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Resins with retention properties for heavy metals. Part 4

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SUMMARY

Resins with adsorption properties for copper(II) and uranium(VI) were synthesized by crosslinking of linear polyethyleneimine and subsequent N-alkylation with dimethyl sulphate. The crosslinking agents used are: 1,9-dibromononane and 1,10-dibromodecane. The influence of the pH on the retention, maximum capacity of load and elution were studied. The morphology of the resins has been examined by scanning electron microscopy and their thermal stability by TGA.

INTRODUCTION

Polymer-metal complexes are now of great interest (1-2). The formation of chelates by polymers has widely been used for concentration, separation and extraction of metal-ions (3-4). In regard to the above, polyethyleneimine (PEI) is well known for its ability to complex with metal ions(5-13).

This paper reports the synthesis and retention properties for copper (II), uranium(VI) and iron (III) of resins obtained by crosslinking of linear polyethyleneimine with 1,9-dibromononane, 1,10-dibromodecane and subsequent alkylation with dimethyl sulphate. Analytical assays determined were: pH dependence; maximum capacity of load and elution of the ion. The thermal stability and morphology of the resins has been studied by TGA and scanning electron microscopy respectively.

EXPERIMENTAL PART

Reagents : 2-methyl-2-oxazoline and dimethyl sulphate were purified by distillation. Other chemicals were used without purification.

Homopolymerization: Linear polyethyleneimine was synthesized by cationic polymerization of 2-methyl-2-oxazoline in solution at 70°C using BF_3Et_2O (1 mol%) as initiator. Its molecular weight determined by vapor pressure osmometry was 2095 (14).

Crosslinking of linear polyethyleneimine : This reaction was carried out in heterogeneous phase using Span 65 as emulsifier. The polyethyleneimine: crosslinker derivative ratio was 3:1 (9).

N-alkylation of crosslinked polyethyleneimine : Crosslinked PEI was been N-alkylated with an excess of dimethyl sulphate at 50°C in acetonitrile(10).

Electron micrographs : The surface of the resin was coated with gold for 4 min to obtain approximately 150 A° thickness using an Edwards sputter coater. Electron micrographs were obtained by using a scanning electron

microscope (ETEC Austoscan U-1 Model).

Measurements : Uranium was analyzed on a PMQ II Carl Zeiss spectrophotometer. Iron and copper were analyzed on a Perkin Elmer 306 Atomic absorption spectrometer. Molecular weight was determined on a Knauer Vapor Pressure Osmometer. The analyses were carried out on a Perkin Elmer TGS-1 Thermobalance at a heating rate of 10°C min^{-1}. About 60 mg of the compound were heated to various temperatures. The weight loss at different temperatures were calculated from the respective TGA curves.

RESULTS AND DISCUSSION

Linear polyethyleneimine was synthesized by ring opening polymerization of 2-methyl-2-oxazoline in acetonitrile using BF_3Et_2O (1 mol%) as initiator and subsequent basic hydrolysis.

To obtain insoluble resins the linear PEI was crosslinked with dibromoalkanes and these subsequently were N-alkylated with dimethyl sulphate.

Retention properties of crosslinked polyethyleneimine.

pH dependence for copper.

Ion solution was prepared by dissolving 1.0 g per liter of copper from copper sulphate pentahydrate in water at the corresponding pH. Ten ml of the solution were mixed with constant stirring. Copper analyses were carried out by atomic absorption spectrometry. Results are summarized on Table 1.

Table 1.- Percent adsorption of copper.

Resin	pH				
	0	1	2	3	4
IML-2	0.0	1.0	13.0	32.3	22.7
IML-2M	0.0	0.0	0.5	6.2	0.0
IML-3	0.0	0.0	19.6	27.2	26.0
IML-3M	0.8	0.8	3.2	15.3	15.8

None of the resins retain copper at pH 0.0 and 1.0. Only the IML-2 resin retained more than 30% copper at pH=3.0.

pH dependence for uranium.

An aqueous solution containing 1.0 g/l in uranium (from uranyl acetate) was prepared. Ten ml of this solution was contacted with 0.1 g of dry resin for 1 h. Uranium analysis was performed by a spectrophotometric method (15).

None of the resins retained above 20% uranium in the pH range assayed. Four resins show similar behaviour with the pH. N-alkylated resins did retain around 5% more uranium than crosslinked resins. The optimum pH for all resins is 1.0.

Table 2.- Percent adsorption of uranium.

Resin	pH				
	0	1	2	3	4
IML-2	22.5	61.4	26.9	16.8	16.1
IML-2M	25.2	64.5	52.5	27.1	25.4
IML-3	31.6	75.9	22.1	22.7	25.4
IML-3M	34.1	85.5	79.0	59.0	52.7

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

One g of dry resin and 100 ml of an aqueous solution of 2.0 g per liter of copper or uranium at the optimum pH were placed in a 250 ml beaker at 25°C. The mixture was shaken for 1 h at 200 cycles per minute. The aqueous solution was decanted from the resin, which was washed several times with water. This process was repeated twice . Ions were analyzed on the filtrates.

Table 3.- Maximum capacity of load.

