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Studies on Selective Adsorption Resins XXVII. Preparation and Properties of Macroreticular Chelating Resins Containing Amidoxime Groups from Chloromethylstyrene–Divinylbenzene Copolymer Beads

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ABSTRACT: Macroreticular chelating resins (RCSNHs) containing amidoxime groups were prepared from chloromethylstyrene–divinylbenzene copolymer beads (RCSs). The RCSs were synthesized by a suspension polymerization in the presence of cyclohexane as a diluent. The introduction of nitrile groups to the RCS could be effectively carried out by treatment with KCN using 18-Crown-6 as a phase transfer catalyst. The products were treated with hydroxylamine in methanol to obtain RCSNH. The influence of macroreticular structure and degree of crosslinking on the adsorption ability of the RCSNH for metal ions was investigated. The RCSNH was prepared from RCS synthesized using 10 mol% of DVB and 120 vol% of cyclohexane and it showed the highest adsorption ability for Ag^+, UO_2^{2+}, and Cu^{2+}. The adsorption ability was greatly affected by macroreticular structure. RCSNHs have high physical stability and resistance against acid solution. Therefore the RCSNHs will be very effective for the recovery and separation of metal ions.

KEY WORDS Amidoxime Group / Chelating Resin / Recovery of Uranium / Macroreticular / Adsorption of Metal Ion /

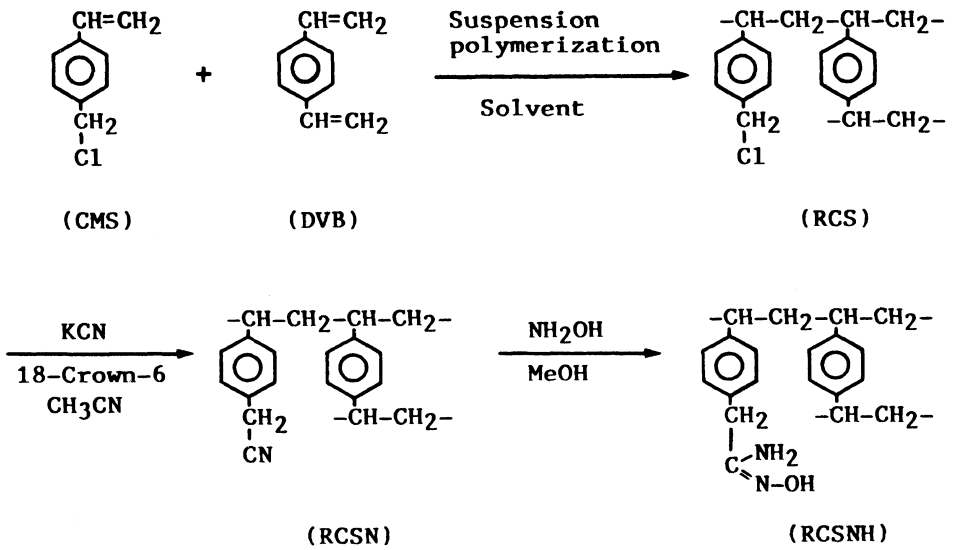
We prepared and studied many kinds of macroreticular chelating resins containing various ligands and reported that they are more practical than gel-type resins for the removal and recovery of heavy metal ions from industrial waste.[1-5] We also reported that the chelating resins containing amidoxime groups prepared from acryronitrile–divinylbenzene (DVB) copolymer beads were most effective for recovery of uranium from seawater.[6-11] Later, chelating adsorbents containing amidoxime groups prepared from polyacryronitrile have been widely investigated by many workers.[12-17] However, study on adsorbents containing amidoxime groups prepared from other polymer matrices such as polystyrene is rarely reported.[13,18]

In the present work, we prepared macroreticular chelating resins (RCSNHs) containing amidoxime groups from chloromethylstyrene (CMS)–DVB copolymer beads (RCSs), and investigated influence of macropore and degree of crosslinking of the resins on the adsorption ability for metal ions.

