Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Krishna, M. V. Balarama , Arunachalam, J. , Prabhu, D. R. , Manchanda, V. K. and Kumar, Surendra(2005) 'Removal of ^{106}Ru from Actual Low-Level Radioactive Waste Solutions Using Polyaniline as Anion-Exchanger', Separation Science and Technology, 40: 6, 1313 — 1332
To link to this Article: DOI: 10.1081/SS-200053317
URL: http://dx.doi.org/10.1081/SS-200053317

Separation Science and Technology, 40: 1313–1332, 2005

ISSN 0149-6395 print/1520-5754 online
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Removal of ^{106}Ru from Actual Low-Level Radioactive Waste Solutions Using Polyaniline as Anion-Exchanger

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Abstract: Polyaniline (PANI) was found to exhibit high affinity for ruthenium (Ru) with comparatively easy desorption and recovery. Based on this, both batch and column experiments were carried out to assess the feasibility of using PANI for the removal of radioruthenium (^{106}Ru) in low-level radioactive waste (LLW) streams. Various experimental parameters such as pH, contact time, ratio of PANI:volume of solution, and desorption of Ru from PANI were studied using inactive (spiked with known amount of Ru) and actual LLW solutions. In the case of inactive experiments, inductively coupled plasma-mass spectrometry (ICP-MS) was used for the estimation of ruthenium whereas the high purity Germanium gamma detector (HPGe) detector was used for the assay of radioruthenium in active experiments. Quantitative ($>$95%) removal of Ru occurs at pH $>$ 4.5 with high K_d ($\sim$8300) values in both the cases. Kinetic studies showed that a contact time of 10–15 min was sufficient to reach equilibrium. Column experiments demonstrated that the polyaniline is capable

Received 6 October 2004, Accepted 7 January 2005
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of removing about 29 ± 2 mg/g of Ru from actual LLW solutions, with near complete removal of active ruthenium from treated samples. The sorbed Ru from the column could be leached out using 4 M HCl. The regenerated sorbent exhibited relatively the same initial binding capacity of Ru even after five cycles of reuse. Polyaniline appears very effective for the removal of radioruthenium from actual LLW solutions.

Keywords: ICP-MS, Polyaniline, ^{106}Ru, low-level radioactive waste

1. INTRODUCTION

Environmental impact of the release of toxic and radioactive pollutants from nuclear industries has led to a wide variety of studies on the removal of such pollutants. Low-level radioactive waste (LLW) solutions in large volumes are generated mainly during operation of nuclear reactors and spent fuel reprocessing plants. Also the radiochemical laboratories engaged in research and process control work generate large volumes of radiotoxic liquid wastes (1). These waste streams are contaminated with fission products, ranging in atomic mass from 70 to 160, produced by the ^{235}U fission process (2). Different nuclides of about 40 elements have been observed in spent nuclear fuels including those of ruthenium. The half-lives of radioactive fission products range from fractions of a second to a million years. Some of the most important fission products are ^{95}Zr, ^{103}Ru, ^{106}Ru, ^{129}Te, ^{131}I, ^{140}Ba, ^{144}Ce, ^{90}Sr, and ^{137}Cs. Their percentage yield depends on the mode of fission under specific nuclear reactor conditions. Some specific radioisotopes can be separated from the nuclear fuels as main or by-products and utilized as radiotracers in a variety of chemical and medical studies.

Among the fission products, three platinum group metals (PGMs) Pd(II), Rh(III), and Ru(III) are produced in nuclear reactors (3). Among the PGMs, ruthenium is particularly a critical radionuclide, first because of its high versatility in changing oxidation states (up to VIII as in RuO_4) and in entering many stable complexes and second, because of its easy transfer into various ecosystems (4). Another characteristic is its high refractory character as an element (melting point: 2310°C) in contrast with its tetroxide form (melting point: 26°C). Therefore, radioruthenium produced in a relatively fission yield shows complex behavior in nuclear fuel reprocessing, radioactive waste treatment, environmental samples, and the human body. ^{103}Ru (γ-energy 497 keV) and ^{106}Ru (γ-energies 512.15 keV and 622.37 keV) with a half-life of 40 days and 1 year, respectively, are the most stable among ruthenium radionuclides. Hence, ^{106}Ru can be an important source of radiological risk for humans (at high concentrations damaging lungs and eyes) and animals (5). Because of its complex chemistry and high radioactivity, ^{106}Ru is one of the major radionuclides of concern in aqueous radwastes generated at spent fuel reprocessing plants (6). Based on these facts, the

necessity to develop various effective methodologies for the quantitative removal of radioruthenium from various radioactive streams has grown in recent years.

Selective removal of radionuclides from nuclear waste effluents is an important task in nuclear waste management (7). Radionuclide contaminants are usually removed by ion-exchange, reverse osmosis, microfiltration, precipitation, or flocculation (8). Various methods of isolating and separating of six platinum metals was reported and reviewed (9, 10). Solvent extraction using various extractants, such as 4-octyl aniline was reported to be used widely for the separation of platinum group metals from various aqueous streams (11). Extractants reported for Ru(III) consist of the use of triphenylphosphine (12), tri-butyl phosphate (13), and octyl(phenyl)-N,N-diisobutyl carbamoylmethyl phosphine oxide (CMPO) (14). The lead oxide extraction method; an adsorption method using activated carbon; various ion exchange methods; and precipitation methods by formic acid, hydrazine, hypophosphorous acid, and ascorbic acid, have been reported for the separation of platinum group metals from various waste streams (2, 9, 10).

