Separation of Gold from Nickel, Cobalt and Zinc by a Poly(hydroxamic acid) Ion-exchange Resin

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ABSTRAK

Kelakuan resin poli(asid hidroksamik) yang disediakan dari poli(etil akrilat) terhadap ion-ion emas, perak, tembaga, besi, nikel, kobalt dan zink di dalam larutan-larutan asid cair telah dikaji. Kajian dengan kaedah kelompok mendapati walau pun resin ini sangat tinggi afinitinya terhadap ion emas tetapi ia juga boleh digunakan untuk pengekstrakan ion-ion logam lain. Erapan ion-ion logam yang dikaji dengan kaedah turus adalah lengkap dan nyaherapan boleh dilakukan secara kuantitatif dengan pengelusi yang sesuai. Kajian lanjut menunjukkan resin ini boleh memisahkan emas dari nikel, kobalt atau zink di samping juga boleh digunakan untuk memisah emas dari perak, besi dan tembaga.

ABSTRACT

Behaviour of poly(hydroxamic acid) resin prepared from poly(ethyl acrylate) towards gold, silver, copper, iron, nickel, cobalt, and zinc in dilute acid solutions was evaluated. Batch method study shows that although this resin shows high affinity towards the gold ion, it can also be used for the extraction of other metal ions. Sorptions of these metal ions by the resin column are complete and their desorptions from the column can be carried out quantitatively by suitable eluants. Further investigations show that gold can be completely separated from nickel, cobalt and zinc in addition to its separations from silver, iron and copper.

Keywords: separation, gold, poly(hydoxamic acid)

INTRODUCTION

Poly(hydroxamic acid) chelating resin has been described as useful for many analytical applications. Vernon and Eccles (1976) showed that this resin can be used for extraction of iron from various salts and analytical standards in addition to separation of iron from copper, nickel and cobalt. Vernon and Wan Md Zin (1981) studied the behaviour of this resin towards gold(III), silver, iron (III) and copper ions and reported that the gold and silver ions could be completely sorbed in addition to separation of these Wan Md. Zin Wan Yunus, Md. Jelas Haron and Tan Lai Heong

metal ions from each other, iron (III) and copper. Other examples of its applications include extraction and separation of uranium (Vernon 1982), copper from lead (Shah and Devi 1985), uranium from neodymium (Mohammed 1987), cobalt from copper and nickel (Shah and Devi 1987) and separation of chromium (III), copper and iron (III) from plating bath effluent (Mendez and Pillai 1990).

Selectivity of a chelating ion-exchange resin depends not only on the properties of its chelating group but is also affected by the matrix to which it is attached (Sahni and Reedijk 1984). Recently the authors have described a simple step for converting poly(ethyl acrylate) into its hydroxamic acid and studied sorption and desorption of the resin for iron(III), copper, nickel, cobalt and zinc ions (Wan Yunus and Ahmad 1988). As part of a systematic evaluation of this resin the authors have investigated further its sorption and desorption properties for gold, silver, iron, copper, nickel, cobalt and zinc ions in dilute acid solutions and found that it can also be used for separation of gold from nickel, cobalt or zinc in addition to gold-iron, gold-copper and gold-silver separation.

MATERIALS AND METHODS

Materials

Poly(hydroxamic acid) resin was prepared as described by Wan Yunus and Ahmad (1988). A gold stock solution was prepared from sodium chloroaurate (BDH). All other chemicals were of analytical grade.

Batch Technique

Sorption studies for gold, silver, copper, iron, cobalt, nickel and zinc were carried out by shaking 0.5 g (accurately weighed) of wet polymer with 50 ml of a chosen metal solution (25 mg/l) for 2 h (Wan Yunus and Ahmad 1988). Distribution coefficient was defined as follows: D = (mmol of metal/g of dry resin)/(mmol of metal/ml of solution).

