

## **Modified poly(ethyleneimine) supports for vanadium, molybdenum, and rhenium removal**

**B. L. Rivas\*, H. A. Maturana, I. M. Peric, A. M. Fierro**

Facultad de Ciencias Químicas, Universidad de Concepción, Casilla 3-C,  
Concepción, Chile

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### **SUMMARY**

Sorption characteristics of modified poly(ethyleneimine) supports which contain ammonium, carboxymethyl or phosphonomethyl groups have been determined for uptake of molybdenum(VI), rhenium(VII) and vanadium(V). Results suggest the separation of rhenium(VII) toward molybdenum(VI) from loaded N-carboxymethyl derivative by selective elution with 1M sulfuric or perchloric acid. Moreover, vanadium(V) should be also selectively eluted from molybdenum(VI), iron(II) or iron(III).

### **INTRODUCTION**

Economics of some copper mines frequently depend heavily on the revenues derived from leaching the waste to recover additional copper as well as from such by-products as molybdenum, silver, gold, selenium, and tellurium (1).

Nowadays, the growing interest in metals having a high melting point for applications in electronic equipment has led to an industrial process for recovering and purifying the element rhenium from molybdenites associated with copper, which provide the commercial source of this metal (2).

Most of the work on the recovery of molybdenum and rhenium has been carried out by solvent extraction (2,3), but the system's disadvantages include extractant loss and the additional aqueous pollution (4). Consequently, functionalized polymeric supports, so-called resins, have been considered, where extractant loss is clearly eliminated; the polymer support is the diluent and so no additional solvent is required; and the system is readily adaptable to the long-term continuous operation most appropriate to metal ion recovery from dilute solutions. Moreover, it is possible to select the fixed ionogenic groups and the degree of crosslinking of the matrix according to the intended applications (4,5).

Crosslinked poly(ethyleneimine) forms very stable complexes with different metal ions (6-9). Recently, the synthesis and preliminary characterization of a crosslinked poly(ethyleneimine) using epichlorohydrin as crosslinker and subsequently modified through polymer-analogue reactions for resins containing ammonium, carboxymethyl and phosphonomethyl groups have been described (10). At present, the sorption characteristics of these resins by a batch

\* Corresponding author

equilibration technique, for uptake of Cu(II), Fe(II), Fe(III) and uranyl ions from aqueous solutions as well as water contents, thermal decomposition and selective sorption of uranyl ions from UO<sub>2</sub>(II) - Cu(II) ion mixture were carried out.

Results obtained in the previous work have encouraged us to determine, in addition, the sorption characteristics of these resins for uptake of Mo(VI) and Re(VII) due to the possibility to separate them from molybdenite concentrates (1). Also, V(V) has been tested due to its analytical interest as well as the possibility to recover it from molybdenum, which is contained in desulfurization waste catalyst and also in oil boiler slag (11).

## EXPERIMENTAL

**Resin form preparations.** The synthesized resins (10) were converted to the hydrochloride form prior to analysis. The resin sample was treated with 1M HCl by a batch method. The sample was then transferred to a glass filter and rinsed with portions of deionized water until the filtrate was neutral to methyl orange, each followed by suction to remove adherent liquid and dried under vacuum till constant weight.

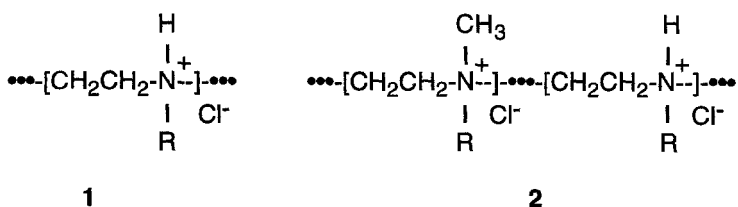
**Sorption and elution of metal ions by batch operation.** Data for metal uptake were determined by shaking 100 mg of dry resin for 1 h with 10.0 mL of 1g/L vanadium(V) (from vanadium(V) oxide, extra pure Merck) or 1g/L molybdenum(VI) (from molybdenum(VI) oxide, GR. Merck) or 0.5 g/L rhenium(VII) (from rhenium powder, Aldrich Co.) aqueous solution at different pH values. Sulfuric acid and sodium hydroxide were used to adjust the pH to the desired value. The metal ions were determined in the supernatants colorimetrically (12-14).

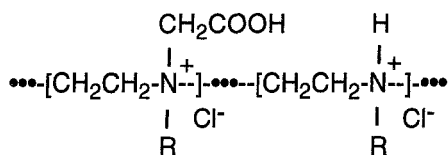
Similarly, the maximum capacity for metal ions were determined at pH 2, but with 1 g of the resin and 50.0 mL of 1g/L metal ions aqueous solution. Two additional contacts with the same resin to ensure loading were performed and the supernatants were combined.

Elution assays were carried out with the metal ions-loaded resins at maximum capacity. These were eluted by shaking 100 mg of the resin with 10.0 mL of 1M and 4M sulfuric acid, 1M and 4M perchloric acid and 0.25M and 0.75M sodium carbonate for 1 h.

