CHEMISTRY LETTERS, pp. 1577-1580, 1988.

Synthesis of Copper(II) Selective Chelating Resin Bearing a Tetraaza Macrocyclic Schiff Base Ligand

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The chelating resin bearing a tetraaza macrocyclic Schiff base ligand as a pendant group has been synthesized and found to have a high selectivity for copper(II) over nickel(II). This resin can be applied to a useful adsorbent for efficient separation of these metal ions in a column system.

Selective separation and recovery of heavy metal ions are a very important subject in the fields of industrial and analytical chemistry. Many extractants and chelating resins have been synthesized for this purpose and some of them are applied to practical uses.1) Crown ethers and related macrocyclic ligands have been found to form complexes selectively with alkali and alkaline earth metal ions, and so the chelating resins bearing these compounds have been synthesized for selective separation of the above metal ions.1)

On the other hand, there have been only a few reports on chelating resins bearing polyaza macrocyclic ligands so far. For example, the chelating resin containing 1,4,8,11-tetraazacyclotetradecane (cyclam) has been shown to bind copper(II) effectively. However, its selectivity for binding copper(II) is not so high, judging from the distribution coefficients of other metal ions such as zinc(II), nickel(II), and cobalt(II).2) Recently, it has been pointed out from the solvent extraction experiments that unsaturated tetraaza macrocycles show a high selectivity for copper(II) over other transition metal ions such as nickel(II), zinc(II), and cobalt(II).3) We also reported that the complexing abilities and extractabilities of the novel tetraaza macrocyclic Schiff base ligands for transition metal ions were in the order of copper(II) >> nickel(II) > zinc(II).4,5)

Based on these experimental results, we have synthesized a chelating resin (CR-1) bearing a tetraaza macrocycle as a pendant group for the purpose of selective separation between copper(II) and nickel(II) (Fig. 1). This resin showed a high selectivity for binding copper(II) over nickel(II), but the incorporated macrocycle of the copper(II)-loading resin was partially decomposed when it was treated with hydrochloric acid for the recovery of copper(II).6) Hence, we have prepared a new chelating resin containing L (CR-2, Fig. 1) which might be more resistive against acid-hydrolysis than CR-1 because of hydrophobicity of the phenylene groups in the macrocyclic molecule. However, when the macrocycle (L) was allowed to react directly with chloromethylated polystyrene beads in dioxane, the extent of its incorporation onto them was very low. Thus, the diamino derivative of L was synthesized and then incorporated onto the polymer beads according to the scheme shown in Fig. 1. The dinitro and diamino derivatives of L were confirmed by elemental analyses and mass spectra.7)

To a suspension of chloromethylated styrene-divinylbenzene (3%) copolymer beads (8.0 g) in dioxane (150 ml) was added a dioxane solution (30 ml) of the diamino derivative of L (7.6 g) and dried pyridine (15 ml), and the mixture was stirred for 24 h at 80 °C in a nitrogen atmosphere. After cooled to room temperature, the solid was filtered, washed with methanol, chloroform and ether successively, and dried in vacuo. Anal. Found: C, 72.65; H, 6.45; N, 5.51%. From the analytical data, the extent of incorporation of the macrocycle onto the polymer beads was estimated to be 0.66 mmol·g^{-1}. In addition, the incorporation of L was confirmed by its characteristic bands (1620 and 1580 cm^{-1}) in the IR spectrum of CR-2.

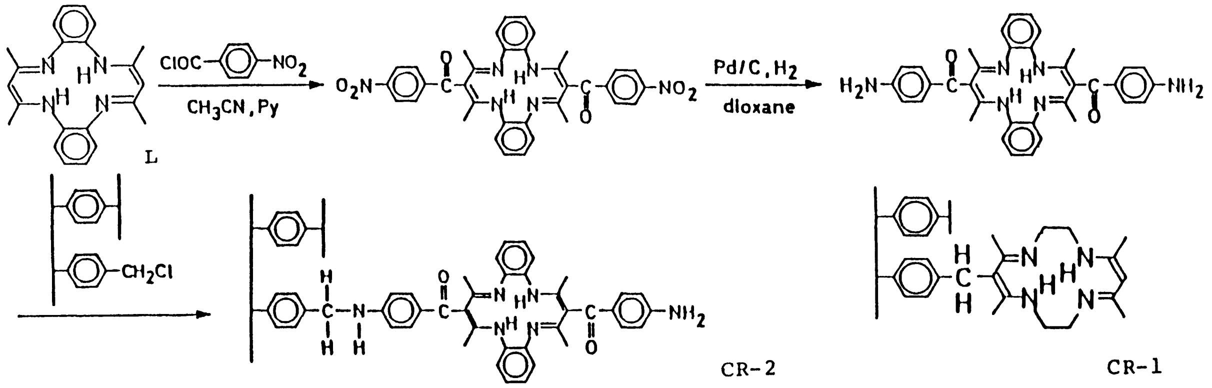

Fig. 1. A scheme for synthesis of the chelating resin.

The binding of metal ions by CR-2 in a batch system was examined as follows. The resin CR-2 (10 mg) was taken into a 10 ml test tube with a stopper which contained an aqueous solution of metal(II) acetate [copper(II) or nickel(II), 10 ml, 1×10^{-3} M, (1 M = 1 mol dm^{-3})]. It was shaken for an appropriate time (1 to 48 h) at room temperature. The loading capacity was calculated from the concentration of the metal ion remaining in the aqueous solution, which was determined by atomic absorption spectrometry. The bound copper(II) on CR-2 increased with shaking time (Fig. 2A). In this case, the initial pH of the copper(II) solution was 5.6 and not adjusted with a buffer solution. Under the same conditions, no binding of nickel(II) was observed after shaken for 48 h. In addition, it was confirmed that the binding of copper(II) took place by complex formation with the incorporated macrocycles in CR-2, from comparison of the visible diffused reflectance spectra between the copper(II) complex with the diamino derivative of L (644 nm) and the copper(II)-loading CR-2 (650 nm).

