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Separation of Pd(II) and Cu(II) in chloride solutions on a glycol methacrylate gel derivatized with 8-hydroxyquinoline

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Abstract

The adsorption of Pd(II) ions on Spheron Oxine 1000, a hydrophilic glycol methacrylate gel bearing 8-hydroxyquinoline groups, was investigated. The work was undertaken in flow conditions, using columns with different inner diameters packed with 1 g of the dry polymer. The adsorption and desorption isoplanes were determined under different hydrodynamic and chemical conditions. The breakthrough volume (95% removal efficiency) and the corresponding capacities were calculated from the isoplanes at different flow-rates and compared with batch results. The dynamic capacity obtained under saturation conditions was 57 ± 1 mg Pd(II)/g resin, at a flow-rate of 1.0 ml/min. High concentration and almost complete elution of Pd(II) were achieved using acidified thiourea solution, which also allowed the recycling of the chromatographic material. The separation of mixtures of Pd(II) and Cu(II) was achieved by appropriate adjustment of the pH of the feed solution to ensure selective sorption. Separation via appropriate acidic elution did not accomplish good selectivity.

1. Introduction

The use of chelating sorbents has been successfully applied as an alternative to liquid–liquid extraction for the concentration and selective separation of noble metals [1–3]. Functional groups capable of interacting selectively with metal ions have been introduced into different polymeric matrices. The organic matrices most extensively used are based on styrene–divinylbenzene copolymers [4]. However, supports obtained by addition of methacrylates are distinguished by their hydrophilicity and a high degree of porosity, which provide a rapid attainment of equilibrium. This is useful with platinum group of metals (PGM) because of the slow

kinetics of their coordinating reactions. For this reason, methacrylate-based polymers bearing chelating groups have appropriate characteristics to be used for sorption–desorption processes under dynamic conditions.

A chelating molecule that has received much attention is 8-hydroxyquinoline (8-HQ), used extensively in solvent extraction [5,6]. 8-HQ has been immobilized on different supports in order to be used in ion-exchange or chromatographic applications [7–9].

Spheron Oxine 1000 is a chelating ion exchanger containing 8-HQ moieties bonded via azo groups in the side-chains of the modified hydroxyethyl methacrylate gel. This resin was developed by Slovák et al. [10] and has been shown to be suitable for the chromatographic separation of base metals.

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This work was undertaken to study the processes of both sorption and elution of Pd(II) in chloride media using Spheron Oxine 1000. The influence of different parameters on the achievement of the selective separation of metal ions from solutions containing Pd(II) and base metals, mainly Cu(II), was investigated. The study was carried out under flow conditions with a chromatographic column and took advantage of previous batch sorption results to determine the optimum operating conditions [11].

2. Experimental

2.1. Reagents and solutions

A $9.4 \cdot 10^{-3}$ M stock standard solution of Pd(II) was prepared from solid $PdCl_2$ (for synthesis; Merck, Darmstadt, Germany). Working standard solutions with metal concentrations ranging from $1.0 \cdot 10^{-3}$ to $2.3 \cdot 10^{-3}$ M were prepared by dilution and then standardized gravimetrically with dimethylglyoxime [12]. A $1.57 \cdot 10^{-2}$ M stock standard solution of Cu(II) was obtained from solid $CuCl_2$ (analytical-reagent grade; Panreac, Spain) and was standardized volumetrically [12]. From this, working standard solutions with Cu(II) concentrations in the same range as for Pd(II) were obtained by dilution. Sodium chloride (analytical-reagent grade; Panreac) was purified as described elsewhere [13] and was employed to adjust the ionic strength of the metal solution to 0.1 M. The pH was varied between 0.0 and 2.0 using standarized HCl solution. For solutions with pH < 1.0 no sodium chloride was added, the ionic strength being determined by the HCl present. Solutions of thiourea (analytical-reagent grade; Pancreac), 0.5 M at pH 2.0, and hydrochloric acid, 0.5–2.0 M, were used in metal elution processes.

Spheron Oxine 1000, a glycol methacrylate support functionalized with 8-HQ moieties, was kindly supplied by Lachema (Brno, Czech Republic). The particle size and the pore diameter of the supported polymer were 40–63 μm and 37–50 nm, respectively.

