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Functional copolymers with retention properties for heavy metal ions

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SUMMARY

Poly (N-phenylmaleimide-*co*-2-methylaziridine); poly [p-methylphenylmaleimide-*co*-1-(2-hydroxyethyl)aziridine]; poly [p-methoxyphenylmaleimide-*co*-1-(2-hydroxyethyl)aziridine] and poly [N-phenylmaleimide-*co*-1-(2-hydroxyethyl) aziridine] were synthesized by spontaneous coplymerization. All the resins were insoluble in water. It was found that the resins with 1-(2-hydroxyethyl)aziridine moiety showed the highest adsorption ability for uranium.

INTRODUCTION

The polymers as metal ion complexing agents have been extensively studied (1-10) and have also been important in solvent extraction chemistry. Thus, principles that are applied in liquid-liquid extraction processes are extrapolated to solid-liquid extraction processes by the synthesis of resins with different ligands. The development of these polymers continue to be a subject of paramount importance, undoubtedly because of their wide application for the separation and monitoring of metal ions. Much of the work on these polymers is concerned with the uptake of metal ions from aqueous solution in the wide 1-10 pH range.

One disadvantage particularly in strong acid media is the instability of most of these resins, specially because the refining of some metals takes place in strong acidic solutions.

In this paper the retention properties for copper, iron and uranium, of the water-insoluble resins by zwitterion copolymerization of N-phenylmaleimide derivatives and aziridine derivatives are reported. Maximum load capacity and elution of the UO_2^{2+} by sulfuric acid and sodium carbonate are discussed.

EXPERIMENTAL PART

Materials: 1-(2-hydroxyethyl)aziridine and 2-methylaziridine were purified by distillation under nitrogen. N-phenylmaleimide, p-methylphenylmaleimide, p-methoxyphenylmaleimide were synthesized by a published method (11). Solvents were purified by the usual methods (12).

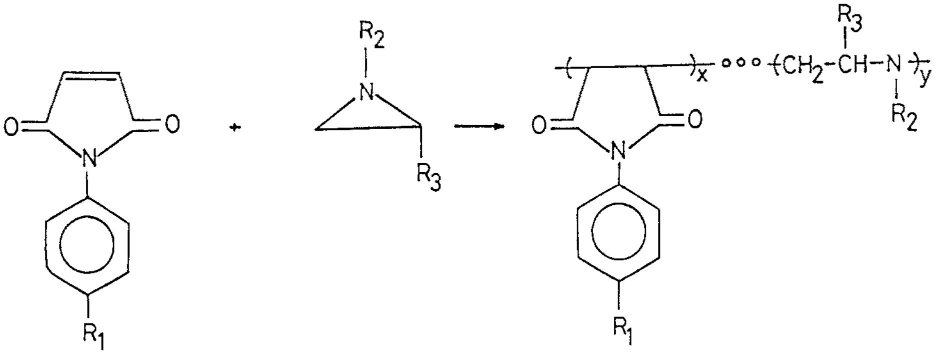
Water-insoluble resins: These materials were synthesized under nitrogen atmosphere according to the pattern of zwitterion copolymerization (13). The copolymers are purified and characterized by elemental analyses, infrared spectroscopy (14).

Measurements: Copper and iron were analyzed on Perkin Elmer 306 atomic absorption spectrophotometer. Uranium was analyzed on a Gilford 250 Spectrophotometer.

RESULTS AND DISCUSSION

The ability of poly(ethyleneimine) to form complexes with metal ions is well known (15-17). Its complexing properties depend essentially on the microstructure. For example, the branched poly(ethyleneimine) has an overall stability constant for divalent ions as Ni, Cu, Zn, Cd, greater than that of linear poly(ethyleneimine) (17). On the other hand, it is well known that the polymers from N-phenylmaleimides showed good physical, mechanical and thermostable properties (18-20).

