

## Preparation of a Poly (Hydroxamic Acid) Ion-Exchange Resin from Poly (Ethyl Acrylate-Divinyl Benzene) Beads and its Properties.

WAN MD ZIN BIN WAN YUNUS and ZAHARUDDIN BIN AHMAD<sup>1</sup>

Department of Chemistry,

Faculty of Science and Environmental Studies,

Universiti Pertanian Malaysia,

43400 UPM, Serdang, Selangor, Malaysia.

**Key words:** Poly (hydroxamic acid) ion-exchange resin; preparation; properties.

### ABSTRAK

Satu kaedah ringkas untuk menyediakan resin penukar ion poli (asid hidroksamik) daripada poli (etil akrilat-divinil benzena) dan beberapa sifatnya dilaporkan. Resin disediakan dengan menggunakan poli (etil akrilat-divinil benzena) dengan larutan hidrosilamina dalam larutan natrium hidroksida. Muatan asid hidroksamik polimer yang dihasilkan adalah 2.29 mmol/g dan kadar erapannya, yang diukur berdasarkan erapan ion kuprum pada pH 4, cepat. Muatan erapan bagi ion Fe(III), Cu, Co, dan Zn bergantung kepada pH dan tertib kepilihan resin bagi ion-ion ini seperti berikut: Fe(III) > Cu > Ni > Co > Zn. Kebolehan resin untuk mengekstrak dan memisahkan logam-logam ini juga dilaporkan.

### ABSTRACT

A method to synthesize a poly (hydroxamic acid) chelating ion-exchange resin from poly (ethyl acrylate-divinyl benzene) and its behaviour towards some metal ions are described. The resin was prepared from this copolymer by treatment with hydroxylamine in the presence of sodium hydroxide. The hydroxamic acid capacity of the product is 2.29 mmol/g and its sorption rate, based on sorption of copper ion at pH 4, is rapid. Sorption capacities of Fe(III), Cu, Co, Ni and Zn ions are pH dependent and its selectively towards these metal ions is in the following order: Fe(III) > Cu > Ni > Co > Zn. The ability of this resin to extract and to separate these metal ions are also reported.

### INTRODUCTION

Chelating ion exchange resins containing hydroxamic groups have been known for more than 30 years and various analytical applications using this polymer have been demonstrated. Examples of the proposed application include: extraction and purification of uranium (Vernon, 1982); extraction and separation of gold and silver (Vernon and Wan Md Zin, 1980); separations of iron from copper, nickel and cobalt (Vernon and Eccles, 1976A), copper from lead (Shah and Devi, 1985), uranium from neodymium (Moham-

med, 1987), and cobalt from copper and nickel (Shah and Devi, 1987), purification of various reagents and extraction of some metal ions from aqueous solutions.

This type of chelating resin is currently not commercially available but can be synthesized by various methods using several starting materials. Petri *et al.* (1965) reported that the resin could be prepared from a conventional weak cation exchanger (IRC 50 resin) by an esterification reaction and followed by treatment with hydroxylamine. The conversion of the carboxylic

<sup>1</sup>Nuclear Energy Unit,  
Prime Minister's Department,  
Kompleks PUSPATI,  
Bangi, 43000 Kajang, Malaysia.

groups to the required functional groups was about 29%. Attempts to produce the resin from this polymer through its acid chloride were also made but the study showed that the conversion was poor (Vernon and Eccles, 1975). Phillips and Fritz (1982) synthesized the resin from styrene-divinyl benzene copolymer (XAD-4 resin) and in the four-step reactions they produced the hydroxamic acid with a nitrogen content of about 1.7 mmol/g. Poly(acrylonitrile) is another starting material used to synthesize the hydroxamic resin. This polymer can be converted into the required resin either through formation of its amide (Vernon and Eccles, 1976B) or carboxylic acid (Shah and Devi, 1985) followed by treatment with hydroxylamine or by direct reaction with hydroxylamine in an alkaline solution (Vernon, 1982 and Wan Yunus, 1980). The latter procedure is a one-step reaction but the product may be contaminated with amidoxime groups. This paper describes a simple method to prepare a hydroxamic acid resin from poly(ethyl acrylate-divinyl benzene) copolymer (by a one-step reaction) and the hydroxamic acid capacity of the product is 2.29 mmol/g. The ion exchanger behaviour of this resin towards iron (III), copper, nickel, cobalt and zinc ion is also reported.

