

## Formation of Metal Complex in a Poly(hydroxamic acid) Resin Bead

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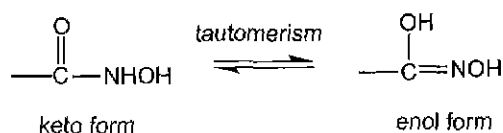
(Received January 22, 2001; Revised March 2, 2001; Accepted March 9, 2001)

**Abstract:** Poly(hydroxamic acid) resin beads were prepared and complexed with various metal ions. We used IR spectroscopy to investigate the structure of metal complex. It proved that the products formed by introduction of metal ions gave stable and colored complex. It was found that the resin bead as synthesized would be a good column packing material for continuous extraction. Energy dispersive spectroscopy was used to study the distribution of metal ions in the resin matrix. It could be tentatively concluded that adsorption and diffusion of metal ions in the chelating resins mainly depended on the loading of the resin matrix which indicated interacting sites with metal ions.

**Keywords:** Chelating resin, Poly(hydroxamic acid), Column extraction, Metal-ligand complex, Energy dispersive spectrum

### Introduction

Chelating resins have received considerable attention in the removal of harmful trace metal ions because of their highly selective adsorption capacity for heavy metal ions[1-4]. The hydroxamic acid group is well-known for its ability to form a stable chelates with various heavy metal ions. The hydroxamic acids are regarded as derivatives of the nitrogen-bound hydrogen in the hydroxylamine molecules, and have a general formula R-CO-NHOH (R = alkyl or aryl) having a tautomerism of keto and enol forms[5].



These groups have a special chelating ability with heavy metals. They have been known for effective chelation with Cu<sup>2+</sup>, Fe<sup>3+</sup>, V<sup>5+</sup>, UO<sub>2</sub><sup>2+</sup>, and others. A number of study has been accomplished to introduce this chelating group into polymer chain[6-11]. Kern and Schulz synthesized poly(hydroxamic acid) by reacting with poly(methyl acrylate) and hydroxylamine, which formed the characteristic red-brown Fe<sup>3+</sup> complex. The ratio of iron to the hydroxamic acid groups in the complex has been found to be 1:3. Crumbliss and coworkers used UV-VIS spectroscopy with photoacoustic detection to assign the co-ordination environment of Fe<sup>3+</sup> in the poly(hydroxamic acid) as tris-(FeL<sub>3</sub>) chelates.

There have been some studies on the distribution of metal ion in the chelating resin beads by electron probe X-ray

microanalysis[12,13]. They thought density of chelating groups and hydrophilicity and flexibility of the resin matrix determined the diffusion and adsorption of each metal ion.

We have synthesized poly(hydroxamic acid) from ethyl acrylate and various crosslinking agents and reported their morphology, metal binding properties, resin-metal kinetics, and selectivity[14-17]. In this report, we have closely investigated continuous extraction of metal ion with previously prepared resin beads for practical use in separation. Distribution of metal ions in the resin matrix was observed via electron dispersive spectroscopy.

### Experimental

For the preparation of poly(hydroxamic acid) resins from ethyl acrylate (EA) and divinylbenzene (DVB), conventional suspension polymerization technique was employed as detailed procedure was published elsewhere[14]. 2,2,4-Trimethylpentane (TMP) was used to enhance porosity of the resin and the amount was indicated as a dilution. Metal ion solutions were prepared according to previously published method[16].

Metal complexed resin beads were prepared to investigate distribution of metal ions in the polymer matrix. Poly(hydroxamic acid) beads were soaked in each metal solutions at room temperature for 24 hr (to reach 90-100% extraction of metal ion). After sufficient soaking, the beads were filtered, washed several times with deionized distilled water several times and methanol, and dried in a vacuum oven at 40°C for 24 hours.

