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ORIGINAL PAPER

Extraction–electrodeposition (EX–EL) process for the recovery of palladium from high-level liquid waste

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Abstract Extraction–electrodeposition (EX–EL) process has been developed for the quantitative recovery of palladium from nitric acid medium and fast reactor-simulated high-level liquid waste (FR-S-HLLW). The process exploits some characteristic properties of room temperature ionic liquid, tri-*n*-octylmethylammonium nitrate (TOMAN), for quantitative and favorable recovery of palladium. Extraction of palladium (II) from FR-S-HLLW and nitric acid medium by a solution of 0.5 M TOMAN in chloroform has been studied in detail. More than 60% of palladium was extracted in a single contact of equal volumes of organic and aqueous phases and nearly five contacts were required for quantitative extraction. The electrochemical behavior of palladium (II) present in the organic phase was investigated at stainless steel electrode by cyclic voltammetry. A surge in cathodic current occurring at a potential of –0.5 V (vs. Pd) was due to the reduction of palladium (II) to palladium (0). The kinetics of electrodeposition was followed by the UV–VIS absorption spectrum of palladium present in organic phase and under the given conditions nearly 20 and 35 h were required for the quantitative deposition of palladium from organic phase, which was obtained after extraction of palladium from 4 M nitric acid and FR-S-HLLW, respectively. Decontamination of palladium from other fission products during extraction and electrodeposition was studied and the results are reported in this article.

Keywords Palladium · Extraction · Electrodeposition · Fission products · Room temperature ionic liquid · Tri-*n*-octylmethylammonium nitrate

1 Introduction

Spent nuclear fuel is a valuable resource of man-made noble metals [1]. Significant quantities of platinum group metals (PGMs namely ruthenium, rhodium, and palladium) are formed as by-products of nuclear fission in a nuclear reactor. Most of the fission PGMs are non-radioactive. For example, fission palladium comprises stable isotopes ^{104}Pd (17 wt%), ^{105}Pd (29 wt%), ^{106}Pd (21 wt%), ^{108}Pd (12 wt%), ^{110}Pd (4 wt%), and a radioactive ^{107}Pd (17 wt%) isotope, which has a half-life of 6.5×10^6 y. The intrinsic radioactivity of ^{107}Pd (soft β-emittor with $E_{\max}$ of 35 keV) is very weak and it can be tolerated for many industrial applications.

PUREX process is being adopted for the recovery of uranium and plutonium from spent nuclear fuel [2]. The process involves the dissolution of spent nuclear fuel in nitric acid medium followed by extraction of uranium and plutonium by a solution of 1.1 M tri-*n*-butyl phosphate in *n*-dodecane. The raffinate rejected after the extraction is known as high-level liquid waste (HLLW), which contains ~70% of fission noble metals existing in the form of nitrate and nitrosyl complexes [3]. Presently, there is no commercial process available for the recovery of fission noble metals from HLLW. However, there are several methods and materials reported for the recovery of PGMs from HLLW [3–6]. Among them, solvent extraction and electrochemical procedure are reported as promising methods. The electrochemical method for the separation

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and recovery of palladium is one of the easiest and promising techniques due to its simplicity and accessibility of reduction potential of palladium in nitric acid medium. Besides, this method does not demand the addition of external reagents to HLLW.

Koizumi et al. [7] reported the electrolytic extraction of fission platinoids from nitric acid medium. A recovery of 90, 23, and 10% was reported, respectively, for the deposition of Pd, Rh, and Ru, and the deposition rates were reported to decrease with increase of nitric acid concentration. Kirshin et al. [8] studied the electrolytic recovery of palladium from nitric acid solutions and reported the efficiency of the process in the presence of HNO_3, $NaNO_3$, uranium, and other admixtures. Recently, we have also studied the electrochemical behavior of palladium (II) in fast reactor-simulated high-level liquid waste (FR-S-HLLW) and the effect of various interfering metal ions during recovery of palladium [9]. The study revealed that the palladium (II) in 3–4 M nitric acid medium exists as neutral palladium (II) nitrate species and undergoes an irreversible single step two-electron transfer to metallic palladium at the working electrode. While the palladium nitrate present in nitric acid medium could be quantitatively recovered by electrolysis at −0.5 V (vs. Pd), serious problems were encountered in the presence of ions such as nitrate, iron (II), uranium (IV), silver (I), etc. that were present in FR-S-HLLW during electrolysis. Due to these, the recovery was incomplete and below 40%. The study, therefore, suggested the requirement of other separation methods either independent or coupled with electrochemical method for the quantitative recovery of palladium from HLLW.

