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Adsorption studies with some chelating ion exchange resins derived from guaran

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A hydrophilic polysaccharide matrix of guaran has been used for the preparation of some new chelating resins, i.e. glycine hydroxamate in guaran (GH-G), acetic acid hydroxamate in guaran (AAH-G) and iminodiacetic acid dihydroxamate in guaran (IDAAH-G) after its crosslinking with epichlorohydrin. Various physico–chemical characteristics of the synthesised resins are studied. The distribution coefficient values of different metal ions, namely Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Ca(II), U(VI) and W(VI) on these resins are given as a function of pH. By using IDAAH-G resin in a column mode of operation, copper–calcium and iron–cobalt separations are quantitatively achieved at pH 5 and 5.5, respectively. © 1997 Elsevier Science Ltd

INTRODUCTION

Guar gum or guaran, derived from the seeds of the guaran plant *Cyamoposis tetragonalobus*, is a naturally occuring hydrophilic polysaccharide consisting of linear chains of β (1→4)-D-mannopyranose units with α-D-galactopyranosyl units attached by a (1→6) linkage (Fig. 1). It finds extensive applications in paper industries, waste water treatment and mineral processing industries as a flocculant and a depressant (Mazor, 1956; Bhatnagar and Mathur, 1977; Menaria *et al.*, 1986, 1989; Mathur *et al.*, 1988; Mackenzie, 1980).

Since the selectivity of guaran for metal ions is not very high, incorporation of chelating groups of known selectivity into the polysaccharide are likely to result in chelating ion exchange resins of predictable selectivity.

The most commonly used chelating resins like Chelex-100 (Tremillion, 1968; Lee *et al.*, 1977; Riley and Taylor, 1968), Dowex-1 (Leyden and Underwood, 1964) and others (Moyer and Fritz, 1977; Orf and Fritz, 1978; Syamal and Singh, 1993) are based on DVBS (a petrochemical product) which is costly and scarce, therefore, in the continuation of our work on chelating resins (Ahuja *et al.*, 1995, 1996a, b), we have attempted to incorporate amino acid hydroxamate and fatty acid hydroxamate groups into the hydrophilic matrix of guaran, which is cheap and easily available.

The choice of hydroxamic acids is based on their extensive use as collectors in the floatation of haematite, pyrolusite, chrysocolla and rare earth bastnaesite ores (Palmer *et al.*, 1975; Natarajan and Fuerstenau, 1983; Peterson, 1965; Rosenbaum, 1969). The success of these collectors is attributed to their better selectivity towards metal ions as compared to carboxylic acids (Bogdanov, 1977).

EXPERIMENTAL

Reagents

Guaran powder (200 mesh size) was obtained from the local guar gum industry. Glycine, chloromethyl acetate, iminodiacetic acid, epichlorohydrin and hydroxylamine hydrochloride were reagent grade chemicals. The solvents were distilled before use.

Physical measurements

Nitrogen analysis was done by the Kjeldahl method. Infrared spectra of the synthesised resins were recorded on the Shimadzu IR-400 spectrophotometer using KBr pellets. A Perkin-Elmer-2380 atomic absorption spectrophotometer was used for the quantitative determination of metal ions.

The resin characteristics, namely bulk density, moisture content and ion-exchange capacity, were determined by the standard methods.

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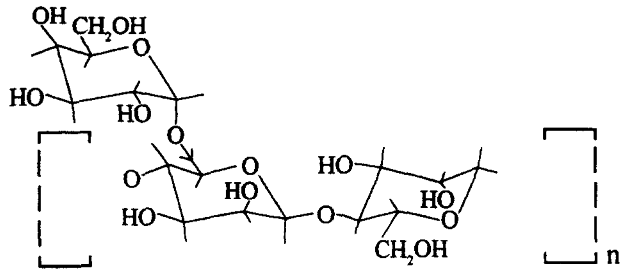


Fig. 1. Structure of guaran.