### Column extraction and recovery of metal ions

A gravity column (1.2 cm i.d., 30 cm height) packed with about 1.0 g resin was used to determine the extent of

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extraction of copper ( $\text{Cu}^{2+}$ ) and iron ( $\text{Fe}^{3+}$ ) ions, respectively. The column was conditioned by flowing deionized distilled water through it. The packed resins were treated with 100 ppm of copper solution at pH 4 or iron solution at pH 2.5 at a flow rate of 1-2 ml/min. Samples of effluent were checked periodically by atomic absorption spectrometer (AAS, GBC 904AA) until the metal uptake had ceased. The column was rinsed and backwashed with deionized distilled water to remove any precipitated metal, then eluted with aqueous 0.1 M hydrochloric acid solution (for copper ion) or aqueous 0.1 M oxalic acid in aqueous 1 M hydrochloric acid solution (for iron ion) at the rate of 1-2 ml/min. Amount of metal eluted was measured by AAS.

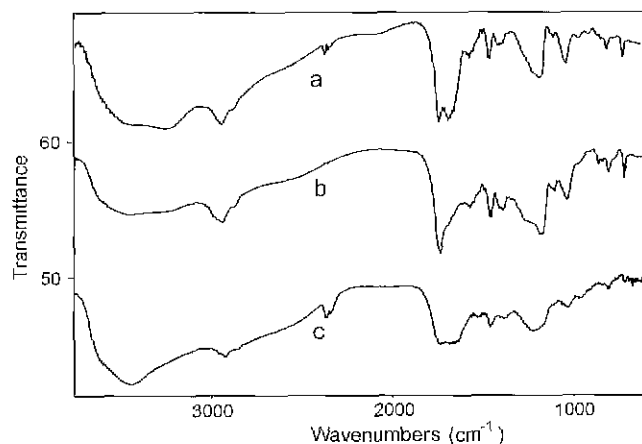
### Characterization

Infrared spectra were obtained from KBr pellets of various resins with FT-IR spectrophotometer (Perkin-Elmer 1725X). Energy dispersive spectrometer (EDS, Kevex Instruments Inc.) was used to investigate the distribution of metal atom inside the beads. Beads of polymer were bisected so that the transverse sections of the beads appeared on the surface. Carbon was evaporated onto the cross-sectional surface of these samples. EDS was carried out on a scanning electron microscope (SEM, Hitachi S-2500C).

### Results and Discussion

The chelating resin with hydroxamic acid groups were prepared via conventional suspension polymerization technique. More details on the identification, characterization, and metal ion binding properties including resin-metal kinetics of the resins have been published[14-17].

The IR spectra of the poly(hydroxamic acid) exhibit the characteristic C=O absorptions at 1680 and 1730  $\text{cm}^{-1}$  and amine stretching at 3400  $\text{cm}^{-1}$  along with bands at 700-1000

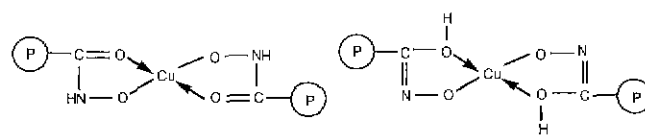


**Figure 1.** IR spectra of poly(hydroxamic acid) from EA/DVB copolymer: (a) poly(hydroxamic acid) resin, (b) Cu chelate, and (c) Fe chelate.

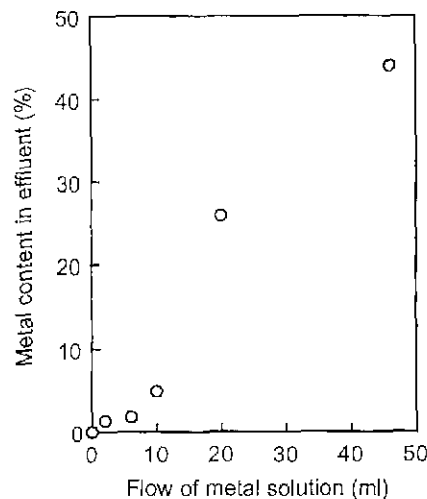
$\text{cm}^{-1}$  caused by the aromatic rings in the DVB portion of the polymer as shown in Figure 1(a). Metal complex formation by an introduction of various metal ions is clearly shown as the sharp absorption band observed near 1700  $\text{cm}^{-1}$  becomes blunt and broadened. This means that the formation of chelating complex weakens the double bonding character of carbonyl group in the hydroxamic acid owing to the coordinate bond between oxygen atom of carbonyl groups and metal ions. The weakening of double bonding is more pronounced in chelating with  $\text{Fe}^{3+}$  (Figure 1(c)) which complexed in 1:3 than with  $\text{Cu}^{2+}$  (Figure 1(b)) which in 1:2, because  $\text{Fe}^{3+}$  is a hard acid which co-ordinates strongly to ligands made up of small, nonpolarizable, highly negative oxygen donor atoms (hard bases), while  $\text{Cu}^{2+}$  is a borderline acid which binds strongly with borderline bases[18].