Resin	meq copper per g dry resin	meq uranium per g dry resin
IML-2	1.0	2.6
IML-2M	-	2.7
IML-3	0.9	2.7
IML-3M	-	4.6

Maximum capacity for copper was not determined for IML-2M and IML-3M since they did not retain copper. In relation to uranium, IML-3M shows a similar maximum capacity as IRA-400, a commercial resin (10).

pH dependence for iron.

One tenth of a gram of dry resin was contacted with 10 ml of an aqueous solution containing 1.0 g per liter ion iron at various pH's between 0 and 2. None of the resins retain iron.

Copper elution.

One tenth of a gram of each loaded resin with copper to maximum capacity and at the optimum pH were contacted in one stage separately with 10 ml of H_2SO_4 1M and 3M and with 0.5M and 1.0M Na_2CO_3 solutions. The resin was separated by filtration and washed.

Table 4.- Percent elution of copper.

Resin	H_2SO_4		Na_2CO_3	
	1M	3M	0.5M	1M
IML-2	79.5	79.5	9.9	2.9
IML-2M	77.2	67.8	2.0	2.0
IML-3	88.3	83.4	2.1	2.3
IML-3M	71.4	69.8	1.0	1.0

Nevertheless, retention of copper is not quantitative (see Table 1, pH=3.0), the elution results show that this ion is better eluted in acid medium.

Uranium elution.

It was performed in a similar way that for copper. Uranium was analyzed by a spectrophotometric method (15).

Table 5.- Percent elution of uranium.

Resin	H_2SO_4		Na_2CO_3	
	1M	3M	0.5M	1M
IML-2	82.0	85.3	71.8	88.3
IML-2M	74.3	72.8	74.7	54.8
IML-3	33.6	46.4	64.5	69.0
IML-3M	61.2	62.1	54.9	47.7

Only the IML-3 resin exhibited a medium effect. None of the resins show a significant effect relative to the H_2SO_4 or Na_2CO_3 concentration.

According to the earlier results, the resins show a selective pH range between 0 and 1. At pH=2 and 3 retention of copper and uranium occurs. In this case it would be possible to separate these ions by elution since in basic medium copper is not eluted significatively and uranium is eluted above 50% in all cases.

Thermal stability.

All resins are stable till 140°C. IML-2 is stable till 140°C, but up to 400°C it looses 85%. IML-3 does not loose weight till 150°C and then it looses a 70% up to 400°C. N-alkylated resins IML-2M and IML-3M show a similar behaviour. IML-2M is stable till 150°C and at 400°C it looses 58%. IML-3M starts to loose weight from 160°C. At 400°C it looses 43% of weight (see Fig.1).

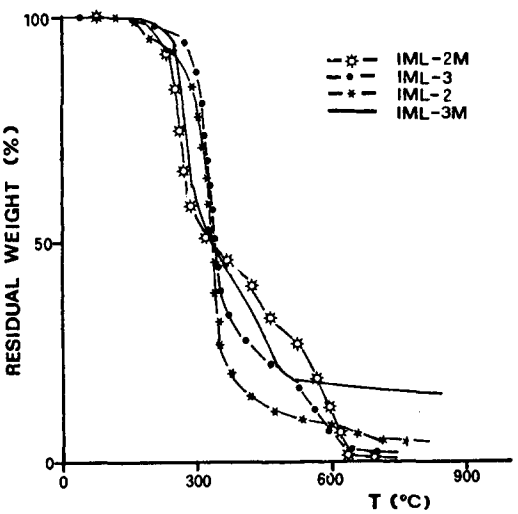

Figure 1.- Thermograms of resin IML-2 (—*—) IML-2M(—☼—) IML-3 (—•—) and IML-3M(———)

Electron microphaphs.

Figures 2 and 3 show the electron micrographs of unloaded resins.

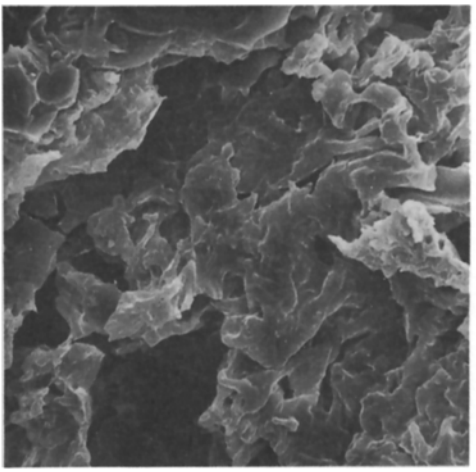

Figure 2. Resin IML-2. Unloaded 800x

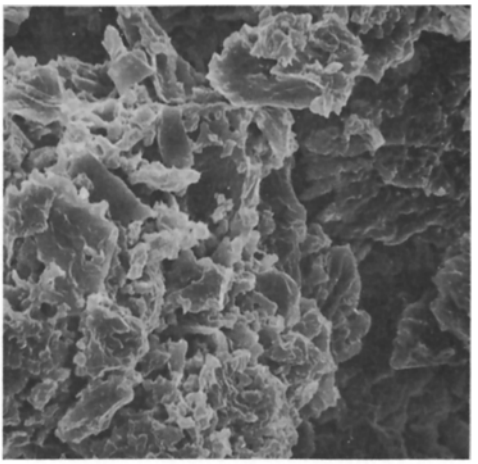

Figure 3. Resin IML-3. Unloaded 800x

The resins show an irregular craked surface with holes and fissures.

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