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Polyethyleneimine Supports for Resins with Retention Properties for Heavy Metals
Part I

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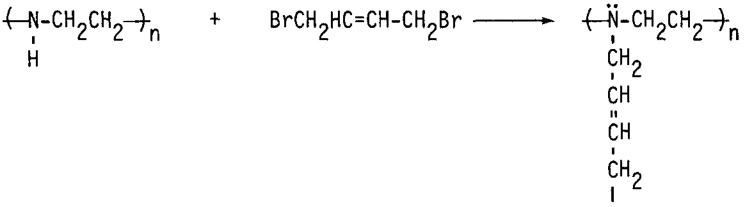
SUMMARY

Resins with retention properties for copper (II), and uranium (VI) have been synthesized by crosslinking of polyethyleneimine with 1,4-dibromo-2-butene and subsequent alkylation with dimethylsulphate. The influence of pH on the retention maximum capacity of load and elution assays were determined.

INTRODUCTION

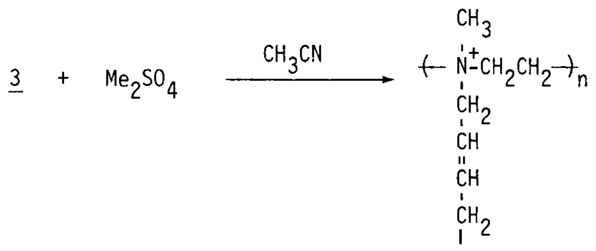
Separation procedures employing ion exchange resins are frequently made more selective by the addition of complexing agents during adsorption or elution. Although the most stable and most selective complexes often involve chelating compounds, some of these, because of size and solubility characteristics, are not suitable for usual ion exchange techniques. To avoid these difficulties and still take advantage of the selectivity of chelating agents, resins have been prepared which incorporate the chelating compound or atom in the structure of the resin itself. In regard to the above, polyethyleneimine (PEI) is well known for its ability to complex with heavy metals (1-9).

This paper reports the synthesis and retention properties for copper (II), uranium (VI), iron (II) and (III) of resins obtained by crosslinking of polyethyleneimine with 1,4-dibromo-2-butene(IM-1) and subsequent alkylation with dimethylsulphate (IM-1M).



$$\left(\underset{\displaystyle H}{\underset{|}{N}}-CH_2CH_2\right)_n + BrCH_2HC{=}CH{-}CH_2Br \longrightarrow \left(\underset{\displaystyle CH_2-CH{=}CH-CH_2-}{\underset{|}{\ddot{N}}}-CH_2CH_2\right)_n$$

1 2 3



$$\underline{3} + Me_2SO_4 \xrightarrow{CH_3CN} \left(\overset{CH_3}{\underset{CH_2CH=CHCH_2I}{N^+}}-CH_2CH_2 \right)_n$$

4

EXPERIMENTAL PART

Materials: Polyethyleneimine (Aldrich Chemical Co.). All the chemicals used were chemically pure. They were used as such, except dimethylsulphate which was distilled previously (b.p. 188 °C).

Crosslinking of Polyethyleneimine: The branched polyethyleneimine was crosslinked with 1,4-dibromo-2-butene. The reaction was carried out in heterogeneous phase. Fifty mg Span 65 (emulsifier) and 0.04 mole dibromoderivative (dissolved in 60 ml petroleum ether, b.p. 100-140 °C) were added to a solution of polyethyleneimine (0.12 mole). The reaction was heated to 95 °C for 24 h. The resin was washed wit NaOH (0.1N) and dried under vacuum at 60 °C; Yield = 100%.

Alkylation of Crosslinked Polyethyleneimine. To a suspension of 0.1 eq/g of crosslinked polyethyleneimine 3 in 50 ml acetonitrile, 0.24 mol of dimethylsulphate was added. The mixture was stirred for 8 hrs at 50 °C. Then, the resin was filtered, washed with water and dried under vacuum at 50 °C till constant weight.

pH dependence for copper.

The copper solution was prepared by dissolving 1.0 g/l copper in the form of $CuSO_4 \cdot 5H_2O$ in water at different pH's (0 to 4). Ten ml of these solutions were contacted with 0.5g dry resin over 2 hrs with constant stirring; the copper was analyzed in the aqueous solution.

pH dependence for uranium.

Uranium solution was prepared containing 1.0 g/l uranium (VI) at different pH's (between 0 to 4). The procedure is similar to that used for copper. The uranium was determined in the filtrates by spectrophotometry.

pH dependence for iron (II) and (III).

Iron solution was prepared containing 1 g/l iron (II) and (III) at pH between 0 and 2. The procedure is similar to the above described ions. The ion was analyzed in the filtrates.

Determination of the maximum capacity of load for copper and uranium.

This parameter was carried out at pH 2.0. A beaker containing a solution pH 2.0, 1.0 g/l in uranium and 1.0 g dry resin was placed in a thermostatically controlled bath at 25 °C. The mixture was stirred for 1 hr at 200 cycles/min. The aqueous solution was separated by decanting and washed several times. This process was repeated three times using the same resin and taking a uranium solutio (50 ml) of the same initial concentration. The uranium was analyzed in the filtrates by spectrophotometry. The maximum capacity of load for copper (II) was carried out in analogous way to a solution of 2.0 g/l copper.

Electron micrograph.