A wide variety of sorbents are reported in the literature for the uptake of radioruthenium from various radioactive waste streams (15–19). A mixture of zinc metal powder and coconut shell–activated carbon was used for removal of radioruthenium from intermediate level radioactive waste solutions (18). Co-precipitation processes with chemicals like copper sulfate, potassium ferrocyanide, ferric nitrate, barium chloride, and sodium sulfate for the removal of Ru along with Cs and Sr from LLW solutions at pH 8.0 to 8.5, have been extensively studied (20). A co-precipitation method with chitosan was studied for the preconcentration of Ru in water samples (21). Various ion-exchange processes using various organic and inorganic exchangers were developed for the removal of various radionuclides as an alternative to precipitation processes (19). Ion-exchange and elution characteristics of Pd(II) and Ru(III) by several anion exchangers, including Dowex 1×8-400 and IRA-900, in the batch and column experiments were investigated (2). Zeolite Y, erionite, and bentonite were used for the removal of ^{239}Np and ^{235}U fission products from aqueous solutions at different pH conditions (22).

Polyaniline (PANI) is established as a novel material in the field of conducting polymers (23). It is an oxidation product of aniline that was found to have anion exchange properties and can be synthesized electrochemically as a film and chemically as powder (24). The oxidation is carried out using ammonium peroxodisulfate or potassium dichromate in HCl or H_2SO_4 medium. The anions of the medium, i.e., Cl^- or SO_4^{2-} are incorporated in the matrix. These anions can be replaced by another suitable anion upon equilibration. The synthesis and the physicochemical properties of polyaniline and its potential applications in diverse fields were reviewed (23). The advantages of using PANI include the inexpensive starting materials and the simple method of synthesis.

Various studies on the ion-exchange properties of PANI have been reported in the literature. Polyaniline has been used as an anion exchanger for the separation of noble metals Pt, Pd, Ir, and Au, which form stable anionic chloro-complexes prior to their determination in meteorite and rock samples (25). Polyaniline also has been used as the base material for the preparation of a mercury standard for use in neutron activation analysis (26). The anion exchange capability of polyaniline for the estimation of Cd, Cu, Pb, and Sb in the KI medium in biological matrices also was studied (27). Despite the extensive literature on various applications of PANI, to our knowledge, no information on the application of PANI to nuclear waste management is reported.

In this work, the applicability of polyaniline as an ion exchanger, probably for the first time, was examined to remove ^{106}Ru from actual LLW solutions. Both batch and column experiments were carried out to investigate the ion-exchange characteristics of ruthenium on polyaniline. Synthetic inactive solution spiked with Ru as well as actual LLW solution were used to optimize the various experimental parameters such as pH, contact time, ratio of PANI, and volume of solution as well as desorption of Ru from polyaniline. Using this optimal procedure, capacity studies were carried out using breakthrough curves.

2. EXPERIMENTAL

2.1. Instrumentation

A VG Plasma Quad 3 inductively coupled plasma mass spectrometer (ICP-MS) (VG Elemental, Winsford, Cheshire, UK) located in the class 200 area, was used for the determination of inactive ruthenium (inactive experiments). The ICP-MS system is equipped with a Meinhard concentric nebulizer and Scott-type double pass cooled spray chamber. The ion lens voltage settings and other parameters of the instrument are tuned everyday with 10 ng mL^{-1} solution containing Be, Co, In, Pb, and Bi. The data were collected by monitoring m/z 102 and m/z 104 using peak jump mode.

2.2. Reagents and Analyses

Millipore water was used throughout. All the chemicals and reagents used in this work were of analytical grade. A stock solution of Ru(III) was prepared by dissolving 100 mg of ruthenium(III) chloride trihydrate in 10% sub-boiled HCl and diluting it to 100 mL with Millipore water. A working standard solution of Ru was made by diluting the stock solution with an appropriate amount of Millipore water. Other standard solutions of anions Cl^-, NO_3^-, CO_3^-, and SO_4^{2-} used to study the effect of foreign ions were prepared by

dissolving weighed quantities of their sodium salts, and these were diluted to the required concentrations. Actual LLW was used in all the radioactive experiments. The γ-spectra of a sample of LLW solution were recorded with a high-resolution γ-ray spectrometer equipped with p-type coaxial HPGe detector. An HPGe detector coupled to a 4 K multi-channel analyzer was also used for gamma activity measurements. The ^{106}Ru activity originally present in the LLW was used for distribution data measurements. In the experiments on determining the capacity of polyaniline, desired quantities of inactive carriers of Ru were added.

All the pH adjustments were done with solutions of HCl and NaOH. The pH of the solution was recorded using an EMCO digital pH meter, type EE 330 A with ± 0.01 unit accuracy. The mean values of the activity measurements for duplicate samples were used for calculations and the mean values are within 5%–10% error limits. Distribution coefficients and final equilibrium concentrations of Ru were calculated from the mean activity/concentration data.

2.3. Preparation of Polyaniline

The PANI was prepared by the oxidative action of ammonium persulfate on aniline (23). In general, polymerization proceeds via the radical cation of the monomer, which then reacts with a second radical cation of the monomer to give the dimmer by eliminating two protons. At the potential required to oxidize the monomer, the dimer or higher oligomer would also be oxidized and, thus, could react further with radical cation of the monomer to build up the aniline chain. The PANI was synthesized by a method described by Syed and Dinesan (23).

Doubly distilled aniline, 15.35 g (0.33 mol/L), was initially dissolved in 500 mL of 1 mol/L HCl. To this 36.5 g (0.32 mol/L) of ammonium peroxydisulphate was slowly added during stirring. The reaction was allowed to continue for 1.5 h at room temperature. The insoluble black precipitate of polyaniline thus formed was filtered, washed thoroughly with Millipore water followed by acetonitrile (in order to remove soluble species), and dried. The resultant material was ground in a ceramic mortar and sieved to get 100–150 mesh.

3. BATCH EXPERIMENTS

3.1. Inactive Batch Experiments

Preliminary inactive batch experiments were performed with PANI to determine the optimal binding pH and exposure time. In all the batch sorption studies, screw cap centrifuge tubes (50 mL) made of polyacrylic (Tarsons CAT No. 546010), which yielded a quantitative material balance,

were used throughout this work. All the equilibrations were done in a water bath at 25 ± 1°C. In the case of inactive experiments, 10 mL of aqueous solution spiked with 0.1 μg/mL of inactive Ru, was adjusted to the desired pH and equilibrated with 25 mg of PANI powder. After equilibration, the suspension was centrifuged at 3000 rpm for 2 to 3 min and decanted. Each supernatant fraction was subsequently analyzed by ICP-MS for the measurement of residual Ru. All the batch experiments were conducted simultaneously as a function of pH in the range of 1–10. After equilibration the residual content of Ru was determined by ICP-MS.