We have also developed a new extraction–electrodeposition (EX–EL) process [10, 11] for the separation and recovery of palladium by exploiting the characteristic properties of room temperature ionic liquids (RTILs). RTILs are compounds comprised entirely of ions and molten at temperatures lower than 373 K [12]. The preliminary studies indicated the feasibility of extracting palladium (II) from nitric acid medium by a solution of tri-*n*-octylmethylammonium nitrate (TOMAN) in chloroform followed by direct electrodeposition from loaded organic phase. However, the EX–EL process has not been demonstrated for the simulated HLLW (Table 1) [13] that mimics the HLLW arising from fast reactor fuel reprocessing. Therefore, the aim of the present study was to investigate in detail the electrochemical behavior of palladium (II) in organic phase obtained after extraction from nitric acid and simulated HLLW, coulombic efficiency of the process, scaling-up studies, etc. and to report the feasibility of adopting EX–EL process for the recovery of fission palladium from fast reactor HLLW.

Table 1 Elemental composition of simulated high-level liquid waste (HLLW)

Element	Elements present ($g\ L^{-1}$)
Antimony	0.01
Barium	0.41
Cadmium	0.04
Cerium	0.69
Cesium	1.12
Chromium	0.1
Dysprosium	0.005
Europium	0.31
Gadolinium	0.07
Iron	0.5
Lanthanum[a]	0.48
Molybdenum	1.09
Neodymium	1.13
Nickel	0.1
Palladium	0.6
Promethium	0.34
Promethium	0.05
Rhodium	0.26
Rubidium	0.06
Ruthenium	0.81
Samarium	0.05
Selenium	0.01
Silver	0.13
Sodium	3
Strontium	0.14
Technetium	0.26
Tellurium	0.16
Terbium	0.01
Tin	0.02
Uranium	2.64
Yttrium	0.08
Zirconium	0.89
Acidity (M)	4

It is based on the HLLW arising from fast reactor fuel [13] that has reached a burn-up of 85,000 MW d Te^{-1}

Tc, Mo not added, *Co* added for Ni, *Ru, Rh, Rb* added for Pd, *Sn, Sb, Te* not added due to poor solubility

[a] *La* added for Y, Pm, Te, and Dy

2 Experimental

2.1 Materials

All the chemicals and materials used in the study were of analytical grade. Tri-*n*-octylmethylammonium chloride (TOMAC) was procured from ACROS and converted to nitrate form (TOMAN) by equilibrating 1 M TOMAC solution in benzene with 4 M $NaNO_3$. The organic phase was separated and equilibrated again with a fresh solution of 4 M $NaNO_3$. This procedure was repeated four times. The organic phase was then separated and scrubbed with water. Benzene present in the organic phase was distilled off using a rotary evaporator. The chemical composition of FR-S-HLLW is presented in Table 1 [13].

2.2 Solvent extraction studies

All the solvent extraction studies were performed at 298 K (using a constant temperature water bath) with organic (100 mL) to aqueous (100 mL) phase ratio of unity. The initial concentration of palladium in aqueous phase was fixed at 0.6 g L^{-1}, which corresponds to the concentration of palladium present in HLLW arising from fast reactor fuel reprocessing (Table 1). The organic phase was pre-equilibrated with desired concentration of nitric acid. The extraction experiments involved equilibration of organic phase (0.5 M TOMAN/$CHCl_3$) with palladium nitrate solution in desired concentration of nitric acid or FR-S-HLLW for 1 h (3 min are sufficient for equilibration). The concentration of palladium present in aqueous phase before and after the equilibration was estimated by a spectrophotometric method using Arsenazo (III) as coloring agent [14] or by ICP-OES. The amount of palladium extracted into organic phase was determined by using Eq. 1.

$$\text{Palladium extraction}\,(\%) = \left(1 - \frac{[\mathrm{Pd}]^{\mathrm{fin.}}_{\mathrm{aq.}}}{[\mathrm{Pd}]^{\mathrm{ini.}}_{\mathrm{aq.}}}\right) \times 100 \qquad (1)$$

where $[\mathrm{Pd}]^{\mathrm{ini.}}_{\mathrm{aq.}}$ and $[\mathrm{Pd}]^{\mathrm{fin.}}_{\mathrm{aq.}}$ are the concentration of palladium present in aqueous phase before and after the extraction. For quantitative extraction, the aqueous phase obtained after the first contact was equilibrated again with a fresh solution of organic phase and the percentage of extraction was determined as above.

