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Diglycolic acid modified zirconium phosphate and studies on the extraction of Am(III) and Eu(III) from dilute nitric acid medium

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Abstract: Diglycolic acid modified zirconium phosphate (ZrP-DGA) was prepared and studied for the extraction of Am(III) and Eu(III) from dilute nitric acid medium. The distribution coefficient (K_d , mL·g⁻¹) of Am(III) and Eu(III) was measured as a function of time, pH and concentration of Eu(III) ion etc. The K_d of Am(III) and Eu(III) increased with increase of pH, reached a maximum value of distribution coefficient at pH 1.5 – 2, followed by decrease in K_d values. Rapid extraction of Am(III) and Eu(III) in ZrP-DGA was observed followed by the establishment of equilibrium occurred in 100 min. Kinetics of extraction was fitted in to pseudo second order rate equation. The amount of Eu(III) loaded in ZrP-DGA increased with increase in the concentration of Eu(III) ion in aqueous phase and the isotherm was fitted in to Langmuir and Freundlich adsorption models. The extraction of Am(III) in ZrP-DGA was higher as compared to Eu(III) and the interference of Eu(III) on the extraction of Am(III) was studied. The distribution coefficient of some lanthanides in ZrP-DGA was measured and the K_d of lanthanides increased across the lanthanide series. The extracted trivalent metal ions were recovered in three contacts of loaded ZrP-DGA with 0.5 M nitric acid.

Keywords: Diglycolamic acid, modified zirconium phosphate, americium, europium, distribution coefficient.

1 Introduction

The PUREX raffinate rejected after the extraction of U(VI) and Pu(IV) from the spent nuclear fuel dissolver solution is known as high-level liquid waste (HLLW) [1]. The trivalent actinides such as Am(III) and Cm(III) are inextractable by the PUREX solvent, and therefore they are rejected to HLLW. The radiotoxicity of HLLW is essentially arising from these alpha emitting nuclides [2], even though they are present in very low concentrations in HLLW [3, 4], and therefore, it calls for the safe management of HLLW. At present, partitioning of trivalent actinides from HLLW followed by transmutation of them into short-lived or stable products (P & T strategy) is considered as a viable strategy for the long-term safe management of HLLW [5–8]. However, the separation of trivalent actinides from HLLW is not an easy task, due to the presence of chemically similar lanthanides, in high concentrations, and in 3–4 M nitric acid medium prevailing in HLLW. Under such conditions, the separation factor of actinides over lanthanides is extremely difficult to achieve. In view of this, the current approach for the P & T strategy is a two-cycle [9, 10] solvent extraction process, in which the trivalent lanthanides and actinides are extracted together as a group from HLLW, followed by their recovery together using dilute nitric acid in the first-cycle. The concentration of nitric acid employed during recovery usually falls in the range of 0.001 M to 0.1 M. The transmutation of actinides demands the separation of trivalent actinides from lanthanides present in dilute nitric acid medium, since the presence of lanthanides in the actinides product reduces the efficacy of transmutation. Therefore, the mutual separation of lanthanides and actinides is carried out from dilute nitric acid medium, in the second-cycle [11–13]. This is followed by transmutation of actinides.

Mutual separation of lanthanides (Ln) and actinides (An) is a challenging task, since both actinides and lanthanides exist in trivalent oxidation state in the feed solution. The methods developed so far, for the Ln-An separation usually exploits the finer differences in the chemical

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behavior of lanthanides and actinides towards various ligands. Several solvent extraction based separation methods have been reported for the mutual separation of lanthanides and actinides [11–13]. However, the studies on the mutual separation of lanthanides and actinides using solid phase adsorbents are very limited. Even though, the methods based on solvent extraction are popular for the separation and recovery of target metal ions, the solid phase extraction method is an apt method for the mutual separation of lanthanides and actinides owing to the fact that actinides are present in very small concentrations in the feed solution.

Inorganic adsorbents are proven candidates for the separation and recovery of hazardous metal ions from aqueous waste streams [14]. It is well recognized that inorganic ion adsorbents are the suitable candidates for the separation of fission products, especially ^{137}Cs and ^{90}Sr from nuclear wastes [15]. They are characterized by the extraordinary selectivity towards fission products and excellent radiation stability. In addition, the fission product trapped inorganic material can be directly immobilized to a ceramic or glass form for final disposal [16–18]. Excellent reviews by Clearfield [19–21]; Mimura [22] and others [23, 24] describe the recent developments in inorganic adsorbents and their applications in the treatment of nuclear waste. Zirconium phosphate (Zr-P) [25], ammonium molybdophosphate (AMP) [26] and crystalline silico-titanate [27] are proposed as the promising inorganic sorbents for the efficient separation of ^{137}Cs and polyanTIMONIC acid [28] for ^{90}Sr from acid solution. However, the studies on the extraction of trivalent actinides and lanthanides from dilute nitric acid medium (pH 1 to pH 3) are very limited owing to the poor selectivity exhibited by these inorganic materials.