EXPERIMENTAL

Preparation of Macroreticular Chelating Resins (RCSNHs)

In this article, the macroreticular chelating resins containing amidoxime groups were prepared by the route in Scheme 1. RCSs were synthesized by a suspension polymerization in the presence of cyclohexane as a diluent. Nitrile groups were introduced to the RCS by reaction of RCS (1 g) with KCN (0.8 g) in



Scheme 1. Preparation of RCSNH.

acetonitrile (50 ml), using 18-Crown-6 (0.8 g) as a phase transfer catalyst, for 24 h under reflux. The products (RCSNs) were filtered off, washed with methanol–water (1 : 1) and methanol, and were dried. The RCSNs were treated with hydroxylamine in methanol at 80°C for 10 h to obtain RCSNH.

Measurement of Macroreticular Structure (Macropores)

Specific surface areas of resins were 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).

Measurement of Adsorption Capacity for Metal Ions

The resin (0.125 g) and 50 cm^3 of 0.01 mol dm^{-3} metal ion solution were shaken in a glass-stoppered Erlenmeyer flask at 30°C for 24 h. The amounts of metal ion adsorbed on the resin were determined by chelatometric titration of metal ion in the supernatant. Metal ion solution was prepared from nitrates of reagent grade.

Adsorption of Uranium from Uranium-Spiked Seawater

The resin (0.1 g) and 25 cm^3 of U-spiked seawater (494 μg of $UO_2(NO_3)_2 \cdot 6H_2O$ were added in it) were shaken at 30°C. Percentage of uranium adsorbed on the resin was calculated by spectrophotometric determination of uranium in the supernatant with arsenazo-III.

RESULTS AND DISCUSSION

Preparation of RCSNH

First, in order to prepare RCS with large specific surface area, various organic solvents were used as diluents in the suspension polymerization (Table I). In the use of toluene or *s*-butyl alcohol, gel type resins which have no macropore were obtained. In the use of 2,2,4-trimethylpentane or *n*-heptane, RCSs with large pore and small specific surface area were obtained and they were soft. The RCS with high mechanical strength and high specific surface area (40.7 $m^2 g^{-1}$) was obtained using 100 vol% of cyclohexane.

Next, the introduction of nitrile groups to RCS was carried out and evaluated from the nitrogen content in the RCSN. Appropriate

amounts of KCN and 18-Crown-6 for the cyanomethylation of the RCS were determined (Figure 1). It was found that about 2.4 mol of KCN per chloromethyl group and 0.12 mol of 18-Crown-6 per KCN were enough to complete the reaction.

Amidoximation was carried out by treatment of RCSN with various concentrations of hydroxylamine (Figure 2). The RCSNHs with high anion exchange capacity, which indicates high content of amidoxime groups, were obtained using the above 3.7 mol of hydroxylamine per cyanomethyl group. Table II shows that the maximum value of the anion exchange capacity of the resins was obtained by reaction for more than 6 h and that the anion exchange capacity corresponds to the nitrogen content in the resin.

The introduction of nitrile groups to RCS

Table I. Specific surface area, pore volume, and pore radius of RCS[a]

Diluent		SSA[b]	Pore volume	Pore radius/Å	
vol%		$m^2 g^{-1}$	$cm^3 g^{-1}$	Peak	Av
2,2,4-Trimetyl pentane	100	3.6	1.112	1190	1716
	75	0.3	0.790	824	869
n-Heptane	100	0.7	1.157	1829	1957
Cyclohexane	100	40.7	0.243	91	125
Decaline	100	19.4	0.577	127	1190
Toluene	100	0	—	—	—
s-Buthyl alcohol	100	0	—	—	—
2-Ethyl hexyl alcohol	100	11.4	0.689	664	675

[a] DVB, 10 mol%.
[b] Specific surface area.