2.3 Cyclic voltammetric studies

The cyclic voltammetry of organic phase (5 mL) was recorded at stainless steel working electrode at 298 K. Platinum wire and palladium wire were used as counter and quasi-reference electrodes, respectively. All the electrochemical investigations were carried out using Autolab (PGSTAT-030) equipped with an IF 030 interface.

2.4 Electrodeposition studies

Electrolysis experiments were performed at a constant potential of −1.6 V (vs. Pd) at 298 K. The electrolytic cell consisted of a stainless steel working electrode (6 cm^2) and platinum foil counter electrode (2 cm^2). Palladium wire was used as quasi-reference electrode. The electrochemical cell had a single compartment and all the electrodes were placed in the same compartment. The working electrode was replaced by a fresh electrode every 10 h. Electrolysis was stopped when the current flowing through the electrodeposition cell reached a steady-minimum value. The electrodes were then removed from the cell, washed with acetone and distilled water. The electrodes were dried at 373 K and weighed to determine the amount of palladium deposited during electrolysis. The product was characterized by X-ray diffraction.

2.5 Kinetics of electrodeposition

The experiments involved electrolysis of palladium present in organic phase (100 mL) extracted either from 4.0 M nitric acid medium or from FR-S-HLLW. The electrolysis was conducted at a constant potential of −1.6 V (vs. Pd) using stainless steel working electrode (6 cm^2) for several hours until the recovery was quantitative. At various time intervals, a known amount of aliquot (0.5 mL) was drawn from organic phase and diluted to 10 mL with 0.5 M TOMAN/$CHCl_3$, which was pre-equilibrated with 4 M nitric acid. The rate of deposition was followed by monitoring the UV–VIS absorption spectrum of palladium nitrate in organic phase that gives an absorption maximum around 425 nm as shown in Fig. 1. The calibration plot (inset in Fig. 1), was obtained by extracting the known amount of palladium (II) from 4.0 M nitric acid medium by 0.5 M TOMAN/$CHCl_3$. The organic phase was then diluted with appropriate addition of 0.5 M TOMAN/$CHCl_3$, which was pre-equilibrated with 4.0 M nitric acid. It is

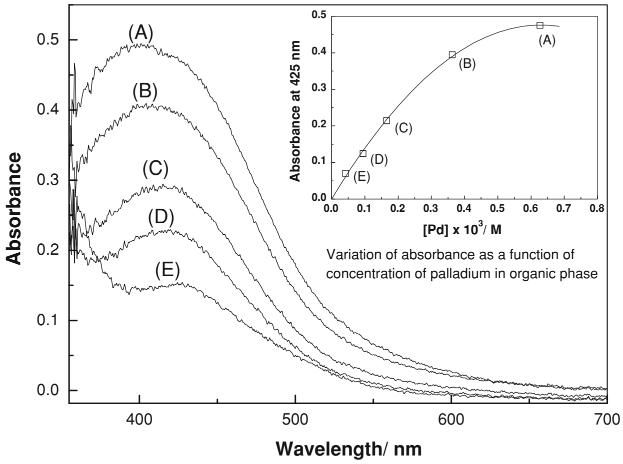

Fig. 1 Comparison of UV–VIS absorption spectrum of palladium nitrate in 0.5 M TOMAN/$CHCl_3$. The concentration of palladium is 0.627 mM (A), 0.363 mM (B), 0.165 mM (C), 0.0949 mM (D), and 0.0423 mM (E). *Inset*: Calibration plot. Variation in the absorbance (at 425 nm) of palladium nitrate as a function of its concentration in organic phase

observed from the Fig. 1 that there is a shift in the λ_{max} with the concentration of palladium (II) in organic phase. Figure 1 (inset) also shows the plot of absorbance as a function of palladium concentration in organic phase. The data were deviating significantly from linear regression for constructing a calibration plot. However, the data were fitted by non-linear equation of the form $Y = A + BX + CX^2$, where $A = 5.71 \times 10^{-4}$, $B = 1.51 \times 10^3$ and $C = -1.19 \times 10^6$. Using this equation, the concentration of palladium remaining in the organic phase during the course of electrolysis (both for nitric acid medium and FR-S-HLLW) was determined and presented in this article. Alternatively, the rate of deposition was also confirmed by weighing the amount of palladium deposited after every 10 h.

