

Poly(hydroxamic acid) Chelating Resin: The Synthesis and Uses

Rahmatollah Khodadadi, S. Ali Fakhri and Ali Akbar Entezami
Polymer Laboratory, Faculty of Chemistry, Tabriz University, Tabriz, I.R.Iran

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ABSTRACT

Two methods for the synthesis of poly (hydroxamic acid) chelating ion exchange resins: A- from copoly(acrylamide-divinylbenzene) by treatment with hydroxylamine hydrochloride in the presence of potassium hydroxide, and B-acrylhydroxamic acid with divinylbenzene by free radical solution polymerization are described. Sorption capacities of Fe(III), Cu(II), Co(II) and Pb(II) ions are pH dependent and the selectivity towards these metal ions is in following order: Fe(III) > Cu(II) > Pb(II) > Co(II).

The ability of the above resins to extract and separate these metal ions are reported. The hydroxamic acid capacity of the products from two methods is also compared.

Key Words: poly(hydroxamic acid) resin, chelating ion exchangers, ion exchange resin

INTRODUCTION

Chelating ion exchange resins containing hydroxamic acid groups have been known for more than 30 years and various analytical applications using these polymers have been demonstrated. A number of poly(hydroxamic acid) resins have been synthesized by various methods and for various purposes. Kern *et. al.* [1] synthesized the resins from polymethacrylate and studied the sorption of Fe(III), Cu(II), Ag(I), Zn(II), Hg(II), Al(III), Pb(II) and TiO. Petrie *et. al.* [2] studied the retention of V(V), Fe(II), Fe(III), Mo(VI), Ti(IV), Hg(II), U(VI) and Ce(IV) with poly(hydroxamic acid) resins synthesized from Amberlite IRC-50. Wan Yunus [3] studied the separation of Fe(III) and Al(III) from Ca(II) and Mg(II) using poly(hydroxamic acid) resins. Philips *et. al.* [4,5] synthesized the resins from Amberlite XAD-4 and

styrene-divinylbenzene copolymer in order to study the extraction of various metal ions, the purification of reagents, the concentration of metal ions and chromatographic separations of Th(IV) and V(IV). Veron *et. al.* [6-10] synthesized resins from acrylonitrile-divinylbenzene copolymers and studied their chelating abilities for various metal ions and used them for the recovery of metals from metal salts and the recovery of uranium from simulated sea water. They also reported the separation of vanadium from iron, copper from iron nickel and cobalt from copper, uranium from thorium, gold from silver and iron(II) from iron(III). Ajay Shah *et. al.* [11] synthesized resins from acrylonitrile-divinylbenzene and studied the separation of zinc from cadmium and of cobalt from copper and nickel. Wan and co-workers [12] synthesized resin from ethyl acrylate-divinylbenzene and studied the sorption of Fe(III), Cu(II), Ni(II),

Co(II) and Zn(II). They also reported the separation of iron (III)-copper-nickel, iron(III)-copper-cobalt and iron(III)-copper-zinc on a hydroxamic acid column. Katoh, and co-workers [13] synthesized resin from acrylonitrile and divinylbenzene and studied the structure of resin and the recovery of uranium from sea water. This paper describes two different methods for preparation of hydroxamic acid resins from copolymer (acrylamide divinylbenzene i.e., resin-A) and acryl hydroxamic acid with divinylbenzene (by a one-step reaction i.e., resin-B). The hydroxamic acid capacity of the products are compared. The ion exchanger behaviour of this resin towards iron(III), copper (II), cobalt(II) and lead (II) ions and the effect of the pH of the metal solutions on the cation-exchange capacities of the resin are also reported.

EXPERIMENTAL

Poly(hydroxamic acid): Resin-A

Crosslinked Polymer: DVB-crosslinked polyacrylamide was prepared by free radical solution polymerization. For the preparation of 18% DVB-crosslinked polymer acrylamide (17.28g) and divinylbenzene (7g) were dissolved in ethanol (100 mL). Benzoylperoxide (200 mg) was added, and the mixture was heated with stirring at 70 °C for 4h. The polymer was collected by filtration, washed several times with water, ethanol, benzene and methanol and dried at 70 °C [14].