Synthesis of resins

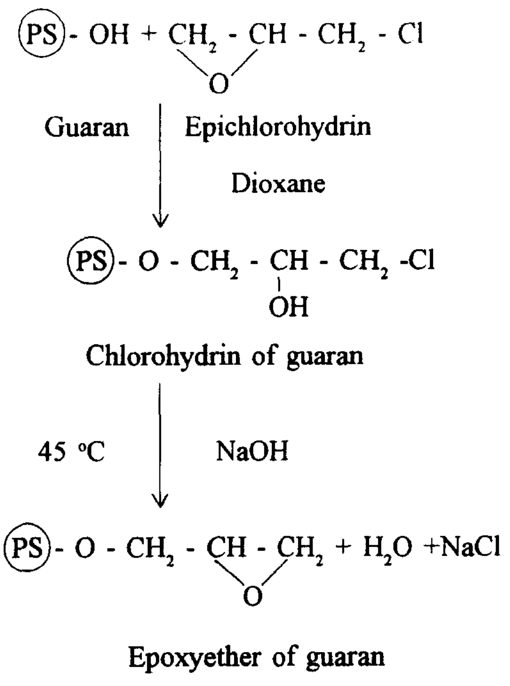
For the synthesis of different derivatives of guaran, it was first cross-linked with epichlorohydrin into epoxyether form which was then utilised for derivatization.

Preparation of epoxyether of guaran

0.1 mol (48.6 g) of guaran powder was slurried with excess dioxane. 50 ml of 50% (w/v) aqueous sodium hydroxide was added to it and the mixture was stirred at 45°C for 2 h. 0.1 mol (9.65 g) of epichlorohydrin was then added to the reaction mixture with continuous stirring. The pH of the reaction mixture was adjusted to between 9 and 10 and the stirring was continued for another 5 h at 45°C. The compound was filtered and washed with 80% aqueous methanol containing nitric acid in order to remove inorganic impurities and excess alkali. The washed product was dried in an oven at 50°C (Scheme 1).

Synthesis of glycine hydroxamate in guaran (GH-G)

Glycine hydroxamate was prepared by first preparing its ester, and subsequently treating the ester with hydroxylamine hydrochloride.



Scheme 1. Synthesis of epoxyether of guaran.

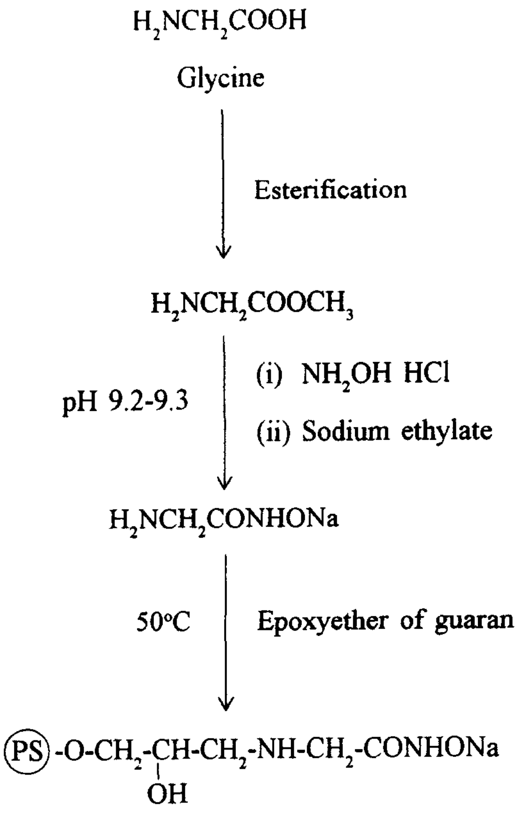
For the synthesis of ester, 0.5 mol (37.5 g) of glycine was taken in a round bottomed flask with excess methanol and cooled to −5–10°C. Thionyl chloride (4.62 ml) was added to it dropwise and the temperature was raised to 40°C. The reaction mixture was kept at this temperature for 2 h on a rotavapour and then dried completely. The methyl ester of glycine was thus formed.

The glycine hydroxamate was prepared by treating 0.1 mol (8.9 g) of methyl ester of glycine with equal moles of hydroxylamine hydrochloride solution in methanol at pH 9.2–9.3 which was adjusted by adding freshly prepared sodium ethylate solution. The reaction mixture was stirred for 5 h at −5°C. The product was filtered and washed with 80% ethanol and dried.

0.01 mol of epoxyether of guaran was added in small amounts to 0.02 mol (1.38 g) of glycine hydroxamate in methanol, stirring at 50°C and the stirring was continued for 5 h. The product formed was filtered and treated successively with N/10HCl, N/10NaOH and N/10HCl, respectively. Finally, it was washed with absolute alcohol and dried in a vacuum (Scheme 2).