Hydroxamic acids metal complexes, therefore, are considered to contribute to stabilization by such a structure as constituted from the co-ordinate bonding of the metal ions formed through the intermolecular and intramolecular linkage in molecular chains regardless of tautomerism (Figure 2). Because the nitrogen lone pair on hydroxamic acid group is tied up by resonance with C=O, chelation with metal occurs at oxygen atom[19].

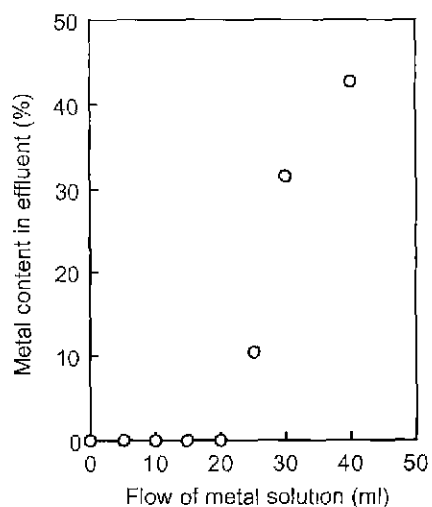
Quantitative studies of the retention of copper and iron ions on the column of the poly(hydroxamic acid) resin were carried out to investigate continuous extraction of metal



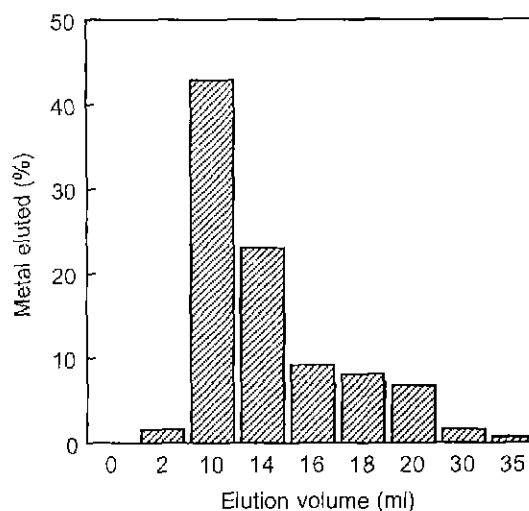
**Figure 2.** Formation of copper complex of hydroxamic acid group.



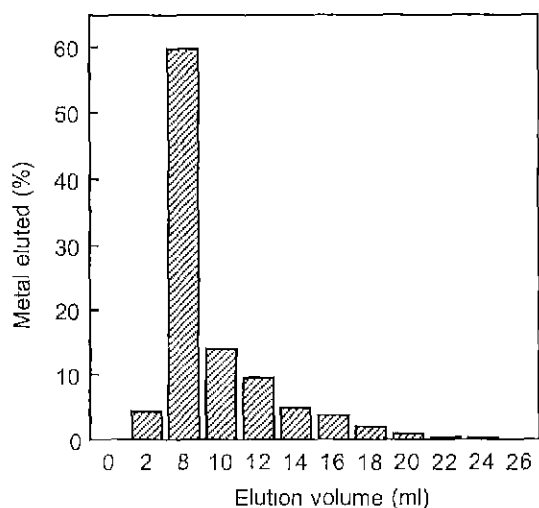
**Figure 3.** Metal binding in flow-through column. resin: 1 g of the resin; 8 mol% crosslinking, 120 vol% dilution, metal: 100 ppm, pH 4 copper solution, flow rate: 1-2 ml/min.



