**SHORT PAPER**

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# New polymer bearing hydroxamic acid chelating resin for binding of heavy metal ions[†]

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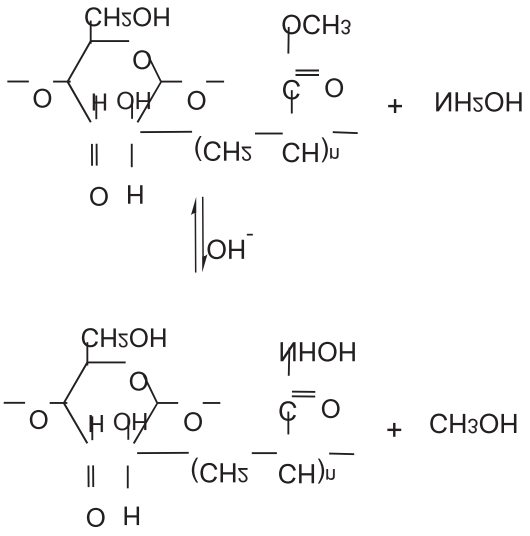
A new polymer containing the hydroxamic acid functional group was prepared from poly(methyl acrylate) grafted sago starch and the binding capacities of copper, iron, chromium, nickel, dysprosium, gadolinium and uranium were found excellent; other metal ions have significant sorption capacities.

**Keywords:** polymer bearing hydroxamic acid chelating resin

Ion exchange resins bearing chelating functional groups have long been of interest for removing specific metal ions from water. The resin chelating can be designed to extract a complex of metal ions from various sources. The design of such chelating resins depends on the stability of the basic macromolecular network, which is suited to the desired chelating functional groups for specific metal ions. The polymeric chelating resins are able to bind the heavier transition, lanthanide and actinide metal ions in the presence of calcium, magnesium, sodium and potassium.[1,2] The poly(hydroxamic acid) resin has potential commercial importance with the knowledge that hydroxamic groups are able to form complexes with wide range of metal ions.[3–5] Such a resin can be used for the recovery of heavy metals from aqueous media and uranium extraction from seawater.[6,7] A characteric feature of the chelating resins is the preservation of their high selectivity with respect to individual ions in the presence of large quantities of other ions. This is of great practical importance as chelating resins are often used to extract microelements from a complex solution. Regarding the potential applications, we have prepared a new polymeric resin containing hydroxamic acid groups and the chelating behaviour was investigated using some metal ions.

In this paper, poly(methyl acrylate) (PMA) grafted sago starch was used as a new starting polymer to obtain the poly(hydroxamic acid) resin. The sago starch starting material for the resin preparation is abundant and it is also a renewable source. The PMA grafted sago starch was prepared by a free radical initiating process, in which ceric ammonium nitrate was used as an initiator. The reaction mechanism and procedure of graft copolymerisation were described in our earlier paper.[8] The optimum reaction conditions were used to obtain the grafted copolymer at the concentration of $8.77 \times 10^{-3}$, 0.803, 0.135 and 0.175 mol/l of ceric ammonium nitrate, methyl acrylate, sago starch (AGU, anhydro glucose units) and sulfuric acid, respectively. The ester group of the PMA grafted copolymer was converted to the hydroxamic acid using the hydroxylamine in an alkaline solution. Based on the mechanism suggested by Domb *et al.*[7] the reaction of poly(acrylate ester) with hydroxylamine is shown in Scheme 1; the top structure is PMA–graft–sago starch and bottom is hydroxamic acid with sago starch grafted polymer.



**Scheme 1**

Infrared spectra of PMA grafted sago starch shows an absorption band of PMA at 1741 $cm^{-1}$ due to the C=O stretching mode in addition to the characteristic absorption bands of sago starch.[8] In the spectrum of the derived hydroxamic acid, the C=O band of the ester group at 1741 $cm^{-1}$ disappeared and new bands appeared of the hydroxamic acid at 1646 $cm^{-1}$ (C=O) stretching, and the amide II band (N–H) at 1568 $cm^{-1}$. This new band of the hydroxamic acid proves that the poly(hydroxamic acid) was successfully prepared from the PMA grafted copolymer.