3.2. Radioactive Batch Experiments

In the case of batch sorption studies with actual LLW solution, 10 mL of LLW solution containing ^{106}Ru were adjusted to the desired pH (in the range of 1–10) and equilibrated with 25 mg of PANI powder. After centrifugation as described previously, at each respective pH, 5 mL aliquots were removed and the residual Ru activity in the solution was determined with the HPGe detector.

3.3. Kinetic Experiments

The time dependency studies in batch mode also were performed using a procedure similarly to that of the pH experiments but at a constant pH of ~5. The equilibration tubes were removed at different time intervals ranging from 5 min to 180 min. Separate sample aliquots were used for each respective pH and time experiment. In both the cases, after equilibration followed by centrifugation, supernatants were removed for residual concentration/activity measurements of Ru.

3.4. Effect of PANI to Inactive/LLW Solution Ratio on Distribution Coefficient Values

For the determination of distribution coefficient (K_d) and percentage removal of Ru, different volumes of inactive/LLW solutions were equilibrated for about 15 min with PANI while keeping the initial pH (~5) of the solution and weight of the PANI (25 mg) constant. Percentage of Ru removed (R) from aqueous/LLW solution and the distribution coefficient K_d, are calculated by:

$$R = \frac{A_i - A_e}{A_i} \times 100 \quad (\%) \tag{1}$$

$$K_d = \frac{A_i - A_e}{A_e} \times \frac{V}{W} \quad (mL/g) \tag{2}$$

A_i = the concentration (μg/mL)/activity (cpm/mL) of Ru in solution initially

A_e = the concentration/activity of Ru in solution after equilibration

V = Volume of the inactive/LLW solution (mL)

W = Weight of the PANI (g)

K_d values are also determined when LLW solution is spiked with varying concentrations of Cl^-, NO_3^-, SO_4^{2-}, and CO_3^{2-} at pH 5.

3.5. Effect of Gamma Irradiation on the Stability of PANI

To investigate the effect of radiation dose on the polymeric properties of PANI, it was irradiated at different doses with gamma rays using a ^{60}Co irradiation chamber at a dose rate of about 0.2 Mrad/h. The maximum dose given was 15 Mrad. At different intervals of irradiation, 25 mg of irradiated PANI was taken out of the irradiation chamber and batch experiments were carried out as described earlier for obtaining distribution coefficients for Ru with irradiated PANI.

4. COLUMN STUDIES

Instead of removing Ru from LLW solution from batch experiments, it would be most useful if the PANI could be packed into a column so that LLW solutions could simply be passed through the column. But restricted flow rates were obtained when the powdered PANI (200–300 mesh) was loaded in the column. Hence, the solutions were pumped through the column with the help of a peristaltic pump.

4.1. Column Experiments

A homemade mini column (5 × 0.4 cm internal diameter) made of polytetrafluoroethene (PTFE) with end caps at both sides was used for column studies. A weighed quantity (about 200 mg) of air-dried PANI was loaded in the column and solutions were passed using a peristaltic pump. The flow rate was initially adjusted to about 2 mL/min. Aqueous feed solution containing 5 μg/mL of Ru as inactive carrier at pH ~5 with a fixed volume interval of 25 mL was passed through the column at a constant flow rate of 2 mL/min. During the course of the column run, the flow was found to fluctuate slightly but was kept at a flow rate of 2 mL/min by adjusting the pump speed. Samples of effluent were collected at regular intervals and analyzed for residual ruthenium by ICP-MS. A similar procedure was used on actual LLW solution spiked with 5 μg/mL of Ru as the inactive carrier to see the

efficacy of PANI for the removal of radioruthenium; effluents were taken periodically and analysed for residual ^{106}Ru activity.

4.2. Breakthrough Capacity Curves

Column experiments were carried out to assess the breakthrough capacity of PANI. During the loading known volumes of inactive feed solution containing a known amount of Ru (5 μg/mL) were passed through the column at an optimized flow rate of 2 mL/min and the effluent fractions of known volumes (25 mL) were collected and analyzed for residual Ru concentration by ICP-MS.

A similar procedure was followed on actual LLW solution spiked with 5 μg/mL Ru as inactive carrier and periodically assayed for ^{106}Ru residual activity in the effluent fractions using an HPGe detector. If the concentration/activity of Ru is not released in the effluent, it was expressed as no breakthrough (BT). Release of concentration/activity of Ru in the effluent with respect to feed expressed in percentage is termed as percentage BT. A breakthrough capacity curve for Ru was obtained by plotting the percentage breakthrough $[(C/C_0) \times 100]$ against volume of aqueous/LLW solution, where C_0 and C are the concentration (μg/mL)/counting rates (cpm/cm^3) of the initial solution and the effluent respectively.

4.3. Elution Studies with HCl

The recovery study of the bound Ru on the column was carried out using different acid strengths of HCl at a flow rate of 2 mL/min. The eluents of HCl were collected at different intervals of effluent volume and the concentration/γ-activity of Ru was measured. A breakthrough elution curve for Ru was obtained by plotting Ru concentration/γ-activity against volume of solution passed. In order to determine the recyclability of the PANI, four sorption-desorption cycles were performed using the same column.

5. RESULTS AND DISCUSSION

The radiochemical composition of a typical LLW solution is given in Table 1. The γ-spectra of a sample of LLW solution recorded with an HPGe detector showed the presence of such major radio contaminants as ^{137}Cs and ^{106}Ru. The γ-spectra of a sample of LLW solution before and after removal recorded with HPGe detector are shown in Fig. 1(a) and Fig. 1(b), respectively.