To enhance the selectivity of inorganic adsorbents towards trivalent actinides, it is necessary to modify the surface of the adsorbent with task specific ligands suitable for actinide extraction [29]. In the recent past, the task specific ligands anchored on inorganic solid supports such as silica, titania etc. are receiving increased attention and they are being investigated for the adsorption of radiotoxic metal ions [30–32]. In the present paper, we report the synthesis of diglycolic acid modified zirconium phosphate (ZrP-DGA) and studies on the extraction of Am(III) and Eu(III) from aqueous nitric acid medium. Diglycolic acid is similar to diglycolamic acid which is regarded as a promising candidate for the mutual separation of Am(III) and Eu(III) from dilute nitric acid medium. Since diglycolic acid possesses two carbonyl group and an etheric oxygen atom, it is expected to exhibit high extraction of trivalent lanthanides and

actinides from dilute nitric acid medium. In view of this, diglycolic acid was chemically attached on the surface of zirconium phosphate and studied for extraction of Am(III) and Eu(III) from dilute nitric acid medium. Since the nitric acid concentration range in the feed solution for Ln-An separation falls in the range of 0.001 M to 0.1 M, this acid concentration range was chosen for extraction studies. The effect of various parameters such as duration of equilibration, concentrations of nitric acid and europium ion on the distribution coefficient of Am(III) and Eu(III) in ZrP-DGA was studied. The conditions needed for efficient separation of americium(III) from europium(III) was identified. The results are reported in this paper.

2 Experimental

2.1 Materials and methods

All the chemicals and reagents used in the study were of analytical grade. Zirconyl chloride was procured from SD Fine Chemicals Limited. Ortho Phosphoric acid (85%) was procured from E-Merck. Diglycolic anhydride (98% purity) was procured from Sigma Aldrich Chemicals. All these chemicals were used without any purification. $(^{152}+^{154})\text{EuCl}_3$ tracer was purchased from Board of Radiation and Isotope Technology, Mumbai and $^{241}\text{Am(III)}$ was received from Oak Ridge National Laboratory as Am_2O_3 and dissolved in nitric acid.

2.2 Preparation of ZrP-DGA

Zirconium phosphate was prepared by the procedure described elsewhere [33]. It involved the addition of 1 M phosphoric acid solution (250 mL), drop-wise, to 0.1 M zirconyl chloride (250 mL) taken in a round bottom flask. The mixture was stirred efficiently and adjusted to pH 1 to obtain white colored zirconium phosphate. To this zirconium phosphate, the diglycolic anhydride (DGAn) was added and the mixture was refluxed for about 3 h at 333 K. The quantity of DGAn added to the mixture was varied from 2 to 6 g. The precipitate obtained was filtered, washed thoroughly with distilled water (till Cl^- was free) and dried at 343 K. The reaction scheme is shown in Figure 1. The product obtained without DGAn was abbreviated as ZrP and with DGAn was abbreviated as ZrP-DGA.

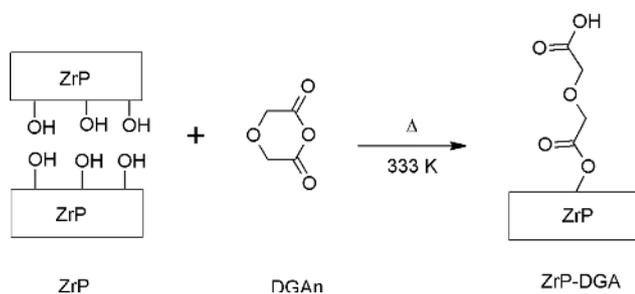


Figure 1: Reaction scheme for the synthesis of ZrP-DGA.

2.3 Batch studies

All the extraction experiments were conducted at 298 K. The batch equilibration experiments involved mixing of 0.05 g ZrP-DGA with 10 mL of dilute nitric acid solution spiked with ^{241}Am or $^{(152+154)}\text{Eu}$ tracer. The solution and ZrP-DGA were taken in a 20 mL stoppered tube and mixing was achieved by rotating the test tube, at 50 rpm, in upside-down rotation. After 3 h of equilibration the mixture was allowed to settle and an aliquot (1 mL) was taken from the supernatant aqueous phase. The radioactivity of ^{241}Am or $^{(152+154)}\text{Eu}$ present in aqueous phase was measured using a well-type NaI(Tl) scintillation detector coupled with single channel analyser. The distribution coefficient was determined from the radioactivity measurement of aqueous phase and using equation 1.

$$K_d \text{ (mL} \cdot \text{g}^{-1}\text{)} = \left(\frac{A_0 - A_f}{A_f} \right) \times \left(\frac{V}{m} \right) \quad (1)$$

where A_0 and A_f are the initial and final radioactivity of aqueous phase. V (in mL) is the volume of aqueous phase, and m (in gram) is the mass of the adsorbent taken for equilibration.

