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SYNTHESIS AND PROPERTIES OF POLY(HYDROXAMIC ACID) FROM CROSSLINKED POLY(METHACRYLATE)

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Summary—Poly(hydroxamic acid) chelating ion-exchange resin was prepared from crosslinked poly(methacrylate) beads. The starting polymer was prepared by a suspension polymerization of methacrylate and divinyl benzene. Conversion of the ester groups into the hydroxamic acid was carried out by treatment with hydroxylamine in an alkaline solution. Hydroxamic acid capacity of the product was 2.71 mmol/g. The resin exhibited high affinity towards Fe(III) and Pb ions and its capacities for Fe(III), Pb, Cu, Ni and Co ions were pH dependent. The ability of the resin to carry out the separation of Fe(III)–Cu–Co/Ni and Pb–Ni ions is also reported.

Poly(hydroxamic acid) ion exchange resins have been used for extraction and separation of metal ions.[1–7] This type of chelating ion exchanger is still not commercially available but has been synthesized by either converting the functional groups such as carboxylic acid,[8] nitrile,[9,10] ester,[11] amide,[12] or maleic acid[13] in a polymer into the hydroxamic acids or polymerization of monomers containing hydroxamic acid groups.[14,15] This paper describes a method to synthesize a polymer bearing hydroxamic acid groups from crosslinked poly(methacrylate). Conversion of the starting material to the resin is a one step reaction and the product is in bead form with a reasonable high hydroxamic acid capacity. The study on the properties of this resin shows that it can be used for lead–nickel separation which is a new application for a resin having an hydroxamic acid functional group.

EXPERIMENTAL

Reagents

Methacrylate and divinyl benzene were purchased from Aldrich (U.S.A.) and Merck (Germany), respectively. These monomers were passed through activated alumina columns to remove any inhibitor. Other chemicals were of analytical-grade reagents.

Polymer preparation

Preparation of poly(methacrylate-divinyl benzene) was carried out by suspension polymerization technique[2] of 90.0 g methacrylate and 10.0 g divinyl benzene solutions. To synthesize the hydroxamic acid groups the dry copolymer in the particle size range between 180 and 500 μm (20 g) was treated with 200 cm^3 of water–methanol (75%) solution containing 27.8 g hydroxylammonium chloride and 80 g sodium hydroxide for 24 hr at 45°C. The resulting polymer was washed with distilled water, 2*M* hydrochloric acid solution, and with distilled water again until free from chloride. This resin was stored in the fully swollen form for further study.

Characterization

Nitrogen content of the dry polymer was determined by CEC Elemental Analyser Model 440. Qualitative analysis of hydroxamic acid groups on the polymer was carried out by shaking a few beads of the resin with vanadium(V) ions in dilute hydrochloric acid solution. The complex formation of iron(III) and copper ions was tested in pH 3.5 acetate buffer solution. Drying of the moist polymer for water content determination was performed using a vacuum desiccator containing phosphorus pentoxide. Swelling behaviour of the resin was observed by comparing the volume of a resin bed packed in a glass column of 1.2 cm internal diameter after it was eluted with 100 cm^3 of selected eluants. Hydrogen capacity was determined based on the amount of sodium hydroxide reacted after 50 cm^3 (0.02*M*) of this solution was shaken with about 0.5 g (accurately weighed) wet polymer for 4 hr. Metal ion capacity was calculated from the amount of the metal ion sorbed by of the wet resin which was in equilibrium with 100 cm^3 of its solution ($0.01M$) at required pH on a rotary shaker for 16 hr. Adjustment of pH of metal ion solution was made using acetate buffer or dilute hydrochloric acid solutions.

For a separation study a resin bed of 5 cm height in a glass column (1 cm I.D.) was used. Conditioning of this column was carried out by washing with pH 4 acetate buffer solution. Separation of metal ions was based on selective elution. In a typical procedure, solution containing selected metal ions (1 mg each) was first applied to the column and this was followed by stripping selectively of the retained metal ions by suitable eluants. Column effluent was collected in 10 cm^3 fraction and analysed by atomic absorption spectroscopy using an IL Spectrophotometer (Model 651).