5.1. Effect of pH on the Removal of Ru

Since LLW solutions are often found at different pH, studies were performed to determine the effects of pH upon Ru binding by PANI. Ruthenium must be

Table 1. Radiochemical composition of the low-level radioactive waste solution

Cs^{137}	125.5 Bq/mL
Ru^{106}	94.5 Bq/mL
Cs^{134}	9.0 Bq/mL
Ce^{144}	31.5 Bq/mL
Nb^{95}	9.5 Bq/mL
Zr^{95}	8.5 Bq/mL
Cl^-	15 ppm
NO_3^-	18 ppm
SO_4^{2-}	14 ppm

Source: Research reactor; pH of the solution: ~6.7; Gross beta-gamma: 389 Bq/mL; Gross alpha: 1.03 Bq/mL; TDS: 1200 ppm.

present in an appropriate oxidation state to ensure strong adsorption onto PANI and the charge of the Ru complex may change depending upon the pH of the solution. As seen in Fig. 2, removal characteristics of Ru by PANI are pH dependent. Figure 2 shows the percentage removal of Ru by PANI as the pH of the inactive aqueous solution containing Ru varied from 2 to 10. The K_d values obtained at different pH conditions are presented in Table 2. At lower pHs, the binding is relatively low (<40%), the percentage removal of Ru by PANI increases from 40% to ~96% when the pH of the solution is raised from 2 to 5. Maximum K_d value of about 8300 was

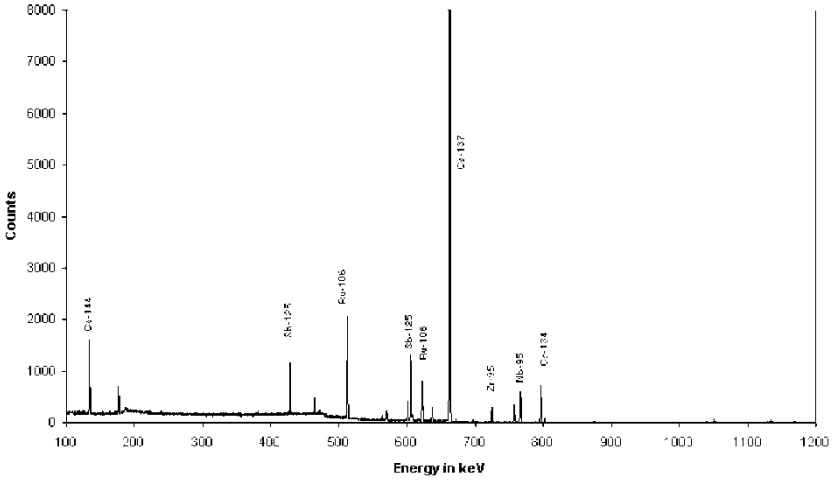

Figure 1a. Gamma ray spectrum of LLW solution.

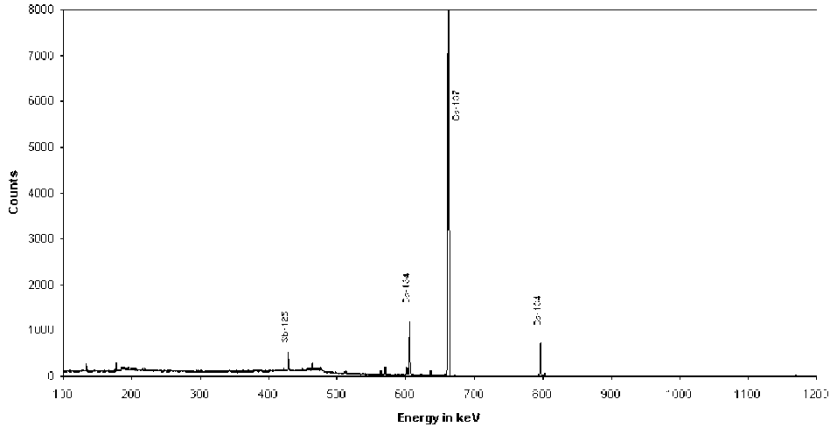

Figure 1b. Gamma ray spectrum of LLW solution after treatment with PANI.

obtained for Ru at pH ~5. However, following pH 5, the percentage of bound Ru remains almost constant. Similar results were obtained when the pH of the LLW solution varied from 2 to 10. But for all subsequent experiments, a pH of ~5 was employed in order to ensure the quantitative removal of ruthenium.

Kumar et al. also observed a decrease in the distribution coefficients of Pd(II), Pt(IV), Ir(IV), and Au(III) with PANI when acidity of the solution increases (25). Studies with other ion exchangers such as Dowex 1 and Amberlite-CG4B also showed similar observations (28, 29).

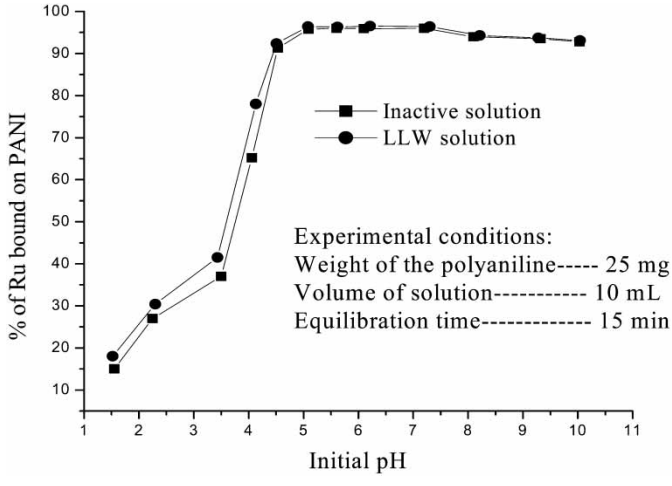

Figure 2. Effect of pH on the removal of Ru.