As shown in Fig. 2B, the loading capacity of CR-2 for copper(II) increased almost linearly with increasing the pH of the copper(II) solution up to ca. pH 6.0 and was kept constant (0.61 mmol·g^{-1}) in the range from pH 6.0 to 7.0. It is noted from these results that CR-2 is available as an adsorbent to separate copper(II) and nickel(II) by a column method under the following conditions. A column (i.d. = 10 mm) was packed with CR-2 (3.0 g in dry weight) which was fully swollen with an acetate buffer solution (0.02 M, pH 5.97) in advance. A mixed acetate buffer solution of copper(II) and nickel(II) (1×10^{-3} M) was eluted at a flow rate of 0.2 ml/min.

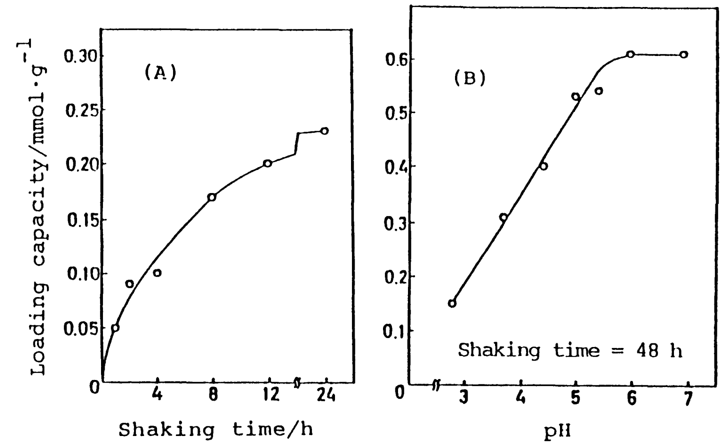

Fig. 2. Effects of shaking time(A) and pH(B) on loading capacity of CR-2(10 mg) for copper(II) (1×10^{-3} M, 10 ml).

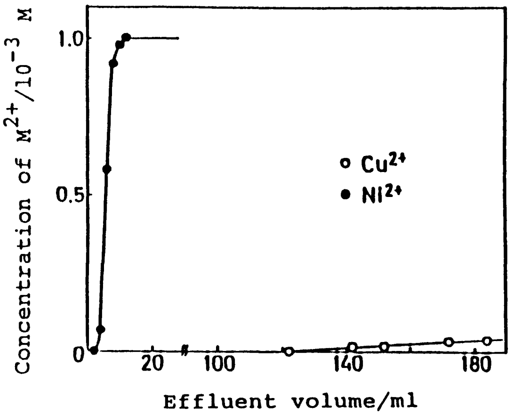

Fig. 3. Breakthrough curves for copper(II) and nickel(II) in a column system.

As shown in Fig. 3, nickel(II) was rapidly eluted and its concentration in the effluent reached the initial one (1 x 10^{-3} M) at the effluent volume of 10 ml. On the other hand, copper(II) was adsorbed completely on CR-2 and began to elute when the effluent volume exceeded 120 ml.

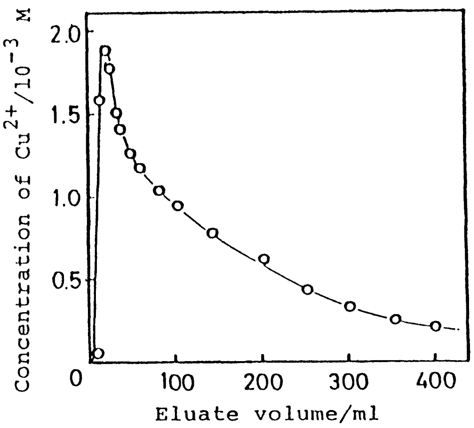

Fig. 4. Elution of copper(II) adsorbed on CR-2 with 0.01 M HCl in a column system.

Figure 4 shows the elution curve of copper(II) when the copper(II)-loading resin was eluted with 0.01 M HCl at a flow rate of 0.35 ml/min. The concentration of copper(II) in the eluate increased quickly to give a peak at the elution volume of 20 ml and then decreased gradually. When the elution volume reached 400 ml, most of the copper(II) on the resin was recovered. Moreover, the same column which the bound copper(II) on the resin had been eluted was employed again to adsorb copper(II) under the same conditions as mentioned above. No copper(II) was eluted till the effluent volume reached 100 ml. These results indicate that the present CR-2 can be used as an adsorbent for separation of copper(II) and nickel(II), and also the copper(II)-loading resin can be regenerated by treatment with 0.01 M HCl without loss of its loading capacity.

References

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7) For the dinitro derivative of L, Found: C, 66.73; H, 4.69; N, 12.97%; M^+, 642. Calcd for $C_{36}H_{30}N_6O_6$: C, 67.28; H, 4.70; N, 13.08%; M, 642. For the diamino derivative of L, Found: C, 73.77; H, 5.80; N, 14.58%; M^+, 582. Calcd for $C_{36}H_{34}N_6O_2$: C, 74.21; H, 5.88; N, 14.42%; M, 582.

(Received April 30, 1988)