## MATERIALS AND METHODS

### *Resin Preparation*

Poly(ethyl acrylate-divinyl benzene) was synthesized from 120.00 cm<sup>3</sup> ethyl acrylate and 12.50 cm<sup>3</sup> divinyl benzene solution by suspension polymerization (Wan Yunus, 1980 and Vernon, 1982) at 83–85°C. To convert this polymer into a polymeric hydroxamic acid, 20.00g of the dry polymer was reacted with a solution containing 27.08g of hydroxylammonium chloride and 80.00g of sodium hydroxide in 200 cm<sup>3</sup> of water-ethanol (75%) for 48 hours at 26–27°C. The product was washed with distilled water, then with 2M hydrochloric acid solution to convert the resin into the hydrogen form and again with the water until it was free of chloride. The resin was then stored under distilled water. Polymeric carboxylic acid was prepared by hydrolyzing the poly(ethyl acrylate) (20.00g) in 100 cm<sup>3</sup> sodium hydroxide (10M) for 6 hours at 95–97°C and then washed using the same washing procedures as outlined above for the hydroxamic acid resin.

### *Characterization of Resin*

To show the presence of the hydroxamic acid groups on the product, 0.5g of wet resin was shaken with vanadium(V) ion in dilute hydrochloric acid solution and the dark purple coloured complex produced by the resin on sorption of the vanadium(V) ion was observed. Drying of the wet resin for determination of water content after it was filtered by suction was carried out in a vacuum desiccator containing phosphorus pentoxide. Nitrogen content of the dry hydroxamic acid resin was determined by Microanalytical Unit, School of Chemistry, University of New South Wales.

Hydrogen capacity of the polymer was calculated from the amount of sodium hydroxide reacted with the resin when 0.5000g of the wet polymer was shaken with 50.00cm<sup>3</sup> of sodium hydroxide (0.02M) for 4 hours. Determination of sodium hydroxide concentration was done by titrating with a standard hydrochloric acid solution (0.02M) using phenolphthalein as an indicator.

Total metal sorption capacities for iron(III), copper, nickel, cobalt and zinc ions in acetate buffer at pH 2.5, 3.5 and 5.0 were determined by the following procedure: 0.5g of wet resin was shaken in 100cm<sup>3</sup> of buffered metal solution (0.01M) for 16 hours and then metal ion concentration in the equilibration solution was determined. Sorption of copper ion at pH 4 for different shaking periods were measured to study the resin kinetics.

### *Extraction, Elution and Separation*

The hydroxamic acid resin of 10 cm height in a glass column (1 cm i.d.) was used in all the studies. The resin in the column was conditioned by passing of an appropriate acetate buffer solution. In the extraction study, a sample solution was passed through the column and this was immediately followed by washing with 10 cm<sup>3</sup> buffer at the same pH. Elution was carried out by passing an eluant through a column on which a known weight of metal ion had been applied. In iron(III) – copper-nickel separation, a solution containing iron(III), copper and nickel ions (1 mg each) at pH 3.5 was passed through the column, followed by the passing of acetate buffer (pH 3.5) to remove nickel ion. Copper and iron (III) ions retained on the resin were eluted with

0.1M hydrochloric acid and 0.1M oxalic acid in 1M hydrochloric acid solution respectively. The same procedure was used for iron(III) – copper-cobalt and iron(III)-copper-zinc separations. A flow rate of about 0.5 cm<sup>3</sup>/min was used in all the experiments.

*Analysis of Metal Ions*

Metal ion concentrations were determined by atomic absorption spectrophotometer (1L Model 651) with the air-acetylene flame.

**RESULTS AND DISCUSSION**

The presence of the hydroxamic acid groups on the product was confirmed by a qualitative test based on the ability of the group to form a coloured complex with vanadium(V) in an acidic solution. Vanadium(V) ion gives a dark purple complex on reaction with hydroxamic acid groups. This coloured complex can easily be observed in this case since the resin is white. The formation of a dark purple complex between the polymeric hydroxamic acids and vanadium(V) ion in an acidic solution has been reported in earlier publications (Petri *et al.*, 1965 and Vernon, 1982). The nitrogen content of the dry hydroxamic resin was 3.21% indicating that the presence of the chelating groups on the polymer is 2.29 mmol/g. Hydrogen ion capacity, a measure of acidic group content on the polymer, is 7.54 mmol/g.

Thus there are also 5.52 mmol/g of carboxylic groups in the resin. The carboxylic groups are a side product resulting from the exposure of the hydroxamic group to sodium hydroxide at high concentration in the preparation procedure. Based on the hydroxamic acid and the carboxylic contents and the weight of divinyl benzene used in the polymerization, this hydroxamic acid resin should still contain 4.30 mmol/g of unconverted

ester groups. The resin prepared by the above procedure is in the bead form and the distribution of bead size can be easily altered by changing the rate of stirring during the polymerization step. On the basis of the weight of the divinyl benzene used in the polymerization process the product should be about 5% crosslinked.