2.6 Decontamination studies

The decontamination of fission products during extraction and electrodeposition was studied by equilibrating 100 mL of 0.5 M TOMAN/$CHCl_3$ phase with 100 mL of FR-S-HLLW spiked with actual HLLW arising from fast reactor fuel reprocessing (burn-up 100,000 MW d Te^{-1}). The total β, γ-radioactivities of organic and aqueous phases were measured by using a well-type NaI (Tl) scintillation counter. The organic phase (100 mL) was then subjected to electrolysis at stainless steel electrode. At various intervals of time, a known amount of the aliquot (0.2 mL) from organic phase was drawn and the radioactivity was measured. The decontamination factor was determined from the ratio of initial radioactivity and the radioactivity present in the product.

3 Results and discussion

3.1 Extraction studies

The extraction behavior of palladium (II) from nitric acid medium by a solution of TOMAN in $CHCl_3$ was reported previously [10]. The distribution ratio was reported to increase with increase in the concentration of nitric acid and reached a maximum when the concentration of nitric acid was 1.0 M. Based on those results, the extraction of palladium (II) from 1.0 M nitric acid medium by 0.5 M TOMAN/$CHCl_3$ was performed in a 200 mL scale (100 mL organic: 100 mL aqueous). The results are tabulated in Table 2. Nearly 70% extraction is observed in a single contact and quantitative extraction is achieved in four contacts. Since the concentration of nitric acid in HLLW ranges from 3 to 4 M, the extraction of palladium was also performed from 4.0 M nitric acid medium. The results, shown in Table 2, also indicate that quantitative extraction is achieved in five to six contacts. Similarly, 55–60% of palladium is extracted in a single contact from FR-S-HLLW.

Table 2 Extraction of palladium (II) from nitric acid and FR-S-HLLW medium by 0.5 M TOMAN/$CHCl_3$

[HNO_3]	Contact	Cumulative extraction (%)
1 M HNO_3	Contact 1	74.5
	Contact 2	93.4
	Contact 3	98.7
	Contact 4	99.6
4 M HNO_3	Contact 1	61.0
	Contact 2	90.6
	Contact 3	97.8
	Contact 4	99.2
	Contact 5	99.9
FR-S-HLLW	Contact 1	55.0
	Contact 2	87.2
	Contact 3	92.5
	Contact 4	98.6
	Contact 5	99.1
FR-S-HLLW (500 mL)	Contact 1	60.0

Organic: aqueous (100 mL:100 mL), $T = 298$ K

3.2 Cyclic voltammetry

Figure 2 shows the cyclic voltammogram of palladium (II) in the extracted organic phase (first contact) recorded at stainless steel electrode at 298 K. The onset of reduction

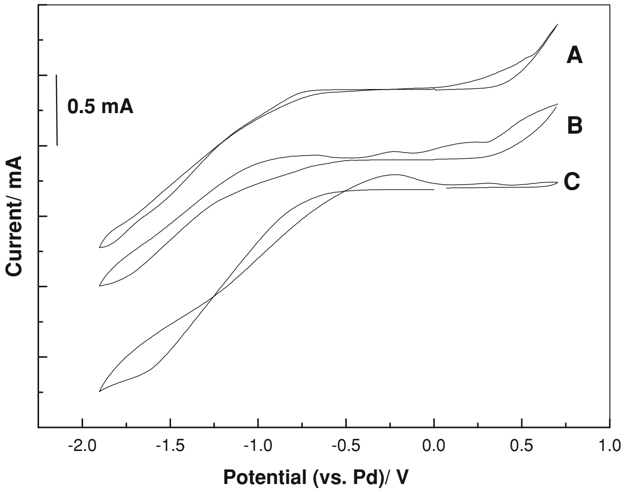

Fig. 2 Cyclic voltammograms of organic phase after extraction of palladium (II) from (A) 1 M and (B) 4 M nitric acid medium and (C) from fast reactor-simulated high-level liquid waste solution by a solution 0.5 M TOMAN/$CHCl_3$. The voltammograms were recorded at stainless steel electrode at a scan rate of 0.01 V s^{-1} at 298 K Counter electrode: platinum, Quasi-reference electrode: palladium