Table II. Effects of reaction time on the introduction of amidoxime groups[a]

Time	N content	C_a[b]	C_c[c]	C_t[d]
h	%	meq g^{-1}	meq g^{-1}	meq g^{-1}
1	7.69	1.52	0.26	1.64
2	8.21	2.04	0.20	2.07
4	8.55	2.38	0.23	2.35
6	8.72	2.53	0.19	2.49
10	8.81	2.53	0.21	2.57

[a] Reaction: RCS, 0.8 g; 3% NH_2OH, 20 cm^3; temp, 80°C.
[b] Anion exchange capacity.
[c] Cation exchange capacity.
[d] Anion exchange capacity calculated from increment in N content.

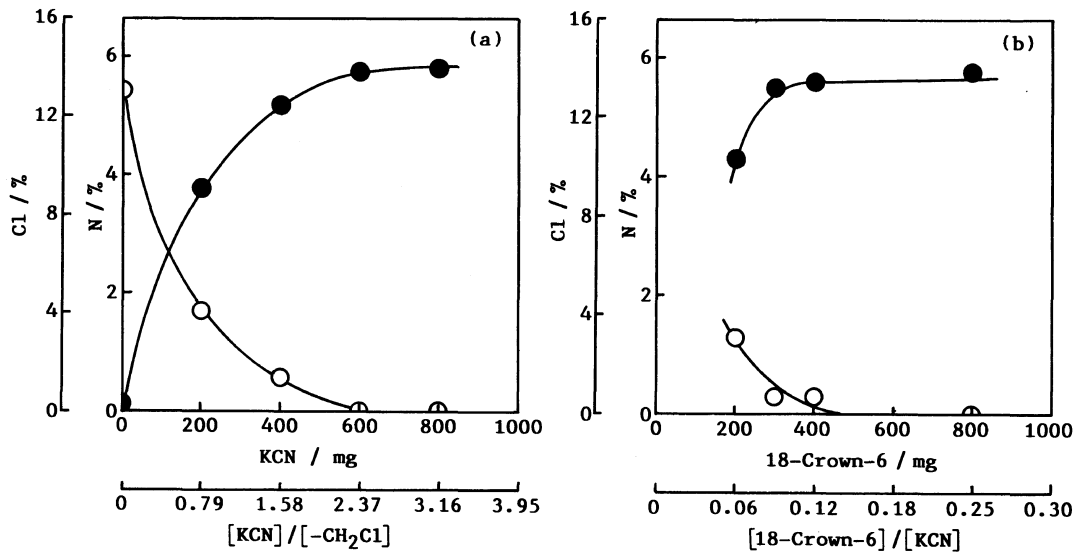


Figure 1. Effects of [KCN]/[$-CH_2Cl$] and [18-Crown-6]/[KCN] on the introduction of nitrile groups: ○, Cl; ●, N; RCS, 1 g; CH_3CN, 50 cm^3; reflux temp; time, 24 h; (a) 18-Crown-6, 800 mg; (b) KCN, 800 mg.

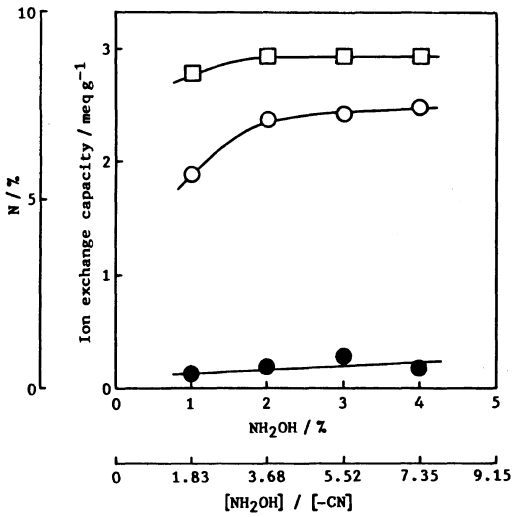


Figure 2. Effects of NH_2OH concentration on the introduction of amidoxime groups: RCSN, 0.8 g; NH_2OH-MeOH, 20 cm^3; temp, 80°C; ○, anion exchange capacity; □, N content; ●, cation exchange capacity.