Table 2. Effect of pH of inactive/LLW solution ratio on the removal of Ru

S. no.	pH of inactive/ LLW solution		% of removal		K_d	
			Inactive solution	LLW solution	Inactive solution	LLW solution
1	1.55	1.52	15.9	17	76	82
2	2.25	2.3	27	30.4	148	175
3	3.5	3.44	40.4	41.5	271	284
4	4.06	4.12	67.4	71.8	827	1,019
5	4.53	4.51	91.4	91.6	4,260	4,371
6	5.09	5.08	95.4	95.5	8,310	8,406
7	5.61	5.62	95.6	95.6	8,609	8,687
8	6.1	6.21	95.4	95.5	8,287	8,397
9	7.24	7.3	95.4	95.5	8,303	8,415
10	8.1	8.21	95.4	95.5	8,341	8,421
11	9.32	9.28	94.8	94.9	7,356	7,484
12	10.03	10.05	94.5	94.6	6,912	7,023

Weight of PANI = 25 mg; Concentration of Ru in inactive solution = 0.1 μg/mL; pH of solution ~5; Volume of inactive/LLW solution = 10 mL; equilibration time = 15 min.

Several researchers have been concerned with the identification of the ruthenium species in aqueous and salt solutions. Olguin et al. showed electrophoregrams for the chemical species of ^{103}Ru at pH values of 1, 3, 5, 7, and 10 (22). The ^{103}Ru was found to be present mainly in the form of a noncharged species (probably RuO_4) and two anionic species, which might be RuO_4OH^- and RuO_4^-. It was reported that the complexes formed in very dilute HCl medium were mainly $Ru(OH)_2Cl_2$ and $Ru(OH)_2Cl_4^{2-}$ (30).

It was also reported that if the fission product solution contains HNO_3, Ru was probably present as a nitrosyl nitrate complex with low NO_3^- content; for instance, $RuNONO_3(OH)_2(H_2O)_2$ as the neutral species and $[RuNO(OH)_4H_2O]^{1-}$ and $[RuNO(OH)_5]^{2-}$ as anionic nitrosyl complexes at a pH of 5 (31).

5.2. Effect of Equilibration Time

In addition to knowing the optimal pH of Ru removal by PANI, it was also necessary to determine the reaction time required for quantitative removal. In the case of inactive experiments, the concentration of ruthenium (0.1 μg/mL) was kept constant. Figure 3 represents the percentage of Ru removal by PANI at different shaking periods. As seen in Fig. 3, because of high D values, the removal of Ru is very rapid since more than 95% removal occurs

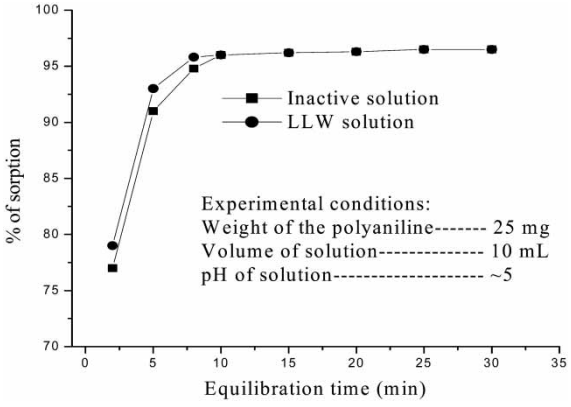

Figure 3. Effect of time on the removal of Ru on polyaniline.

within the first 5 min and reaches equilibrium within 10 min. However, a prolonged shaking for up to 180 min (not shown in the graph) had no significant effect on the removal of Ru. To ensure quantitative removal of Ru, a contact time of 15 min was used for all subsequent experiments with PANI.

5.3. Variation of PANI to Aqueous/LLW Solution Ratio

The K_d and percentage of removal (R%) values (determined in duplicate) for Ru from different ratios of PANI:volume of solution are given in Table 3. The high K_d values ($\sim$8400) were obtained up to a PANI-to-solution ratio

Table 3. Effect of PANI to inactive/LLW solution ratio on the removal of Ru

S. no.	PANI:Volume of inactive/LLW solution	% of removal		K_d	
		Inactive solution	LLW solution	Inactive solution	LLW solution
1	1:200	97.68	97.81	8,430	8,940
2	1:400	95.46	95.56	8,410	8,615
3	1:600	91.3	91.7	6,300	6,650
4	1:800	86.8	87.3	5,260	5,490
5	1:1000	81.13	81.24	4,300	4,330
6	1:1200	68.45	71.5	2,608	2,610
7	1:1600	60.17	60.1	2,417	2,410
8	1:2000	55.55	56.43	2,500	2,590

Concentration of Ru in inactive solution = 0.1 μg/mL; pH of solution $\sim$5; equilibration time = 15 min.

of 1:400 (i.e., 10 mL of solution equilibrated with 25 mg of PANI). The K_d values were found to be about 2500 even with a 1:2000 ratio. As seen from Table 3, it is very clear that PANI has excellent selectivity towards ruthenium.

Based on available information, a number of sorbents and ion exchangers tested for uptake of ruthenium, are compared and listed in Table 4. From the results shown in Table 1, it is seen that the reported sorbents are not significantly effective for ruthenium. Among the sorbents listed in Table 4, coconut-based activated carbon (Hychar SCG7), hydrous ferric oxide loaded on Hychar SCG7 grade active carbon, and iron-activated carbon mixture showed somewhat higher K_d values of 280, 540, and 730 mL/g, respectively.