Functionalization: To convert this polymer into a polymeric hydroxamic acid, 7.22 g of the dry polymer was reacted with a solution containing 10.63 g of hydroxylammoniumchloride and 12.87 g of potassium hydroxide in methanol-water (85% v/v) for 3 days at 75-80 °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 water until it was free of chloride. The resin was stored under distilled water.

Poly(hydroxamic acid): Resin-B

Acrylhydroxamic acid: Acrylhydroxamic acid was

synthesized from 49.75 g (0.5 mol) acrylchloride (Merck) by treatment with a solution containing 69.49 g (1.0 mol) of hydroxylammoniumchloride [10], (Merck), and 84.165 g (1.5 mol) of potassium hydroxide in 500mL of methanol; (yield 70% crude). Acrylhydroxamic acid (16.2g crude) and divinylbenzene (commercial, 55%, 4.9g) were dissolved in ethanol (120 mL). Benzoylperoxide (Merck 150 mg) was collected by filtration, washed several times with water, ethanol, benzene, methanol and again with distilled water then with 2M hydrochloric acid solution to convert the resin into the hydrogen form and again with water until it was free of chloride. The resin was then stored under distilled water [14].

Characterization of Resins

To show the presence of the hydroxamic acid groups on the resin, 0.5 g of wet resin was shaken with vanadium (V) ion in dilute hydrochloric acid and a dark purple coloured complex produced by the resin upon sorption of the vanadium (V) ion was observed [12].

Swelling Studies

The hydroxamic acid resin (0.5g) was equilibrated with 30 mL of distilled water for 4 days. The swollen resin was collected by filtration, adhering traces of water were removed by pressing with filter paper and the sample was weighed. The swollen resin was dried in a vacuum for 24 h and weighed again. From the swollen and dry weight of the sample the equilibrium water content (EWC) was calculated using the following equation [14]:

$$EWC = \frac{\text{wt. of wet resin} - \text{wt. of dry resin}}{\text{wt. of wet resin}}$$

Hydrogen Capacity

A sample of the wet resin (0.5g) was shaken with 50.0 mL of sodium hydroxide (0.02 M) for 4 h. Hydrogen capacity of the resin was calculated from the amount of sodium hydroxide reacted with the resin. Determination of the sodium hydroxide concentration was done by titrating with a standard hydrochloric acid solution (0.02 M), using phenolphthalein as an indicator [12].

Sodium Capacity

Sodium capacity of the resin was calculated from the amount of sodium bicarbonate reacted with the resin when 0.5 g of the wet resin was equilibrated with 25 mL of 0.25 M sodium bicarbonate solution for 12h, then the resin was filtered and washed thoroughly with distilled water. The total filtrate was acidified with 25 mL of 0.25 M hydrochloric acid, boiled to expel carbon dioxide, and back-titrated with 0.25 M sodium hydroxide solution [6].

Metal Ion Capacity

Total metal sorption capacities for iron (III), copper(II), cobalt(II) and lead (II) ions in acetate buffer at pH 2, 3, 3, 5, 4 and 0.5 were determined by the following procedure: 0.5 g of wet resin was shaken in 100 mL of buffered metal solution (0.01 M) for 16h and then metal ion concentration in the equilibration solution was determined [12].

Column Extraction and Recovery of Metal Ions

A glass column (5mm i.d.) packed with about 250 mg of resin (5 cm height) was used to determine the extent of extraction of various ions from their mixture. The resin in the column was conditioned by 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 mL buffer at the same

pH. Elution was carried out by passing an eluent through a column on which a known weight of metal ion had been applied.