2.2. Apparatus

A Varian SpectrAA-300 atomic absorption spectrometer (Varian Australia, Mulgrave, Victoria, Australia) was used to determine metal concentrations.

A Gilson Minipuls 2 peristaltic pump [Gilson Medical Electronics (France), Villiers-le-Bel, France] was employed to propel the solutions through the column. A Gilson FC 203 fraction collector (Gilson Medical Electronics, Middleton, WI, USA) was used to collect effluent samples at the outlet of the column.

All pH measurements were made with a Micro pH 2000 pH meter (Crison Instruments, Alella, Barcelona, Spain) and a Crison Model 50-02 combined glass electrode.

2.3. Column preparation

Glass columns were gravity packed with weighed samples of 1 g of air-dried resin (about 3 ml). The polymer was placed in the column in a suspension with a 0.1 M solution of sodium chloride or hydrochloric acid and allowed to settle. Two columns of different diameter (1.5 and 0.5 cm I.D.) were used.

2.4. Procedure for breakthrough studies

After column preparation, solution volumes of 250 ml containing Pd(II) or mixtures of Pd(II) and Cu(II) were processed through the column at a given flow-rate. In some instances, 350 ml of metal solution were necessary to achieve a higher degree of saturation. Effluent samples of 2.5 ml, for feed solutions containing only Pd(II), or 5 ml, when loading with both metals was studied, were periodically collected for analysis. Breakthrough curves were obtained from these analyses.

The adsorbed metal was eluted at a constant flow-rate (2.0 ml/min). The elution process was monitored as described for the loading process. In some instances, all the eluting solution was collected in several volumetric flasks until no metal was detected in the outlet of the column,

in order to determine the percentage of metal eluted at a given time.

The influence of the chemical and physical conditions on the palladium loading and its separation from copper was studied. Also, the behaviour of the eluting reagent, thiourea or HCl at different concentrations, was checked.

Experiments were carried out at a controlled room temperature of $22 \pm 2°C$ and their reproducibility was verified in duplicate, which also indicated the uncertainty of the experimental data to be ± 1 mg palladium/g resin.

3. Results and discussion

The reaction between 8-HQ and Pd(II) is on the basis of the palladium adsorption process described here. Such a reaction can be expressed by the equation [5]

$$M^{n+} + (n + r)(HOx)_{org} \rightleftharpoons [MOx_n(HOx)_r]_{org}$$
$$+ nH^+ \qquad (1)$$
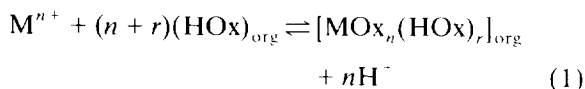
This process depends strongly on the acidity of the medium and the nature of the metal ion (i.e., the variation of the related stability constant is considerable). For palladium, the stability constant is high enough to allow the formation of the corresponding complex in very highly acidic media [5].

The adsorption of palladium by Spheron Oxine 1000 follows the mentioned pattern, as described previously [11]. The total amount of counter ions extracted per unit mass of solid chelating material is commonly called the apparent capacity [14]. The theoretical value of the metal adsorption capacity of Spheron Oxine 1000 (calculated from its nitrogen content and assuming a stoichiometry of 1:1 of the complex formed) was found to be 0.68 mmol/g resin. When the sorption of Pd(II) was determined in batch experiments, this theoretical value was only reached under specific chemical conditions, i.e., ionic strength, as described previously [11]. At pH 2.0 and ionic strength 0.1 M and after 24 h of contact between the resin and Pd(II) solution, a value of 0.536 mmol Pd(II)/g resin [57.03

mg Pd(II)/g resin] was found. Sorption of Pd(II) was not affected at pH values above 1.5.

The breakthrough capacity was determined to characterize Spheron Oxine 1000 under dynamic column operation. The breakthrough capacity is defined as the amount of metal ion that can be adsorbed per unit mass of solid before being detected in the outlet of the column. Different levels of metal in the effluent have been reported to be used to evaluate the breakthrough capacity [15]. In this work, the breakthrough capacity was determined from the volume of metal solution where the sorbent gives a removal efficiency higher than 95% under specified conditions. Breakthrough volumes were determined directly from the curves where $(C/C_0) \cdot 100 = 5$ (C_0 and C are the metal concentrations in the solution at the inlet and outlet of the column, respectively).