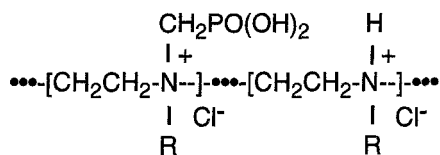
## RESULTS AND DISCUSSION

Synthesis of crosslinked poly(ethyleneimine) **1** as starting material, using epichlorohydrin as crosslinker, with a narrow particle size between 180 and 250  $\mu\text{m}$ , as well as its modification in order to obtain the corresponding N-methylated **2**, N-carboxymethylated **3** and N-phosphonomethylated **4** derivatives has been detailed earlier (10). All the resins, in the current study, were used in the hydrochloride form and they can be schematized as follows:





3



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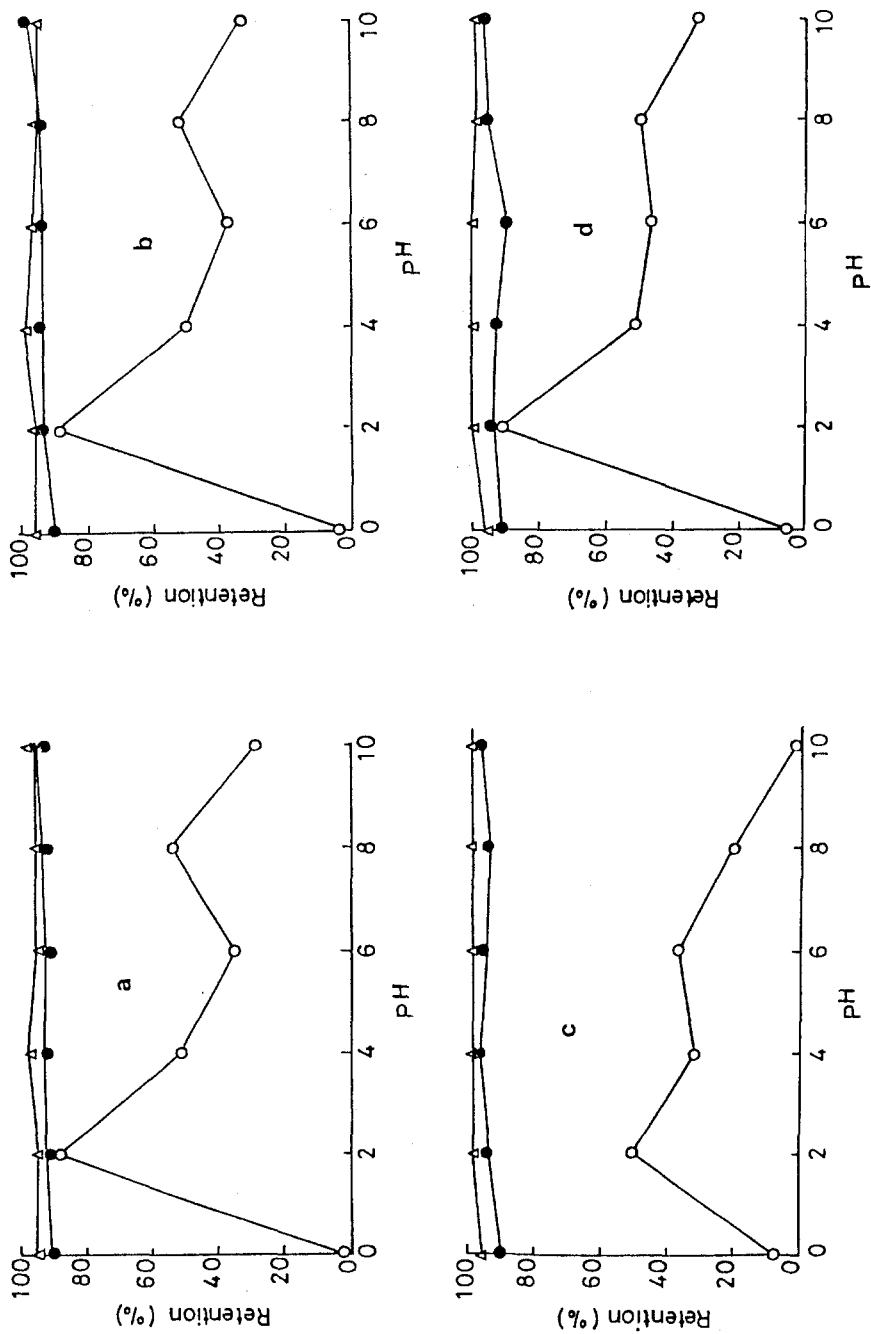
The affinities of these resins for V(V), Mo(VI) and Re(VII) were investigated by a batch operation outlined in Table 1. The retention percentages of the metal ions taken up by the resins, as a function of the pH, are reported in Fig. 1 for each resin under the experimental conditions employed.

Table 1. Sorption ability of resins at pH 2.