5.4. Effect of Foreign Anions on the Removal of Ru

The effluents generated in nuclear fuel reprocessing are expected to contain salts of various anions and cations. The similar batch experiments were

Table 4. Comparison of K_d values obtained for various sorbents with PANI

S. no.	Sorbent	Nature of sorbent	K_d (mL/g)	Ref.
1	Hychar/HFO	Hydrous ferric oxide loaded on Hychar SCG7 grade active carbon	340	19
2	A27(MP)/FeFC	Ferric hexacynoferrate(II) loaded on microporus strong base anion exchange resin	15	19
3	TU-RF	Thiourea-resorcinol formaldehyde resin	10	19
4	Hychar SCG7	Coconut-shell activated carbon	280	19
5	AR1(Modenite)	Molecular sieve zeolite	30	19
6	Hychar/Zn	Mixture (1:1) of zinc powder and Hychar SCG7 grade active carbon	160	18
8	Hychar/Fe	Mixture (1:1) of iron powder and Hychar SCG7 grade active carbon	730	19
9	CoFC	Cobalt (II) hexacynoferrate(II)	210	19
10	Dowex 78	Anion-exchanger	~25	2
11	IRN 78	Anion-exchanger	~20	2
12	PANI	Polyaniline-anion exchanger	~8,300	Present work

carried out to see the influence of various foreign anions on the removal of Ru with PANI by adding different amounts of anions, viz., chloride, nitrate, carbonate, and sulfate to the LLW solution at pH ~5 and the results are presented in Table 5. These results indicate that the presence of foreign anions Cl^-, NO_3^-, SO_4^{2-}, and CO_3^{2-} up to a studied concentration of 1 M, did not interfere and, hence, no significant decrease in the D values was observed. Accordingly, ruthenium could be removed quantitatively from LLW solutions using the proposed procedure.

The LLW effluent generated after ion-exchange treatment contains about 20% $NaNO_3$ (20). Thus, it is necessary to know the effect of $NaNO_3$ concentration on the removal of Ru by PANI. Hence, batch experiments were carried out as described earlier to assess the impact of $NaNO_3$ concentration on removal of Ru. The corresponding solutions were prepared by adding the calculated amounts of $NaNO_3$ and then adjusting the pH to ~5. The K_d values for Ru in the presence of varying concentrations of $NaNO_3$ are presented in Table 6. As seen from Table 6, $NaNO_3$ has no significant effect on the removal of Ru.

5.5. Capacity Studies with a Mini-Column Loaded with PANI

After establishing the feasibility of removal of Ru by PANI using batch experiments, further studies with column experiments were carried out to find the capacity of PANI for ruthenium. The packed column with known weight of PANI (200 mg) in dry form was used. As seen from Fig. 4, concentration of Ru in the effluent was close to the background level up to the time when about 800 mL volume of the feed solution were passed. After passing 1000 mL of feed solution, a small decrease in the binding of Ru was

Table 5. Effect of anions on the removal of Ru by PANI

S no.	Con. of anions (M)	$K_{d(Ru)}$			
		Cl^{-1}	NO_3^-	SO_4^{2-}	CO_3^{2-}
1	0	8,371	8,371	8,371	8,371
2	0.01	8,312	8,384	8,310	8,375
3	0.05	8,380	8,281	8,309	8,198
4	0.10	8,352	8,375	8,150	8,318
5	0.30	8,169	8,360	8,299	8,361
6	0.50	8,249	8,314	8,245	8,276
7	0.80	8,350	8,288	8,295	8,297
8	1.00	8,332	8,311	8,290	8,230

Weight of PANI = 25 mg; volume of LLW = 10 mL; equilibration time = 30 min.

Table 6. Effect of $NaNO_3$ concentration on the removal of Ru from LLW solutions

S. no.	Amount of $NaNO_3$ (%)	% of removal	K_d
1	0	95.6	8,371
1	2	95.4	8,298
2	5	95.5	8,171
3	7	95.4	8,327
4	9	95.6	8,190
5	12	95.6	8,293
6	14	95.4	8,210
7	16	95.6	8,295
8	18	96.0	8,274
9	20	96	8,365

Volume of aqueous solution = 10 mL; weight of PANI = 25 mg; Equilibration time = 15 min.

observed and the column reached about 10% BT only after 1200 mL of the feed solution spiked with 5 μg/mL of Ru were passed.

Similar column experiments were carried out by taking actual LLW solution spiked with a known amount of inactive Ru (5 μg/mL) as feed solution. In this case, release of activity in the effluent with respect to feed activity is expressed as percentage breakthrough. Up to a feed volume of 800 mL no BT was found, whereas about 5% BT was obtained after 1000 mL

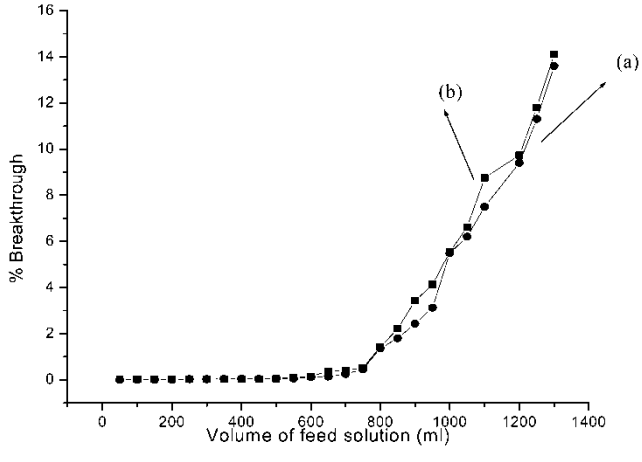

Figure 4. BT curve obtained with PANI and Ru when (a) aqueous solution and (b) actual LLW solution was used as feed solutions.

feed solution had been passed. As seen from Fig. 4, a gradual increase of only about 2% to 3% column breakthrough was found with every 200 mL of feed solution. The column studies were discontinued after attaining about 15% BT.

These studies indicate the possible use of the PANI for the removal of radioruthenium from low-level radioactive waste solutions. From a waste management point of view, it may be advantageous to separate radioruthenium from LLW as it offers an advantage of waste volume reduction.

5.6. Elution Experiments with HCl

The sorption studies of Ru have shown that PANI has a very high affinity for Ru from aqueous streams at pH ~5. But increased acid concentrations favor the removal of Ru from the column, and distribution coefficients fall significantly with an increasing solution of pH. But regeneration of the column is difficult when concentrated acids are used. Hence, the strength of the acid solution used for stripping of bound Ru must be as low as possible. Similarly, to obtain a higher preconcentration factor, volume of the eluent solution must also be as low as possible. Based on these aspects, elution studies were performed in the range of 1.5 to 4 mol l^{-1} of HCl to optimize the eluent concentration. The volume of the eluent solution was fixed at 10, 20, and 30 mL, whereas the flow rate was maintained at 1 mL/min. The results are presented in Table 7. As may be seen from Table 7, elution of Ru was quantitative (>95%) with 20 mL of 4.0 mol l^{-1} HCl whereas lower concentrations of HCl (<2.0 mol l^{-1}) gave only about 70%–85%. To ensure quantitative elution of Ru, 20 mL of 4.0 mol l^{-1} HCl was used as eluent in this work.