Synthesis of acetic acid hydroxamate in guaran (AAH-G)

The acetic acid hydroxamate was prepared by treating 10.8 ml (0.1 mol) of chloromethyl acetate with 0.1 mol hydroxylamine hydrochloride at pH 9–9.5 adjusted by sodium bicarbonate and sodium ethylate solutions and



Scheme 2. Synthesis of glycine hydroxamate in guaran.

stirred the reaction mixture for 7h at 25°C. 0.01mol of epoxyether of guaran was then added to the equal moles of so prepared acetic acid hydroxamate, at 35°C with continuous stirring. The stirring was continued for another 3h. The resin formed was treated with N/10HCl, N/10NaOH and N/10HCl, respectively, and finally it was washed with absolute alcohol and dried in a vacuum (Scheme 3).

Synthesis of iminodiacetic acid dihydroxamate in guaran (IDAAH-G)

It was prepared by the procedure reported in our previous research paper (Bohra and Mathur, 1992) (Scheme 4).

Determination of distribution coefficients

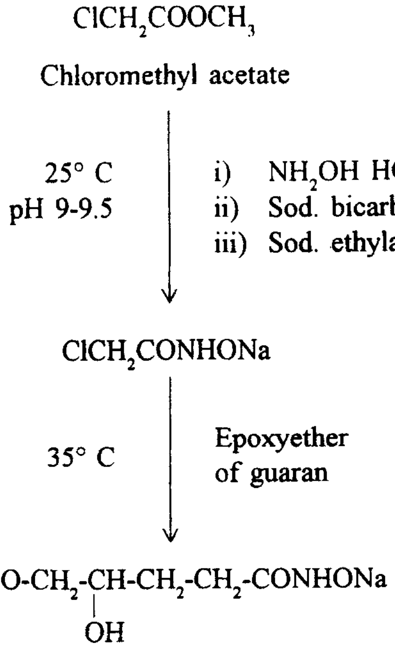
The molar distribution coefficient values (K_d) of metals ions i.e. Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Ca(II), U(VI) and W(VI) on GH-G, AAH-G and IDAAH-G resins were determined by batch equilibrium method.

Portions of resins (1g) in the hydrogen form were placed in glass stoppered conical flasks containing 1ml of 1000ppm metal ion solution and a known volume (40ml) of (0.2M) sodium acetate–acetic acid buffer of varying pH (4–7). The mixture was shaken mechanically for 24h at 25±0.1°C. The two phases were separated by filtration and an aliquot of filtrate was analysed for the metal concerned by atomic absorption spectrophotometer. The calibration curves for different metal ions were plotted using standard metal solutions and the unknown concentration of metal ions was determined from these curves. The distribution coefficient value, K_d, was computed using the formula:

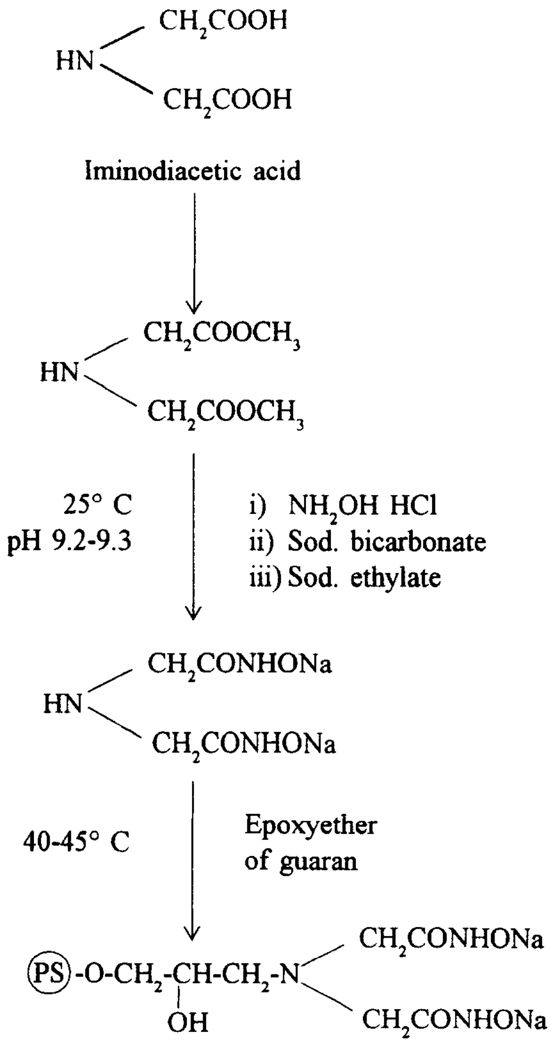
$$K_d = \frac{\text{Amount of metal ion in resin/g of dry resin}}{\text{Amount of metal ion in solution/ml of solution}}$$