RESULTS AND DISCUSSION

Treatments of esters with hyroxylamine is a common procedure to prepare hydroxamic acids. This reaction was used by Kern and Schult[14] to prepare a linear poly(hydroxamic acids) from poly(methyl acrylate). Recently we have reported that a crosslinked polymeric hydroxamic acid was prepared from poly(ethyl acrylate).[11] In this study the starting material was a crosslinked poly(methacrylate) in bead form which was synthesized from methacrylate and divinyl benzene. Based on the amount of divinyl benzene used in the above polymerization procedure and the efficiency of the polymerization obtained of about 98% it could be assumed that the product was about 5% crosslinked.

The water content of the wet form was 2.48 g/g. High water regain is probably due to high hydrophilicity of the groups attached to the polymer matrix and also owing to its lowly crosslinked polymer. High water regain is required for favorable kinetics of extraction.[15] It was also observed that the resin swelled and shrunk when it was exposed to different eluants. The decreases of the bed volume of about 15 and 31% were noted when the resin was eluted with pH 4 acetate buffer and $2M$ acid hydrochloric, respectively. The resin bed returned to its original volume after it was eluted with distilled water. Thus proper column conditioning was required to carry out column separations.

The presence of the hydroxamic acid groups on the polymer was confirmed by the formation of a dark purple complex when reacted with vanadium ions.[8,11] The purple complex was not observed when poly(mehthacrylate) was reacted under similar conditions. It was also observed that brown and dark green complexes were also produced when this polymeric hydroxamic acid was reacted with iron(III) and copper(II) ions, respectively. The same coloured complexes formation has been reported for the polymeric hydroxamic acid prepared from poly(acrylamide).[12]

The nitrogen content of the dry polymer analysed by elemental analysis was found to be 3.80%. This indicated that there was 2.71 mmol/g of hydroxamic acid groups on the polymer. It could be consequently inferred that there was 3.41 mmol/g of carboxylic acid groups on the polymer as its hydrogen exchange capacity was 5.85 g/g. These groups were the product of breaking down of the hydroxamic acid and hydrolysis of the ester groups in concentrated alkaline solution under preparation conditions. The formation of carboxylic acid groups was detected when poly(methacrylate) was treated with sodium hydroxide solution (without the presence of hydroxylamine) under the above preparation conditions.

Exchange capacities for six selected metal ions at various pH are given in Fig. 1. The exchange capacities for iron(III), copper, nickel, cobalt and lead ions are pH dependent as the exchange involves releasing of hydrogen ion. The capacities of iron(III), copper and lead at pH 5 are bigger than nitrogen content suggests that under this condition the exchange of these ions on the polymer involves the carboxylic groups in addition to the formation of a 1:1 complex with the hydroxamic acid groups. Exchange of hydrogen ions from carboxylic acid

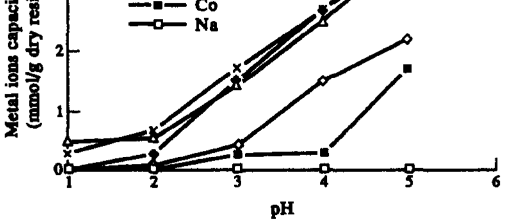

Fig. 1. Metal ions capacities of poly(hydroxamic acid) resin in various pH: about 0.5 g accurately wieghed wet resin equilibrated with 100 cm^3 $0.01M$ metal ion solution for 4 hr.

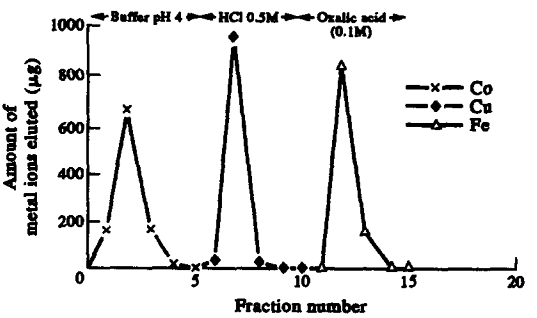

Fig. 2. Co–Cu–Fe separation by poly(hydroxamic acid) resin column (1.0 cm I.D. × 10 cm): eluants; pH 4 sodium acetate–acetic acid, HCl 0.5M and oxalic acid 0.1M in HCl 1M; flow rate 0.5 cm^3/min.