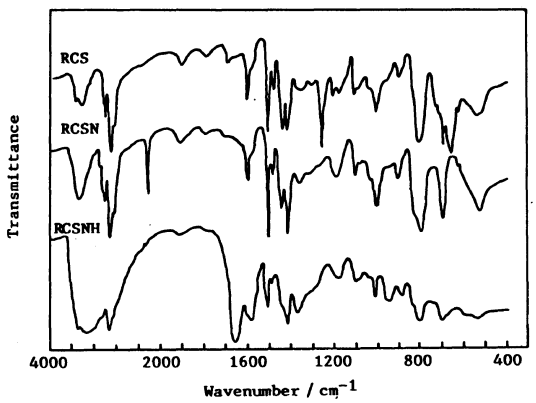


Figure 3. IR spectra of RCS, RCSN and RCSNH.

was confirmed by IR spectra which exhibited the appearance of new peak at 2230 cm^{-1} due to the C≡N stretching vibration and the disappearance of the peak at 1260 cm^{-1} due to the C-Cl stretching vibration (Figure 3). IR spectra of the RCSNH showed the appearance of new peak at 3400 cm^{-1} due to stretching vibration of $-NH_2$ and at 1650 and 950 cm^{-1} due to oxime groups and decrease of the peak at 2230 cm^{-1} due to nitrile groups.

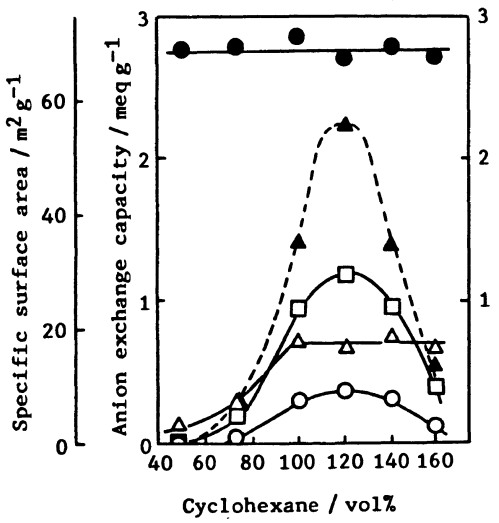


Figure 4. Effects of macroreticular structures of RCSNHs on the adsorption of metal ions: △, Ag^+; □, Cu^{2+}; ○, UO_2^{2+}; ●, anion exchange capacity; ▲, specific surface area.

Effects of Macroreticular Structure of Resin on Adsorption of Metal Ions

In order to obtain resins with various macroreticular structures, RCSs were prepared using the various contents of cyclohexane (50—160 vol% to monomer) in suspension polymerization. In the use of 50 and 75 vol% of cyclohexane, the gel type copolymers with no or small specific surface area were obtained (Table III). The RCSs with macroreticular structure could be prepared using 100–160 vol% of cyclohexane and pore volume and pore radius of the copolymers increased with volume percent of cyclohexane. RCS with maximum specific surface area was obtained using 120 vol%. In the use of above 120 vol%, the specific surface area decreased with increasing cyclohexane content.

RCSNHs were prepared from these RCSs. The adsorption ability of the RCSNHs for UO_2^{2+}, Cu^{2+}, and Ag^+ were measured (Figure 4). The anion exchange capacity and specific surface areas of the RCSNHs are also shown in Figure 4. The RCSNHs prepared by using 50 and 75 vol% of cyclohexane could