The poly(hydroxamic acid) resin was used to study the binding properties of metal ions. From the results one can infer that the relative amount of metal ion taken up by the resin increases steadily with the increase of pH of the sorption medium (Table 1). This resin exhibits high affinity for copper, iron, chromium, nickel, dysprosium, lanthanum and uranium. The binding capacities of copper, iron, chromium, nickel, dysprosium, gadolinium and uranium were 3.46, 2.49, 2.43, 2.34, 2.30, 2.25 and 2.20 mmol/$g^{-1}$ respectively at pH 6. Although the binding capacity of copper is very high, other metal ions also have significant sorption capacity (Table 1). The sorption capacity of metal ions was pH dependent and its selectivity towards these metal ions is in the following order: $Cu^{2+} > Fe^{3+} > Cr^{3+} > Ni^{2+} > Dy^{3+} > Gd^{3+} > U^{6+} > Nd^{3+} > Pr^{3+} > Ce^{3+} > Co^{2+} > La^{3+} > Zn^{2+} > Th^{4+} > Cd^{2+} > Zr^{3+} > As^{3+} > Na^{+} > Ca^{2+} > Mg^{2+}$. The rate of exchange of copper was determined using the resin beads with copper solution for various time intervals. The time required for 50% exchange ($t_{1/2}$) was calculated from the copper ion exchange by the resin according to method

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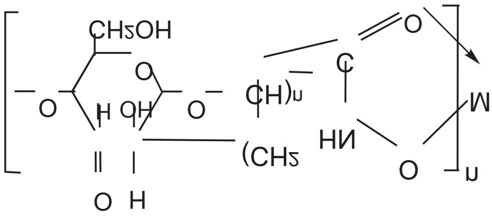
described by Lee *et al*.[9] It was found that the sorption rate of copper ion was very fast *i.e.* $t_{1/2}$ <5 min.

The poly(hydroxamic acid) resin containing divinyl benzene crosslinked has been studied by Vernon and Eccles.[5] They studied the chelating abilities for various metal ions and significant sorption capacities of copper, iron, uranium, silver and gold were obtained with a longer sorption rate *i.e.* $t_{1/2}$ is 43 min. Vernon and Wan Yunus[6] optimised the preparation of poly(hydroxamic acid) resin using the methyl acrylate and acrylonitrile copolymer beads. Metal capacities were high and the kinetics of metal ion exchange were much improved ($t_{1/2}$ = 8 min) in comparison with the earlier poly(hydroxamic acid) resin. Domb *et al*.[7] prepared a poly(hydroxamic acid) in gel or water solution from polyacrylamide and hydroxylamine and the copper capacity was determined to be about 3.0 mmol/g. Although the overall metal ion capacities of this poly(hydroxamic acid) resin are similar to those of other research workers, the rate of exchange is faster ($t_{1/2}$ <5 min) than that for other reported poly(hydroxamic acid) resins.

Most of the hydroxamic acids complexes with transition metal salts are highly coloured. It has been observed that the complex formation requires the hydroxylamine oxygen to be unsubstituted, although the nitrogen may bear a substituent.[10] Much evidence is now accumulating that the hydroxamate anion is a bidentate ligand and forms a complex in which the metal ion is bound by both oxygens.[4,5,10] The chelate complex produced by the hydroxamic acid ligand with a metal ion is presented in Scheme 2, where n is the oxidation state of metal (M).



**Scheme 1**

In conclusion, a new chelating resin containing the hydroxamic acid functional group was obtained from grafted copolymer and the chelating behaviour of the resin with some metal ions was investigated. Preparation of the poly(hydroxamic acid) resin from the PMA grafted copolymer is efficient, cost effective and by a simple work up. It has the advantage of significant binding capacity, faster rate of equilibrium and a little affinity for alkali metal ions. Therefore, it can be considered as an efficient resin for extraction of heavier transition and other metal ions in presence of sodium, calcium and magnesium metal ions.

## Experimental

*Preparation of hydroxylamine ($NH_2OH$) solution*: Hydroxylamine hydrochloride (21.05 g) was dissolved in 150 ml of methanol. The solution was cooled somewhat and HCl was neutralised by 4M NaOH solution. After the NaCl was filtered off, the pH of the $NH_2OH$ solution was adjusted to 13 using 4M NaOH solution and this solution was used in the next step.

*Preparation of poly(hydroxamic acid) resin*: The PMA grafted copolymer (10.0 g) was taken in a round bottom flask and the $NH_2OH$ solution was added, the flask was equipped with a mechanical stirrer, condenser and thermostat water bath. The reaction was continued for 2 h under slow stirring 72°C. The resin was collected by filtration and the product was treated with methanolic 0.2M HCl solution (200 ml) of at least 10 min. Finally, the resin was collected and washed several times with methanolic solution (methanol : water; 5:1) and dried at 50°C to a constant weight.