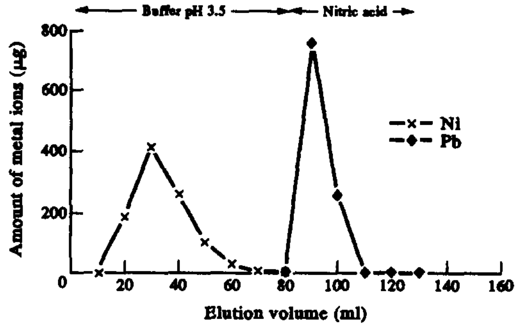

Fig. 3. Ni–Pb separation by poly(hydroxamic acid) resin column (1.0 cm I.D. × 10.0 cm): eluants; pH 3.5 sodium acetate–acetic acid and nitric acid 4M; flow rate 0.5 cm^3/min.

groups with metal ions is effective only if the pH of the solution is 5 or higher.[16] The resin does not show any exchange capacity with sodium ion as it is unable to form a complex with hydroxamic acid. These results also indicate that lead and iron ions were strongly sorbed by the resin.

Properties of this chelating ion exchange resin was also studied based on its ability to carry out metal ions separation using a column technique. Figure 2 shows a chromatogram of iron–copper–cobalt separation. Cobalt, copper and iron(III) ions were selectively eluted from the column by acetate buffer (pH 4), hydrochloric acid (0.1M) and oxalic acid (0.1M dissolved in 1M HCl) solutions, respectively. This procedure can also be used for iron– copper–nickel separation. These separations have been reported for the hydroxamic acid resins prepared from poly(acrylonitrile)[5] and poly(ethyl acrylate).[11] The result of lead–nickel separation is given in Fig. 3. Complete separation was obtained by selective elution of nickel ions from the column by acetate buffer (pH 3.5) and lead ions by 4M nitric acid solution. This separation is a new application of hydroxamic acid ion exchange resins.

REFERENCES

1. F. Vernon and W. M. Zin, *Anal. Chim. Acta.* 1981, **123**, 309.
2. F. Vernon, *Pure Appl. Chem.*, 1982, **54**, 2151.
3. W. M. Z. Wan Yunus, *PhD Thesis*. University of Salford, England, 1980.
4. R. J. Phillips and J. S. Fritz, *Anal. Chim. Acta*, 1982, **139**, 237.
5. F. Vernon and H. Eccles, *Anal. Chim. Acta*, 1976, **83**, 187.
6. D. M. Mohammed, *Analyst*, 1987, **112**, 1171.
7. A. Shah and S. Devi, *Analyst*, 1987, **112**, 325.
8. G. Petri, D. Locke and C. E. Meloan, *Anal. Chem.*, 1965, **37**, 919.
9. F. Vernon and H. Eccles, *Anal. Chim. Acta*, 1976, **82**, 369.
10. A. Shah and S. Devi, *Analyst*, 1985, **110**, 1501.
11. W. M. Z. Wan Yunus and Z. Ahmad, *Pertanika*, 1988, **11**, 255.
12. A. J. Domb, E. G. Cravalho and R. Langer, *J. Polym. Sci. Part A Polym. Chem.*, 1988, **26**, 2623.
13. R. Mendez and V. N. S. Pillai, *Talanta*, 1990, **37**, 591.
14. W. Kern and R. C. Shultz, *Angew Chem.*, 1957, **69**, 153.
15. F. Vernon and H. Eccles, *Anal. Chim. Acta*, 1977, **85**, 317.
16. *Ion Exchange Resins*, BDH, Sixth Edn, September 1988.