Factors that directly affect the breakthrough capacity, i.e., flow-rate, concentration of metal solution and column dimensions, were studied. Breakthrough curves were obtained for Pd(II) solutions at pH 2.0, ionic strength 0.1 M and flow-rates of 1.0, 2.0 and 3.0 ml/min using a column of 1.5 cm I.D. In Fig. 1, the percentage of metal in the effluent outlet is plotted against the bed volume (BV), defined as the ratio of the volume of effluent to the volume of resin. From the isoplanes, breakthrough capacities can be
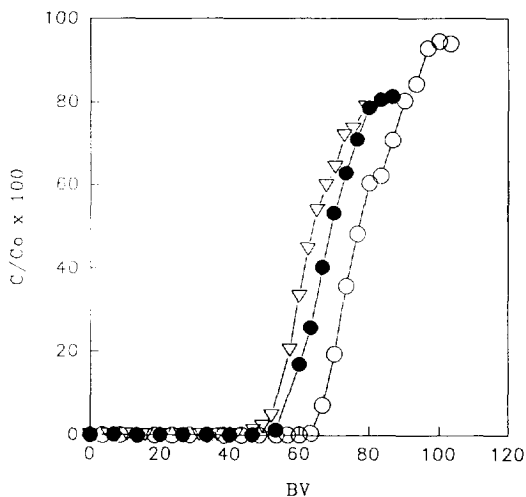

Fig. 1. Breakthrough curves for Pd(II) sorption at different flow-rates: $\bigcirc$ = 1.0; $\bullet$ = 2.0; $\triangledown$ = 3.0 ml/min. Feed solutions as reported in Table 1. Column of 1.5 cm I.D.

Table 1
Breakthrough and dynamic capacities obtained at different flow-rates in a column of 1.5 cm I.D. with feed solutions at pH 2.0 and ionic strength 0.1 M

Flow-rate (ml/min)	Initial metal concentration (10^{-3} M)	Breakthrough capacity (mg/g resin)[a]	Dynamic capacity (mg/g resin)[a]
1.0	1.9	40 ± 1	48 ± 1
2.0	2.0	35 ± 1	44 ± 1
3.0	2.1	36 ± 1	45 ± 1

[a] Mean ± S.D. ($n = 2$).

determined. On the other hand, a better measure of capacity can be expressed as the total amount of metal loaded under flow conditions. This value, termed the dynamic capacity, can be calculated from the experimental points when $(C/C_0) \cdot 100 = 100$. As the achievement of this value occurs very slowly for the uptake of Pd(II) by Spheron Oxine 1000, an approximate dynamic capacity was calculated graphically from the point where $(C/C_0) \cdot 100 = 80$. Different numerical integration methods, i.e., Simpson and trapezium methods, were used in these calculations [16]. Both values are summarized in Table 1. As expected, an increase in the flow-rate reduces both the breakthrough and dynamic capacities, in spite of this effect being more obvious at lower flow-rates [17]. Such a decrease can be ascribed to a lower residence time. As seen in Table 1, the dynamic capacities calculated as mentioned before are lower than the theoretical adsorption capacity. Saturation conditions were reached at a flow-rate of 1.0 ml/min and with 350 ml of feed solution. In this manner, a total amount of Pd(II) loaded of 57 ± 1 mg/g resin was obtained, which is similar to the corresponding batch capacity value.

