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REMOVAL OF ^{243}Am WITH PHENOL BASED RESINS

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ABSTRACT

Long-term radiotoxicity of nuclear waste produced during spent nuclear fuel reprocessing could be reduced if the minor actinides (neptunium, americium and curium) contained within the waste are separated into short-lived radionuclides for their subsequent transmutation or for separate storage. Cross-linked phenolic resins based on different substituted phenol were shown to be very efficient for selective uptake of Eu^{3+} from aqueous solutions containing equal amounts of La^{3+}. In this work, we have prepared and characterized cross-linked phenol based resins to investigate the uptake of ^{243}Am. According to the results obtained for Eu selective extraction and to enhance ^{243}Am sorption, the resins are transformed into their Na^{+}–forms before extraction. The ion selectivi-

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ties of the cross-linked phenol based resins are then compared as a function of the identity of the ion-exchange phenolic matrix. Radiation stability of the resins was studied and each resin was measured for the effect of ionizing radiations with FTIR spectroscopy, moisture regain and ion exchange capacity.

INTRODUCTION

The actinides pose a long-term hazard to the biosphere making their isolation from the environment an important public concern. The separation of actinides from the radioactive waste generated during the nuclear fuel cycle for the separate storage of long-lived minor α emitting actinides (neptunium, americium and curium), or their subsequent transmutation into short-lived radionuclides is a promising strategy for the improvement of the radioactive waste management [1]. For such a strategy, it is necessary to define minor actinide separation methods. The group separation is still one of the most difficult processes. For trivalent actinides Am^{3+} and Cm^{3+}, the main obstacle is the separation from the lanthanides, which are present in major quantities and have similar ionic radii [2] and electronic structures.

The separations of actinide ions are based on the small differences in their ionic radii across the series and/or in the stronger interaction of actinides with soft donor ligands like S or N [3,4]. Indeed, soft donor extractants are known to enhance Ln/An group separations, presumably due to enhanced stability of the actinide extractant complexes (metal-ligand covalent bonding or steric effects) [5].

Organic ligands containing acidic phenol or carboxyl functional groups are known to complex radionuclides under a variety of conditions [6-9]. An improved process for the separation of these ions requires both size-selective complexation and a ligand with the optimum mix of hard and soft donors. Numerous methods based on liquid-liquid extraction [10-12] or solid-liquid extraction [13,14] have been described for effecting this separation [15,16].

The DIAMEX process is currently evaluated for the coextraction of the chemically similar minor actinide(III) and lanthanide(III) ions using hydrophobic malonamides from the highly acidic raffinate issuing from the PUREX process [17]. To achieve the final americium(III) separation from scrubbing solutions, there is a need to develop another efficient process. In a previous paper [18], we demonstrated that phenolic resins are effective in the selective removal of Eu^{3+} from acidic aqueous medium. By combining the formaldehyde condensation of the phenolic compound with 8-hydroxyquinoline, an attempt was made to exploit an expected small increase in covalency in bonding of the actinides [19]. We showed that incorporation of 8-hydroxyquinoline into the phenolic matrix induces an intragroup separation La^{3+}/Eu^{3+} with separation factors from 6 to 10.

The present article deals with the Am^{3+} uptake behavior of synthetic polymers prepared from monomers containing phenolic groups. The effect of introducing 8-hydroxyquinoline into the molecular matrix was studied. The stability of the resins was then determined.

EXPERIMENTAL PROCEDURE

Chemicals And Reagents

Resorcinol, catechol, 8-hydroxyquinoline and formaldehyde (37% aqueous solution) were obtained from Aldrich and used without further purification. The stock solutions of europium were prepared by dissolving the Eu nitrate hexahydrate salt from Aldrich in deionized water.

Synthesis of the Resins

The resins were synthesized by alkaline polycondensation of formaldehyde with phenolic compounds according to references [18,9].

Phenol based resins. A phenolic compound (0.2 M) in 150 mL of 2 N sodium hydroxide was cooled to 0°C; 40 mL of formaldehyde (0.5 M) were then slowly added, keeping the solution at 0°C. The mixture was stirred 1 h at this temperature, left overnight at room temperature and then kept at 100°C in an air oven for curing for 4 days.

Phenol 8-hydroxyquinoline based resins. Formaldehyde (40 mL, 0.5 M) was added to a suspension of 8-hydroxyquinoline (29 g, 0.2 M) in 150 mL of 1.5 N sodium hydroxide. When a deep red solution was obtained, a solution of phenolic compound (0.2 M) in 150 mL of 1.5 N sodium hydroxide was added, followed by 40 mL of formaldehyde (0.5 M). The solution was stirred overnight at room temperature and then kept at 100°C in an air oven for curing for 4 days.