In iron (III)-copper (II)-cobalt (II) separation, a solution containing these ions (1 mg each) at pH 3.0 was passed through the column, followed by passing acetate buffer (pH 3.0) to remove cobalt ion. Copper and iron ions retained on the resin were eluted with 0.1 M hydrochloric acid and 0.1 M oxalic acid in 1M hydrochloric acid solution, respectively [12].

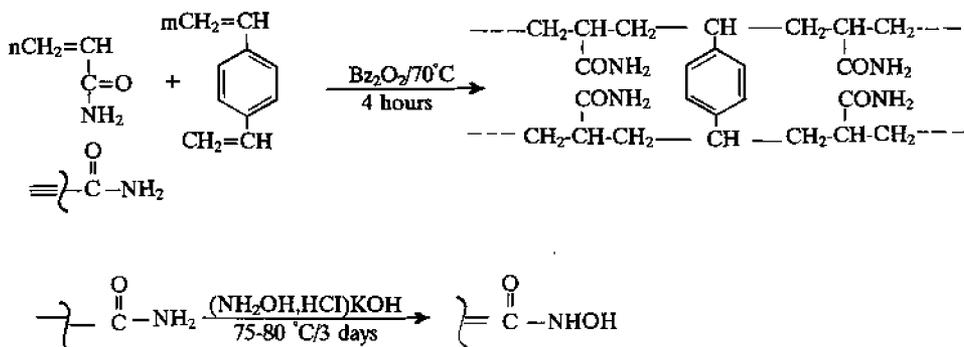
Analysis

Elemental analysis of the dry hydroxamic acid resin was determined by CHN-o-Rapid/Heareus and Carol-Erba Mod 1106 instrument. Metal ion concentrations were determined by atomic absorption spectrophotometer Shimadzu Mod 670 G an air - acetylene flame.

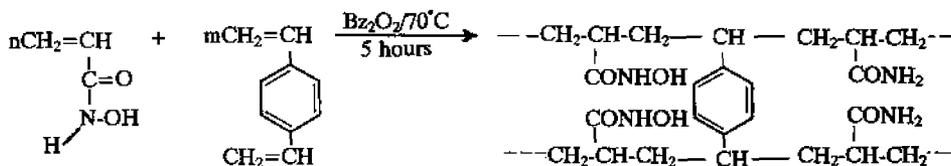
RESULTS AND DISCUSSION

Preparation of Hydroxamic Acid Resins

Poly(hydroxamic acid) resin was prepared by two general methods. Hydroxylamine hydrochloride was reacted with performed copolymer (scheme 1). The hydroxamic acid also was converted to a polymerizable derivative that was subsequently



Scheme 1. Preparation of hydroxamic acid resin-A.



Scheme 2. Preparation of hydroxamic acid resin-B.

copolymerized with divinylbenzene (scheme 2).

Hydroxamic Acid Groups

The presence of the hydroxamic acid groups on the product was confirmed by a qualitative test based on the ability of the groups to form a coloured complex with vanadium (V) and iron (III) in an acidic solution. Vanadium (V) ion gives a dark purple complex and iron (III) ion gives a red complex on reaction with hydroxamic acid groups. These coloured complexes can easily be observed in these cases since the resin is white. The formation of a dark purple and red complexes between polymeric hydroxamic acids and vanadium (V) and iron (III) ion each in an acidic solution has been reported in earlier publications [2,4,10,12]. This is also confirmed by IR spectral evidence (3400, 1500, 1450, 1400 cm^{-1}) of the complexed resin.

Properties of Resins

Table 1 summarizes the properties of the poly-(hydroxamic acid) ion exchanger prepared from two methods. The resin prepared from DVB-cross-linked polyacrylamide is in the powder form of white colour that gives intense colours on sorption of metals. Based on the weight of divinylbenzene used in the polymerization process and elemental analysis of dry resin, the product is about 18% crosslinked. The sodium-hydrogen exchange from hydrogen carbonate solution is a measure of the carboxylic acid groups by hydrolysis of the amide groups.