The sorption and desorption isoplanes of Pd(II) at pH 2.0, flow-rate 2.0 ml/min and initial metal concentration $1.2 \cdot 10^{-3}$ M are shown in Fig. 2. The breakthrough capacity determined from the data obtained was 40 ± 1 mg/g resin. It was also determined that the capacity obtained depends on the metal concentration in the feed
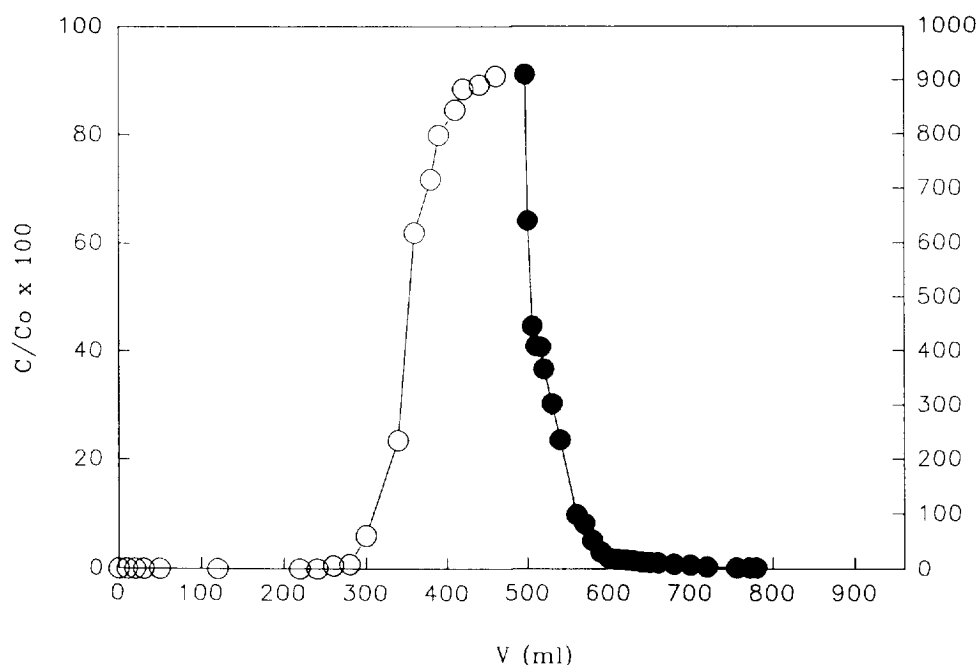

Fig. 2. (○) Sorption and (●) desorption isoplanes for $1.2 \cdot 10^{-3}$ M Pd(II), pH 2.0, ionic strength 0.1 M. Column of 1.5 cm I.D. Elution carried out with 0.5 M thiourea at pH 2.0. Flow-rate, 2.0 ml/min in both processes.

solution. As expected, the capacity increases when the metal concentration decreases. The elution data with 0.5 M thiourea at pH 2.0 show high efficiency.

A comparison of the elution efficiencies with 0.5 M thiourea at pH 2.0 and 2.0 M HCl as eluents is illustrated in Fig. 3. Loading was carried out at a flow-rate of 1.0 ml/min, initial metal concentration $1.9 \cdot 10^{-3}$ M, pH 2.0 and ionic strength 0.1 M in both experiments. Data are expressed as percentage of metal eluted calculated with respect to the total metal loaded [57 ± 1 mg Pd(II)/g resin]. As seen, the elution efficiency obtained with acidified thiourea was 81% and a considerable concentration of initial palladium solution is easily obtained. On the other hand, the efficiency of HCl elution was found to be much lower (only 36% was eluted in this instance).

The following experiments deal with the influence of the column diameter. The results obtained with a 1.5 cm I.D. column were compared with those with a 0.5 cm I.D. column packed with the same mass of resin. Under the same experimental conditions, an increase in column efficiency was obtained when a narrow column was used. Breakthrough capacities were calculated and are given in Table 2. The effect of
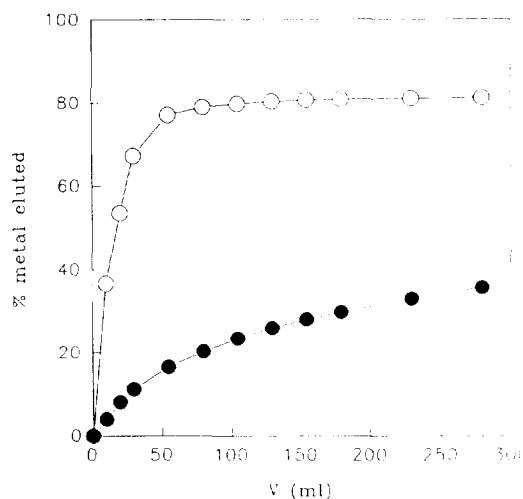
Table 2
Breakthrough capacities as a function of inner diameter of the column

