

Studies of Selective Adsorption Resins. XVIII. The Influence of Porosity of Macroreticular Chelating Resin on Adsorption of Heavy Metal Ions in an Aqueous Solution

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Synopsis

In order to choose the most practical macroreticular chelating resins for the removal and recovery of heavy metal ion from industrial waste solution, the influence of the porosity of macroreticular chelating resins on the adsorption for metal ion was studied. The four macroreticular chelating resins (RST) containing triethylenetetramine side chain with different porosity were used. It was found that the adsorption of zinc ion at its low concentration solution was affected by the porosity of the RST. Among the four resins with average pore radius of 21.0, 24.5, 28.0, and 66.5 nm, a resin with that of 66.5 nm gave the highest initial adsorption rate and the largest breakthrough capacity for zinc ion at a space velocity of 15 h⁻¹.

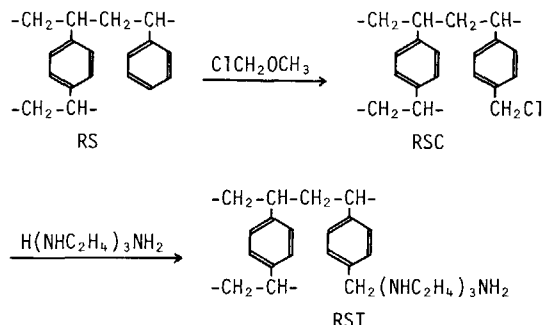
INTRODUCTION

In recent years, chelating resins have been used for the selective removal and recovery of heavy metal ions from industrial waste solution containing much other cations such as sodium ion, calcium ion, and magnesium ion. In the previous papers, we reported^{1,2} that macroreticular chelating resins were more practical than gel type resins for the above purpose because of its high physical stability and its high adsorption rate. We also reported^{1,3} that the macroreticular chelating resins (RST) containing triethylenetetramine side chain exhibited selectivity for certain metal ions which tend to form ammine complexes, and the RST which was prepared from heavily crosslinked matrix (divinylbenzene 42%) could be effectively used for the selective removal and recovery of zinc ion from the waste solution in the viscose rayon industry because of its high physical stability. The adsorption ability of the RST obtained from such a heavily crosslinked matrix seems to be affected by their macropore structure (porosity) because those resins hardly swell in an aqueous solution. However, the influence of porosity of heavily crosslinked resins on the adsorption of metal ion have never been reported. In this article, the influence of porosity of the RST on the adsorption ability for heavy metal ions was investigated in order to choose more practical macroreticular chelating resins.

EXPERIMENTAL

Preparation of Macroreticular Chelating Resins

The macroreticular chelating resins (RST) containing triethylenetetramine side chain were prepared⁴ by the route in Scheme 1:



Scheme 1. Preparation of chelating resin.

The four commercial macroreticular styrene-divinylbenzene copolymer beads (20–60 mesh, Mitsubishi Kasei Kogyo Co., Ltd.) with different porosity were used for the preparation of RST. The copolymer beads (RS) (5 g) were chloromethylated with chloromethyl methyl ether (33 cm³) at 0–5°C for 3 h in the presence of tetrachloroethane (5 cm³) as swelling agent and of aluminum chloride (6.7 g) as catalyst. The chloromethylated copolymer beads (RSC) (5 g) were aminated with triethylenetetramine (10 cm³) in benzene (40 cm³) at 100°C for 3 h. The aminated copolymer beads (chelating resins, RST) were first washed with 1 mol·dm⁻³ HCl solution and next with 1 mol·dm⁻³ NaOH solution and left overnight in the NaOH solution to convert them to OH form. Finally the resins were washed with deionized water until the wash water became neutral.

Measurement of Porosity

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).

Measurement of Anion Exchange Capacity

In a glass-stoppered Erlenmeyer flask, 0.5 g of the RST and 100 cm³ of a 0.1 mol·dm⁻³ HCl solution were placed and then the mixture was allowed to stand at room temperature (about 25°C) for 48 h with occasional shaking. The anion exchange capacity was calculated by determination of HCl concentration in the supernatant.

Measurement of Adsorption Ability for Metal Ions

Batch Method: In a glass-stoppered Erlenmeyer flask, 0.25 g of the RST and 50 cm³ of a metal ion solution in various concentrations were placed and then

the mixture was allowed to stand at room temperature (about 25°C) for 96 h with occasional shaking. The amount of metal ion adsorbed on the resins was calculated by chelatometric determination of the metal ion concentration in the supernatant.

