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Resins

Synthesis of Basic Resins for Uranium and Copper Recovery. (Part IV)

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SUMMARY

A branched polyethyleneimine has been obtained by ionic polymerization of ethyleneimine. These were crosslinked with 1,3 dibromopropane and showed chelating properties in the presence of copper (II) in aqueous solution. The crosslinked polymer was N-alkylated and showed retention properties for uranium (VI).

INTRODUCTION

The ability of ion exchange resins to concentrate selectively many metals of strategic and economic importance coupled with the fact that many of our now important ore reserves are of low grade, have stimulated interest in the use of these resins in hydrometallurgy, the technology of recovering valuable metals from aqueous solutions. Some articles have been published about the synthesis and application of polymers with chelating properties (1,2).

As part our work on the synthesis and study on the analytical properties of polyethyleneimines (3-6), we report here the preparation of a resin by crosslinking branched polyethyleneimine with 1,3 dibromopropane, which shows retention properties for copper (II). Subsequently, this resin was N-alkylated with dimethylsulphate and the product showed good retention for uranium (VI) and adequate selectivity against copper (II) and iron (III).

EXPERIMENTAL

Materials: All the chemicals used were chemically pure. They were used as such, except dimethylsulphate which was distilled before use.

Measurements: Uranium was analyzed on a PMQ II Carl Zeiss spectrophotometer. Copper and iron were analyzed on a Perkin Elmer 306 atomic absorption spectrophotometer. The molecular weights were determined on a Knauer vapor pressure osmometer.

Polymerization of Ethyleneimine.

The branched ethyleneimine was prepared by polymerization of ethyleneimine catalyzed by acetic acid (7). A mixture containing 50 g ethyleneimine, 50 ml methanol and 2.0 g acetic acid was kept at room temperature for 8 days. The viscous product was diluted with water and the solution passed through a column of strong base ion exchange resin (Amberlite CG 45) in the hydroxyl form to remove acetic acid and carbon dioxide.

Crosslinking of Polyethyleneimine.

The branched polyethyleneimine was subsequently crosslinked with 1,3 dibromopropane (8). The reaction was carried out in heterogeneous phase. 250 mg Span 65 (emulsifier) and 8.08 g 1,3 dibromopropane (dissolved in 60 ml petroleum ether, b.p. 100-140°C) were added to a solution of polyethyleneimine(5.16 g dissolved in 20 ml water). The reaction was heated at 95°C for 8 h. The resin was washed with NaOH 1N and dried under vacuum at 60°C.

Alkylation of Crosslinked Polyethyleneimine.

To 1.5 eq/g crosslinked polyethyleneimine suspended in 60 ml acetonitrile, 0.36 mole dimethylsulphate were added. The mixture was stirred for 6 h to 50°C. The resin was filtered and dried under vacuum at 60°C.

RESULTS AND DISCUSSION

The molecular weight of the branched polyethyleneimine, $\bar{M}n$= 1095, was determined by vapor pressure osmometry (water solvent at 60°C).

Retention properties of crosslinked polyethyleneimine.

1. pH dependence for copper.

The solution was prepared by dissolving 2.0 g/l in copper from $CuSO_4 \cdot 5H_2O$ in water at different pH's (0 to 4). Fifty ml of these solution were contacted with 0.5 g dry resin over 2 h with constant stirring; copper analysis was performed by atomic absorption spectrophotometry. See Figure 1.

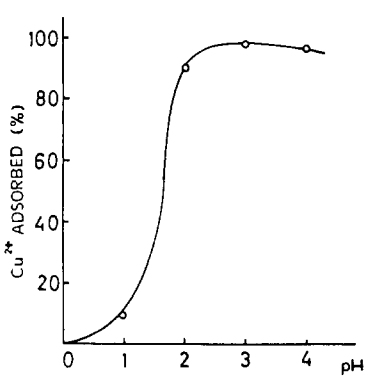

Figure 1.- Percent adsorption of copper by the crosslinked polyethyleneimine.