Procedure for column separation

A 20cm long glass column of uniform diameter was used for the separation of metal ions. The H^+ form of resin was kept overnight in DMF for swelling. The slurry of resin in DMF was poured into the column to a height of 8–10cm. The resin was washed with the same buffer (pH 5.0 in case of copper–calcium separations and pH 5.5 buffer in case of iron–cobalt separations) at which the adsorption of mixture is to be carried out. 20ml aliquot of solution containing 10ml of each metal ion was loaded on the column at a flow rate of 2ml/min. The column was washed with the same buffer solution and the sorbed metal ions were eluted with 0.1NHCl. 5ml of fractions were collected and were analysed for metal ion concentration by an atomic absorption spectrophotometer.



Scheme 3. Synthesis of acetic acid hydroxamate in guaran.



Scheme 4. Synthesis of iminodiacetic acid dihydroxamate in guaran.

Table 1. Resin characteristics

Resin	Moisture content (%)	Bulk density density (g/cm^3)	Nitrogen content (%)	Cation exchange capacity meq/g	Degree of substitution
GH-G	3.3	0.735	3.66	1.31	0.433
AAH-G	18.3	0.823	2.11	1.50	0.476
IDAAH-G	3.8	0.750	7.14	1.70	0.724

RESULTS AND DISCUSSION

The synthesised resins are quite stable over a wide range of temperature and moisture.

The infrared spectra of hydroxamate resins showed a band near 3400cm^{-1} assigned to ν(N-H) vibrations. The ν(C-O) peak present in the spectra of carboxylic acids near 1570cm^{-1} and ν(C-O) peak of esters near 1730cm^{-1} was shifted near 1680cm^{-1} in the spectra of hydroxamate resins.

The resin characteristics, namely moisture content, bulk density, nitrogen content, cation exchange capacity and degree of substitution, are given in Table 1.

Uptake of metals by the resins

The K_d values vs pH contours of GH-G, AAH-G and IDAAH-G resins with various metal ions are represented in Figs 2, 3 and 4, respectively.

The selectivity sequence of various metal ions on GH-G resin (Fig. 2) is as follows

	Ca(II) ≪	Co(II) <	Zn(II) <	Ni(II)
K_d :	112	970	1011	1230
	< Cu(II) <	Fe(II) <	W(VI) <	U(VI)
	1498	1851	2255	2840

The results show that the metal uptake by the resin first increases with increase in pH, attains a maximum value and then decreases with further increase in pH. The metal uptake by the resin was maximum in the pH range 6.0–6.5. The resin exhibits maximum adsorption for Fe(II), Ni(II), U(VI) and W(VI) metal ions at pH 6 and Co(II), Cu(II), Zn(II) at pH 6.5. The adsorption of Ca(II) by the resin was maximum at pH 4.5.

The resin is found to be selective for iron, copper and highly charged metal ions, i.e. uranium and tungsten. The separation possibilities of uranium and tungsten from cobalt, nickel, copper, zinc and calcium and iron from zinc, cobalt and calcium are quite high at pH 6.

