Notes

Selective Preconcentration and Separation of a Trace Amount of Copper(II) with Poly[*N*-(8-hydroxy-5-quinolylmethyl)-4-aminomethylstyrene] Resin

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The selective preconcentration and separation of trace-metal ions have been important subjects in analytical and environmental chemistry. Since chelating resins are characterized by a simple separation procedure and higher concentration factors, some new chelating resins have been synthesized in an effort to develop a selective separation methods for metal ions of interest.¹

Several chelating resins, in which 8-quinolinol was immobilized on different matrices, have been prepared due to the potential ability to form stable metal complexes.^{2,3}

Warshawsky reported a new type of resin for copper(II), in which 8-quinolinol is bonded to a macroporous poly(styrene-divinylbenzene) copolymer through $-\text{CH}_2-\text{NH}-\text{CH}_2-$ bonding.⁴ However, no details concerning the adsorption behavior of copper(II) have been investigated. We have demonstrated that the adsorption rate of copper(II) on PQAS resin is dependent on the kinds of anions, and was accelerated by adding such anions as SO_4^{2-} , NO_3^- , Cl^- .⁵

The adsorption behavior of copper(II), manganese(II), cobalt(II), nickel(II), zinc(II), lead(II), palladium(II), platinum(II) and iron(III) was studied by a batch method. The preconcentration and pre separation of a trace amount of copper(II) by a column method was examined and applied to the preconcentration and determination of copper(II) in a tap-water sample.

Experimental

Preparation of PQAS resin

PQAS resin was synthesized by a reported method⁴ with some modifications. A 4.2 g of aminomethylpolystyrene resin (AMPS) prepared from poly(styrene-divinylbenzene) copolymer (10% cross linking and 50–300 mesh) was refluxed with 8.9 g of 5-chloromethyl-8-quinolinol hydrochloride⁶ in 250 cm³ of 0.1 mol dm⁻³ HCl for 6 h. Analysis: 78.00% C, 7.43% N, 7.41% H.

The incorporated 8-quinolinol groups were calculated to be 0.96 mmol/g-resin.

Working solutions of metal ions were prepared by dissolving the metal salts of chloride, nitrate, and sulfate in 0.01 mol dm⁻³ corresponding acids.

Water was purified by demineralization with a MILLI Q Labo (Nippon Milli Pore Co. Ltd.) after double distillation.

All of the other chemicals were of analytical reagent grade.

Procedure for the batch method

A 50 mg sample of PQAS resin (100–350 mesh) and a 20-cm³ portion of an aqueous solution of a metal ion (2.0×10^{-4} mol dm⁻³) were gently agitated in a 50-cm³ vial for 10 min–6 d. The copper(II) in an aqueous solution was determined using an atomic absorption spectrometer (AAS). The pH of the aqueous solution was adjusted by HCl, HNO₃ or H₂SO₄. The ionic strength was adjusted so as to be constant by the addition of sodium chloride, sodium nitrate, and sodium sulfate, in some cases. All of the experiments were performed in a thermostated room at 25°C.

Procedure for the column method

A 500 mg of PQAS resin (100–350 mesh) was packed into a Pyrex column (0.5 cm i.d. and 6.5 cm in height). Then, a metal solution was passed through a PQAS resin column using a peristaltic pump at a flow rate of 0.92 cm³ min⁻¹. The eluate was collected in 20 or 50 cm³ fractions each. Breakthrough curves for the adsorption of metal ions were obtained by measuring the metal ions in the eluate. Metal ions, except for platinum(II) and palladium(II), were eluted with 10 cm³ of 1.5 mol dm⁻³ H₂SO₄. After the eluate was appropriately diluted with deionized water, metal ions were determined by AAS.