I.D. (cm)	Initial metal concentration (10^{-3} M)	Breakthrough capacity[a] (mg/g resin)
1.5	2.0	35 ± 1
0.5	2.2	50 ± 1

Flow-rate, 2.0 ml/min; feed solutions at pH 2.0 and ionic strength 0.1 M.
[a] Mean $\pm$ S.D. ($n = 2$).

column dimensions on breakthrough capacities can be interpreted as a diffusional effect, because for a large column diameter the diffusion within the column does not occur quickly enough to utilize as many of the available complexation sites [17].

The reuse of the chromatographic material was determined to be efficient. For this purpose, a loaded resin was washed with 300 ml of 0.5 M thiourea solution of pH 2.0, rinsed with 0.1 M NaCl solution of pH 2.0, allowed to dry in air and then loaded again with palladium solution. No relevant differences were observed in the breakthrough capacities between the new and the reused resin [35 ± 1 mg Pd(II)/g resin for both new and reused materials].

Under dynamic conditions, sorption studies of precious metals and selected base metals were carried out with regard to potential applications of the chelating resins in hydrometallurgy. In this sense, results reported previously indicate that Spheron Oxine 1000 could be used for the separation of Pd(II) and Cu(II) taking into account the different apparent capacities obtained for these ions at pH 2.0, where the adsorption of palladium is much higher [11].

In a chromatographic column, separation can be obtained by either selective sorption or elution. Both factors were studied following the same procedure as described for the adsorption of palladium. Breakthrough curves were obtained under the following experimental conditions: initial concentration of Pd(II) $2.3 \cdot 10^{-3}$ M, initial concentration of Cu(II) $2.2 \cdot 10^{-3}$ M
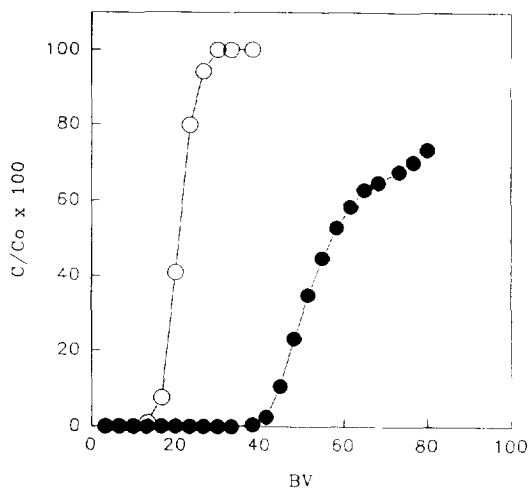

Fig. 3. Elution efficiency: percentage of metal eluted as a function of eluent volume. Flow-rate, 2.0 ml/min. ○ = 0.5 M thiourea, pH 2.0; ● = 2.0 M HCl.

Fig. 4. Breakthrough curves for a solution containing 2.3 · 10^{-3} M Pd(II) and 2.2 · 10^{-3} M Cu(II), pH 1.4. Flow-rate. 2.0 ml/min. ○ = Cu(II); ● = Pd(II).

Fig. 6. Breakthrough curves for a solution containing 2.3 · 10^{-3} M Pd(II) and 2.2 · 10^{-3} M Cu(II), pH 0.3. Flow-rate, 2.0 ml/min. ○ = Cu(II); ● = Pd(II).