The hydroxamic acid units are incapable of reacting with hydrogen carbonate; this was verified by determining the sodium capacity of the

Table 1. Physical and chemical characteristics of the poly(hydroxamic) acid resins.

Physical & Chemical Properties	Resin(A)	Resin(B)
Colour	white	white
Form	powder	powder
DVB content (m/100g)	0.21	0.20
Cross-linking (mol %)	18.6	18
EWC %	6.0	2.4
Total hydrogen ion capacity (mmol/g)		
(carboxylic and hydroxamic acid)	9.12	6.8
Sodium ion capacity (mmol/g)		
(carboxylic acid)	4.38	4
Hydroxamic acid (mmol/g)	4.74	2.8

copper-loaded resin produced by equilibrating the exchanger with copper chloride at pH 4.0. The hydroxamic groups are complexed where the carboxylic groups cannot take up copper at this pH [6]. The sodium capacity of the copper-loaded form of the resin was also 4.0 mmol/g and content of nitrogen (7.7%), the resin contains 2.8 mmol/g of hydroxamic acid groups; therefore in the resin, 40% of amide groups has been hydrolyzed, 26.5% remain as amide, and 34% has been converted to hydroxamic acid. The carboxylic groups are the side product resulting from exposure of the hydroxamic groups to potassium hydroxide at high concentration in the preparation procedure. The nitrogen content of the hydroxamic resin (resin B, 6.63%) indicates that the presence of the chelating groups on the polymer is 4.74 mmol/g. Hydrogen ion

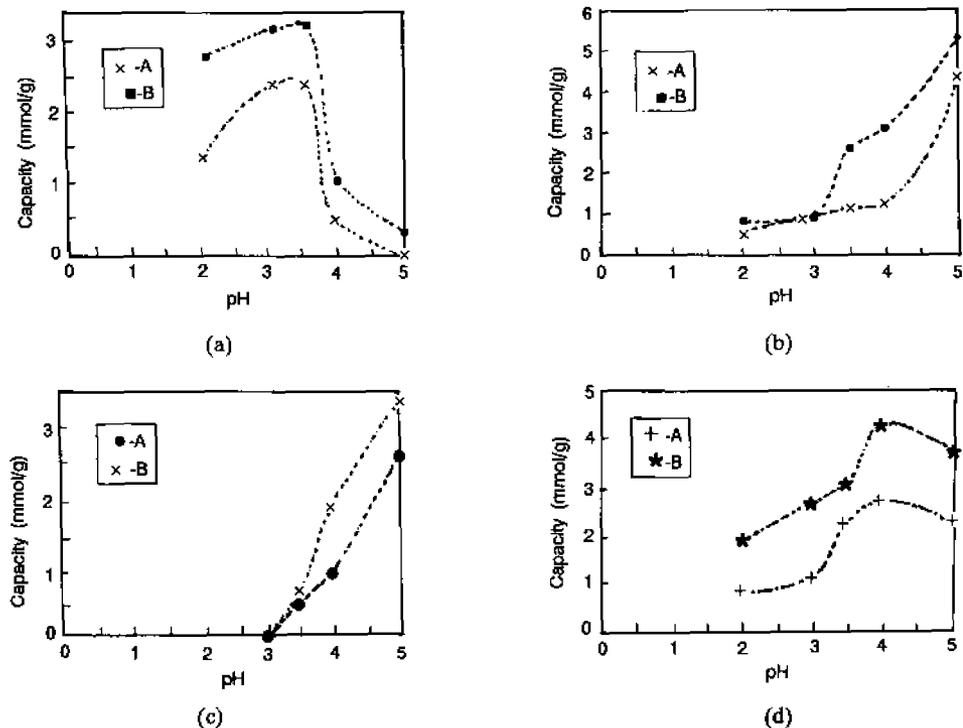


Figure 1. Total capacity versus pH contours for ion exchanger resins and metal ions (a) Fe(III), (b) Cu(II), (c) Co(II), (d)Pb(II).

capacity, a measure of acidic group (hydroxamic and carboxylic groups) content on the polymer, is 9.12mmol/g. Thus there are also 4.38 mmol/g carboxylic groups in the resin [16,17]. The carboxylic groups are side products resulting from the exposure of the hydroxamic groups to potassium hydroxide at high concentration in the preparation procedure.