Column Method: 20 cm³ of 20–60 mesh sample of the RST (OH form) was packed in glass column (10 mm ϕ \times 500 mm). Resin height was about 255 mm. Metal ion solution was passed through the resin bed at a space velocity of 15 h⁻¹. The metal content in the effluent was determined by means of the chelatometric titration. Metal ion solutions were prepared from metal nitrate salts of reagent grade.

Measurement of Adsorption Rate

Two grams of the RST and 50 cm³ of deionized water were placed in a three neck flask. The resins in the flask were degassed in a vacuum for 1 min and then 400 cm³ of deionized water was added to the flask. The mixture was allowed to stand overnight to permeate water into the resins. The flask was set in a bath controlled at 27 \pm 1°C. 50 cm³ of 0.1 mol-dm⁻³ zinc nitrate solution was added to the flask with vigorous agitating. After addition, 5 cm³ of the aqueous phase was collected with volumetric pipet at fixed times and the concentration of zinc ion in it was determined.

RESULTS AND DISCUSSION

Table I shows the characterization of the four RST with different porosity, and Figure 1 shows the pore size distribution of the four RST. The porosity of the four RST was similar to that of the original macroreticular copolymer beads respectively. Table II shows the adsorption capacity of the four RST for heavy metal ions which tend to form ammine complexes. The adsorption capacity was determined by equilibrating these resins with zinc, copper, nickel, and mercury ion solution (10 mmol-dm⁻³) adjusted to pH of 6, 5, 6, and 1 with Clark-Lubs buffer, respectively.

The adsorption capacities of RST-3 and RST-4 for all metal ions in this research were higher than those of RST-1 and RST-2. The differences of the adsorption capacity for those metal ions depended on that of its anion exchange capacity which show the amount of triethylenetetramine side chain introduced.

TABLE I
Characterization of the Macroreticular Chelating Resins Used in This Research

Resin	DVB ^a content (%)	N content (%)	Ligand ^b capacity (mmol/g)	Anion exchange capacity (meq/g)	Pore volume (cm ³ /g)	Specific surface area (m ² /g)	Average pore radius (nm)
RST-1	50	5.25	0.94	3.07	0.95	98	66.5
RST-2	50	5.25	0.94	3.07	0.99	145	28.0
RST-3	42	5.63	1.01	3.53	0.86	189	24.5
RST-4	55	5.98	1.07	3.53	0.67	323	21.0

^a Divinylbenzene.

^b Calculated from actual nitrogen content.⁵

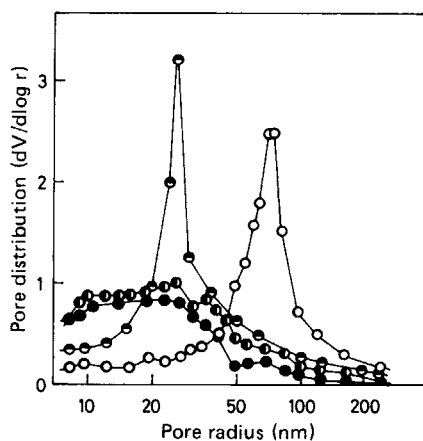


Fig. 1. Pore distribution of chelating resins: r = pore radius; (○) RST-1; (◐) RST-2; (◑) RST-3; (●) RST-4.

Figure 2 shows the adsorption capacity of the macroreticular chelating resins with different anion exchange capacity for zinc ion. The amount of zinc ion adsorbed increased with an increase in the anion exchange capacity of the chelating resins, regardless of the difference of their porosity. These results suggest that the adsorption capacity of the four RST for metal ion in a high concentration solution depend on only the amount of chelating side chain introduced.

Figure 3 shows the adsorption isotherm of the four RST for zinc ion within the range of equilibrium concentration from $0.08 \text{ mg}\cdot\text{dm}^{-3}$ to $23.0 \text{ mg}\cdot\text{dm}^{-3}$ of zinc ion. In this experiment, the initial concentration range of zinc ion was from $0.38 \text{ mmol}\cdot\text{dm}^{-3}$ to $1.53 \text{ mmol}\cdot\text{dm}^{-3}$, and the pH of the solutions at equilibrium was in the range of 6.1–6.9.