**Figure 4.** Metal binding in flow-through column. resin: 1 g of the resin; 8 mol% crosslinking, 120 vol% dilution, metal: 100 ppm, pH 4 copper solution, flow rate: 1-2 ml/min.



**Figure 6.** Elution of copper by eluting reagent. eluting reagent: 0.1 M oxalic acid in 0.1 M HCl, flow rate: 1-2 ml/min.

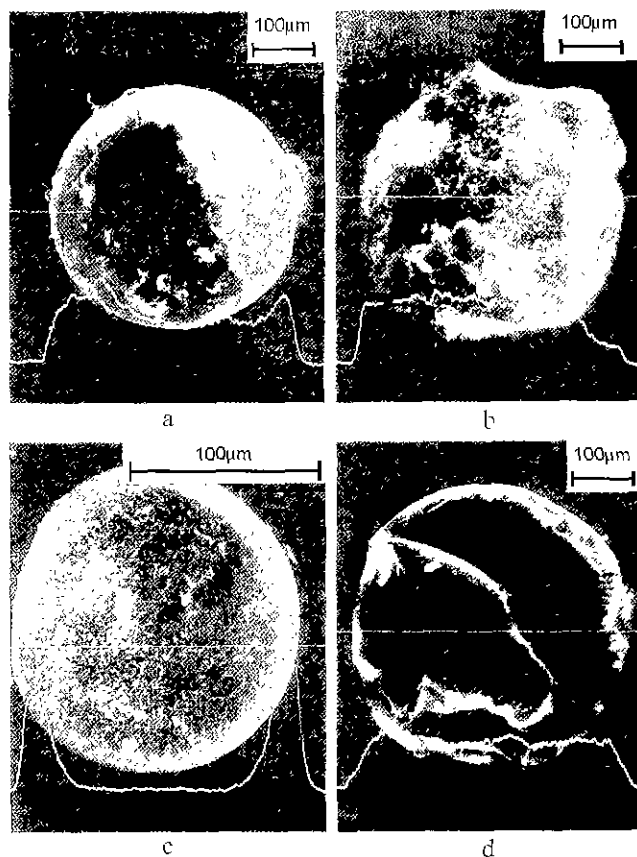


**Figure 5.** Elution of copper by eluting reagent. eluting reagent: 0.1 M HCl, flow rate: 1-2 ml/min.

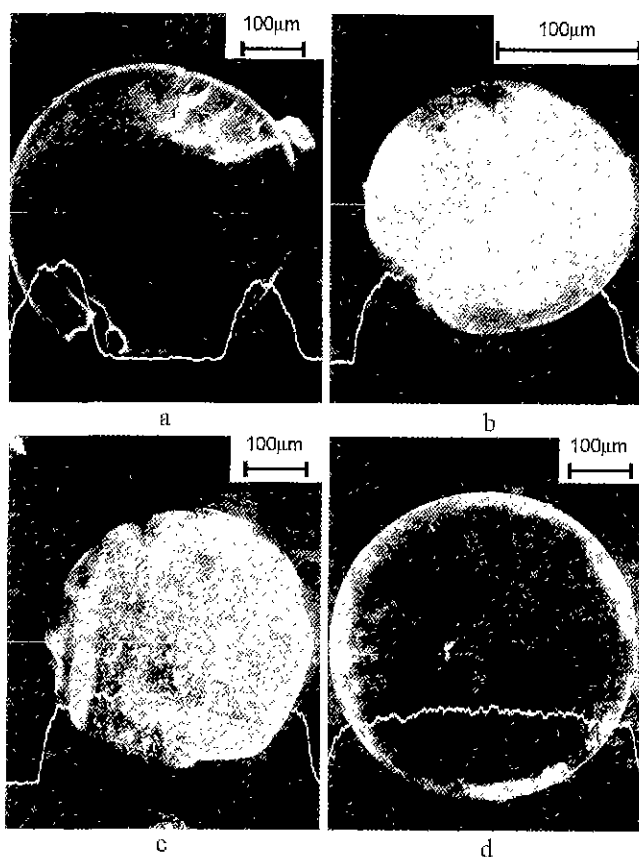
ions. Simply by passing a solution, metal ions in it could be extracted. Results of the column extraction (Figures 3 and 4) demonstrates the feasibility of this approach. Copper ion was retained with the formation of a green-colored band which could be removed by elution with 0.1 M HCl solution (Figure 5). Iron ion was eluted by 0.1 M oxalic acid in 1 M HCl solution (Figure 6), which column band color changed from red to colorless.