current occurring at a potential of −0.5 V (vs. Pd quasi-reference), followed by a continuous increase in cathodic current is due to the reduction of Pd (II) to Pd (0). This indicates that it is possible to recover palladium in metallic form by direct electrolysis from organic phase. Therefore, the electrodeposition studies were conducted in the extracted organic phase, at 298 K, and the results were discussed below.

3.3 Electrodeposition studies

The UV–Visible absorption spectrum of the organic phase obtained after extraction from 4 M nitric acid and FR-S-HLLW are shown in Figs. 3 and 4, respectively. From the absorbance measurements at various intervals of time and using a molar extinction coefficient obtained from Fig. 1, the amount of palladium remaining in organic phase was determined. The rate of decrease in the concentration of palladium in organic phase during electrolysis at stainless steel electrode at 298 K is shown in Fig. 5. When the organic phase obtained after the extraction of palladium from 4 M nitric acid medium is subjected to electrolysis, rapid decrease in the concentration of palladium in organic phase is observed with time. Extrapolation of this trend indicates the requirement of 19–20 h for the quantitative recovery of palladium from organic phase. Significant deposition of palladium was observed during the course of electrolysis, which was accompanied by a gradual change in the color of organic phase from dark-orange to pale yellow (original color of organic phase) occurring after 18–19 h. Therefore, electrolysis was stopped after 20 h and the recovery of palladium was ∼98% (by the weight of palladium deposited also). In contrast, when the electrolysis is carried out in an organic phase obtained after extraction of palladium from FR-S-HLLW, the decrease in concentration of palladium is gradual as shown in Fig. 5. Extrapolation of this trend indicates the requirement of more than 30 h for quantitative recovery of palladium. Nearly 96% of palladium was found to be deposited after 30 h of electrolysis.

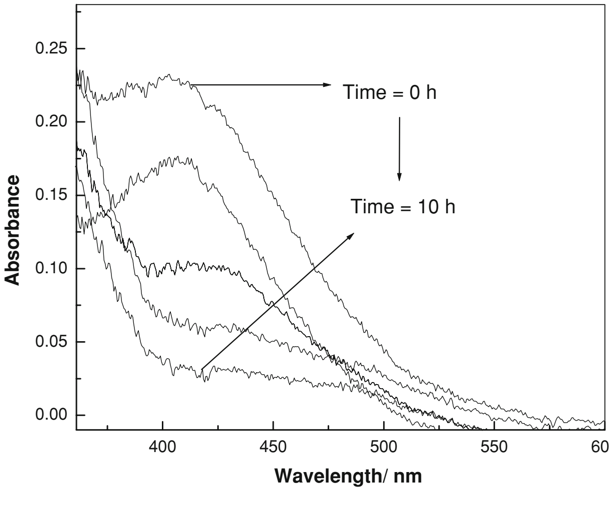

Fig. 3 Comparison of UV–VIS absorption spectrum of the organic phase at various intervals of time during the course of electrolysis. The organic phase is obtained after extraction of palladium (II) from 4 M nitric acid

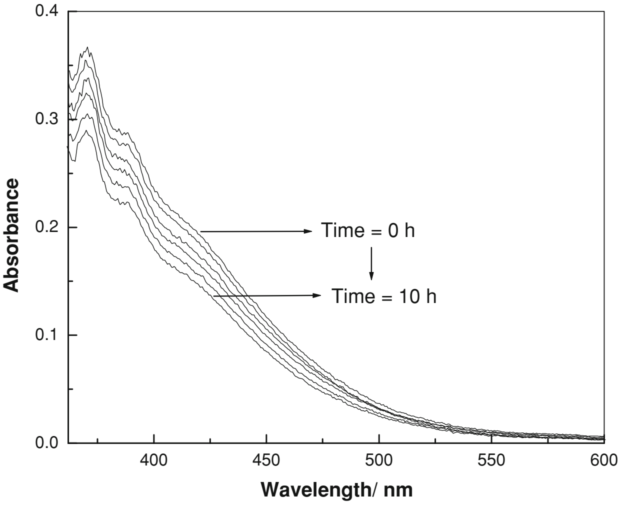

Fig. 4 Comparison of UV–VIS absorption spectrum of the organic phase at various intervals of time during the course of electrolysis. The organic phase is obtained after extraction of palladium (II) from fast reactor-simulated high-level liquid waste solution