Table 1 shows the total sorption of copper ion of the poly(ethyl acrylate), the poly(carboxylic acid) and the poly(hydroxamic acid) resins at various pH. The hydrogen ion capacity of the polymeric carboxylic acid is 10 mmol/g. The results show that the ester groups are not involved in copper ion uptake but the carboxylic acid groups show some sorption capacity at high pH. The results also clearly indicate that the presence of the hydroxamic acid groups on the polymer has greatly increased the ability of the polymer to sorb copper ion. Copper ion uptake by the carboxylic acid groups can be suppressed if the pH of the solution is adjusted to 3.5 or below.

Sorption of copper ion by the hydroxamic acid resin at pH 4 for various shaking periods are given in Table 2. The time taken by the resin to occupy 50% of its total sorption, *t*<sub>1/2</sub>, is 14 minutes which indicates that the sorption rate of the resin is rapid and the resin is suitable for use in a column technique. It is also noticed that the total copper ion sorption capacity at this pH is 2.88 mmol/g, 26% higher than the hydroxamic acid group capacity deduced from the nitrogen content. Further investigation showed that this was caused by the uptake of copper ion by the carboxylic acid groups. Total sorption capacity of copper ion of the polymeric carboxylic acid at pH 4 was 0.58 mmol/g.

Total sorption capacity of iron(III), copper, nickel, cobalt and zinc ions at pH 2.0, 3.5 and 5.0 are reported in Table 3. The resin shows high

TABLE 1  
Total sorption capacities of copper ion for the poly(ethyl acrylate), the poly(carboxylic acid) and the poly(hydroxamic acid) at various pH.

Resin	Total sorption capacity (mmol/g)		
	pH 2.0	pH 3.5	pH 5.0
Poly(ethyl acrylate)	0	0	0
Poly(carboxylic acid)	0	0	1.50
Poly(hydroxamic acid)	0.31	1.70	3.82

TABLE 2.  
Rate of sorption of copper ion at pH 4 by the hydroxamic acid resin.  
Total sorption capacity at this pH is 2.88 mmol/g

Time (min)	5	10	20	40	80	360
Sorption capacity (mmol/g)	0.78	1.17	1.61	1.90	2.05	2.44
(Sorption capacity/total sorption capacity) x 100	27	41	56	66	71	85

selectivity for iron (III) as it is to be expected when hydroxamic acid chelating ion-exchange resin reacts with this metal ion. Based on these results, selectivity of the resin towards these five metal ions was as follows: Fe(III) > Cu > Ni > Co > Zn. The results also suggest that separations of iron(III)-copper-nickel, iron(III)-copper-cobalt and iron(III)-copper-zinc could be carried out using this resin.

Removal of 1 mg of any one of these metal ions from 10 cm<sup>3</sup> aqueous solution, buffered at pH 5.0, by the exchanger in a column was quantitative. The retention of iron(III) and copper ions was also complete at pH 3.5. These metal ions on the column can be eluted by suitable eluants. Nickel, cobalt and zinc ions can be eluted completely with a solution at pH 3.5 or below. Copper and iron(III) ions, which are more strongly retained by the column, can be removed by 0.1M hydrochloric acid and 4M sulphuric acid or 0.1 oxalic acid in hydrochloric acid (1M) respectively. The oxalic acid solution is shown to be a better eluant system than the sulphuric acid solution. The use of oxalic acid for rapid and quantitative elution of iron(III) was suggested by Phillips and Fritz (1980). Table 4 shows the recovery

of iron(III) and copper ions (1mg each) when 100 cm<sup>3</sup> of several concentrated alkaline and alkaline earth metal solutions at pH 3.5 were passed through the ion exchange column followed by elution with sulphuric acid (4M). The quantitative recoveries of these two metal ions under these conditions show that the hydroxamic acid groups which are attached to the polymer matrix are capable of carrying out selective extractions. The high selectivity of chelating ion exchange resin towards some metal ions is one of the main properties which distinguish this type of resin from conventional ones (Schmuckler, 1965).

The iron(III)-copper-nickel separation on the hydroxamic acid column is shown in Figure 1. Nickel was completely washed out by acetate buffer (pH 3.5). Copper ion was eluted by 0.1M hydrochloric acid and iron(III) ion, which was not affected by the earlier solutions, was removed quantitatively from the column by 0.1M oxalic acid in hydrochloric acid. Similar chromatograms were obtained when iron(III)-copper-cobalt and iron(III)-copper-zinc separations were carried out. The chromatographic behaviour shown by this resin is very similar to the resin described by Vernon and Eccles (1976A).