Possibility of extending use of the resin from analytical separation to large scale processing of nuclear fuels should be considered.

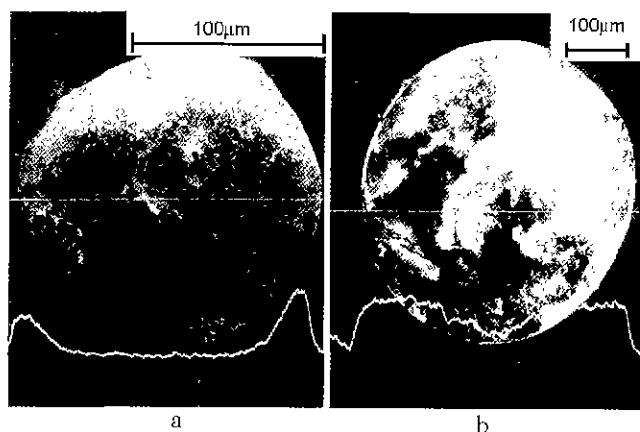
In general, the adsorption of metal is less than the theoretical value of the metal adsorption capacity. Thus the



**Figure 7.** EDS photographs showing distribution of copper in the poly (hydroxamic acid) beads from: (a) 5 mol% crosslinking, 40 vol% dilution; (b) 8 mol% crosslinking, 120 vol% dilution; (c) 8 mol% crosslinking, 120 vol% dilution, NaOH treated, (d) 15 mol% crosslinking, 40 vol% dilution.



**Figure 8.** EDS photographs showing distribution of nickel and vanadium in the poly(hydroxamic acid) beads from: (a) 5 mol% crosslinking, 40 vol% dilution-Ni; (b) 5 mol% crosslinking, 120 vol% dilution-V; (c) 8 mol% crosslinking, 120 vol% dilution-V; (d) 12 mol% crosslinking, 120 vol% dilution-V chelate.



**Figure 9.** EDS photographs showing distribution of uranium in the poly(hydroxamic acid) beads from: (a) 5 mol% crosslinking, 120 vol% dilution, (b) 8 mol% crosslinking, 120 vol% dilution.

metal adsorption capacity is not directly related to the loading of the resin. It can be concluded that all the

hydroxamic acid groups in the beads are not accessible to the metal ions.

EDS was carried out to observe the distribution of the metal in the resin beads loaded with copper, nickel, vanadium, and uranium, respectively (Figures 7-9). The investigation was accomplished by the line profile measurement, showing white straight line in the middle of the each bead. Metal ions located in this line were analyzed for the distribution of metals in the beads. In Figure 7(a), (d), and Figure 9, the metals were located in a surface layer when lower crosslinking ratio was employed, while in the case of more crosslinked system, the metal ions could diffuse deeply inside the beads to look for available chelating sites for coordination. However, diffusion of vanadium was easier than that of copper as shown in Figure 8(b)-(d). It is presumed that the penetration of metal ions into the resin bead depended on the physical properties and the kind of metal ion as shown in Figure 7(a), Figure 8(a) and (b), and Figure 9(a). In Figure 7(b) and (c), copper ions are located in more narrow surface layer in the alkali treated bead, which can be explained that new chelating sites or micropores were formed mainly at the surface by alkali treatment.

## Conclusions

Poly(hydroxamic acid) chelating resin was successfully prepared as a bead form. The ligand formed a coordination complex between oxygen atom of carbonyl groups and metal ions. Continuous metal binding properties were investigated via column extraction and elution. It was presumed that according to the EDS study, the distribution of the metal ions in the resin bead were more affected by the loading of the resin rather than rigidity of the bead. To clarify this relationship porosity measurement is still in progress.

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