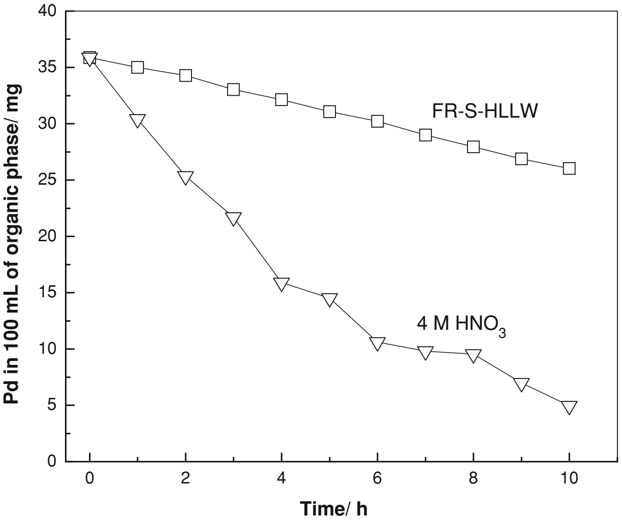

Fig. 5 Variation of palladium concentration in organic phase as a function of time during the course of electrolysis. The organic phase is obtained after extraction of palladium from 4 M nitric acid and fast reactor-simulated high-level liquid waste

The study revealed that the time required for complete recovery of palladium by electrodeposition depends upon the composition of feed solution, from which palladium is extracted. Under the given electrolytic cell conditions, nearly 20 and 35 h are required for quantitative electrodeposition of palladium from organic phase, which is obtained after extraction from 4 M nitric acid and FR-S-HLLW, respectively. A large difference in time requirement for electrodeposition shows that the organic phase obtained after extraction from FR-S-HLLW may be containing several metal ions, which are co-extracted during extraction of palladium. These co-extracted metals may also be contributing the redox reactions in preference to palladium reduction. This is evident from the comparison of absorption spectrum of organic phase obtained after extraction from 4 M nitric acid (Fig. 3) and FR-S-HLLW (Fig. 4). The presence of strong absorption bands occurring in the wavelength region 375–425 nm could, perhaps, be due to the presence of other metal ions.

Mezhov et al. [15] reported the individual distribution ratios of fission products and actinides in a solution of 0.5 M TOMAN in benzene. The distribution ratio of palladium (II) was reported as 20. Among the other metal ions U (VI) ($D = 3$), Pu (IV) ($D = 10^4$), Ru (III) ($D = 0.1$–1), and Am (III) ($D = 0.3$) exhibit higher distribution ratio for their extraction from 3.0 M nitric acid medium and the remaining fission products exhibit D values of the order 10^{-2} or less. Rhodium (III) is inextractable. In addition, nitric acid is co-extracted in 0.5 M TOMAN/$CHCl_3$ [10]. We have also studied the electrochemical behavior of various interfering cations and anions during the electrodeposition of palladium from nitric acid medium [9]. It was shown that the initial deposition of palladium on stainless steel working electrode modifies the electrode surface to metallic palladium and favors the underpotential redox conversions of several ions such as Ag^+, UO_2^{2+}, NO_3^-, Fe^{2+}, if present in electrolytic medium and limits the electrochemical recovery of palladium to <40%. Therefore, the co-extracted metals and nitric acid from FR-S-HLLW are also likely to interfere/lower the electrodeposition of palladium, but to a limited extent in the present case (as their distribution coefficients are less). As a result, the rate of recovery of palladium from the organic phase which is contacted with FR-S-HLLW is significantly lower and required >30 h for quantitative deposition. The study indicates that rejection of fission products and corrosion products to aqueous phase achieved during the extraction of palladium from FR-S-HLLW in the step 1, indeed facilitates the erstwhile inefficient direct electrochemical recovery of palladium (recovery <40% [9]) to a more efficient process (EX–EL process) where the recovery is quantitative.