**Table 1** Metal ions capacity by poly(hydroxamic acid) resin[a]

| Metal ions | Metal ions capacity (mmol/g) | | | | |
|---|---|---|---|---|---|
| | pH | | | | |
| | 2 | 3 | 4 | 5 | 6 |
| $Cu^{2+}$ | 1.25 | 1.42 | 2.08 | 2.83 | 3.46 |
| $Fe^{3+}$ | 1.40 | 1.53 | 1.93 | 2.47 | 2.49 |
| $Cr^{3+}$ | 0.56 | 0.71 | 1.56 | 2.23 | 2.43 |
| $Ni^{2+}$ | 0.51 | 0.88 | 1.18 | 1.86 | 2.34 |
| $Dy^{3+}$ | 0.85 | 1.33 | 1.39 | 2.01 | 2.24 |
| $Gd^{3+}$ | 0.67 | 0.94 | 1.20 | 1.91 | 2.20 |
| $U^{6+}$ | 0.59 | 0.89 | 1.56 | 2.04 | 2.15 |
| $Nd^{3+}$ | 0.58 | 0.78 | 1.12 | 1.68 | 2.04 |
| $Pr^{3+}$ | 0.51 | 0.72 | 1.10 | 1.35 | 2.00 |
| $Ce^{3+}$ | 0.42 | 0.70 | 1.11 | 1.13 | 1.87 |
| $Co^{2+}$ | 0.42 | 0.45 | 0.99 | 1.77 | 1.86 |
| $La^{3+}$ | 0.40 | 0.64 | 0.82 | 1.21 | 1.77 |
| $Zn^{2+}$ | 0.35 | 0.51 | 1.10 | 1.79 | 1.71 |
| $Th^{4+}$ | 0.29 | 0.46 | 1.12 | 1.26 | 1.45 |
| $Cd^{2+}$ | 0.17 | 0.56 | 0.85 | 1.18 | 1.26 |
| $Zr^{3+}$ | 0.12 | 0.19 | 0.25 | 0.40 | 0.71 |
| $As^{3+}$ | 0.04 | 0.10 | 0.27 | 0.35 | 0.43 |
| $Na^{+}$ | 0.12 | 0.19 | 0.29 | 0.32 | 0.36 |
| $Ca^{2+}$ | 0.11 | 0.15 | 0.24 | 0.31 | 0.33 |
| $Mg^{2+}$ | 0.10 | 0.11 | 0.11 | 0.18 | 0.21 |

[a]0.2000 g dry resin and 20 ml of 0.1M metal ion.

*Sorption of metal ions*: Accurately weighed 0.2000 g of dry resin was placed into a series of 100 ml plastic bottle and 25 ml of distilled water was added to equilibrate the resin beads. Exactly 20 ml of 0.1M sodium acetate buffer solution at various pH and 20 ml of 0.1M metal ion solution were added to each bottle; the mixture was shaken for 24h. The 5 ml supernatant solution was collected for metal ion concentration and analysed by AAS (GBC-903) and ICP (Perkin 1000).

*Rate of exchange*: Exactly 0.2000 g of resin beads was treated with 20 ml of 0.1M copper ions in presence of sodium acetate buffer (pH 4) for various time intervals. The copper ion concentration was determined as described above. The time required for 50% exchange ($t_{1/2}$) was calculated from the plot of the copper capacity (mmol/g) versus time.[9]

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## References

1 A. Winston, D. Kirchner, *J. Am. Chem. Soc.*, 1978, **11**, 597.
2 F. Vernon, *Pure. Appl. Chem.*, 1982, **54**, 2151.
3 P. N. Sophiamma, K. Sreekumar, *J. Appl. Polym. Sci.*, 1996, **62**, 1753.
4 W. Kern, R.C. Schulz, *Angew Chem. Int. Ed. Engl.*, 1957, **69**, 153.
5 F. Vernon, H. Eccles, *Anal Chim Acta*, 1975, **77**, 145.
6 F. Vernon, Wan Yunus, *Anal Chim Acta*, 1981, **123**, 309.
7 A.J. Domb, E.G. Cravalho, R. Langer, *J. Polym. Sci., Part A*, 1988, **26**, 2623.
8 R. Lutfor, S. Silong, W.M. Zin, M.Z.A. Rahman, A. Mansor, H. Jelas, *J. Appl. Polym. Sci.*, 2000, **76**, 516.
9 C.H. Lee, J.S. Kim, M.Y. Suh, W. Lee, *Anal. Chim. Acta.*, 1997, **339**, 303.
10 P.A.S. Smith, *The Chemistry of Open-Chain Organic Nitrogen Compounds*, Chapman & Hall, London, 1962, p. 68.