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Resins

Phosphonomethylated Polyethylenimine Resin for Recovery of Uranium from Seawater

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SUMMARY

Branched polyethylenimine (BPEI) was crosslinked by a bis-epoxide to give a resin (CL-BPEI), which was further functionalized by phosphorous acid / formaldehyde leading to phosphonomethylated CL-BPEI (PhosCL-BPEI). The latter resin has been found to recover uranium from natural seawater very efficiently but not the former resin; with column method PhosCL-BPEI recovered 85-64 % of uranium in the original seawater at SV = 170 - 680 hr^{-1}. The highest recovery rate obtained so far was 46.8 µg-U/g-resin/6 hr at SV = 680 hr^{-1}. PhosCL-BPEI could be used repeatedly without appreciable decrease of the efficiency. The molar ratio of phosphonomethyl group to amino groups in the resin affects the adsorption ability very much, the adequate P/N ratio being ~0.25. Both PhosCL-BPEI and CL-BPEI showed a large adsorption capacity from an aqueous solution of uranyl ions. It is stressed, however, that the phosphonomethylation of CL-BPEI is very important for the uranium recovery from seawater.

INTRODUCTION

It has been a challenging problem for chemists to recover uranium from natural seawater because uranium is one of important resources to secure energy (1). Seawater contains only a very small amount of uranyl ion UO_2^{2+} (~3.3 ppb) as a mixture of various metal ions like Na^+, Mg^{2+}, Ca^{2+}, K^+, Sr^{2+} etc in large amounts, and hence, a recovery process is required to be efficient and selective for uranium. Several ways have been examined to recover uranium from seawater; adsorption method, floation method, solvent-extraction method, biological concentration method, etc. Among these, the adsorption method is presently considered most promising. There are a variety of inorganic (2) and organic adsorbents (3) developed so far. Followings can be cited as typical organic resins for the uranium recovery from seawater: resins with macrocyclic hexaketones or hexacarboxylic acids (4, 5), amidoxime type resins (6-8), dithiocarbamate type resins (5, 9), resins with dihydroxyphosphino and/or phosphono groups (10), and aminoalkylene phosphoric acid type resins (11).

In order to recover uranium from seawater, the adsorption properties of chelating resins are most important. Very recently, we have shown that resins of phosphonomethylated poly(allylamine) adsorbed uranium from seawater very effectively and the adsorbed uranium was readily desorbed by treating the resins with an aqueous ammonium carbonate solution (12). From the practical viewpoint, polyethylenimine having branched structure (BPEI) is prepared commercially in a larger scale and hence more readily accessible than poly(allylamine). The present paper describes the preparation of

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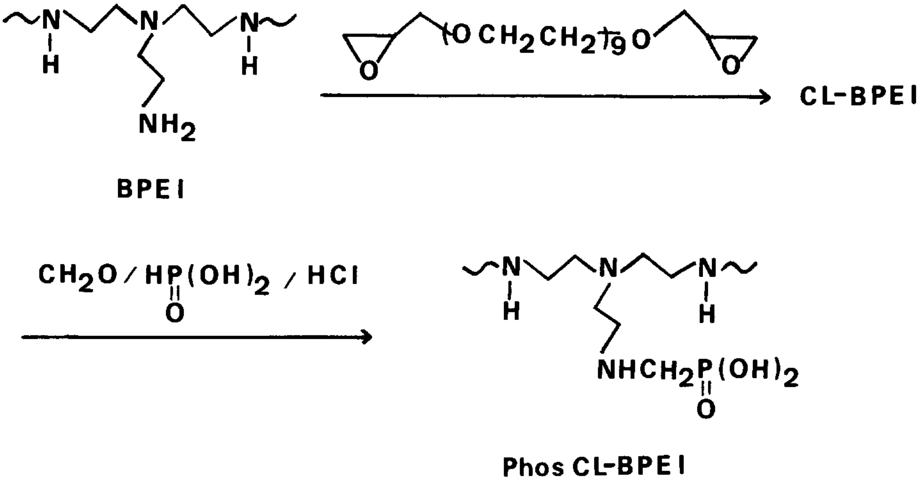
phosphonomethylated BPEI resin and the uranium recovery from seawater by using the resin (13).

RESULTS AND DISCUSSION

Preparation of Resin

Phosphonomethylated BPEI resin (PhosCL-BPEI) has been prepared in a following way; first, BPEI was converted to a resin by crosslinking with a bis-epoxide to give CL-BPEI. Then, CL-BPEI was well swelled in an acidic water and was subjected to the reaction with formaldehyde/phosphorous acid in an aqueous HCl solution (14), giving rise to pale yellow PhosCL-BPEI (One of possible unit structures is given below). The amount of the epoxide for crosslinking was in all cases 5 molar percent for amino groups in BPEI. By varying the amount of $HP(O)(OH)_2$ toward BPEI, the molar ratio of phosphonomethyl group to amino groups (the P/N ratio) in PhosCL-BPEI could be controlled. The P/N ratio was determined by elemental analysis.