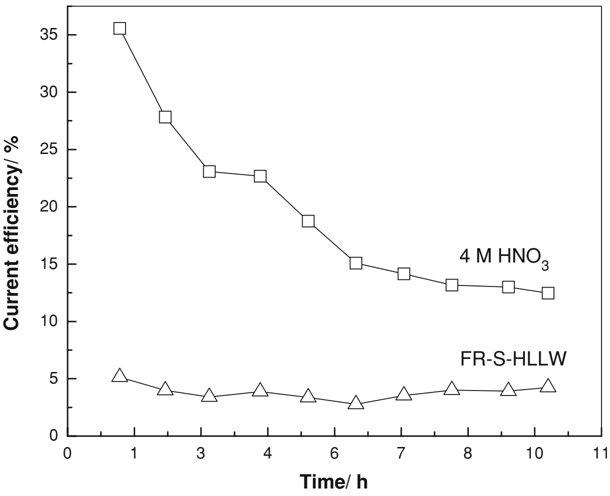

Fig. 6 Comparison of current efficiency for the electrodeposition of palladium on stainless steel electrode from 0.5 M TOMAN/$CHCl_3$. The organic phase is obtained after extraction from 4 M HNO_3 and FR-S-HLLW. Counter electrodeplatinum and quasi-reference—palladium wire

Figure 6 shows the comparison of current efficiencies of electrodeposition during electrolysis of organic phase obtained after extracting palladium from 4 M HNO_3 medium and FR-S-HLLW solution. It is observed that the current efficiency rapidly decreases from 30% in the initial period of electrolysis to the efficiency of ~15% after 10 h of electrolysis. Lower current efficiency could be due to extraction of nitric acid, water from the aqueous phase. These compounds and nitrate ion of TOMAN are likely to undergo underpotential reduction soon after the deposition of palladium on SS electrode, as described above and elsewhere [9]. The current efficiency is only ~6% for the electrodeposition of palladium from organic phase which is extracted with FR-S-HLLW during extraction. The current efficiency of electrodeposition and rate of recovery of palladium are realized under the present experimental conditions and they can be improved and optimized by appropriate design of the cell that will be reported later.

3.4 Recycling of organic phase

The recycling behavior of organic phase after subjecting to extraction of palladium from 4 M nitric acid medium and electrodeposition (20 h) was studied. The organic phase (100 mL) was contacted with aqueous solution (100 mL) containing palladium nitrate in 4 M nitric acid medium. The results are tabulated in Table 3. As expected, 60% of palladium is extracted in a single contact. The organic phase (100 mL) was electrolyzed for 20 h at stainless steel electrode (6 cm^2). The recovery of metallic palladium is also shown in Table 3. It is observed that the recovery is >95%. The organic phase was then washed with 1 M $NaNO_3$ to remove any undesirable by-products of electrolysis formed during the reduction of palladium and also to reconvert the extractant into TOMAN form. Then the 0.5 M TOMAN/$CHCl_3$ was recycled for extraction. The results, shown in Table 3, indicate that there are no

Table 3 Solvent extraction of palladium (II) from 4.0 M nitric acid medium by 0.5 M TOMAN/$CHCl_3$ and recovery of palladium by electrodeposition

[HNO_3]	Cycle	Extraction efficiency (%)	Recovery of electrodeposition (20 h) (%)
4 M	1	61.1	98
	2	60.5	95
	3	60.4	96
	4	59.9	98
	5	60.6	96

Aqueous: organic (100 mL:100 mL), $T = 298$ K

significant changes during solvent extraction of palladium from 4.0 M nitric acid medium and recovery during electrodeposition, when the organic phase is recycled five times.