Column Extraction and Elution

Gravity flow column was prepared by packing the poly(hydroxamic acid) resin (50-100 mesh) in a glass column (1.0 cm I.D.) to a height of 10 cm. This column was conditioned by passing 50 ml 10^{-4} M nitric acid solution. For the extraction study, 10 ml of a solution containing 1 mg of selected metal ion dissolved in 10^{-4} M nitric acid solution was fed into the column. This was followed by washing the column with 10 ml of 10^{-4} M nitric acid solution. Column effluents were collected and analysed for the metal ion concentration.

Elution of the sorbed metal in the column was carried out by passing a suitable eluant. Fractions of 10 ml of column effluents were collected and the elution curve was plotted after the metal ion content in each fraction was analysed. The column flow rate used was 0.5 ml/min.

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Gold Separation

A shorter resin column (5 cm) which was also conditioned with 10^{-4} M nitric acid was used for separation of gold from silver, iron, copper, nickel, cobalt or zinc. Except for gold-silver separation, the sample used was a 10 ml solution containing 1 mg of each metal ion in 10^{-4} nitric acid solution. Sorption of gold and silver (1 mg) in the column was carried out as described by Vernon and Wan Md. Zin (1980). Separations were obtained by selective elution of the metal ions from the resin using suitable eluants.

Water Content Determination

Water content in the wet resin was calculated from the weights of the wet and dried resin. The wet resin was dried in a vacuum desiccator containing phosphorus pentoxide.

Metal Ion Determination

Quantitative analysis of all the metal ions was carried out using a Shimadzu flame A.A. spectrophotometer.

RESULTS AND DISCUSSION

Distribution coefficients of this poly(hydroxamic acid) resin for gold, silver, iron, copper, nickel, cobalt and zinc are given in Table 1. These results indicate that the affinity of the resin towards the gold ion is very high and the gold ion can be separated from the other metal ions if they are dissolved in nitric solutions at appropriate concentrations. Zero distribution coefficients of this resin for silver and the other ions suggest that these metal ions can be easily eluted from this polymer. The behaviour towards silver ions is different from the hydroxamic acid resin prepared from poly(acrylonitrile-ethyl acrylate), which shows that silver ion is strongly sorbed by the resin (Vernon and Wan Md. Zin 1981). High selectivity of that resin for silver ion is probably due to the presence of amidoxime groups on that polymer. These groups are one of the products obtained from

TABLE 1	

Distribution coefficients of poly(hydroxamic acid) for gold, silver, iron, copper, nickel, cobalt and zinc ions in dilute acid nitric solution

[HN03]/M	Au	Ag	Zn	Co	Ni	Cu	Fe
0.0001	∞	∞	16463	∞	∞	2352	∞
0.001	96228	0	0	0	130	372	83
0.01	982	0	0	0	0	31	9
0.10	54	0	0	0	0	0	30
0.50	36	0	0	0	0	0	200
1.00	31	0	0	0	0	0	241
2.00	4	0	0	0	0	0	0

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treatment of poly(acrylonitrile) with hydroxylamine (Vernon 1982). Silver ion is one of the strongly sorbed ions by poly(amidoxime) resin (Egawa *et al.* 1990).

Table 2 shows that extraction of gold, silver, iron, copper, cobalt, nickel and zinc from 10⁻⁴ M nitric acid solution by the column technique is complete. Gold, iron and copper ions are still completely extracted even from 0.01M nitric solution (Table 3). The metal ions retained by the resin can be eluted by the use of suitable eluants. Silver, copper, cobalt, nickel and zinc ions can be completely eluted by 2M nitric acid solution (Table 4). Iron is only partially desorbed from the resin by this acid (Table 4) but a rapid and complete elution is obtained when it is eluted with 0.1 M oxalic acid in hydrochloric acid solution (Table 5), as suggested by Wan Yunus and Ahmad (1988). The gold-resin complex is very stable and the gold ion cannot be desorbed by nitric acid solution even at the concentration of 6M. This indicates that this acid solution is not strong enough to break the resingold complex. However it is quantitatively eluted when a solution of 5% (w/ v) thiourea in 2 M sulphuric acid is used as an eluant (Table 6). Vernon and Wan Md Zin (1981) reported that this ion can be eluted from the poly(hydroxamic acid) resin using potassium cyanide solution. The use of the thiourea solution is a better alternative as potassium cyanide is a very poisonous chemical. However it may be used with proper precautions. Both thiourea and potassium cyanide solutions can completely elute the gold ion from the resin.