The fatty acid hydroxamate resin(AAH-G) (Fig. 3) exhibits the following selectivity series for metal ions at the pH of their maximum adsorption:

	Ca(II) ≪	Co(II) <	Ni(II) <	Zn(II)
K_d :	90	545	845	927
	< Cu(II) =	Fe(II) <	U(VI) <	W(VI)
	1100	1100	1414	1525

The resin shows greater adsorption for tungsten as compared to uranium. The distribution coefficient values of copper and iron are almost same at different pH values. Calcium is again adsorbed minimally by the resin. The selectivity sequence of the resin may be slightly identical to the GH-G resin, but the efficiency of fatty acid hydroxamate resin is quite poor in comparison to amino acid hydroxamate resin. The reason being the presence of nitrogen in the amino acid hydroxamate

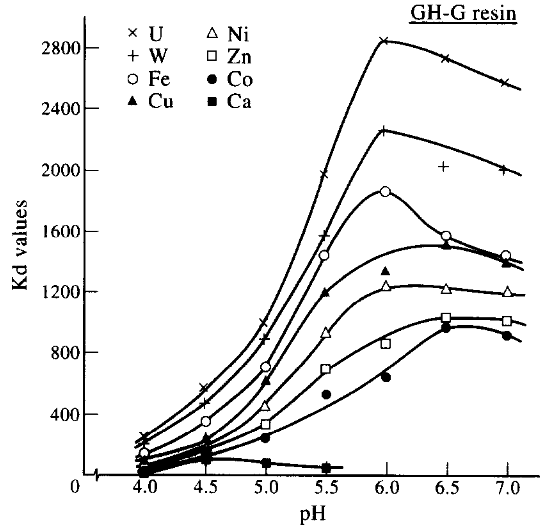


Fig. 2. K_d vs pH contours of GH-G resin with various metal ions.

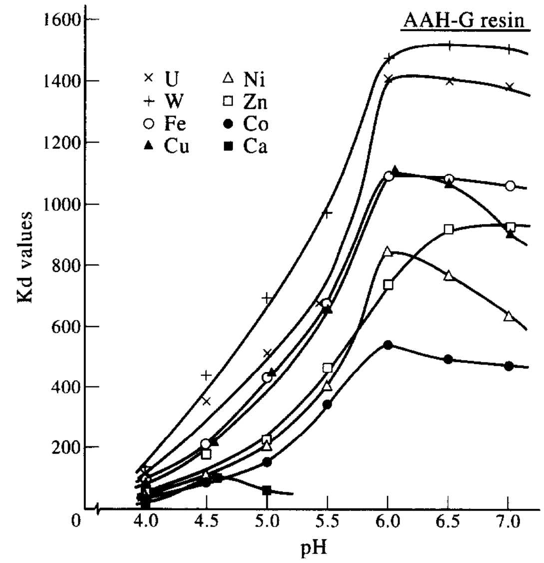


Fig. 3. K_d vs pH contours of AAH-G resin with various metal ions.

resin which increases the electron density on coordinating oxygen. This may also be due to the additional coordination site available in the form of nitrogen of amino acid.

Sorption studies of various metal ions with IDAAH-G resin (Fig. 4) indicate that it is the most effective of the three synthesised resins for the selective adsorption of metal ions owing to the presence of extra coordinating sites on it. At the pH of maximum adsorption, the distribution coefficient values for Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Ca(II), U(VI) and W(VI) are 4947, 1083, 1570, 3884, 1790, 117, 8453 and 7473, respectively. Thus, the metal ions can be arranged in the following ascending order of selectivity:

$$\mathrm{Ca(II)} \ll \mathrm{Co(II)} < \mathrm{Ni(II)} < \mathrm{Zn(II)} < \mathrm{Cu(II)}$$

$$< \mathrm{Fe(II)} < \mathrm{W(VI)} < \mathrm{U(VI)}$$

Ni(II) and Cu(II) metal ions exhibited maximum adsorption at pH 5, Fe(II), Co(II) and Zn(II) at pH 5.5, U(VI) and W(VI) at pH 6 and Ca(II) is adsorbed maximum at pH 4.5. The resin is thus selective for iron, copper, uranium and tungsten.

The order of selectivity of the three hydroxamate resins for various metal ions is inconsistent with the selectivity sequence given by Bogdanov (1977) for hydroxamic acids. Of the two tautomeric forms exhibited by hydroxamic acids, metal complexes are formed through the hydroxamide functional group (a), thus, there is a considerable covalency in the bonds formed and this contributes to the high selectivity in the hydroxamate interaction with metal ions.