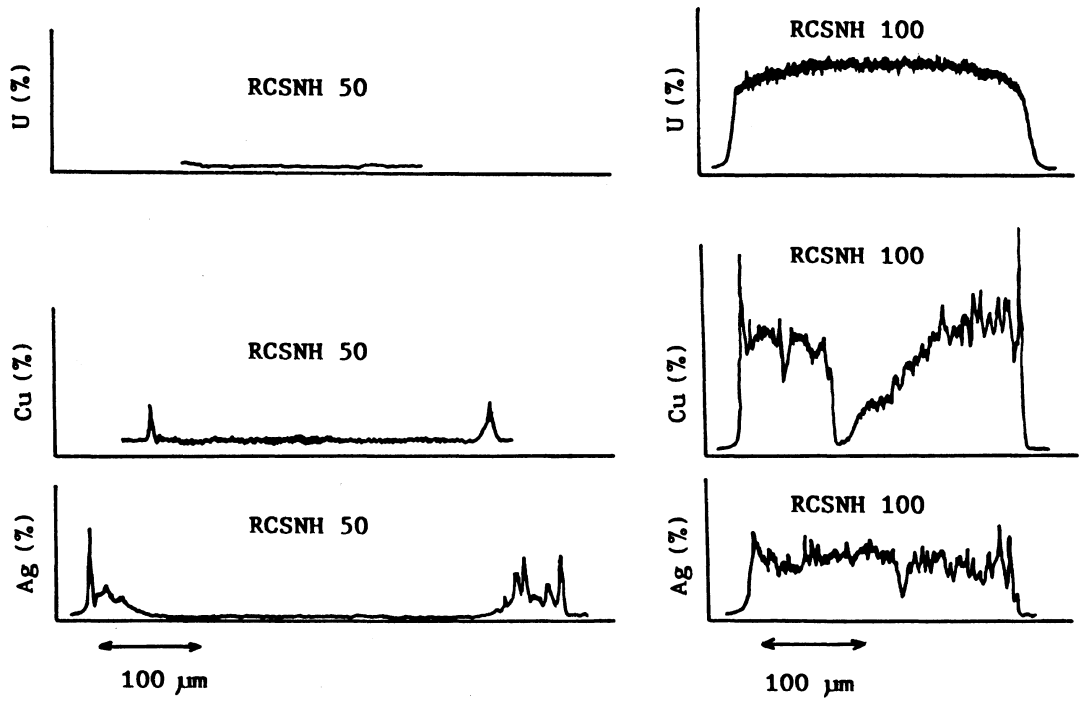


Figure 5. Distribution of metal ions adsorbed on the resins.

Table III. Specific surface area, pore volume, and pore radius of RCS[a]

Cyclohexane	SSA[b]	Pore volume	Pore radius/Å	
vol%	$m^2 g^{-1}$	$cm^3 g^{-1}$	Peak	Av
50	0	—	—	—
75	8.2	—	—	—
100	41.4	0.369	125	156
120	56.6	0.839	267	311
140	39.6	1.332	688	726
160	14.2	1.595	5000	3127

[a] DVB, 10 mol%.
[b] Specific surface area.

adsorb no UO_2^{2+} and very little Cu^{2+}, although they had almost the same anion exchange capacity as the RCSNHs prepared by using above 100 vol%. UO_2^{2+} and Cu^{2+} were adsorbed mostly on RCSNH prepared by using 120 vol% of cyclohexane. Ag^+ was slightly adsorbed on RCSNHs prepared by using 50 and 75 vol% of cyclohexane. The results indicate that metal ions such as Cu^{2+} or UO_2^{2+} are very difficult to diffuse to the inner part of the resins which have no macroreticular structure. This was confirmed by the distribution curves of metal ions adsorbed on the resins prepared by using 50 and 100 vol% of cyclohexane measured by electron-probe microanalyser (Figure 5). Figure 5 indicates that, in the case of RCSNH prepared by using 50 vol%, UO_2^{2+} and Cu^{2+} were hardly adsorbed onto the resin and Ag^+ was adsorbed only on the surface parts of the resin. On the other hand, in the case of RCSNH prepared by using 100 vol%, UO_2^{2+}, Cu^{2+}, and Ag^+ were found to be adsorbed onto whole parts of the resin. The adsorption ability of the RCSNH for uranium in U-spiked seawater was investigated (Figure 6). The RCSNHs prepared by using 50 and 75 vol% of cyclohexane little adsorbed uranium even after 75 h. RCSNH with the highest specific surface area prepared by using 120 vol% of cyclohexane showed the