According to the anterior, water-insoluble resins were synthesized by spontaneous copolymerization (14). N-phenylmaleimide, p-methylphenylmaleimide and p-methoxyphenylmaleimide were used as electrophilic monomers. On the other hand, 1-(2-hydroxyethyl)aziridine and 2-methylaziridine were employed as nucleophilic monomers.



Resin	R_1	R_2	R_3	x/y	Yield (%)
1	-H	-H	$-CH_3$	1.9	54.6
2	$-CH_3$	$-CH_2CH_2OH$	-H	1.3	97.3
3	$-OCH_3$	$-CH_2CH_2OH$	-H	1.5	98.5
4	-H	$-CH_2CH_2OH$	-H	1.0	92.0

Adsorption capacity for metal ions (batch method)

The adsorption of Cu^{2+}, UO_2^{2+} or Fe^{2+} was determined as follows: 0.1 g of the resin was shaken for 2 h in 10 ml of a solution containing 1 g/l Cu^{2+} (from $CuSO_4 \cdot 5H_2O$) or 1 g/l Fe^{2+} (from $FeSO_4 \cdot 7H_2O$), or 1 g/l UO_2^{2+} (from uranylacetate). The experiments were carried out in the pH range 0-4 Cu^{2+} and in the range 0-2 for Fe^{2+}. Then the resin was filtered off. The amount of metal ion adsorbed on the resin was determined in the supernatant by spectrophotometry for uranium (21) and by atomic absorption spectrometry for copper and iron. The results are summarized in Tables 1 and 2.

Table 1. Adsorption percent of copper (II)

	Initial pH				
Resin	0	1	2	3	4
1	15	15	18	42	42
2	0	3	28	35	35
3	9	11	28	32	33
4	6	11	29	30	34

Table 2. Adsorption percent of uranium (VI).

	Initial pH				
Resin	0	1	2	3	4
1	14	21	24	27	27
2	35	44	54	54	52
3	13	33	50	49	49
4	11	20	61	64	69

All the resins were able to take up UO_2^{2+} in pH range examined. However, the adsorption capacity for UO_2^{2+} is higher than that for Cu^{2+}. This effect may be due to the presence of the tertiary amine groups which are assumed to favour the fixation of UO_2^{2+}. All the resins adsorb Cu^{2+} up to pH 2.0 less than 30%. Fe^{2+} was not adsorbed by the resins in the 0-2 pH range.

The resins with 1-(2-hydroxyethyl)aziridine moiety show better retention properties than those with 2-methylaziridine moiety. The differences in the complexing abilities may be attributed to the composition and the structural differences in the repetitive unit. For resin 1 it is possible that crosslinking reaction occurs yielding a resin with different functional groups.

In resins 2-4, moreover of the tertiary amine groups there is a hydroxy group in the side chain which can contribute to the macromolecular binding of metal ions, particularly UO_2^{2+}.

Maximum capacity of load for uranium

The loading capacity for UO_2^{2+} was determined at pH = 3.0 by shaking 1.0 g of the resin for 1 h with 10 ml of 1 g/l solution according to the literature (22). The best resin is 4 which shows a maximum uranium capacity of 4.5 meq/g dry resin.

Elution assays

The UO_2^{2+} adsorbed on the resin 4 was removed by shaking 0.1 g of the resin with 50 ml of H_2SO_4 1 M or sodium carbonate 1 M at room temperature for 1 h. The amount of metal ion desorbed was determined in the filtrates by spectrophotometry. In basic medium, UO_2^{2+} is better eluted (91%) than that in acid medium (43%), due to a more stable complex carbonate $[UO_2(CO_3)_3]^{4-}$ is probably formed.

Assuming that the more stronger ligands are the secondary and tertiary amino groups, the adsorption of copper is probably accompanied with chelate ring formation (22). On the other hand, uranium forms adducts with the different amino groups and does not need the stereochemical arrangements of four nitrogen atoms as copper does (23).

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