On the basis of the weight of the divinyl benzene used in the polymerization process and elemental analysis of dry resin, the product is about 18.6% crosslinked (2.1 mmol/g DVB content).

Metal Ion Capacity

The total capacity versus pH contours for the metals is shown in Fig. 1a,b,c,d for resins. The curves showing the chelation of metal ions with the

resins are highly dependent on pH. By adjusting the pH values, selectivity can be achieved for different metal ions.

The resins show high selectivity for iron (III) as it is to be expected when hydroxamic acid chelating ion exchange resins react with this metal ion. Considering these results, selectivity of the resin towards these 4 metal ions was as follows: Fe(III)>Cu>Pb>Co. The results also suggest that separation of iron (III)-copper-cobalt, iron (III)-cobalt-lead could be carried out using this resin as described before.[12]. It is also noticed in resin (A) that the total copper ion sorption capacity at pH 5.0 is 4.49 mmol/g, 97% higher than the hydroxamic acid group capacity. Further investigation showed that this was caused by the uptake of copper ion by the carboxylic acid groups.

Table 2. Removal of metals from their mixture in aqueous solution on passing through poly(hydroxamic) acid resins column.

Eluate	% of metal in eluate		
	Fe(III)	Cu(II)	Co(II)
Buffer pH=3.0	—	—	100
0.1 M Hydrochloric acid	—	100	—
0.1 M Oxalic acid (1M)	—	—	—
Hydrochloric acid	100	—	—

The carboxylic acid groups show some sorption capacity at high pH.

Column Extraction and Recovery of Metal Ions

Removal of 1 mg of any one of these metal ions from 10 mL aqueous solution, buffered at pH 3.0 by the exchanger in a column, was qualitative. Table 2 show the removal of Fe (III), Cu(II) and Co(II) from their mixture on passing through resin columns. The retention of iron (III) and copper ions were also complete at pH 3.0. Copper and iron (III) ions, which are more strongly retained by the column, can be removed by 0.1 M hydrochloric acid (1M), respectively [12].

The synthesized resin from acrylhydroxamic acid has higher coordination capacity than other resins [12-20]. Table 3 shows this difference.

These resins should find applications in analytical work for the removal of many species from water, and for hydrometallurgical and electroplating solutions for example where gold and silver recoveries from dilute cyanide solutions are required [10].

Infra-red Spectra

The infra-red spectrum of the DVB-crosslinked polyacrylamide shows the characteristic absorptions of amide (N-H), carbonyl and aryl groups in broadening bands at 3450, 1660 and 800 cm^{-1} , respectively and the infra-red spectrum of the resin showed the characteristic absorptions of hydroxamic acid (O-H), amide (N-H), carbonyl and aryl groups in broadening bands at 3500, 3450, 1660 and 800 cm^{-1} , respectively. This broadening originates from intermolecular hydrogen bonding and there

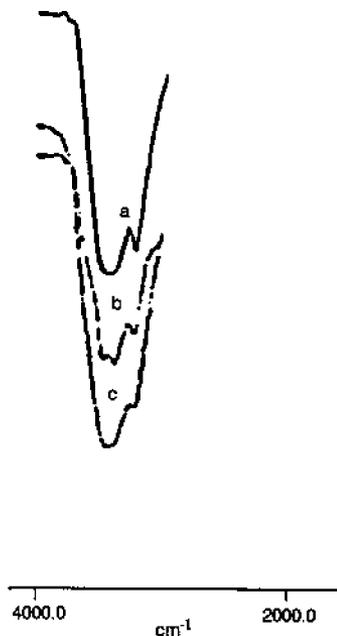


Figure 2. Infra-red absorption of the NH_2 groups of (a) amide (b) hydroxamic (c) Cu(II) complexed resin.

are two bands at 1400 and 1440 cm^{-1} that are also assigned to the NH valence frequency and deformation of the NH moiety.