After attaining 10% BT loading, the column was washed with the same pH solutions as those of the feed until the effluent activity reached near

Table 7. Effect of volume and concentration of HCl on the recovery of Ru

Volume (mL)	Concentration (mol l^{-1})	Recovery (%)
10	1.5	71
20	1.5	78
30	1.5	86
10	3	82
20	3	88
30	3	93
10	4	90
20	4	98
30	4	99

background level. Subsequently the bound Ru was eluted from the column using 4 M HCl solution (Fig. 5). All the HCl fractions were collected separately and analyzed for Ru concentration/activity. Based on these studies, at 10% BT, the capacity of PANI for Ru was found to be 30 ± 2 mg/g when aqueous solution was used as feed solution whereas it was 29 ± 2 mg/g when actual LLW solution was used as the feed solution.

As described earlier, batch studies were carried out with irradiated PANI and the results are presented in Table 8. As may be seen from Table 8, K_d values were found to be almost constant with PANI exposed at different dose rates. These studies indicated that the PANI is very stable even under radiation conditions.

5.7. Reusability of PANI

In order to verify the effect of the recovery cycle on the reusability of PANI, the column was recycled again by passing fresh feed solution spiked with 5 μg/mL of Ru as inactive carrier at pH ~5 at a flow rate of 2 mL/min. As expected, the percentage breakthrough in the second cycle was similar to that seen in the first cycle. This process of removal and elution cycles was repeated five times. These studies indicate that no percentage breakthrough was found even after 800 mL of feed solution was passed in each cycle. The efficiency of the column loaded with PANI remained relatively steady even after five cycles of 4 M HCl were used for the recovery of Ru.

The fission products ^{144}Ce, ^{95}Zr, ^{95}Nb, and to some extent, ^{125}Sb also were found to be removed by PANI along with ^{106}Ru. But data have not

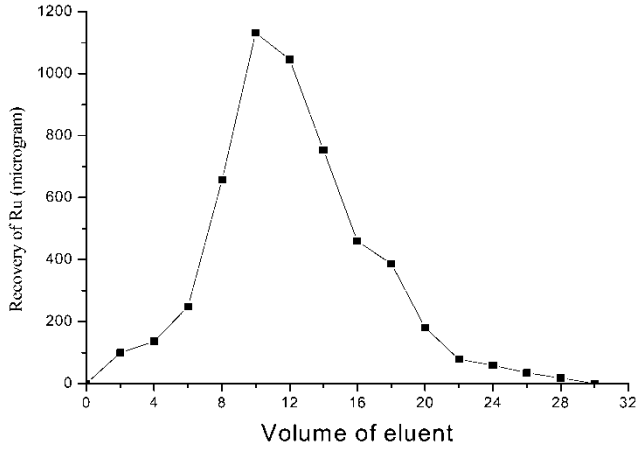

Figure 5. Effect of HCl (4 M) on the elution of Ru from PANI.

Table 8. Effect of gamma radiation on the stability of PANI

S. no.	Total dose (Mrad)	% of removal	K_d
1	0	95.4	8,371
2	0.5	95.3	8,210
3	1.5	95.3	8,180
4	4.3	95.4	8,350
5	5.7	95.4	8,260
6	6.9	95.3	8,149
7	10.2	95.3	8,050
8	11.6	95.4	8,230
9	14.4	95.4	8,310

Weight of irradiated PANI = 25 mg; volume of LLW solution = 10 mL; equilibration time = 15 min.

been collected for those fission products as our study is mainly focused on the removal of ^{106}Ru.

CONCLUSIONS

Applicability of PANI for use as an anion exchanger for the removal of ^{106}Ru from actual LLW solutions was investigated. Using preliminary batch studies with PANI, the operating parameters, in particular, the pH of solution and equilibrium time were optimized. These studies indicate that quantitative removal of Ru occurred at pH $\geq$ 5. The presence of complementary anions such as Cl^-, NO_3^-, SO_4^{2-}, and CO_3^{2-}, even at high concentrations, did not affect the K_d values significantly. Column experiments demonstrated that the PANI was capable of removing considerable amounts of ^{106}Ru from actual LLW solutions under constant flow conditions. The recovery of Ru bound from the column and the regeneration of the column can be achieved by eluting the column with 4 M HCl followed by washing with water. No significant loss on the column capacity for Ru was noticed for three consecutive cycles. Hence, PANI appears promising as an ion-exchange resin for the removal of radioruthenium from actual LLW solutions. Further studies are being planned with PANI for the removal of ^{106}Ru from actual intermediate level radioactive waste (ILW) solutions.

ACKNOWLEDGMENT

The authors thank Dr. T. Mukherjee, Associate Director, Chemistry Group, BARC, and Shri Kanwar Raj, Head, Waste Management Division, BARC,

for their support and encouragement. The help provided by Dr. B. S. Tomar, Head, Actinide Chemistry Section, Radiochemistry Division, BARC, is gratefully acknowledged. The authors thank Shri Sanjiv Kumar for his help during the preparation of polyaniline.