and flow-rate 2.0 ml/min. As the most important parameter affecting the loading of base metals on Spheron Oxine 1000 was found to be the pH of the initial metal solution [10], the pH was varied systematically in order to obtain a selective loading. Experiments at pH 1.4, 0.8, 0.3 and 0.0 were performed and the breakthrough curves obtained are shown in Figs. 4–7. As expected,
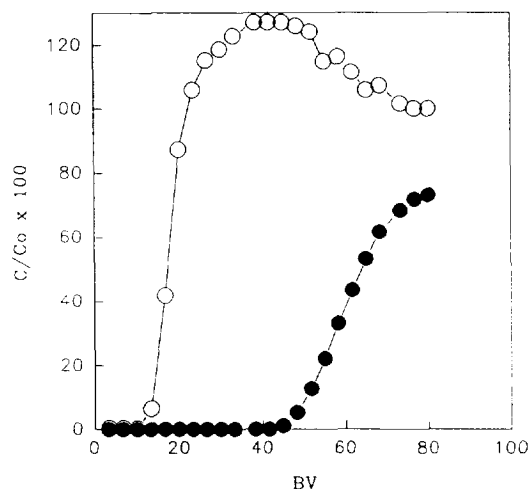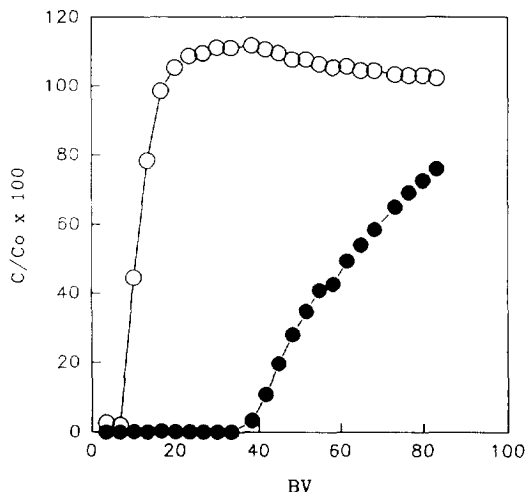
an improvement in the separation is observed when the pH of the solution is decreased. Nevertheless, for high acidity (pH < 0.3) the loading of palladium is also affected: copper is not adsorbed at all and palladium appears in the effluent in a shorter time. The breakthrough curves at pH 0.8 or 0.3 show that the sorption of palladium in the resin displaces the adsorbed
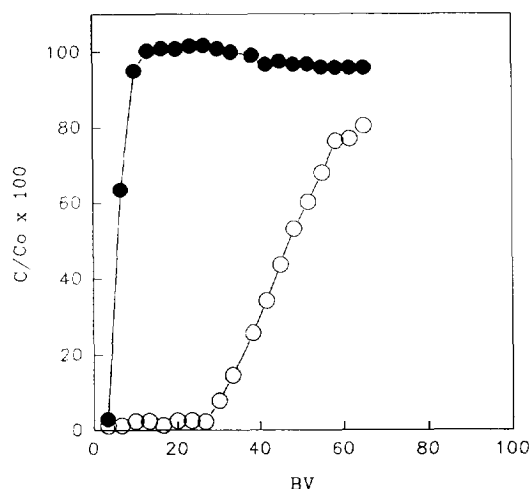

Fig. 5. Breakthrough curves for a solution containing 2.3 · 10^{-3} M Pd(II) and 2.2 · 10^{-3} M Cu(II), pH 0.8. Flow-rate. 2.0 ml/min. ○ = Cu(II); ● = Pd(II).

Fig. 7. Breakthrough curves for a solution containing 2.3 · 10^{-3} M Pd(II) and 2.2 · 10^{-3} M Cu(II), pH 0.0. Flow-rate, 2.0 ml/min. ○ = Pd(II); ● = Cu(II).

copper, producing the values of the ratio $(C/C_0) \cdot 100$ greater than 100.

Dynamic capacities for loading of palladium and copper at pH 0.3 were determined as the difference between the total metal concentration and the concentration in the effluent after a certain volume of solution has circulated through the column. In this instance, the volume corresponds to an efficiency of 20% with respect to palladium. The values obtained are summarized in Table 3. The breakthrough and dynamic capacities obtained for Cu(II) are similar whereas for Pd(II) a considerable difference in these values can be observed, in agreement with the shape of the isoplanes in Fig. 6. The value of the dynamic capacity obtained experimentally agrees with the value calculated by means of numerical integration methods, which was found to be 46 mg Pd(II)/g resin. At pH 0.3, complete separation of the two metals is not obtained, but the copper sorbed in the resin is only 6% of the initial value. Only at pH 0.0 is Pd(II) selectively adsorbed, according to the results shown in Fig. 7.