The surface of the resin was coated with gold for 4 min to obtain a 150 Å thickness using an Edwards S 150 Sputter coater. The electron micrographs were obtained by using a scanning electron microscope ETEC Autoscan U-1 Model.

Measurements.

Uranium was analyzed on a PMQ II Carl Zeiss spectrophotometer. Copper (II) and iron (III) were analyzed on a Perkin Elmer 306 atomic absorption spectrophotometer. Iron (II) was analyzed by dichromatometry (10).

RESULTS AND DISCUSSION

The branched polyethyleneimine was crosslinked with 1,4-dibromo-2-butene, obtaining an insoluble resin. This resin was N-alkylated with dimethylsulphate to convert all the groups or the majority of them to ammonium ions. Elemental analys show that crosslinking was quantitative (See Table 1).

Table 1. Elemental analyses[a] of the Resin IM-1.

	C%	H%	N%
Theoretical	65.93	10.99	23.07
Experimental	66.20	10.55	22.90

[a] Assuming that the ratio polymer/crosslinking derivative in the resin is 3 to 1.

The retention properties for the resins were studied under different experimental conditions. The results are shown in Tables 2 and 3.

Table 2. Retention percent of copper (II).

Resin	Initial pH				
	0	1	2	3	4
IM-1	2.0	2.0	94.0	94.0	94.0
IM-1M	0.0	1.1	8.2	7.0	8.4

The resin IM-1 practically does not retain copper up to pH 1.0. However, fro pH = 2.0 to pH = 4.0 it retains, 94% of the copper. It is very important for recovery of the resin. When the crosslinked resin is N-alkylated the retention of copper is very small (lower than 9%).

Table 3. Retention percent of uranium (VI).

Resin	Initial pH				
	0	1	2	3	4
IM-1	41.3	73.7	86.9	83.4	85.9
IM-1M	44.8	83.3	94.0	93.4	99.9

In general, both resins show a similar retention behaviour. As the pH increases, the retention for uranium increases but the resin IM-1M is better than IM-1, which is expected. Resin IM-1M practically does not retain copper between pH 0 to 4 and retains 44.8 - 99.9% uranium in this range. Evidently this resin is selective practically over the entire pH range assayed.

On the other hand, the two resins did not retain iron (II) and (III) under th experimental conditions examined.

Also, resin IM-1M has a greater maximum capacity for uranium (3.2 meq/g) than IM-1 (2.8 meq/g). (See Table 4).

Table 4. Maximum capacity for uranium (VI) and copper (II).

Resin	IM-1	IM-1M
Maximum Capacity (meq/g) for uranium	2.8	3.2
Maximum Capacity (meq/g) for copper	1.74	- [a)

[a)] It was not determined as the resin IM-1M practically does not retain copper (II).

According to these results the resins retain copper and uranium but by different mechanisms. Usually copper is retained by an ion exchange and possibly chelate ring formation (2) and uranium by adduct formation with the tertiary amine i.e. ammonium group (11). The ammonium shows a greater afinity to uranium. For this reason, when the crosslinked resin (IM-1) is N-alkylated, a resin (IM-1M) that is obtained is more selective for uranium than to copper in this pH range.

Elution assays were carried out in acidic (H_2SO_4 1M, 3M) and basic media (Na_2CO_3 0.25M, 0.75M). In all cases the ions were eluted quantitatively after two contacts.

Morphology

The morphology of loaded and unloaded resins was studied. In general, the resins show a rough surface with holes, however, the change on the surface during the ion adsorption is unimportant (See Figs. 1 and 2).

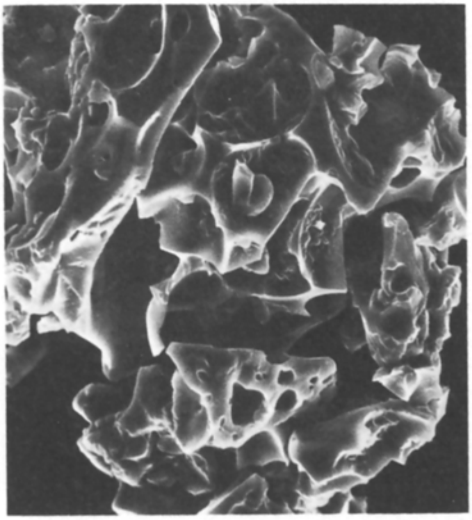


Figure 1. SEM micrograph of Resin IM-1 (310x). Unloaded.

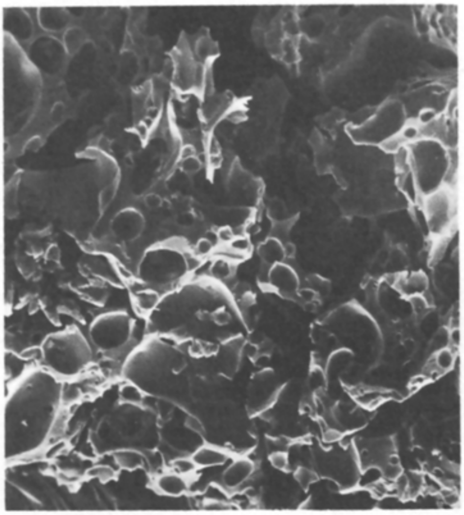


Figure 2. SEM micrograph of Resin IM-1M (152x). Unloaded.

ACKNOWLEDGEMENT

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