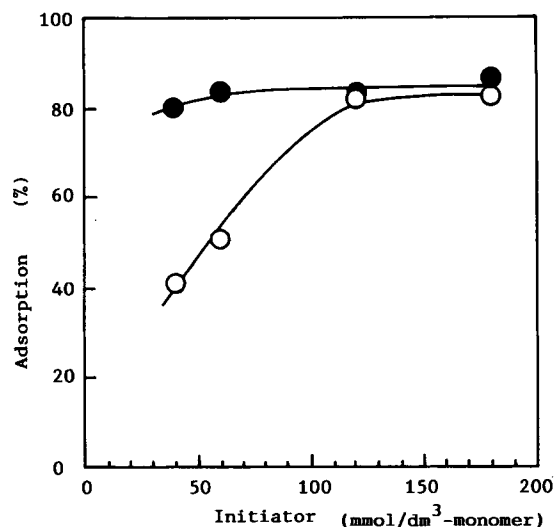


Figure 2 Adsorption of uranium from spiked seawater with RNH (1)–(8) by the batch method: resin 0.1 g; spiked seawater 25 cm³ (250 μg of uranium was added to it); shaking at 30°C (1 h); (○) RNH (1)–(4); (●) RNH (5)–(8).

we were not able to elucidate the difference in adsorption rate on the basis of physical properties, such as specific surface area and swelling ratio of these RNHs, shown in Table III.

Although RNHs derived from RNs synthesized by varying the amount of polymerization initiator have the same physical and chemical properties, the

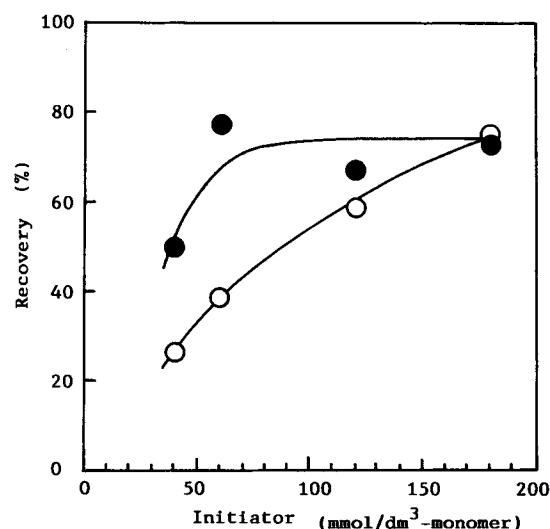


Figure 3 Recovery of uranium from natural seawater with RNH (1)–(8) by the column method: resin 1.5 cm³; loading, seawater 20 dm³, SV 300 h⁻¹, temp. 30°C; elution, 0.5 mol dm⁻³ H₂SO₄, 10 dm³/dm³-resin (SV 3 h⁻¹); resin 1.5 cm³; (○) RNH (1)–(4); (●) RNH (5)–(8).

Table III Physical Properties of RNH

RNH	Specific Surface		Swelling Ratio V ₂ /V ₁
	Area (m ² /g)	V ₁ ^a V ₂ ^b (cm ³ /g)	
(1)	45.1	2.3 2.9	1.3
(2)	46.7	2.3 2.8	1.2
(3)	43.5	2.1 2.6	1.2
(4)	44.2	2.0 2.5	1.3
(5)	42.7	2.3 2.9	1.3
(6)	39.6	2.1 2.6	1.2
(7)	35.3	2.2 2.5	1.1
(8)	38.1	2.2 2.6	1.1

^a Dry volume of RNH.^b Wet volume of RNH.

pore structure in the swollen state of RNH was presumed to be the most important factor for the adsorption rate. Kuga⁸ developed a method for the porous structure analysis of gel substances in swollen state by means of gel permeation chromatography (GPC). We have tried to obtain information on the pore structure of swollen macroreticular chelating resins by this method. A series of dextran and the oligomers of sugar were used as solutes in aqueous medium, and the typical calibration curves for RNH (1)–(8) are shown in Figure 4. The different calibration curves demonstrate the formation of various pore structures of RNHs in the swollen state. The adsorption ability of RNH (1)–(8) for uranium in seawater can be correlated to the pore structure produced by varying the amount of polymerization initiator. In order to clarify this point, porosity (D₂O), porosity (T₁₀), and porosity (T₄₀) were calculated by the following equation:

Table IV Porosity of RNH and Recovery of Uranium

RNH	Porosity (%)			Recovery of Uranium (%)
	D ₂ O	T ₁₀	T ₄₀	
(1)	72.5	0.0	0.0	27
(2)	70.6	36.1	1.1	39
(3)	70.2	48.0	20.0	60
(4)	70.2	49.4	37.4	76
(5)	71.9	43.7	0.0	49
(6)	70.2	57.2	40.7	79
(7)	70.9	53.3	46.9	66
(8)	70.5	53.7	51.6	72

$$\text{Porosity (D}_2\text{O)} = (V_D - V_0)/V_x \times 100 (\%),$$

$$\text{Porosity (T}_{10}\text{)} = (V_{10} - V_0)/V_x \times 100 (\%),$$

$$\text{Porosity (T}_{40}\text{)} = (V_{40} - V_0)/V_x \times 100 (\%),$$

and where V_D, V₁₀, and V₄₀ are the elution volume of heavy water, Dextran (T₁₀), and Dextran (T₄₀), respectively, V₀ is the void volume and V_x is the total bed volume. Porosity (D₂O) indicates the volume occupied with water in the swollen resins, namely total porosity. The porosities (D₂O) of each RNH prepared from RNs, which were polymerized using the same amount of the diluent, had almost the same value, as shown in Table IV. The RNH (1), which showed the lowest adsorption rate among all RNH, did not have the pore that makes it possible for T₁₀ to permeate the internal phase of resins. Kuga⁸ reported that the hydrodynamic diameter of T₁₀ is 48 Å. On the other hand, uranyltricarbonate

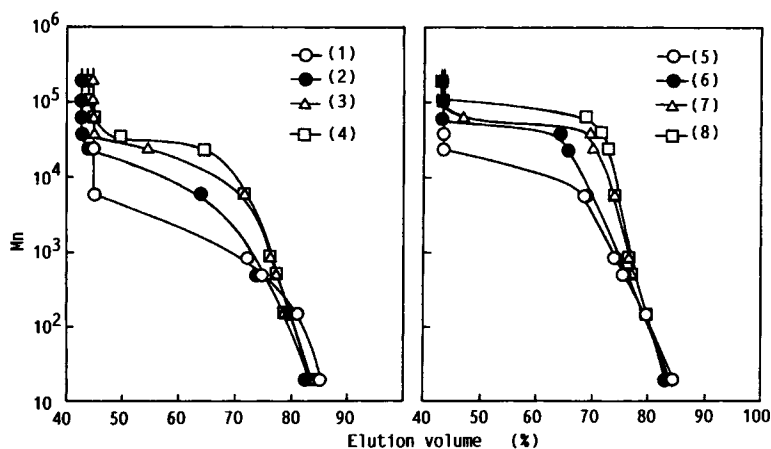


Figure 4 Calibration curves of GPC for RNH (1)–(8) in aqueous solution: eluent, deionized water; flow rate 0.5 cm³/min; column, 30 cm × 5 mm I. D.

was estimated to be as large as 9.7 Å in diameter by single-crystal, X-ray analysis.⁹ Since the hydrodynamic diameter of uranyltricarboxylate can be assumed to be larger than 9.7 Å, the formation of a pore, through which the dextran of a molecule larger than T10 is able to permeate, was defined as being important for the increase of the adsorption rate of uranium. It was found that the polymerization initiator was one of the most important factors in the control of micropore formation of RNH.

CONCLUSION

It has been found that the RNH-DVB, derived from RN synthesized by varying conditions of polymerization, formed the different pore structure in the swollen state. It was concluded that the formation of favorable micropore was important to improve the adsorption rate for uranium.

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