As shown in Figure 3, the adsorption ability for zinc ion in a low concentration solution decreased in the following order: RST-1 > RST-2 > RST-3 > RST-4. This result suggests that the adsorption ability of the RST for metal ion in a low concentration solution is affected by not only the amount of chelating side chain introduced but also their porosity.

The adsorption of metal ions on the four RST was examined under column operation which is practical process for the removal and recovery of heavy metal ion from industrial waste solution. Figure 4 shows the breakthrough curves obtained for zinc ion by using the four RST. Metal ion solution containing zinc ion ($5 \text{ mmol}\cdot\text{dm}^{-3}$, pH 6) was passed through the resin bed at a space velocity of 15 h^{-1} .

TABLE II
Adsorption Capacity of Chelating Resins^a

Resin	Metal ion adsorbed (mmol/g)			
	Zn ²⁺	Cu ²⁺	Ni ²⁺	Hg ²⁺
RST-1	0.60	0.68	0.63	0.41
RST-2	0.59	0.70	0.64	0.41
RST-3	0.74	0.92	0.84	0.46
RST-4	0.72	0.91	0.82	0.46

^a Initial concentration of metal ion: $10 \text{ mmol}\cdot\text{dm}^{-3}$, zinc, copper, nickel, and mercury ion solution was adjusted to pH of 6, 5, 6, and 1 with Clark-Lubs buffer, respectively.

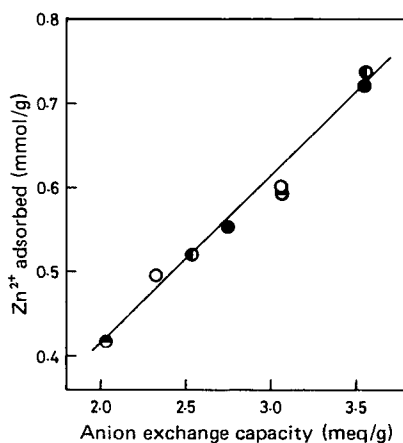


Fig. 2. Relation between Zn^{2+} adsorbed and anion exchange capacity: (○) RST-1; (◐) RST-2; (◑) RST-3; (●) RST-4.

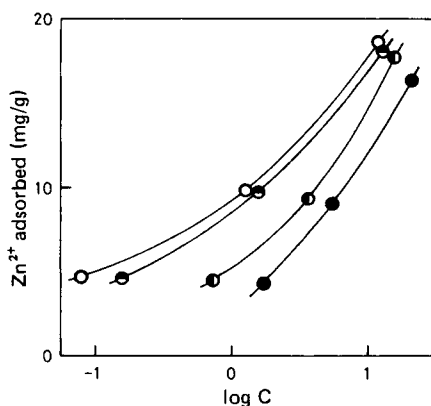


Fig. 3. Adsorption isotherms for Zn^{2+} : C = equilibrium concn ($\text{mg}\cdot\text{dm}^{-3}$); initial concn of Zn^{2+} = $25\text{--}100\text{ mg}\cdot\text{dm}^{-3}$; (○) RST-1; (◐) RST-2; (◑) RST-3; (●) RST-4.

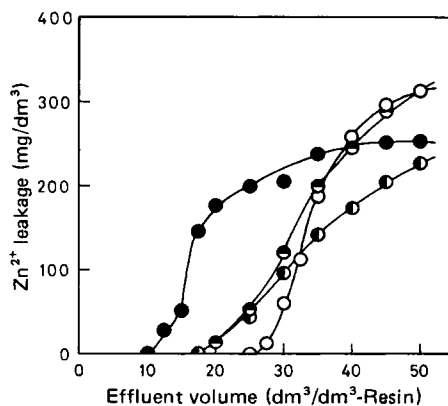


Fig. 4. Breakthrough curves for Zn^{2+} : resin bed = RST, 20 cm^3 ($10\text{ mm}\phi \times 255\text{ mm}$); void volume = $8\text{--}9\text{ cm}^3$; metal ion solution: $0.005\text{ mol}\cdot\text{dm}^{-3}\text{ Zn}(\text{NO}_3)_2$; flow rate: space velocity (SV) 15 h^{-1} ; (○) RST-1; (◐) RST-2; (◑) RST-3; (●) RST-4.