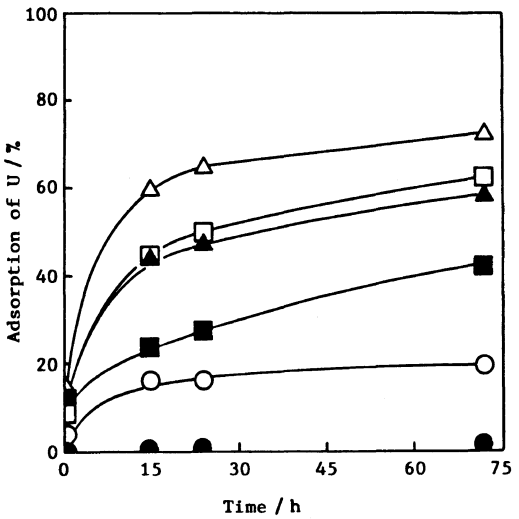


Figure 6. Effects of macroreticular structure on the adsorption uranium from U-spiked seawater: cyclohexane/vol%; ●, 50; ○, 75; □, 100; △, 120; ▲, 140; ■, 160.

Table IV. Cl content of RCS[a]

DVB	Cl content/%	
mol%	Found	Calcd
2.5	14.7	22.7
5	15.8	21.6
10	13.6	19.9
15	13.3	18.1
20	12.2	16.3
30	8.7	13.1

[a] Cyclohexane, 100 vol%.

highest adsorption rate and adsorption capacity of uranium. But the adsorption rate of uranium on RCSNH from the U-spiked seawater is much slower than that of uranium on RNH. Further investigations for this are now in progress.

Effects of Degree of Crosslinking of Resin on Adsorption of Metal Ions

RCSs were synthesized using various DVB contents (2.5—30 mol%) and constant cyclohexane content (100 vol%). The Cl contents in the RCSs were 8.7—15.8% (Table IV). These values were smaller than those calculated from the contents in the feed. This decrease in Cl content is attributed to the hydrolysis of the chloromethyl groups during a suspension polymerization. This phenomena was ascertained from the release of Cl^- into the dispersion medium after the suspension polymerization and from adsorption bands due to hydroxyl groups in the IR spectra of the RCS. Table V shows the specific surface area of the RCSNH to increase with DVB content, whereas the pore volume and pore radius to decrease with

Table V. Specific surface area, pore volume, pore radius of RCSNH[a]

DVB	SSA[b]	Pore volume	Pore radius/Å	
mol%	$m^2 g^{-1}$	$cm^3 g^{-1}$	Peak	Av
2.5	3.7	0.502	1056	968
5	17.3	0.336	156	164
10	37.3	0.249	83	110
15	64.1	0.249	87	103
20	91.9	0.333	89	114
30	157.4	0.344	125	120

[a] Cyclohexane, 100vol%.
[b] Specific surface area.

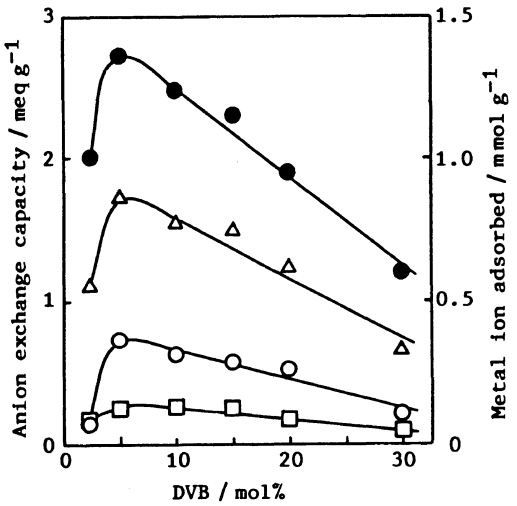


Figure 7. Effects of the degree of crosslinking on the anion exchange capacity and adsorption of metal ions: ○, UO_2^{2+} (pH 3); □, Cu^{2+} (pH 3); △, Ag^+ (pH 3); ●, anion exchange capacity.

