NOTES

Removal and Recovery of Nickel Ion in Sodium Citrate Solution with Chelating Resin Containing Triethylenetetramine Side Chain

SYNOPSIS

Removal and recovery of nickel ion in sodium citrate solution with the macroreticular chelating resin containing triethylenetetramine side chain was investigated. The resin (RMT) exhibited high affinity for nickel ion in a solution containing 100 mmol/dm³ of sodium citrate over the pH range of 7.4–11.5. The adsorption of nickel ion was above 98%. In the column method, the breakthrough capacity of the RMT for nickel ion was 3.0 g/dm³-resin, when the solution containing 0.5 mmol/dm³ of nickel(II) nitrate and 100 mmol/dm³ of sodium citrate was passed through the RMT column at a space velocity of 7.5 h⁻¹. The nickel ion adsorbed was eluted by allowing 1 mol/dm³ hydrochloric acid to pass through the column. The recycle of adsorption and elution was found to be satisfactory.

INTRODUCTION

The removal of metal ion such as nickel ion from the waste solution of chemical plating is important either for pollution control or for material recovery. However, it is difficult to recover nickel ion in the waste solution because the chemical plating solution contains large amounts of complexing agents such as citrate ion. There have been few studies on adsorption of nickel ion in the solution containing complexing agents.[1] In a previous paper, we reported on a macroreticular chelating resin containing triethylenetetramine side chain.[2] In this article, the adsorption of nickel ion in the presence of sodium citrate is investigated with such a resin.

EXPERIMENTAL

Preparation of Macroreticular Chelating Resin

The macroreticular methyl methacrylate/divinylbenzene (5 vol %) copolymer beads were synthesized by suspension polymerization in the presence of 2,2,4-trimethylpentane

(50 vol %/monomer) as diluent. The macroreticular copolymer beads (35–60 mesh, pore volume 0.47 cm³/g, specific surface area 8.3 m²/g, average pore radius 82 nm, 1 g) were aminated with triethylenetetramine (5 cm³) at 175°C for 7 h. The anion-exchange capacity of the resin obtained was 6.2 meq/g.

Measurement of Adsorption Ability for Nickel Ion

Batch Method. In a glass-stoppered 100 cm³ Erlenmeyer flask were placed 0.125 g of the resin and 25 cm³ of nickel(II) nitrate solution (0.5 mmol/dm³) and the mixture was shaken for 24 h at 30 ± 1°C. The concentration of nickel ion in the supernatant liquid was analyzed by a spectrophotometric procedure based on dimethylglyoxime. The amount of nickel ion adsorbed on the resin was calculated by the change in the nickel ion concentration.

Column Method. A 2 cm³ sample of the resin was packed into a glass column (6 mmφ × 200 mm). Resin height was about 70 mm. Nickel ion solution was passed through the resin bed at a space velocity (volumes [cm³] of loading solution per unit volume [cm³] of resin-hour) of 3–15 h⁻¹. The nickel content in the effluent was determined by the spectrophotometric procedure based on dimethylglyoxime. Nickel ion solutions were prepared from nickel(II) nitrate of reagent grade. Nickel ion adsorbed on the column was eluted by passing 1 mol/dm³ hydrochloric acid through the resin at a space velocity of 7.5 h⁻¹. After elution, the resin was washed with 10 bed volumes of deionized water and then 1 mol/dm³ sodium hydroxide solution was passed through the resin bed at a space velocity of 15 h⁻¹. After the resin was washed with 10 bed volumes of deionized water, the adsorption–elution procedure was repeated several times.

Measurement of Adsorption Rate

One-half gram of the resin and 225 cm³ of sodium citrate solution or ammonia–ammonium chloride buffer solution were placed in a 300 cm³ three-neck flask. The resins in the flask were degassed under vacuum for 1 min. The mix-
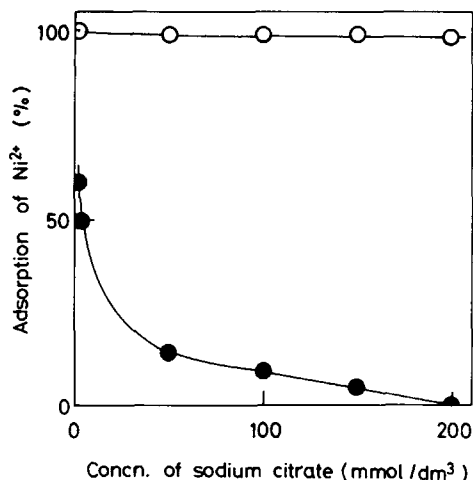
Figure 1 Effect of sodium citrate on the adsorption of Ni^{2+}; resin: (O) RMT; (●) IRC 50; initial concentration of Ni^{2+}, 0.5 mmol/dm^3; pH 7.2–8.5.

ture was allowed to stand overnight to allow water to permeate into the resins. The flask was set in a fixed temperature bath. After 25 cm^3 of nickel nitrate solution (5 mmol/dm^3) was added to the flask with vigorous agitation, 2 cm^3 of the aqueous phase was collected with a volumetric pipet at fixed times and the concentration of nickel ion in it was determined.