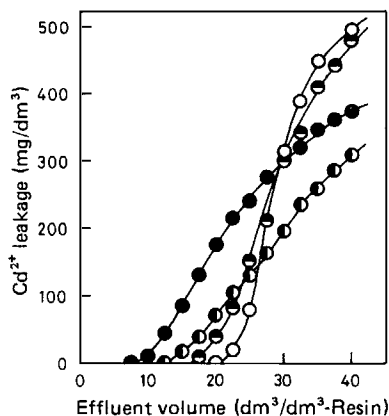


Fig. 5. Breakthrough curves for Cd^{2+} : metal ion solution = $0.005 \text{ mol-dm}^{-3} \text{ Cd}(\text{NO}_3)_2$; other conditions are the same as those described for Figure 4; (○) RST-1; (◐) RST-2; (◑) RST-3; (●) RST-4.

The breakthrough capacities of RST-1, RST-2, RST-3, and RST-4 for zinc ion were 8.8 , 6.3 , 6.6 , and 3.7 g-dm^{-3} resin, respectively. In practical column operation, large differences of the breakthrough capacities for zinc ion among the four RST were recognized, indicating that the breakthrough capacity of RST-1 for zinc ion was about 2.4 times as much as that of RST-4. Similar results were also obtained for cadmium ion and nickel ion, and the results were shown in Figures 5 and 6. From these results, it was found that the adsorption ability of the RST for metal ions in column operation is also greatly affected by their porosity. It is assumed that the adsorption band of metal ions on the RST-4 column is broader than that of the RST-1 column under the present experimental conditions by observing the forms of these breakthrough curves.

From Figure 1, it is clear that the two chelating resins (RST-1, RST-4) which exhibited particularly different adsorption abilities for metal ions have the large difference in the pore size distribution. Namely, many of the pore sizes of the RST-1 were in the range of radius from 50 nm to 100 nm , while the pore size of the RST-4 was in the radius below 50 nm .

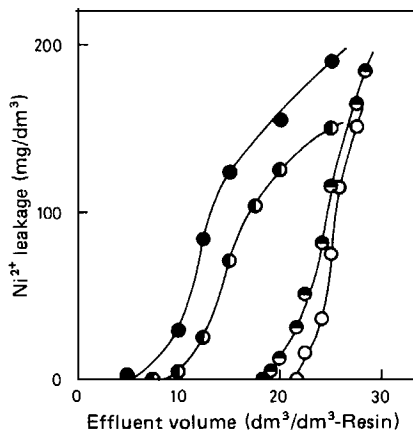


Fig. 6. Breakthrough curves for Ni^{2+} : metal ion solution = $0.005 \text{ mol-dm}^{-3} \text{ Ni}(\text{NO}_3)_2$; flow rate: $\text{SV } 5 \text{ h}^{-1}$; other conditions are the same as those described for Figure 4; (○) RST-1; (◐) RST-2; (◑) RST-3; (●) RST-4.

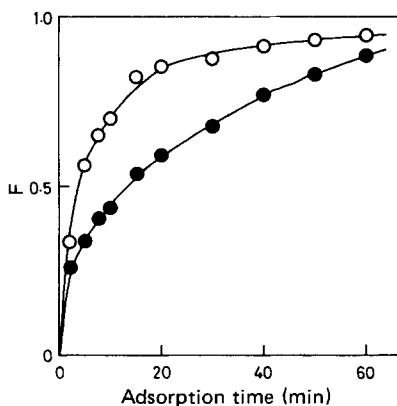


Fig. 7. Adsorption rates of Zn^{2+} on RST; F = fractional attainment of equilibrium; (O) RST-1; (●) RST-4.

Figure 7 shows the initial adsorption rates of zinc ion on RST-1 and RST-4 in terms of the fractional attainment of equilibrium. The pH of the solution during the measurement was in the range of 5.70–6.03. The initial adsorption rate of zinc ion on the RST-1 was higher than that on the RST-4, indicating that the time to 50% equilibration of the RST-1 and the RST-4 were about 3 min and 13 min, respectively. It seems that the adsorption rate of the macroreticular chelating resins in the earlier stage depends on the rate of the intraparticle diffusion of metal ion into the resin; therefore, the adsorption ability of the macroreticular chelating resin in the column operation was affected by its porosity.

From the results mentioned above, it was proved that the heavily crosslinked macroreticular chelating resin such as RST-1 with a larger pore radius is more practical for the removal and recovery of heavy metal ion from industrial waste solution because of its high adsorption rate and high physical stability.

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