Recovery of Uranium from Seawater

PhosCL-BPEI resins were pulverized and the powdery resins of 48-80 mesh were employed. The uranium recovery experiment was carried out with a column method by using a continuous up-flow of seawater. After adsorption, uranyl ions were desorbed by treating three times with 8% $(NH_4)_2CO_3$ aqueous solution. The amount of recovered uranium was determined by spectrophotometry according to the method using Arsenazo III (15, 16) (Table 1).

In all cases except for run no 6 the resin adsorbed uranium very rapidly within a relatively short period of contact, e.g., >50 μg/g-resin/24 hr. It is seen from run no 1 and 2 that the amount of uranium recovered was almost doubled when seawater was allowed to flow for a longer period from 24 hr to 48 hr at the space velocity (SV) of 170 hr^{-1}. The same tendency has been observed at SV = 340 hr^{-1} from 12 hr to 24 hr (run no 3 and 4). Even at a high velocity of SV = 680 hr^{-1} the resin recovered 71% of uranium present in the original seawater (run no 5). CL-BPEI itself (without phosphonomethylation) showed very reduced adsorption abilities (run no 6), indicating that the phosphonomethylation of CL-BPEI is essential to enhance the adsorption properties. As to the uranium adsorption

Table 1
Recovery of Uranium from Seawater by PhosCL-BPEI Resins[a]

Run no	Resin[b]		Seawater (25 °C)			U recovered	
	no	mg	l	hr	SV(hr^{-1})[c]	µg/g-resin	(%)[d]
1	A	250	5	24	170	55.9 / 24 hr	(85)
2	B	125	5	48	170	106 / 48 hr	(80)
3	A	250	5	12	340	42.4 / 12 hr	(64)
4	B	125	5	24	340	90.7 / 24 hr	(69)
5	B	125	2.5	6	680	46.8 / 6 hr	(71)
6	C	250	5	24	170	7.5 / 24 hr	(11)

a) A column used was 8.0 mm in diameter and 60 cm in length.

b) Resin A : P/N ratio of 0.21. Resin B : P/N ratio of 0.23. Resin C : CL-BPEI without phosphonomethylation (P/N ratio=0) obtained by crosslinking of BPEI with 17 molar % of the bis-epoxide. All were powdery resins of 48-80 mesh.

c) Space velocity.

d) The value in the parenthesis corresponds to the percent for the total uranium present in the original seawater.

rate from seawater, the following two examples are to be cited; $\sim$10 µg/g-resin/24 hr for a polystyrene phosphonic acid type resin at SV = 60 hr^{-1} (10), and $\sim$6 µg/ g-resin /24 hr for a polystyrene aminoalkylene phosphonic acid type resin at SV = 50 hr^{-1} (11).

PhosCL-BPEI resin can be used repeatedly. The recovery efficiency did not appreciably decrease after the repeated use, i.e., 50.3 µg/g-resin/24 hr for the fourth use of resin A under the similar experimental conditions of run no 1.

PhosCL-BPEI resin has aminomethylphosphonic acid group as well as amino groups, and hence, is of buffer system. The acid-base balance in the resin may play a very important role for the high rate of uranium adsorption. Figure 1 shows the relationships between the amount of uranium recovered (µg/g-resin/24 hr) and the phosphonic acid group/the amino group molar ratio (P/N ratio) in the resin. It is clear that the adsorption ability is very much dependent on the P/N ratio; the optimum P/N ratio being around 0.25. These observations suggest a strong synergic effect of phosphonic acid and amino groups. The reason for these observations is now under investigation using corresponding soluble (non-crosslinked) polymers.

Adsorption Capacity

PhosCL-BPEI is characterized by a high concentration of functional groups. In principle, phosphonomethyl group is introduced up to the equal amount of N-H group, if the N-H group which reacts with a crosslinking agent is not taken into account. So, following relationships hold; $P/N \leq 1$, $P \times 3 = 0$ and $2 < C/N \leq 3$. Carbon is a main, indispensable atom to constitute a resin form chemically and physically. With this respect, PhosCL-BPEI is the limiting case, in which the content of hetero-atoms of phosphorus, nitrogen, and oxygen toward carbon is conceivably the highest. This leads to the high adsorption capacity of the present resin as shown by exhaustive adsorption experiments. A powdery sample resin was allowed to adsorb uranyl acetate exhaustively in an aqueous solution (500 ppm) with

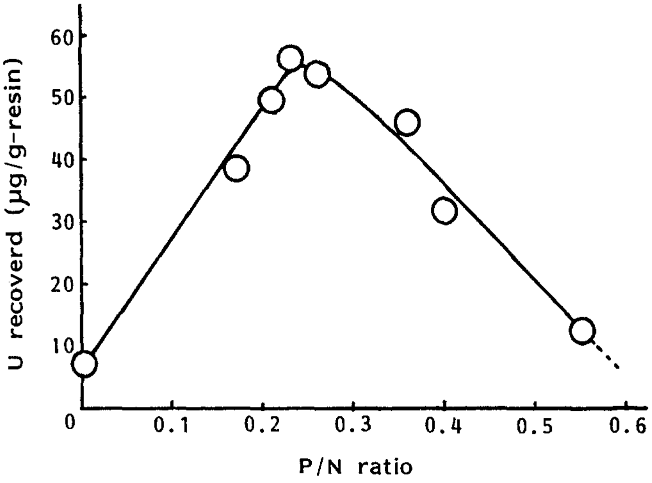


Figure 1. Relationships between the amount of uranium recovered and the P/N ratio in PhosCL-BPEI resins. The amount of resin (48-80 mesh) was 250 mg. 5 1 of seawater was allowed to up-flow at SV = 170 hr^{-1} for 24 hr at 25 °C.

stirring at 25 °C for 72 hr, and then, the adsorbed uranyl ions were desorbed (Table 2). From the color change of the solution and of the resin the adsorption appeared to finish actually within few hours.