RESULTS AND DISCUSSION

Effect of Sodium Citrate on the Adsorption of Nickel Ion

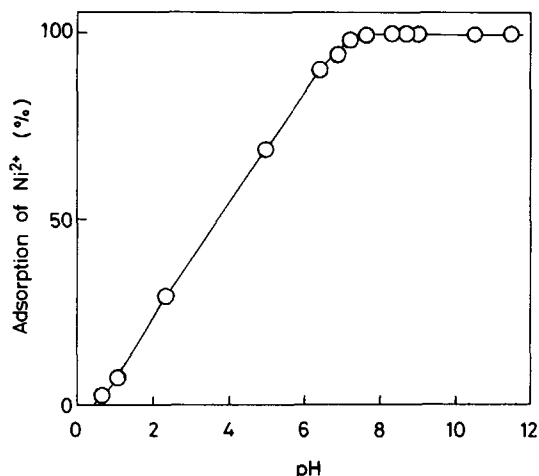The effect of complexing agent on the adsorption of nickel ion on the RMT containing triethylenetetramine side

Figure 3 Breakthrough curves of Ni^{2+}; resin bed, RMT 2 cm^3 (6 mmϕ × 70 mm); flow rate, SV 7.5 h^{-1}; loading solution: (O) Ni^{2+} 30 mg/dm^3, sodium citrate 100 mmol/dm^3, pH 7.9; (●) Ni^{2+} 30 mg/dm^3, NH_3—NH_4Cl buffer solution (100 mmol/dm^3), pH 8.7.

chain was investigated. Figure 1 shows the adsorption ability of nickel ion on the RMT in the presence of sodium citrate. The adsorption capacity was determined by equilibrating the resin with nickel ion solution (0.5 mmol/dm^3). The value of a commercial cation-exchange resin, Amberlite IRC 50, containing carboxyl groups is also shown for comparison.

Although the adsorption ability of the cation-exchange resin for nickel ion in the sodium citrate solution remarkably decreases with an increase in the amount of sodium citrate, the adsorption of nickel ion in the solution on the RMT is not influenced by the presence of sodium citrate in the concentration range of 1–200 mmol/dm^3. From these results, it is clear that the RMT exhibits high

Figure 2 Effect of pH on the adsorption of Ni^{2+}; initial concentration of Ni^{2+}, 0.5 mmol/dm^3.
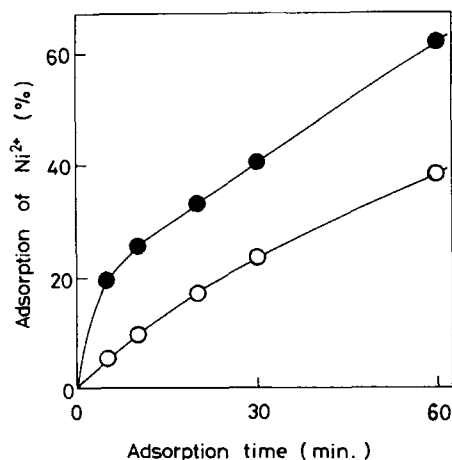

Figure 4 Adsorption rate of Ni^{2+} on the RMT; concentration of Ni^{2+}, 30 mg/dm^3; pH 8.9–9.1; (O) sodium citrate solution (100 mmol/dm^3); (●) NH_3—NH_4Cl buffer solution (100 mmol/dm^3).
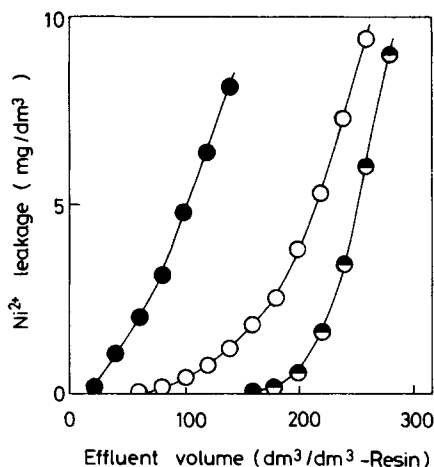
Figure 5 Effect of flow rate on the adsorption of Ni^{2+}; resin bed, RMT 2 cm^3 (6 mmϕ × 70 mm); loading solution, Ni^{2+} 30 mg/dm^3, sodium citrate 100 mmol/dm^3; flow rate: (●) SV 15 h^{-1}; (○) SV 7.5 h^{-1}; (◑) SV 3 h^{-1}.

affinity for nickel ion in the solution containing large amounts of complexing agent such as citrate ion at equilibrium of adsorption.

Figure 2 shows the pH dependence of adsorption ability for nickel ion in a sodium citrate solution on the RMT. The pH of the solutions was adjusted with hydrochloric acid or sodium hydroxide. Obviously, the RMT has a high affinity for nickel ion in the solution over the pH range of 7.4–11.5, indicating that the adsorption of nickel ion is above 98%.