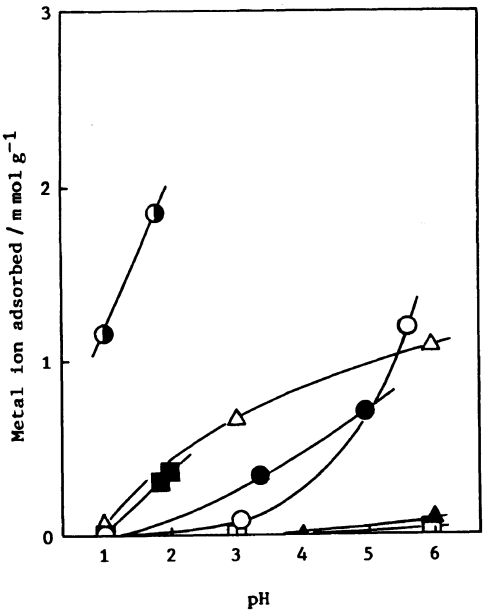


Figure 8. Adsorptions of various metal ions by RCSNH: ◑, Hg^{2+}; △, Ag^{+}; ■, Fe^{3+}; ○, Cu^{2+}; □, Pb^{2+}; ▲, Zn^{2+}; ●, UO_2^{2+}.

increasing DVB content up to 10 mol%. The RCSNH prepared by using 2.5 mol% of DVB showed very small specific surface area and remarkably large pore radius.

The RCSNH prepared by using 2.5 mol% of DVB and having very low specific surface area showed a very low adsorption ability for UO_2^{2+}, although the resin has a high anion exchange capacity, and a high adsorption ability for Ag^{+} (Figure 7). The RCSNHs prepared by using above 5 mol% of DVB and having high specific surface areas exhibited the adsorption ability which corresponds to the anion exchange capacity of the resins.

Effects of pH on the Adsorption of Metal Ions

The adsorption ability of the RCSNH prepared by using 10 mol% of DVB and 120 vol% of cyclohexane for various metal ions in an aqueous solution with different pH was investigated (Figure 8). The pH in the abscissa figure are equilibrium values after adsorption. The RCSNH showed a high adsorption ability

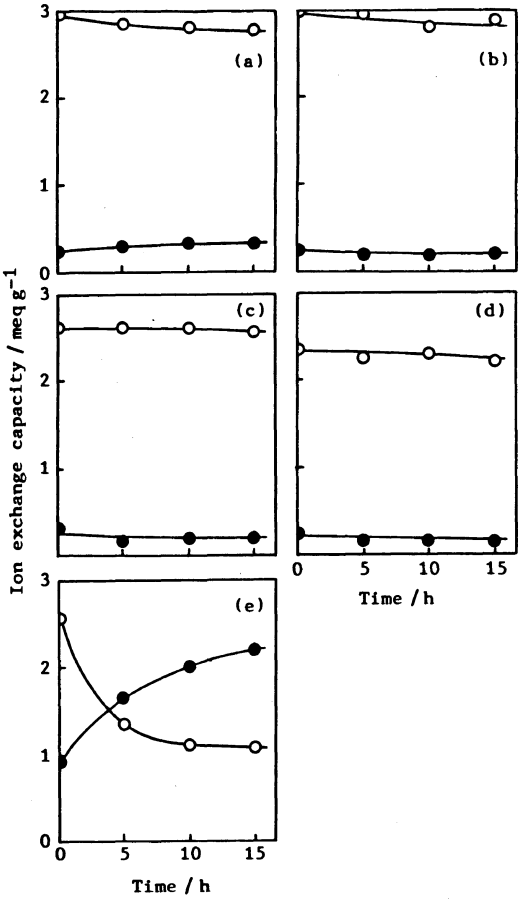


Figure 9. Effects of acid treatment on ion exchange capacity: ○, anion exchange capacity; ●, cation exchange capacity; (a) RCSNH (DVB, 5 mol%); (b) RCSNH (DVB, 10 mol%); (c) RCSNH (DVB, 15 mol%); (d) RCSNH (DVB, 20 mol%); (e) RNH (DVB, 10 mol%).

for Hg^{2+} in the solution with low pH (1—2). Fe^{3+} and Ag^{+} could be adsorbed from the solution with pH above 2, whereas Cu^{2+} and UO_2^{2+} could be adsorbed from the solution with pH above 3. Pb^{2+} and Zn^{2+} could hardly be adsorbed even at pH 6. From these results, it is recognized that metal ions can be separated by adjusting the pH of the solution. For example, Hg^{2+} and Ag^{+} (or Fe^{3+}) can be separated at pH 1 and Ag^{+} (or Fe^{3+}) and Pb^{2+} (or Zn^{2+}) at pH 3—4.