Table 2
Exhaustive Adsorption Experiments of Uranyl Ions[a]

Resin[b]	Recovery[c] (%)	Adsorption capacity (g-U/g-resin)
PhosCL-BPEI (resin A)	77	0.51
CL-BPEI	52	0.34

a) Batch method using resin powders stirred in an aqueous uranium acetate solution (500 ppm) at 25 °C for 72 hr.
b) 80-120 mesh.
c) Recovered amount (%) toward that of uranium originally present.

From an aqueous solution containing only uranyl ions in a higher concentration (500 ppm), the adsorption capacity of both PhosCL-BPEI and CL-BPEI was not different so much, the former being 1.5 times larger in capacity than the latter. A polyethylenimine resin also showed a capacity close to CL-BPEI (17). However, the recovery ability of uranium from natural seawater is very much different in these two resins (Table 1), indicating the superior selectivity of PhosCL-BPEI. Therefore, functionalization of CL-BPEI by phosphonomethylation is very important. The similar tendency was already observed for the resins derived from poly(allylamine) (12).

In conclusion, the present resin of PhosCL-BPEI has been found to adsorb uranium very efficiently from natural seawater and the adsorbed uranium was recovered readily by desorption. The resin is characterized by the following points; i) the very rapid adsorption rate, at least the highest of the initial rate ever reported for powdery resins, ii) both chemically and physically stable for the repeated use, iii) a synergic effect of phosphonic acid groups and amino groups for the adsorption, and iv) a high adsorption capacity of uranium due to a high concentration of the functional groups.

We are currently undertaking the exploitation works of new chelating resins for uranium and other heavy metal ions by using several functionalized polyethylenimines (13). Detailed results will appear in a forthcoming full paper.

EXPERIMENTAL PROCEDURES

Preparation of Resins

A mixture of a commercial, 30 weight % aqueous solution of BPEI (mol. wt. = 60,000-80,000, Nakarai Chemical Co. Kyoto) and a crosslinking agent of nonaethylene glycol diglycidyl ether (5 mol % for the unit mol of BPEI, Nagase Chemical Co. Hyōgo, Japan) in water was stirred for 4 hr at room temperature to give jelly like solids (CL-BPEI) quantitatively. CL-BPEI was pulverized and dried at 100 °C in a vacuum oven. Then, CL-BPEI was subjected to phosphonomethylation in conc. HCl aqueous solution by using phosphorous acid (0.5 mol equivalent for the BPEI unit mole in the case of resin A) and 35% formaldehyde aqueous solution (12, 14). The mixture was neutralized by NaOH. The resulting resin (PhosCL-BPEI) was separated and well pulverized. The fraction of 48-80 mesh was obtained by sieving the powdery resins in water and dried in a vacuum oven to give PhosCL-BPEI (resin A).

Adsorption, Desorption and Spectroscopic Determination of Uranium

Seawater used was taken at the Straits of Kanmon in the Inland Sea of Japan. PhosCL-BPEI resin was placed in a glass column (8.0 mm inner diameter, 60 cm height) having glass filter at the lower end. From the bottom of the column, 5.0 l of the seawater was allowed to up-flow at the constant rate at 25 °C. After the adsorption, the resin was separated. The adsorbed uranyl ions were desorbed by treating the resin with 8% $(NH_4)_2CO_3$ aqueous solution at 50 °C for 1 hr. This desorption procedure was repeated three times. Then, the amount of uranyl ions in the combined $(NH_4)_2CO_3$ solution was determined by the Arsenazo III method using spectrophotometry as described previously (12, 15, 16).

Exhaustive Adsorption of Uranyl Ions

PhosCL-BPEI (resin A, 20 mg, 80-120 mesh) in an aqueous $UO_2(OAc)_2 \cdot 2H_2O$ solution (40 ml, 500 ppm) was allowed to stir at 25 °C for 72 hr. After the separation of the resin, adsorbed uranyl ions were desorbed by treating the resin three times with ca. 3 ml of 10% $(NH_4)_2CO_3$ aqueous solution at 50 °C for 1 hr. The spectroscopic analysis (Arsenazo III method) revealed the amount of 10.1 mg of uranium, which corresponds to the adsorption capacity = 0.51 g of U/g-resin. Analogously, CL-BPEI was found to be the adsorption capacity = 0.34 g of U/g-resin (Table 2).

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