After curing, the resins were crushed, sieved to -80+200 ASTN mesh size particles, washed and conditioned by subjecting them to two 1 N HCl/0.1 N NaOH cycles. The resins were finally converted into acid form and washed thoroughly with water until neutral.

Preparation of the ^{243}Am Stock Solution

Am was separated from U, Np and Pu by anion exchange chromatography and assayed by α spectroscopy. The total α activity was 91% of ^{243}Am and 9% of ^{241}Am + ^{244}Cm. On a mole basis, this is ^{243}Am / (^{243}Am+^{241}Am+^{244}Cm) =

99.7%. Am hydroxide was precipitated and redissolved in order to prepare an initial solution of pH 4 and ionic strengh (NaCl) of about 0.01 M.

Convertion of the Resins into their Na^+–Form

0.05 g of resin into H^+-form was shaken for 2 hours with 10 mL of 1M NaOH. The resin was then filtered and washed with water until neutral.

Analytical Section

FTIR Spectroscopy. FTIR spectra were recorded on a 1600 Perkin-Elmer spectrophotometer. The measurements were done using KBr pellets in the range 4000-400 cm^{-1}.

ICP-AES Measurements. Eu and La concentrations were determined by inductively coupled plasma – atomic emission spectrometry (ICP-AES) with a standard deviation of ± 2%. The system used for this work was the Spectro D system from Spectro Analytical Instruments.

Activity Measurements by α-Spectrometry and β-Counting. The alpha spectrometer used to determine the Am and Cm isotopic composition consisted of a Tennelec 257 alpha spectrometer and a Nucleus PC-based MCA system. Total alpha and beta measurements were carried out by liquid scintillation spectrometry (liquid scintillation counting : LSC) with a Packard Instrument Company 2500 TR liquid scintillation analyser. The instrument was normalized using a NIST-traceable background, H-3 and C-14 standards from Packard Instrument Company.

Characterization of the Resins

Moisture Regain. Moisture regain was determined by heating 0.1 g of resin in an air oven at 100°C for 24 hours. The weight loss gave the percentage of water in the resin.

Ion-Exchange Capacity. For determining the total ion-exchange capacity, 0.25 g of resin in H^+ form, of known moisture content, was equilibrated overnight with 50 mL of 0.1N NaOH solution containing 5% NaCl. The amount of NaOH consumed in the H^+—õNa^+ exchange was determined by titrating the remaining NaOH in the supernatant with 0.1M HCl solution.

Europium Uptake

Eu^{3+} sorption was performed according to a standard procedure previously described [10] in order to get comparable results between various resins. Batch extraction was performed at room temperature. A known amount of resin was equilibrated for 20 hours with a solution of Eu salt. After separation, the concentration of non sorbed Eu^{3+} in solution was determined by ICP-AES. The standard deviation was determined from six independent ion-exchange experiments. The distribution coefficient (D (mL/$g_{(dry)}$)) was calculated as follows:

$$D = \left(\frac{C_i - C_f}{C_f}\right) \times \left(\frac{V}{m}\right) \tag{1}$$

where C_i and C_f are the initial and final concentrations of metal ion in solution, V is the volume of the equilibrated solution (mL) and m is the weight of dry resin (g). The pH of the solutions was determined before extraction.

Americium Uptake

A weighted quantity (~ 0.1 g) of resin was placed in a plastic tube and stirred for 20 hours with 10 mL of Am stock solution. After stirring the resin was allowed to settle in the plastic tube for 1/2 hour for the first assay. A second assay was made after 72 h. Liquid Scintillation Samples of the experiment were taken by pipetting 50 μL of the supernatant and placed into 18 mL of Ecolite scintillation fluid. For each resin two samples, corresponding to 20.5 h and 92 h of contact time, were then counted on the Packard spectrometer.

Irradiation of the Resins

Plugged glass containers filled with ~ 0.5 g of phenolic based resins were all gamma irradiated in the spent fuel pool of the Massachusetts Institute of Technology's nuclear reactor. The position of the samples from the bottom of the spent fuel rack was evaluated and the value of the highest gamma flux in the spent fuel pool was determined to be 475.6 Gy h^{-1}. The absorbed dose was determined after calibration to be 200 kGy. After irradiation, the resins were characterized again for their moisture regain and ion-exchange capacity.

RESULTS AND DISCUSSION

Condensation polymer of resorcinol (RF), catechol (CF) and copolymer of resorcinol and 8- hydroxyquinoline (RQF), catechol and 8- hydroxyquinoline (CQF) (Figure 1) were evaluated at pH 4.

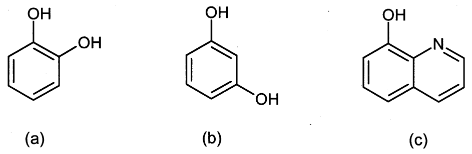

Figure 1. Formo phenolic resins were synthesized with catechol (a) (CF), resorcinol (b) (RF) and copolymers were synthesized with catechol (a) and 8-hydroxyquinoline (c) (CQF) or with resorcinol (b) and 8-hydroxyquinoline (c) (RQF).