3.5 Decontamination studies

Utilization of the end product, metallic palladium, depends upon its purity and the degree of decontamination achieved from the fission products and other elements during extraction and electrodeposition. To examine this, the FR-S-HLLW was spiked with actual HLLW (Burn-up 100,000 MW d Te^{-1}) and measuring the decontamination achieved during extraction with 0.5 M TOMAN/$CHCl_3$. The β, γ-radioactivities of aqueous and organic phases are tabulated in Table 4. A decontamination factor of 13 was achieved during extraction of palladium. The organic phase was then subjected to electrolysis at -1.6 V (vs. Pd) and radioactivity of organic phase was monitored at various intervals of time. Figure 7 shows the variation in the radioactivity of organic phase during the course of electrolysis. It is observed that the decrease in radioactivity of organic phase is insignificant. Therefore, the contamination of fission products in the deposit is minimal and the decontamination factor achieved during electrodeposition is very high. Mezhov et al. [15] reported that among the metal ions present in HLLW, U (VI), Pu (IV), and Am (III) exhibit higher distribution ratio in 3.0 M nitric acid medium. However, these metals even if extracted in TOMAN phase may not contaminate the palladium deposit, as they require large negative potentials for deposition. Moreover, the other fission platinoids namely rhodium (III) ($D < 10^{-3}$) and ruthenium ($D < 10^{-2}$) are poorly extracted by 0.5 M TOMAN/$CHCl_3$ and thus they are unlikely to contaminate the palladium deposit. Thus, by adopting the EX–EL process for the recovery of palladium from HLLW, the end product palladium metal is decontaminated substantially from other fission products by a factor of ~ 13 during extraction and fairly a high decontamination (~ 100) is achieved during electrodeposition.

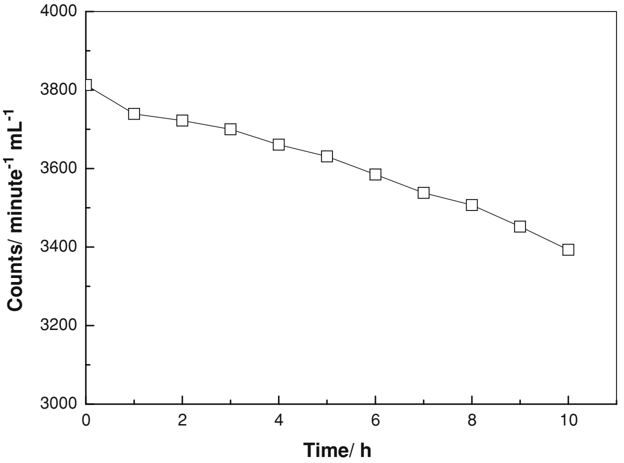

Fig. 7 Variation of organic phase radioactivity with time during the course of electrolysis. The organic phase is obtained after the extraction of palladium (II) from FR-S-HLLW spiked with actual HLLW

4 Conclusions

The extraction–electrodeposition (EX–EL) process has been demonstrated for the quantitative recovery of palladium from FR-S-HLLW. The process exploited a few remarkable properties of RTIL namely, liquid ion exchange behavior and wide electrochemical window of TOMAN to develop a congenial procedure for quantitative recovery of palladium. More than 60% of palladium can be extracted using 0.5 M TOMAN/$CHCl_3$ in a single contact and complete extraction was achieved in five contacts. The extracted palladium was quantitatively recovered by

Table 4 Comparison of β, γ-radioactivity recorded for samples drawn from aqueous and organic phases

Sample	Counts per minute per mL				$DF_{extraction} = \frac{Activity_{aqueous}}{Activity_{organic}}$
	Aqueous feed FR-S-HLLW	Aqueous phase after extraction with 0.5 M TOMAN in $CHCl_3$	Organic phase after extraction (before electrolysis)	Organic phase after 10 h of electrolysis	
Run 1	51,247 ± 200	48,850 ± 200	3,813 ± 100	3,393 ± 100	13.4
Run 2	51,080 ± 200	48,157 ± 200	3,715 ± 100	3,483 ± 100	13.7

electrodeposition at stainless steel electrode. Nearly 20 h were required for complete recovery of palladium from organic phase which was contacted with a solution of palladium nitrate in 4.0 M nitric acid while more than 35 h were needed for recovery form organic phase, which was contacted with FR-S-HLLW. The process holds promise of decontaminating β, γ-radioactivity by an order of magnitude during extraction of palladium from HLLW and also provides a large decontamination factor (of ~ 100) during electrodeposition step. The study revealed that rejection of fission products and corrosion products to aqueous phase during the extraction of palladium from FR-S-HLLW in the step 1, indeed facilitates the erstwhile inefficient direct electrochemical recovery of palladium (recovery <40%) to a more efficient process (EX–EL process) where the recovery is quantitative.

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