The effect of pH on the retention behaviour of the resin is very interesting. No copper retention was observed at pH=0; however, the retention increases to 96.5% at pH=3.0. The retention is 90% at pH=2.0 which is the normal pH for the acid lixiviated copper mineral.

2. Determination of the maximum capacity for copper.

This parameter is determined at optimum pH (see Figure 1). A beaker (containing a solution pH=3.0; 6.0 g/l in copper and 1 g dry resin) was placed in a thermostatically controlled bath at 25°C. The mixture was stirred for 1 h at 200 cycles per minute. The aqueous solution was separated by decanting and washed several times with water. This process was repeated three times using the same resin and taking a copper elution (50 ml) of the same initial concentration. The copper was analyzed on the filtrates by atomic absorption spectrophotometry and the copper fixed in the resin is determined from the difference. The maximum capacity for copper is 0.14 g Cu^{2+}/g dry resin (4.5 meq/g dry resin).

3. Copper Elution.

The resin loaded with Cu^{2+} at pH=2 and 3 were contacted with 25 ml H_2SO_4 1M and 2M respectively. The mixture was stirred for 1 h and then the resin was separated by filtration. The percentage of eluted copper was 57.5% and 95.2% respectively.

Retention properties of the N-alkylated polyethyleneimine.

1. pH dependence for uranium.

Uranium solutions were prepared containing 2.0 g/l in uranium (VI) at different pH's (between 0 and 5). The procedure was similar to that used for copper. The uranium was analyzed on the filtrates by spectrophotometry (9). The results are shown in Figure 2.

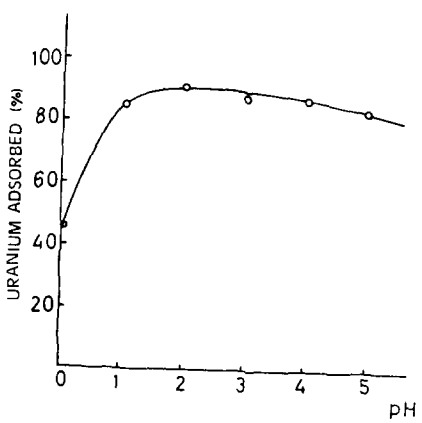

Figure 2.- Percent adsorption of uranium by the N-alkylated resin.

2. Determination of the maximum capacity for uranium.

It was determined at the optimum pH, according to Figure 2. A beaker (containing an aqueous solution at pH=2; 6 g/l in uranium from uranyl acetate and 1 g dry resin) was placed in a thermostatically controlled bath at 25°C. The procedure was similar to that used for copper. The uranium was analyzed on the filtrates after 4 contacts. The value is 0.36 g of uranium per 1 g dry resin (9.1 meq/g dry resin). In addition the values of adsorbed uranium by each one contact were recorded. The results are shown in Table 1.

Table 1.- Percent adsorption of uranium by each contact.

Contact (Nº)	1	2	3	4
Uranium (%)	87.4	22.0	4.7	0.1

At the first contact there is a 87.4% adsorbed uranium and during 4 additional contacts the resin does not adsorb uranium.

3. Studies of selectivity.

1.0 g dry resin was contacted with 50 ml of 2 g/l iron (III) solution at pH=0, 1 and 2. The same procedure was carried out with a solution containing 2g Cu^{2+}/l at pH between 0 and 4. Copper and iron were determined on the filtrates by atomic absorption spectrophotometry. The resin does not retain iron in all the pH ranges assayed. The results for copper are shown in Table 2.-

Table 2.- Percent adsorption of copper for the resin.

Initial pH	0	1	2	3	4
Copper (%)	0.0	2.0	4.5	2.5	8.0

The synthesized resin has a high selectivity for uranium, since it retains copper and iron only in a very low percentage. (See Table 2).

Ion exchange chemistry for copper and uranium.

The crosslinked polyethyleneimine forms a stable complex with copper (II) by the chelate ring formation (10). For the N-alkylated resin, the uranium forms an adduct with the ammonium nitrogen of the resin (11).

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