Results and Discussion

Adsorption isotherm for copper(II)

A 50-mg portion of the dry resin was gently agitated with 50 cm³ of a copper(II) (5×10^{-5} mol dm⁻³ – 5×10^{-2} mol dm⁻³) solution at pH 2.0 for 2 h–6 d in order to attain adsorption equilibrium. After the resin was filtered off, the adsorbed copper(II) was eluted with at least 10 cm³ of 1.5 mol dm⁻³ H₂SO₄, and was determined by AAS. A plot of $\log q$ vs. $\log c$ gave a straight line, where q and c are the adsorbed copper(II) concentration and the residual concentration of copper(II) in an aqueous solution, respectively. The adsorption isotherm for copper(II) is a typical Freundlich isotherm. This type of the isotherm has often been observed in the adsorption of metal ions by a resin.⁷

Adsorption behavior for metal ions by a batch method

Figure 1 represents the adsorption curves of metal ions by a batch method. The pH was adjusted with HCl. As reported in a previous paper⁵, the adsorption of the copper(II) on the PQAS resin was dependent on not only the pH, but also on the kinds of acids used for the pH adjustment. In the cases of H₂SO₄, the copper(II) was completely adsorbed above pH 2.0. However, the adsorption decreased along with increases in the pH in the 2–4 range in the cases of HNO₃ and HCl (*cf.* Fig. 1). This unusual adsorption behavior of copper(II) on PQAS resin was ascribed to a difference in the adsorption rate, which depended on the anions in the aqueous solution. The increasing order of the rate was NO₃⁻ < Cl⁻ < SO₄²⁻. Although copper(II) is almost completely adsorbed at pH 2.0, manganese(II) is not adsorbed at all. Nickel(II), cobalt(II) and zinc(II) are slightly adsorbed at pH 2.0. Platinum(II) and palladium(II) are completely adsorbed in the acid region below pH 1.

The effect of sodium sulfate on the adsorption of metal ions was observed, as represented in Table 1. In the presence of 0.1 mol dm⁻³ sodium sulfate, manganese(II), cobalt(II) and nickel(II) were not adsorbed at all, and only 3% of zinc(II) was adsorbed. The adsorption of copper(II) was also affected by sodium sulfate, and slightly decreased from 100% to 97%. Adsorbed metal

Fig. 1 Effect of the pH on the adsorption of 2.0×10^{-4} mol dm⁻³ metal ion (20 cm³) onto PQAS resin (50 mg) at 25°C. Shaking time: 2 h. The pH values were adjusted with HCl.

ions, except for platinum(II) and palladium(II), were easily eluted with 1.5 mol dm⁻³ H₂SO₄. The adsorbed platinum(II) and palladium(II) were eluted with a 0.3 mol dm⁻³ thiourea solution.

Adsorption behavior of metal ions by a column method

The effect of the flow rate of a feed solution containing 5.0×10^{-7} mol dm⁻³ copper(II) on the adsorption was investigated at pH 1.9, which was adjusted with H₂SO₄. More than 97% of the adsorption of copper(II) was obtained at flow rates of 0.62–1.92 cm³ min⁻¹. Figure 2 shows breakthrough curves for the adsorption of copper(II), nickel(II), iron(III) and zinc(II) on PQAS resin. The concentration of metal ions in the feed solutions was 2.0×10^{-4} mol dm⁻³. The pH of the feed solutions was adjusted to pH 2.0 with H₂SO₄. The copper(II) was completely adsorbed even at 185 cm³ of the feed solution. The adsorption quantity for copper(II) obtained by the column method is almost coincident with that obtained by the batch method. Whereas the breakthrough curve for iron(III) is fairly different from those for other metal ions, 45% of iron(III)

Table 1 Adsorption of metal ions onto PQAS resin (50 mg) under various conditions