Results of elution experiments are shown in Figs. 8 and 9. In Fig. 8 the elution profiles were obtained using 2.0 M HCl as eluent (loading at pH 1.4). As can be seen, this stripping is very effective for Cu(II), even though a small amount of Pd(II) is eluted simultaneously. It must be taken into account that the resin contains much more palladium than copper (see Fig. 4). Lower concentrations of hydrochloric acid did not improve the palladium–copper separation. However, a high efficiency of separation was achieved
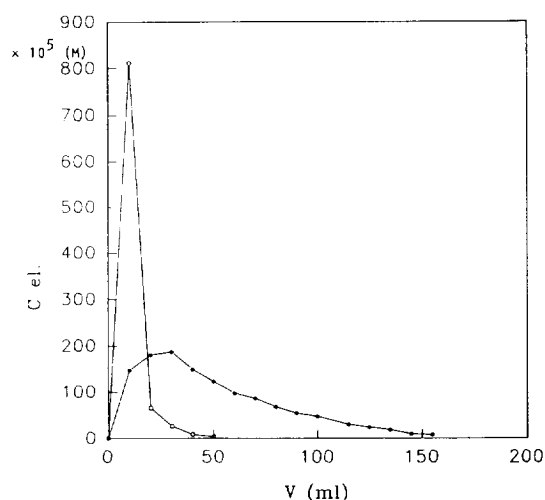

Fig. 8. Elution profiles of loaded Pd(II) and Cu(II) from the experiment shown in Fig. 4 using 2.0 M HCl as eluent at 2.0 ml/min. Results expressed as concentration of metal [Pd(II) or Cu(II)] in the elution outlet as a function of volume of eluent. $\bigcirc$ = Cu(II); $\bullet$ = Pd(II).

by loading the mixture under very acidic conditions (pH < 0.3). Under these conditions copper is virtually unadsorbed. Elution in this in-
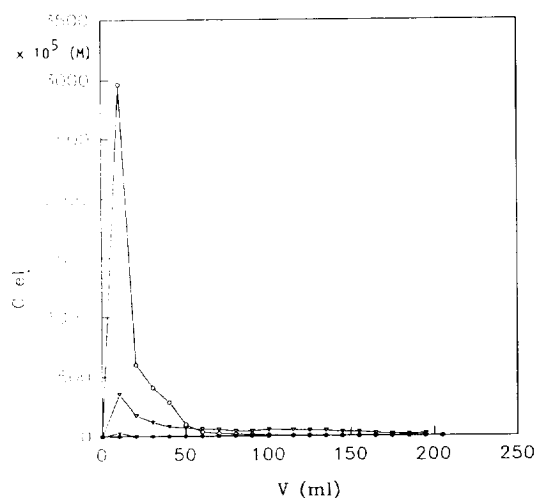

Fig. 9. Elution profiles of loaded Pd(II) and Cu(II) from the experiment shown in Fig. 6 using either 2.0 M HCl or 0.5 M thiourea at pH 2.0 as eluent at 2.0 ml/min. Results expressed as concentration of metal [Pd(II) or Cu(II)] in the elution outlet as a function of volume of eluent. $\bigcirc$ = Pd(II) and $\bullet$ = Cu(II) with 0.5 M thiourea at pH 2.0; $\triangledown$ = Pd(II) and $\blacktriangledown$ = Cu(II) with 2.0 M HCl.

Table 3
Breakthrough and dynamic capacities obtained for a mixture of Pd(II) and Cu(II)

Metal	Breakthrough capacity[a] (mg/g resin)	Dynamic capacity (mg/g resin)[a]
Pd(II)	28 ± 1	45 ± 1
Cu(II)	3 ± 1	2 ± 1

[Pd(II)] = 2.3 · 10⁻³ M; [Cu(II)] = 2.2 · 10⁻³ M; pH = 0.3; flow-rate, 2.0 ml/min.
[a] Mean ± S.D. ($n = 2$).

stance (see Fig. 9), both with 0.5 *M* thiourea of pH 2.0 and 2.0 *M* HCl, verifies the separation by the loading process. The experiments also reveal the higher efficiency of thiourea than hydrochloric acid solutions.

Acknowledgement

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