REFERENCES

1. Negri, M.C. and Hinchman, R.R. (2000) Phytoremediation of toxic metals; the use of plants for the treatment of radionuclides, edited by Ilya Raskin and B.D. Ensley, John Wiley & Sons, Inc., New York, 107–150.
2. Lee, S.H. and Chung, H. (2003) Ion-exchange characteristics of Pd and Ru from a simulated radioactive liquid waste. *Sep. Sci. Technol.*, 38 (14): 3459–3472.
3. Naito, K., Matsui, T., and Tanaka, Y. (1986) Recovery of noble metals from insoluble residue of spent fuel. *J. Nucl. Sci. Technol.*, 23 (6): 540–549.
4. Ronneau, C., Cara, J., and Rimski-Korsakov, A. (1995) Oxidation-enhanced emission of Ru from Nuclear fuel. *J. Environ. Radioactivity*, 26: 63–70.
5. Rachubik, J. and Kowalski, B. (2002) Radioruthenium transfer into hen eggs after repeated administration. *Bull. Vet. Inst. Pulawy*, 46: 139–142.
6. Marciniak, M. and Baltrukiewicz, Z. (1989) Evaluation of the doses of ionizing radiation absorbed in organs and the whole body of rats and their offsprings after intravenous contamination of females with ruthenium radioisotopes. *J. Chas', Nukleonika*, 34: 65–76.
7. Lehto, J. and Harjula, R. (1999) Selective separation of radionuclides from nuclear waste solutions using inorganic ion-exchanger. *Radiochimica Acta*, 86: 65–70.
8. Dushenkov, S., Vasudev, D., Kapulnik, Y., Gleba, D., Flesher, D., Ting, K.C., and Ensley, B. (1997) Removal of U from water using terrestrial plants. *Environ. Sci. Technol.*, 31: 3468–3474.
9. Beamish, F.E. (1960) A critical review of methods of isolating and separating the six platinum group metals. *Talanta*, 5: 1.
10. Jensen, G.A., Platt, A.M., Mellinger, G.B., and Bjorklund, W.J. (1984) Recovery of noble metals from fission products. *Nucl. Technol.*, 65: 305.
11. Lokhande, T.N., Kolekar, G.B., Anuse, M.A., and Chavan, M.B. (2000) Extraction of ruthenion (IV) from HCl medium with N-octylaniline and uts determination spectrophotometrically with pyridine-2-thiol. *Sep. Sci. Technol.*, 35 (1): 153–168.
12. Mojski, M. (1980) Extraction of platinum group metals from HCl medium with triphenyl phopshine solution in 1,-dichloroethane. *Talanta*, 27: 7.
13. Rozen, A.M., Kartasheva, N.A., and Nikolotova, Z.N. (1995) *Radiokhimiya*, 37: 232.
14. Mathur, J.N., Murali, M.S., and Natarajan, P.R. (1992) Extraction of actinides and fission products by CMPO from nitric acid media. *Talanta*, 39 (5): 493–496.
15. Siczek, A.A. and Steindler, M.J. (1978) *At. Energy Rev.*, 16: 575.
16. Berak, L., Uher, E., and Marhol, M. (1975) *At. Energy Rev.*, 13: 325.
17. Dyer, A., Keir, D., Hudson, M.J., and Leung, B.K.O. (1984) The removal of ^{106}Ru from simulated liquid nuclear wastes. *J. Chem. Soc., Chem. Commun.*, 1457.
18. Samantha, S.K. (1992) Studies on the removal of ruthenium from radioactive wastes, Nuclear and Radiochemistry Symposium. Andhra University: Visakhapatnam, India.

19. Samantha, S.K. and Theyyunni, T.K. (1994) Removal of radioruthenium from alkaline intermediate level radioactive waste solution: A laboratory investigation. BARC report, BARC/1994/E/012.
20. Kore, S.G., Prasad, V., Singh, U.S., Yeotikar, R.G., Mishra, A., and Ali, S.S. (2002) Removal of Ru along with Cs and Sr from the LLW of reprocessing plant by chemical treatment method, Bhabha Atomic Research Centre (BARC) News letter, Founder's Day Special, Issue No. 225, October 2002, 64–68.
21. Minanisawa, M., Kuroki, H., Arai, N., and Okutani, T. (1999) Coprecipitation of Ru with chitosan and its determination by GFAAS. *Analytica Chimica Acta*, 398: 289–296.
22. Olguin, M.T., Solache-Rios, M., Bosch, P., and Bulian, S. (1996) Sopriton of ^{239}Np and ^{235}U fission products by zeolite. *Sep. Sci. Technol.*, 31 (15): 2021–2044.
23. Syed, A.A. and Dinesan, M. (1991) Polyaniline—A novel material: review. *Talanta*, 38: 815–837.
24. Syed, A.A. and Dinesan, M. (1992) Polyaniline: A conducting polymer as a novel anion-exchange resin. *Analyst*, 117: 61–66.
25. Kumar, S., Verma, R., and Gangadharan, S. (1993) Application of polyaniline as an anion exchanger for the separation of Pd, Ir, Pt and Au prior to their determination by NAA. *Analyst*, 118: 1085–1087.
26. Verma, R., Kumar, S., and Parthasarathy, R. (1997) Polyaniline as a base material for preparation of a mercury standard for use in neutron activation analysis. *J. Radioanl. Nucl. Chem.*, 218 (2): 189–191.
27. Sahayam, A.C. (1998) Determination of Cd, Cu, Pb and Sb in environmental samples by ICP-AES using polyaniline for separation. *Fresenius J. Anal. Chem.*, 362: 285–288.
28. Korkisch, J. and Klakl, H. (1968) Anion exchange behavior of the platinum group metals and gold in hydrochloric acid-organic solvent media. *Talanta*, 15: 339.
29. Kuroda, R., Ishida, K., and Kiriyama, R. (1968) Adsorption behavior of number of metals in HCl on a weakly basic anion-exchange resin. *Anal. Chem.*, 40: 1502.
30. Beamish, F.E. and Van Loon, J.C. (1972) *Recent Advances in the Analytical Chemistry of the Noble Metals*; Pergamon Press: New York, 16.
31. Serrano, J., Granades, F., Bertin, V., and Bulbulian, S. (2002) Speciation of some ^{235}U fission products in nitrate solution and their sorption behavior in thermally treated hydrotalcites. *Sep. Sci. Technol.*, 37 (2): 329–341.