TABLE 3.  
Total sorption capacities of some metal ions of the poly(hydroxamic acid) resin at various pH

Metal ion	Total sorption capacity (mmol/g)		
	pH 2.0	pH 3.5	pH 5.0
Fe(III)	1.38	2.10	—
Cu	0.31	1.70	3.82
Ni	0.26	0.66	2.18
Co	0	0.14	1.97
Zn	0	0	1.58

TABLE 4.  
 Recoveries of iron(III) and copper ions from various concentrated salt solutions

Solution	metal ion recovered (%)	
	Fe	Cu
NaCl	103	102
KCl	98	100
CH <sub>3</sub> COONa	100	100
BaCl	99	98
CaCl	100	100

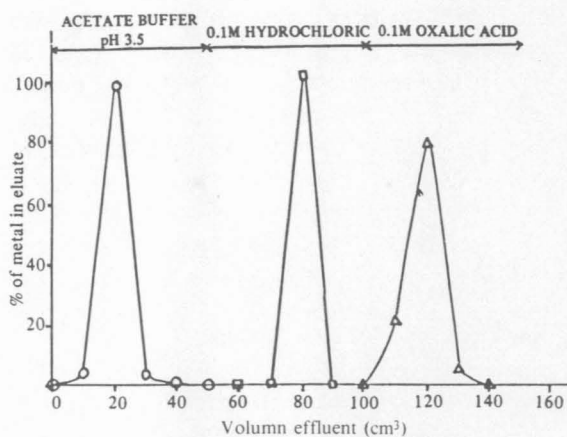


Fig. 1. Iron-copper-nickel separation. (○) nickel.  
(□) copper. (△) Iron.

### ACKNOWLEDGEMENTS

The authors would like to thank the School of Chemistry, University of New South Wales, for the elemental analysis.

### REFERENCES

- MOHAMMED, D.M. (1987): Separation of uranium from neodymium in a mixture of their oxides. *Analyst* 112: 1171-1181.
- PETRIE, G., D. LOCKE and C.E. MELOAN. (1965): Hydroxamic acid chelate ion exchange resin. *Anal. Chem.* 37(7): 919-920.
- PHILLIPS, R.J. and J.S. FRITZ. (1980): Synthesis and analytical properties of an N-phenyl-hydroxamic acid resin. *Anal. Chim. Acta* 121: 225-232.
- PHILLIPS, R.J. and J.S. FRITZ. (1982): Extraction of metal ion by N-phenyl, N-methyl- and N-unsubstituted hydroxamic acid resins. *Anal. Chim. Acta* 139: 237-246.
- SCHMUCHLER, G. (1965): Chelating resins. Their analytical properties and applications. *Talanta* 12: 281-290.
- SHAH, A. and S. DEVI. (1985): Separation of lead and copper on a series of chelating ion exchange resins. Part I. *Analyst* 110: 1501-1504.
- SHAH, A. and S. DEVI. (1987): Poly(hydroxamic acid) chelating resin. Part II. Separation of zinc from cadmium and of cobalt from copper and nickel. *Analyst* 112: 325-328.
- VERNON, F. and H. ECCLES. (1975): Chelating ion exchangers containing N-substituted hydroxylamine functional group. Part II. N-acylphenylhydroxylamines. *Anal. Chim. Acta* 79: 229-236.
- VERNON, F. and H. ECCLES. (1976A): Chelating ion exchangers containing N-substituted hydroxylamine functional group. Part IV. Column separation on a hydroxamic acid resin. *Anal. Chim. Acta* 83: 187-193.
- VERNON, F. and H. ECCLES. (1976B): Chelating ion exchangers containing N-substituted hydroxylamine functional group. Part III. Hydroxamic acids. *Anal. Chim. Acta* 82: 369-375.
- VERNON, F. and WAN MD ZIN (1981): Chelating ion-exchangers containing N-substituted hydroxylamine functional group. Part IV. Sorption and separation of gold and silver by a polyhydroxamic acid. *Anal. Chim. Acta* 123: 309-313.
- VERNON, F. (1982): Chelating ion exchangers. The Synthesis and uses of poly (hydroxamic acid) resin. *Pure & Appl. Chem.* 54(II): 2151-2158.
- WAN YUNUS, W.M.Z.B. (1980): Synthesis optimization and application of a poly(hydroxamic acid) ion-exchange resin. PhD. Thesis, University of Salford.

(Received 20 October, 1987)