Resistance against Acid Solution

We reported that RNH had not sufficient stability against acid solution and the adsorption ability for uranium in seawater decreased gradually during repeated use. The changes of anion exchange capacity of resins after acid treatment with 1 mol dm^{-3} HCl at 60°C are shown in Figure 9. In the case of RNH, the anion exchange capacity decreased and the cation exchange capacity increased with time of acid treatment. This suggests that the amidoxime groups decrease and acidic groups such as carboxyl groups etc. are formed by acid treatment. But the decrease in the anion exchange capacity and increase in the cation exchange capacity of the RCSNHs could hardly be observed. This indicates that RCSNHs have high resistance against acid solution.

CONCLUSIONS

It was found that the adsorption ability of RCSNH for metal ions is greatly affected by macroreticular structure of resin and RCSNHs have high resistance against acid solution. Therefore, the RCSNHs which have appropriate macroreticular structures should be very effective for the recovery and separation of metal ions.

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REFERENCES

1. H. Egawa and K. Sugahara, *Kogyo Kagaku Zasshi*, **74**, 236 (1971).
2. H. Egawa, T. Nonaka, and Y. Fujiyama, *Nippon Kagaku Kaishi*, 888 (1977).
3. H. Egawa, T. Nonaka, and M. Ikari, *J. Appl. Polym. Sci.*, **29**, 2045 (1984).
4. H. Maeda and H. Egawa, *J. Appl. Polym. Sci.*, **29**, 2281 (1984).
5. H. Egawa and T. Nonaka, *J. Appl. Polym. Sci.*, **31**, 1667 (1986).
6. H. Egawa and H. Harada, *Nippon Kagaku Kaishi*, 958 (1979).
7. H. Egawa, H. Harada, and T. Nonaka, *Nippon Kagaku Kaishi*, 1767 (1980).
8. H. Egawa, H. Harada, and T. Shuto, *Nippon Kagaku Kaishi*, 1773 (1980).
9. H. Egawa, M. Nakayama, T. Nonaka, and E. Sugihara, *J. Appl. Polym, Sci.*, **33**, 1993 (1987).
10. H. Egawa, M. Nakayama, T. Nonaka, H. Yamamoto, and K. Uemura, *J. Appl. Polym. Sic.*, **34**, 1557 (1987).
11. M. Nakayama, K. Uemura, T. Nonaka, and H. Egawa, *J. Appl. Polym. Sic.*, **36**, 1617 (1988).
12. K. Sugasaka, S. Katoh, N. Takahashi, and Y. Umezawa, *Sep. Sci. Technol.*, **16**, 971 (1981).
13. L. Astheimer, H. J. Schnenk, E. G. Witte, and K. Schwochau, *Sep. Sci. Technol.*, **18**, 307 (1983).
14. J. Okamoto, T. Sugo, A. Katakai, and H. Omichi, *J. Appl. Polym. Sci.*, **30**, 2967 (1985).
15. T. Hori, S. Furusaki, T. Sugo, and J. Okamoto, *Nippon Kagaku Kaishi*, 1071 (1987).
16. T. Hirotsu, S. Katoh, and K. Sugasaka, *Ind. Eng. Chem. Res.*, **26**, 1970 (1987).
17. N. Takagi, T. Hirotsu, J. Sakakibara, S. Katoh, and K. Sugasaka, *Nippon Kaisui Gakkaishi*, **42**, 279 (1989).
18. H. Kise and H. Sato, *Makromol. Chem.*, **186**, 2449 (1985).