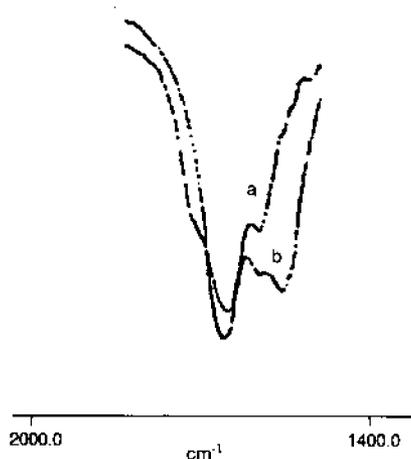
The N-H stretching frequencies of polyacrylamide and (N-H, O-H) of poly(hydroxamic acid) and Cu(II) complex are given in Figure 2. When hydroxamic acid resin is complexed with metal ions, the bond of stretching frequencies of O-H groups disappear. The broad band around 1660-1550 cm^{-1} observed in infra-red spectra of complexes of metal ions with hydroxamic acid resin shows shifts of about 100-110 cm^{-1} when compared with the metal-free resin. This strongly suggests the complexation of the carbonyl groups Figure 3. [14,15,16]

The infra-red spectra of the resin-B shows the characteristic absorptions of hydroxamic acid (O-H), amide (N-H), carbonyl and aryl groups in broadening bands at 3490, 3200, 1660 and 800 cm^{-1} respectively. Its broadening originates from

Table 3. Comparison of total sorption capacity of poly(hydroxamic) acid resins with some other resin.

Resins type	hydroxamic acid mmol/g	carboxylic acid mmol/g	Fe(III) absorption mmol/g(a)	Cu(II) absorption mmol/g(b)	Co(II) absorption mmol/g(b)
A	2.8	2.7	2.42	4.49	2.6
B	4.74	4.38	3.21	5.38	3.37
C	2.29	5.52	2.10	3.82	1.97

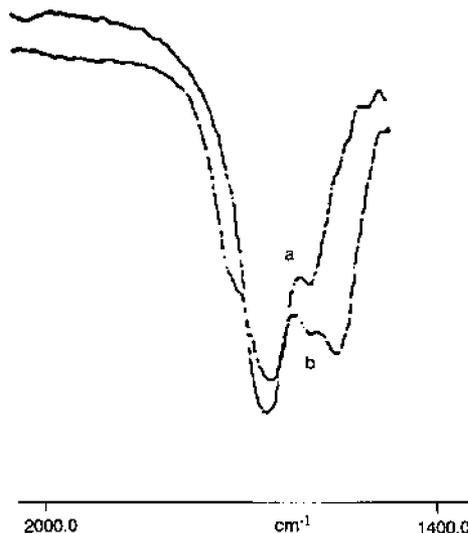
(a) Maximum absorption at pH=3.5; (b) Maximum absorption at pH=5; and C from Ref. [12].

**Figure 3.** Infra-red absorptions of the C=O groups of (a)resin, (b) Cu(II) complexed resin.

intramolecular hydrogen bonding and there are two bands at 1400 and 1440 cm^{-1} that are also assigned to the NH valence frequency and deformation of the NH moiety. The broad band around 1660-1550 cm^{-1} observed in infra-red spectra of complexation of metal ions with resin shows shifts of about 100-110 cm^{-1} when compared with the metal - free resin. This strongly suggests the complexation of the carbonyl oxygen atoms [14,18, 19] (Figure 4).

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**Figure 4.** Infra-red absorptions of the C=O groups of (a)resin, (b) Cu(II) complexed resin.

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