	Mn ²⁺	Fe ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Pd ²⁺	Pt ²⁺
HCl ^a	1.7%	48.1%	9.1%	3.9%	99.0%	0.3%	100%	100%
(pH)	(2.2)	(2.1)	(2.2)	(2.2)	(2.0)	(2.2)	(2.0)	(2.0)
HCl ^b	0%	79.1%	5.3%	14.8%	100%	2.3%	100%	100%
(pH)	(2.2)	(2.2)	(2.2)	(2.2)	(2.0)	(2.2)	(2.4)	(2.2)
H ₂ SO ₄ ^c	0%	82.4%	0%	0%	97.0%	3.0%	100%	
(pH)	(2.1)	(2.1)	(1.9)	(1.9)	(2.1)	(2.1)	(2.1)	
H ₂ SO ₄ ^d	0%	82.4%	0%	2.7%	98.0%	3.0%		
(pH)	(2.1)	(2.0)	(2.1)	(2.1)	(2.4)	(2.0)		

Metal ions: 20 cm³ of 2.0×10^{-4} mol dm⁻³. Shaking time: a, 2 h; b, 1 h (in the presence of 0.1 mol dm⁻³ sodium chloride); c, 1 h; d, 1 h (in the presence of 0.1 mol dm⁻³ sodium sulfate).

Fig. 2 Breakthrough curves for the adsorption of 2.0×10^{-4} mol dm^{-3} metal ions onto PQAS resin at pH 1.9 (H_2SO_4). Column: 500 mg of PQAS resin was packed into a Pyrex glass tube (0.5 cm i.d. and 6.5 cm in height). Flow rate: $0.8 \text{ cm}^3 \text{ min}^{-1}$. C_0 and C are the initial concentration of the feed solution and the concentration of the feed solution passed through the column, respectively.

in the feed solution was still adsorbed even after passing 280 cm^3 of the feed solution. The unusual adsorption behavior of iron(III) may be due to the hydrolysis of iron(III). The amounts of the zinc(II), cobalt(II) and nickel(II) adsorbed were remarkably smaller than that of copper(II).

Elution of copper(II) from the PQAS resin column

The desorption behavior of copper(II) was investigated with H_2SO_4 and HCl . About 98% of the copper(II) was eluted with 10 cm^3 of $1.5\text{--}2.0 \text{ mol dm}^{-3}$ H_2SO_4 . However, a 97.2% of the copper(II) adsorbed was eluted with as much as 40 cm^3 of 4.0 mol dm^{-3} HCl . The recovery of copper(II) in varying quantities was examined by passing a feed solution ($290\text{--}1000 \text{ cm}^3$) containing $2.0 \times 10^{-8} \text{ mol dm}^{-3}\text{--}2.0 \times 10^{-4} \text{ mol dm}^{-3}$ copper(II) and by subsequently eluting the adsorbed copper(II) with 1.5 mol dm^{-3} H_2SO_4 .

The recovery was more than 98%, independent of the copper(II) concentration in the feed solution when copper(II) adsorbed was eluted with 10 cm^3 of 1.5 mol dm^{-3} H_2SO_4 .

Application

The present method was applied to the preconcentration and the determination of a trace amount of the copper(II) in a tap-water sample. The procedure was as follows. The tap-water sample was filtered with a membrane filter (TM-80 TOYO FILTER), the pH of the water was then adjusted to $1.9\text{--}2.0$ with H_2SO_4 . A 2-dm^3 portion of the water sample was passed through a PQAS resin column (0.5 cm i.d., 6.5 cm in height) at a flow rate of $0.92 \text{ cm}^3 \text{ min}^{-1}$. The copper(II) adsorbed was eluted with 10 cm^3 of 1.5 mol dm^{-3} H_2SO_4 and determined by AAS. The copper(II) concentration was determined to be 1.22 ppb and 0.257 ppb for the tap-water sample and for a distilled water sample, respectively. A blank experiment was carried out using purified water instead of a tap-water sample under the present experimental conditions. A blank value of copper(II) was 0.039 ppb and negligibly smaller than the amount of copper(II) in the tap-water sample.

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