Europium Uptake

At pH 4, CF and RF resins in their H^+–form are inefficient for Eu sorption, whereas introduction of 8- hydroxyquinoline in the bulk of the polymer clearly induces an extraction (Table 1). Indeed, at pH 4, no $H^+ \rightarrow zEu^{3+}$ exchange occurs.

Phenolic resins contain the weakly acidic phenolic —OH group (pKa = 9.9) as the functional group responsible for ion exchange. It is expected that complete manifestation of their ion-exchange properties will be possible only when the —OH groups are ionized to the maximum extent, i.e., at high pH where precipitation of the lanthanides occurs [20]. To avoid precipitation of Eu^{3+} and still enhance its sorption, it is necessary to transform the resins into their Na^+–form before extraction. Though the resins in Na^+–form show high affinity for Eu^{3+}, a marked decrease in the compound's ability to extract Eu^{3+} is observed as 8-hydroxyquinoline group is introduced into the matrix of the polymers. The decrease from the parent resins CF and RF is significant, decreasing by several orders of magnitude. Nevertheless, the 8-hydroxyquinoline based resins are most efficient in their Na^+–form than in their H^+–form.

Table 1. Ion-Exchange Capacity and Eu Distribution Coefficients for Substituted Phenol-formaldehyde Resins in their H+–Form and their Na+–Form. C_i Eu^{3+} = 0.005 M, V = 10 mL, pH = 4, m = 0.05 g, T (Shaking) = 20 h

Resin	Ion-Exchange Capacity (meq/$g_{(dry)}$)	D (mL/$g_{(dry)}$) H^+–form	D (mL/$g_{(dry)}$) Na^+–form
CF	8.6	0	6450000
RF	11.5	0	946000
CQF	9.6	12.6	216
RQF	9.9	17.8	411

Americium Uptake

The resins were then applied for the sorption of ^{243}Am. The distribution coefficients were determined for CF, RF and the 8-hydroxyquinoline derivatives at pH 4. The results obtained after 20.5 h and 92 h of contact time are summarized in Table 2.

The resins behave differently with Am^{3+} than with Eu^{3+}. It can be seen by comparing the results in Table 1 to those in Table 2 that $D(Am^{3+})$ is significantly lower for the CF and RF resins that one could expect from Eu^{3+} experiments. Comparable $D(Eu^{3+})$ and $D(Am^{3+})$ are observed for the CQF and RQF resins probably because of the similar affinity of Eu^{3+} and Am^{3+} for N-donor extractants. But, influence of the phenolic compound in the 8-hydroxiquinoline based resins is different for Eu^{3+} than for Am^{3+}. For Eu^{3+}, distribution coefficient with RQF resin is superior to the one obtained with CQF resin when it is the opposite for Am^{3+}. Although the kinetics of the extraction is slower for Am^{3+}, the ability of the resins to remove Am^{3+} from pH 4 solutions is clearly brought to the fore.

The alpha and beta activities in the aqueous solutions were measured before and after extraction and the β-to-α?activity ratios were determined. Table 3 lists the β-to-α?activity ratios obtained after 20.5 h and after 92 of contact time before sampling and counting.

Table 3 shows that in all cases the β-to-α?activity ratio in the solution is larger after 92 h than at 20.5 h of contact. In addition, the CF and RF resins show the highest affinity for ^{243}Am, and for these resins, β-to-α?activity ratios are greater than one after 92 h of contact. An explanation for these results is that ^{239}Np daughters of ^{243}Am bound to the resin are being released back into the solution while the resin continue to extract ^{243}Am from the solution. In opposition, CQF and RQF resins kept in ^{239}Np. Such behavior suggests that the CF and RF resins show an affinity for ^{243}Am(III) over ^{239}Np while 8-hydroxyquinoline based resins show a ^{239}Np affinity

Table 2. ^{243}Am Distribution Coefficient D of ^{243} Am Extracted by Substituted Phenol-Formaldehyde Resins in their Na^+–Form as the Function of Time. Stock Solution ^{243}Am Activity = 1.40 10^8 dpm / mL, V = 10 mL, pH = 4, m = 0.05

Resin	^{243}Am D (mL/$g_{(dry)}$) contact time = 20.5 h	^{243}Am D (mL/$g_{(dry)}$) contact time = 92 h
CF	6659	42809
RF	8012	83560
CQF	272	575
RQF	116	761

Table 3. β-to-α Activity Ratios of the Solution After ^{243}Am Extraction by Substituted Phenol-Formaldehyde Resins in their Na^+–Form

Resin	β-to-α activity ratio contact time = 20.5 h	β-to-α activity ratio Contact time = 92 h
CF	0.98	2.6
RF	0.96	5.7
CQF	0.43	0.67
RQF	0.36	0.69

Radiation Stability of the Resins

Gamma irradiation of ion-exchange resins used for radioactive effluents processing may lead to prejudicial modifications of the molecular structure and macroscopic properties. Phenol formaldehyde polycondensates are known to be quite stable to irradiation by gamma radiation [21,22]. The effects of gamma radiation to phenol based resins were studied by comparing moisture regain, ion-exchange capacity (Table 4) and by FTIR spectra before and after irradiation (Figure 2). The maximum integrated dose was 200 kGy.