Resin	Sorption Capacity (meq/g-resin)		
	V(V)	Mo(VI)	Re(VII)
1	4.2	9.3	3.7
2	4.6	7.7	3.3
3	2.6	4.7	1.7
4	2.4	3.1	2.7

Examination of the uptake data by the resins (Fig. 1) shows that all of them retain over 89% V(V) and Mo(VI) over the whole pH range studied. On the other hand, all the resins show a maximum retention for rhenium(VII) at pH 2, but with a second maximum peak at pH 8, except resin 3 which shows this maximum at pH 6. This behaviour can be explained by considering the mechanism of retention as an anionic exchange where the species like  $\text{VO}_4^{2-}$ ,  $\text{MoO}_4^{2-}$  and  $\text{ReO}_4^-$  are involved. Vanadium and molybdenum are easily retained due to their high charge, in spite of the polymeric derivatives that were formed as the pH decreased (15).

Percentages of the metal ions taken up by resins as a function of shaking time were determined at room temperature and are reported in Table 2 for resin 1. All the resins show a higher adsorption rate. The time needed for perfect saturation of the capacity of the resin for the metal ions was about 15 min, which was a sufficiently short time for the polymer to be used for the removal of the metal ions.



**Figure 1.** Metal ion uptake (%) by resins as a function of pH; a: resin 1, b: resin 2, c: resin 3, d: resin 4 ( $\Delta$ ) V(V), ( $\bullet$ ) Mo(VI) and ( $\circ$ ) Re(VII).

Table 2. Percent vanadium(V), molybdenum(VI) and rhenium(VII) adsorbed as a function of contact time for resin 1, at pH 2.0.

Metallic ion	Time (min)				
	15	30	60	90	120
V(V)	94.5	94.4	94.5	94.6	--
Mo(VI)	96.3	98.4	99.4	--	--
Re(VII)	65.8	67.0	67.2	67.8	68.2

Evaluation of the maximum capacity for the considered metal ions were carried out at pH 2.0 and results are shown in Table 1. Examination of these results indicates that resin 1 shows the greatest maximum capacity for Mo(VI) (9.3 meq/g), Re(VII) (3.7 meq/g) and V(V) (4.3 meq/g) within experimental error. Consequently, retention was not improved with the proposed modifications.

However, analysis of the elution percentages of metal ions from loaded resins in acid as well as basic media suggest the possibility to elute selectively rhenium (Table 3) from a binary mixture, which includes molybdenum (Table 4) by using 1M sulfuric or perchloric acid when the N-methylcarboxylated resin 3 is used. This behaviour should not be possible to observe for resin 1. This must be due to the stable complex formation in acidic media between molybdate ion and methyl carboxylic groups of the resin, because of the evidence of this kind of complexes with hydroxo compounds like tartrate ion (16).

Table 3. Percentage of rhenium(VII) recovery in acid and basic media.

Resin	$H_2SO_4$		$HClO_4$		$Na_2CO_3$	
	1M	4M	1M	4M	0.25M	1M
1	78.6	75.3	69.5	77.4	68.6	75.3
2	87.5	85.6	71.8	71.8	72.2	76.9
3	99.9	99.9	95.2	99.9	99.9	99.9
4	84.9	88.2	83.7	88.8	91.7	89.4

Table 4. Percentage of molybdenum(VI) recovery in acid and basic media

Resin	$H_2SO_4$		$HClO_4$		$Na_2CO_3$	
	1M	4M	1M	4M	0.25M	1M
1	35.0	55.1	36.5	60.6	46.6	62.3
2	35.4	52.2	13.9	57.2	77.3	78.7
3	5.6	22.6	2.2	5.6	97.7	99.9
4	21.9	63.6	6.1	72.4	79.4	87.4

Likewise, the high retention of molybdenum by resin 1 can be due to the complex formation between molybdate ion and amine groups in the resin as it is reported in the literature (17).

This result suggests that resin 1 may have a suitable stereochemical arrangement for molybdenum complex formation, where secondary amine groups may be involved. On the contrary, Mo(VI) sorption with resins 2, 3 and 4 could be accounted by the loss of secondary amine groups by conversion to tertiary and/or quaternary ammonium groups; hence, the complexation was hindered.

In contrast, vanadium was significantly eluted with 1M and 4M sulfuric acid (see Table 5) from the N-methylated resin 2. It suggests a possible separation of V(V) from a binary mixture including Fe(II) or Fe(III), because these latter ions were not retained significantly by this resin (10).

Table 5. Percentage of vanadium(V) recovery in acid and basic media.

Resin	H <sub>2</sub> SO <sub>4</sub>		HClO <sub>4</sub>		Na <sub>2</sub> CO <sub>3</sub>	
	1M	4M	1M	4M	0.25M	1M
1	76.4	81.1	81.1	84.2	78.0	92.1
2	96.5	96.5	69.5	83.7	62.4	75.2
3	94.4	97.0	68.9	76.5	76.5	81.7
4	67.4	72.8	97.1	99.9	67.4	89.0

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