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Weak and strong basic resins for uranium recovery
Part 6

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SUMMARY

Resins were synthesized by crosslinking of linear polyethyleneimine and subsequent N-methylation. The retention properties of these resins, for copper (pH=0 to 4); for uranium (pH=0 to 3) and for iron (pH=0 to 2) were studied. The maximum capacity of adsorption for uranium and the elution of uranium with sulphuric acid and sodium carbonate were determined. The resins, in general, do not retain iron. The thermal stability was also studied.

INTRODUCTION

Polymer-metal complexes are of great current interest (1,2). The formation of chelates and adducts by polymer has widely been used for concentration, separation and extraction of metal ions (3,4). Polyethyleneimine (PEI) is known to complex with heavy metals (5-8). In order to utilize this polymer as an adsorbent for specific metal ions in aqueous solution, it is necesary to make the polymer insoluble. For this purpose the water-soluble polymer is crosslinked to give water-insoluble product. PEI crosslinked with dibromoethane (5) and dichloroethane (6) has been studied for their ability to bind metal ions such as Ni^{2+}, Cu^{2+}, Co^{2+}

This communication presents the preparation of resins prepared by crosslinking of linear PEI (LPEI) with 1,3-dibromo-2-propanol; 1,4-dibromo-2,3-butanedione followed by N-methylation; the adsortion properties for copper, iron, and uranium; elution assays for uranium; and thermal stability properties.

EXPERIMENTAL PART.

Materials : All the chemicals used were chemically pure. Acetonitrile was purified by distillation over P_2O_5. Dymethyl sulphate was distilled. 2-Methyl-2-oxazoline was purified by distillation from KOH.

Synthesis of Linear Polyethyleneimine (LPEI) . It was obtained by cationic polymerization in CH_3CN of 2-methyl-2-oxazoline and subsequent basic hydrolisis (9).

Crosslinking of linear polyethyleneimine . It was carried out in heterogeneous phase using Span 65 as emulsifier. The ratio LPEI/crosslinking agents was 3:1 (7). All the resins are insoluble in water.

N-Methylation of crosslinked resin . It was carried out with an excess of dimethyl sulphate.

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 thermal stability was studied by a Perkin Elmer TGS-1 Thermobalance. Heating rate 10°/min.

RESULTS AND DISCUSSION

The LPEI was crosslinked with 1,3-dibromo-2-propanol; and 1,4-dibromo-2,3-butanedione and subsequently these resins were N-methylated with dimethyl sulphate (See Table 1). All the resins are totally insoluble in water.

Table 1.- Dibromo-crosslinking agents and symbols of the resins.

Crosslinker	Name	
	Crosslinked Resin	N-Methylated Resin
1,3-dibromo-2-propanol	IML-4	IML-4M
1,4-dibromo-2,3-butanedione	IML-8	IML-8M

Adsorption Properties for Cu^{++}, Fe^{++}, UO_2^{++} *(Batch Method)*

The adsorption of these ions was analyzed as follows: A mixture of 0.1 g of the resin and 50 ml if an aqueous solution containing 1 g/l in Cu^{++} or Fe^{++} or UO_2^{++} were shaken by 2 h. The adsorption experiments were carried out in the pH range 0 to 4 for copper and uranium, and in the pH range 0 to 2 for iron.

The resin was filtered and the ions was analyzed in the filtrates. The results are summarized in Tables 2 and 3.

Table 2.- pH influence on copper adsorption(in percentage).

Resin	pH				
	0	1	2	3	4
IML-4	0.0	2.0	78.0	77.0	82.0
IML-4M	2.0	32.0	21.0	33.0	36.0
IML-8	3.0	3.0	29.0	69.0	66.0
IML-8M	7.0	12.0	16.0	14.0	13.0

Table 3.- pH influence on uranium adsorption (in percentage).

Resin	pH			
	0	1	2	3
IML-4	36.7	61.4	89.0	93.4
IML-4M	36.2	58.6	84.6	78.8
IML-8	28.1	52.0	91.9	96.4
IML-8M	29.7	54.9	84.8	79.8
IRA-400	14.2	31.9	70.9	28.5

IML-4 and IML-8 resins adsorb copper above 60% at pH 3.0 and lower than 4% at pH 0.0 and 1.0. This behaviour is very important as is possible to recover the resin by changing the pH. In respect to uranium, all the resins adsorb this ion in the pH range assayed. At pH=2.0, the four resins adsorb above 80% uranium. The high adsorption capacity for uranium may be due to the presence of the tertiary amine and ammonium groups which favour the adsorption of uranium. All resins show a better adsorption behaviour than IRA-400 a commercial resin under these experimental conditions.

Maximum capacity of adsorption for uranium . This parameter was determined at pH=2.0 similarly to the pH influence on adsorption. In this case three contacts were carried out. Uranium was analyzed in the filtrates by spectrophotometry. The results are summarized in Table 4.

Table 4.- Maximum uranium adsorption capacity.

Resin	IML-4	IML-4M	IML-8	IML-8M	IRA-400
(meq/g)	4.5	5.6	3.2	4.6	6.7

Uranium elution.

Adsorbed uranium was eluted by shaking 0.1 g of the resin with 50 ml of an aqueous solution of sulphuric acid or sodium carbonate at different concentrations. The adsorbed uranium was determined in the filtrates. See Tables 5 and 6.

Table 5.- Uranium elution with sulphuric acid (in percentage).

Resin	H_2SO_4			
	1.0M	2.0M	3.0M	4.0M
IML-4	48.6	54.9	60.3	61.3
IML-4M	38.0	37.6	37.9	30.8
IML-8	47.9	54.8	56.4	56.6
IML-8M	43.2	56.4	57.4	61.5
IRA-400	73.0	86.7	91.7	93.7

Table 6.- Uranium elution with sodium carbonate (in percentage).

Resin	Na_2CO_3			
	0.25M	0.50M	0.75M	1.00M
IML-4	86.0	84.1	84.3	81.6
IML-4M	47.9	54.8	56.4	56.6
IML-8	99.0	99.0	99.0	99.0
IML-8M	87.8	84.8	87.0	87.5
IRA-400	47.0	53.5	56.5	72.3

Uranium is better eluted in basic medium than in acid medium. In basic medium a more stable complex carbonate $[UO_2(CO_3)_3]^{4-}$ is probably formed. The resin IML-8 which adsorbs above 80% of uranium at pH=2.0 after one contact is completely recovered by 0.25M Na_2CO_3 after one contact. The resin IML-4M shows in basic medium a similar elution behaviour to IRA-400 resin, up to 0.75M.

Thermal Stability.

All the resins loose only a weight up to 200°C. The resin IML-8M is more stable than IRA-400. On the other hand, the N-methylated resins are also more stable than the crosslinked resins (See Table 7).

Table 7.- Thermogravimetric analyses of the crosslinked and N-methylated Resins.

Resin	weight loss at various temperatures (%)				
	100°C	200°C	300°C	400°C	500°C
IML-4	0.0	2.5	10.0	88.5	92.5
IML-4M	0.0	1.9	27.0	51.9	74.1
IML-8	0.0	3.3	12.3	47.2	61.3
IML-8M	0.0	0.0	7.4	13.4	18.5
IRA-400	0.0	7.4	20.0	36.8	68.4

In addition four resins were synthesized. These shows similar properties to IRA-400 resin. The IML-8 resin adsorbs uranium above 90% at pH=2.0 and it is recovered completely in basic medium . Up to pH=1 essentially no copper is adsorbed. None of the resins adsorb iron.

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