Metal Ion	mg in sample	mg retained	% of extraction
Au	1.00	1.00	100
Ag	1.00	1.00	100
Ag Co	1.00	1.00	100
Cu	1.00	1.00	100
Fe	1.00	1.00	100
Ni	1.00	1.00	100
Zn	1.00	1.00	100

TABLE 2

Column extraction of gold, silver, iron, cobalt, nickel, copper and zinc ions from 0.0001M nitric acid solution

TABLE 3

Column extraction of gold, iron and copper ions from 0.01M nitric acid solution

Metal Ion	mg in sample	mg retained	% of extraction
Au	1.00	1.00	100
Cu	1.00	1.00	100
Fe	1.00	1.00	100

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TABLE 4

Efficiency of eluting 1 mg of metal ions from the resin column by various amount of 2M nitric acid solution

Metal Ion	Volume of Eluant/mL	Recovery	
		mg	%
Ag	10.0	0.96	96
	20.0	1.00	100
Fe	10.0 30.0 40.0 50.0	$0.03 \\ 0.15 \\ 0.26 \\ 0.39$	3 15 26 39
Со	10.0	0.60	60
	20.0	0.99	99
	30.0	1.01	101
Cu	10.0 20.0	0.91 1.00	91 100
Ni	10.0	0.52	52
	20.0	0.94	94
	30.0	1.01	101
Zn	10.0	0.20 -	20
	20.0	0.73	73
	30.0	0.91	91
	40.0	0.98	98
	50.0	1.00	100

TABLE 5

Efficiency of elution of 1 mg of iron from the resin column by various amounts of 0.1 M oxalic acid in 1 M hydrochloric acid solution

Volume of eluant/mL	Reco	very
	mg	0/0
10.0	0.52	52
20.0	0.94	94
30.0	1.00	100

Separation of gold from nickel, cobalt or zinc is carried out by selective elution of the sorbed metal ions from the resin. Nickel, cobalt or zinc ions are eluted by 2M nitric acid solution and the gold is desorbed by the thiourea solution. A typical chromatogram is shown in *Fig. 1*. In the presence of iron ions in the sample solutions, elution of nickel, cobalt or zinc ions by 2M nitric is unable to elute these ions selectively as the iron is Wan Md. Zin Wan Yunus, Md. Jelas Haron and Tan Lai Heong TABLE 6

Efficiency of elution of 1 mg of gold from the resin column by
various amounts of 5% $\left(w/v\right)$ of thiourea in 2M sulphuric acid
solution

Volume of	Reco	covery
eluant/ml	mg	%
10.0	0	. 0
20.0	0.07	7
30.0	0.43	43
40.0	0.77	77
50.0	0.93	93
60.0	0.99	99
70.0	1.00	100

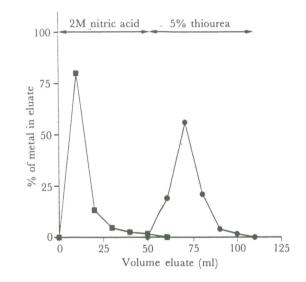


Fig. 1. Gold-nickel separation (•) gold and (•) nickel

partially eluted by this eluant. To avoid the contamination, hydrochloric acid solution (0.1M) is used to eluate nickel, cobalt or zinc ion. Clean threecomponent separation is obtained if the column is later eluted with the oxalic acid and thiourea solutions to strip iron and gold ions respectively. *Fig. 2* shows zinc-iron-gold separation.

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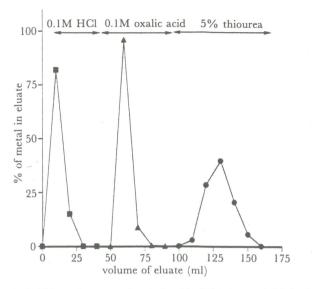


Fig. 2. Gold iron-zinc separation (\bullet) gold, (\blacksquare) iron and (\blacktriangle) zinc

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