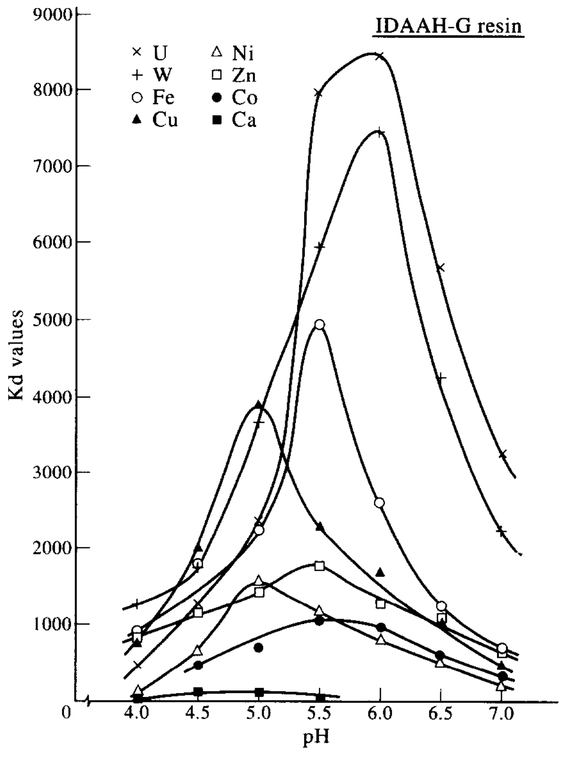


Fig. 4. K_d vs pH contours of IDAAH-G resin with various metal ions.

The synthesised resins show lit"tle adsorption for alkaline earth metal, i.e. calcium. Therefore, the resins can be utilised for the separation of transition and highly charged metal ions from alkaline earth metals and the disadvantages of the most widely used resin, Chelex-100 (its high cost and same affinity for transition as well as alkaline earth metals) can be overcome, to a great extent, by utilising the synthesised guaran resins which are cheap, easily available, selective and biodegradable.

Separation of metal ions by the resin

A study of distribution coefficient values of various metal ions suggests that there are separation possibilities for a large number of metal ions on these resins. The differences in the distribution coefficient values between

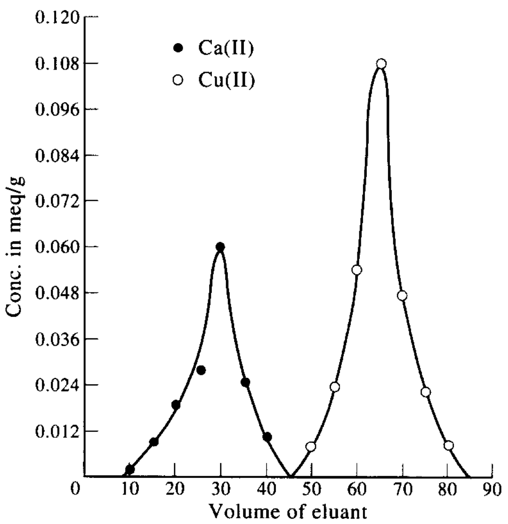


Fig. 5. Column separation of Cu(II) and Ca(II).

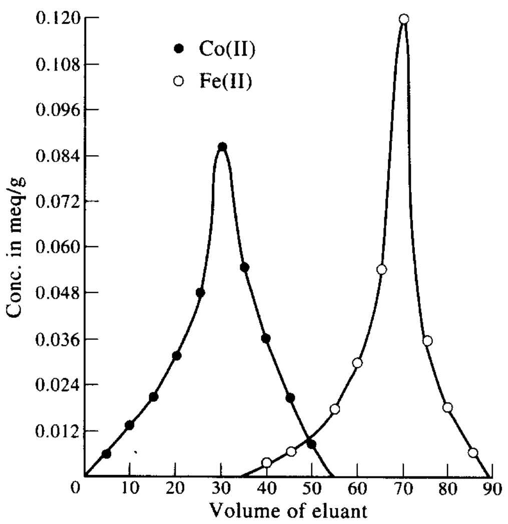


Fig. 6. Column separation of Fe(II) and Co(II).

the metal ions are large enough to permit good separations on columns. We have utilised IDAAH-G resin for the separation of copper–calcium and iron–cobalt mixtures at pH 5 and 5.5, respectively (Figs 5 and 6).

Copper and iron, having high Kd values, were strongly held by the resin while calcium and cobalt moved down the column more rapidly and their fractions were collected before copper and iron.

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