The adsorption ability of the RMT for nickel ion in the solution containing the complexing agent was examined under column operation, which is a practical process for recovery of nickel ion from aqueous solution. Two nickel ion solutions containing sodium citrate (100 mmol/dm^3) or ammonia–ammonium chloride buffer (100 mmol/
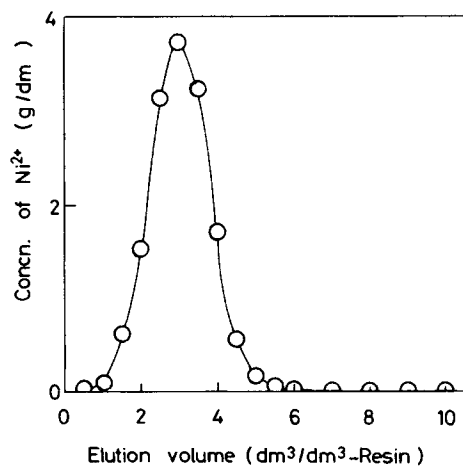

Figure 6 Elution curve of Ni^{2+}; eluent, 1N HCl; flow rate, SV 7.5 h^{-1}.

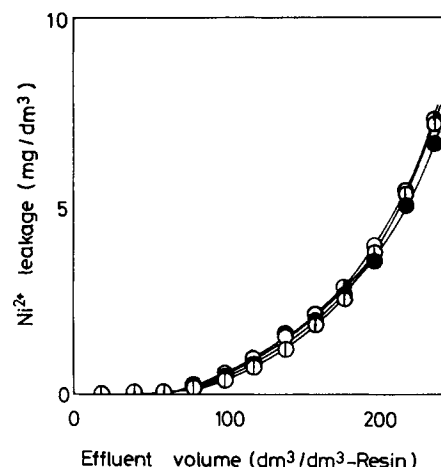**Figure 7** Recycle test; resin bed, RMT 2 cm^3 (6 mmϕ × 70 mm); loading solution, Ni^{2+} 30 mg/dm^3, sodium citrate 100 mmol/dm^3; flow rate, SV 7.5 h^{-1}; elution, 1 mol/dm^3 HCl, 10 dm^3/dm^3-resin, SV 7.5 h^{-1}; cycle number: (①) 1; (○) 2; (◑) 3; (●) 4.

dm^3) were passed through the resin bed at a space velocity of 7.5 h^{-1}, respectively. Figure 3 shows the breakthrough curves of nickel ion.

In practical column operation, the adsorption ability of the RMT for nickel ion in the solution containing sodium citrate is lower than that of the resin for nickel ion in ammonia–ammonium chloride buffer solution. Figure 4 shows the initial adsorption rates of nickel ion on the RMT. The initial adsorption rate of nickel ion in the solution containing sodium citrate is very slow in comparison with that of nickel ion in ammonia–ammonium chloride solution. It seems that the adsorption of nickel ion in the sodium citrate solution on the RMT in the column operation is affected by forming a nickel–citrate complex, because the initial adsorption rate of nickel ion in the sodium citrate solution on the RMT is slow.

The effect of flow rate on the adsorption of nickel ion in the sodium citrate solution was tested. Figure 5 shows the breakthrough curves of nickel ion, in the case that the nickel ion solution was passed through the column at various flow rates.

The adsorption ability of nickel ion on the RMT in practical column operation is greatly affected by the change of space velocity of 3–15 h^{-1}. Accordingly, reducing the flow rate as much as possible is required for effective recovery of nickel ion in the solution containing sodium citrate.

Elution of Nickel Ion Adsorbed on the Resin

It is necessary for nickel ion adsorbed on the resin to be eluted easily, in order to use this resin repeatedly for recovery of nickel ion. The elution of nickel ion adsorbed on the RMT was investigated by the column method,

which is a practical process for recovery of nickel ion. Figure 6 shows the elution curve of nickel ion with 1 mol/dm^3 of hydrochloric acid. The recovery of nickel ion was 99.3%. Almost complete removal of nickel ion from the resin was achieved by passing 6 bed volumes of 1 mol/dm^3 hydrochloric acid through the column at a space velocity of 7.5 h^{-1}, indicating that tailing phenomenon was not observed.

Recycle Test

Repeated adsorption and elution of nickel ion in the solution containing sodium citrate was examined by the column method by using 1 mol/dm^3 hydrochloric acid as eluent. Figure 7 shows the breakthrough curves of nickel ion for several adsorption–elution cycles. A decrease of adsorption ability of the RMT for nickel ion was not observed on repeated cycling. The breakthrough capacity of the RMT for nickel ion was 3.0 g/dm^3-resin, when the breakthrough point was taken at the point that the concentration of nickel ion in the effluent solution became 0.5 mg/dm^3. From these results, it was found that the recycle of adsorption and elution was satisfactory.

From the results mentioned above, it is clear that the RMT containing triethylenetetramine side chain is of practical use for the recovery of nickel ion in the solution containing large amounts of sodium citrate as complexing agent.

References

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