The moisture regain is not significantly affected whereas ion-exchange capacities are decreased (Table 4). This decrease can be ascribed to a crosslinking or an oxidative degradation of the polymer matrix. Globally, the pattern and the intensities of the FTIR vibration bands remain very similar before and after irradiation. Figure 2 illustrates how the spectrum changes for RQF resin upon submitting the resin to gamma ray.

Similar features are observed for irradiated RF, CF and CQF resins. After irradiation, four absorption bands occur at 1738, 1720, 1702 and 1686 cm^{-1} are observed, corresponding to carbonyl stretching vibrations of chelated carboxylic acid functions [23]. Nevertheless, the absorption bands intensity is fairly small, confirming the well-known stability of the phenolic polycondensates.

Table 4. Ion-Exchange Capacity and Moisture Regain of Irradiated Resins

Resin	Moisture Regain (%wt/wt)	Ion-Exchange Capacity (meq/$g_{(dry)}$)
CF	20	6.8
RF	33	7.5
CQF	16	5.5
RQF	14	5.8

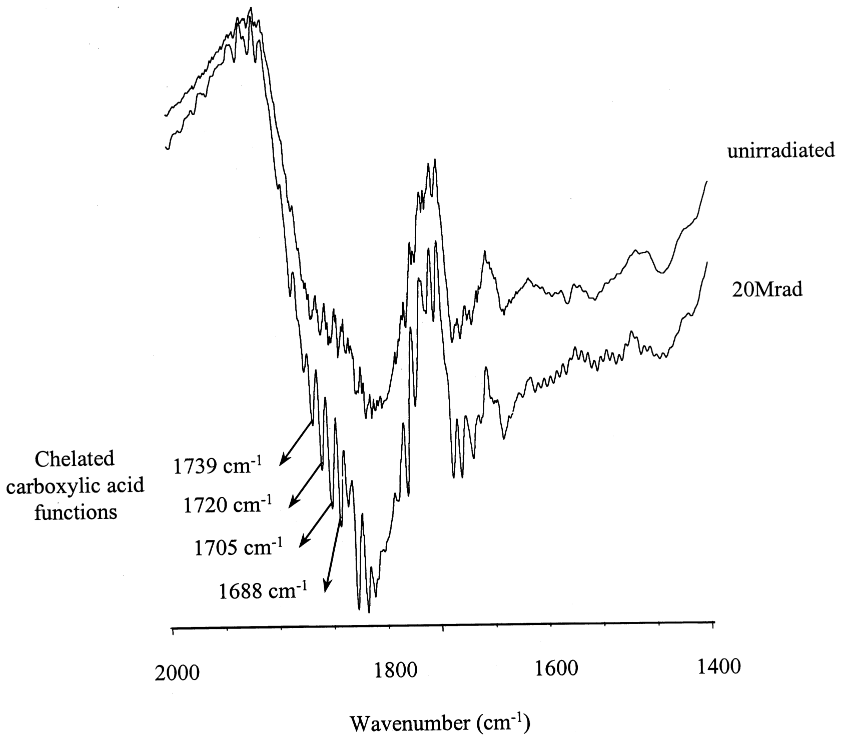

Figure 2. FTIR spectra of the RF resins before and after irradiation.

CONCLUSION

The purpose of this paper was to develop an improved process for ^{243}Am removal. Polymers prepared from simple phenolic monomers were found to have high affinities for Eu(III) and Am(III) of pH 4 solutions. At pH 4, CQF and RQF 8-hydroxyquinoline based resins in their H^+–form are efficient for Eu extraction, whereas CF and RF parent resins need to be transformed ito their Na^+–form to show a high affinity for Eu extraction. CF and RF resins show a Am(III) versus Np(V) selectivity while 8-hydroxyquinoline based resins show an affinity toward Np(V).

The effects of gamma radiations to phenol based resins were studied by comparing moisture regain, ion-exchange capacity and by FTIR spectra before and after irradiation. The maximum integrated dose was 200 kGy. The ion-exchange capacities are by half decreased and low intensity absorption bands of chelated carboxilic acid functions are observed.

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