2.4 Kinetic studies

The rate of uptake of Am(III) or Eu(III) in ZrP-DGA was studied by equilibrating 0.05 g of ZrP-DGA with 10 mL of dilute nitric acid solution (pH 2) spiked with ^{241}Am or $^{(152+154)}\text{Eu}$ tracer. At various intervals of time the equilibration was stopped and an aliquot (1 mL) was taken from the aqueous phase. From the initial activity and the activity after equilibration, the percentage of Am(III) or Eu(III) extracted in ZrP-DGA was calculated by using equation 2.

$$\% \text{ Extraction} = \left(\frac{A_0 - A_f}{A_0} \right) \times 100 \quad (2)$$

2.5 Adsorption isotherm

Batch experiments were conducted at 298 K by equilibrating 0.05 g of ZrP-DGA with 10 mL of nitric acid solution (pH 2) containing various concentrations of europium nitrate (europium concentration varied from $10 \text{ mg} \cdot \text{L}^{-1}$ to $1000 \text{ mg} \cdot \text{L}^{-1}$) spiked with $^{(152+154)}\text{Eu}$ tracer. The test-tubes were rotated with a constant speed of 50 rpm for a period of 3 h. Aliquots were withdrawn from the aqueous phase before and after extraction. The amount of Eu(III) extracted in ZrP-DGA was determined, as described above.

2.6 Interference study

The extraction of Am(III) in presence of Eu(III) was conducted by equilibrating 0.05 g of ZrP-DGA with 10 mL of nitric acid solution (pH 2) containing various concentrations of europium nitrate (europium concentration varied from $10 \text{ mg} \cdot \text{L}^{-1}$ to $1000 \text{ mg} \cdot \text{L}^{-1}$) spiked with ^{241}Am tracer. The test-tubes were rotated with a constant speed of 50 rpm for a period of 3 h. Aliquots were taken from the aqueous phase before and after extraction. The radioactivity of ^{241}Am in the aqueous solution was measured by using a well – type NaI(Tl) scintillation detector. The amount of Am(III) extracted in ZrP-DGA was measured from the initial and final radioactivity values, as described above.

2.7 Instrumentation

The X-ray diffraction pattern of the sorbent was obtained using a Philips 1011 X-ray diffractometer (operating with 40 KV and 45 mA) with $\text{Cu K}\alpha$ (1.5406 \AA) radiation. Ultima C spectroanalyser (Jobin Yvon, France) equipped with ICP excitation source was used in the present study.

3 Results and discussion

3.1 Characterization of ZrP-DGA

Zirconium phosphate (ZrP) was prepared by the procedure [33] described in Section 2.2. The quantity of diglycolic anhydride added to ZrP during synthesis was varied from 2 to 6 g. After the synthesis, the distribution coefficient of Am(III) was measured in ZrP at pH 2 as well as DGA modified ZrP, namely ZrP-DGA at pH 2, and the results are displayed in Table 1. It can be seen that the

Table 1: Distribution coefficient of Am(III) at pH 2 in ZrP and ZrP-DGA prepared at various quantities of DGAn.

Diglycolic anhydride (DGAn)/g	K_d of Am(III) at pH 2/mL·g ⁻¹
Nil	51 ± 2
2	2348 ± 20
3	3154 ± 20
5	5582 ± 20
6	5587 ± 20

Volume of 0.1 M zirconyl chloride taken for synthesis = 250 mL.
Volume of 1 M phosphoric acid taken for synthesis = 250 mL.

distribution coefficient of Am(III) in ZrP is ~50 mL·g⁻¹. However the distribution coefficient increased to the value of ~2300 mL·g⁻¹ when 2 g of diglycolic anhydride (DGAn) was added to ZrP during synthesis. This indicates that DGAn modifies the surface of ZrP and enhances the distribution coefficient of Am(III). Diglycolic anhydride contains an etheric oxygen and a couple of >C=O groups. During the reaction of DGAn with ZrP, it is quite likely that DGAn undergoes a reaction with ZrP leading to the formation of diglycolic acid over the surface of ZrP, as shown in Figure 1. Since diglycolic acid is similar to diglycolamic acid which is a well-known reagent [11] for the extraction of trivalent metal ions from dilute nitric acid medium, the distribution coefficient of Am(III) in ZrP-DGA increased to ~2300 mL·g⁻¹ when DGAn was added to ZrP during synthesis. Moreover, the distribution coefficient of Am(III) in ZrP-DGA further increased with increase in the quantity of DGAn added during

synthesis, as shown in Table 1. However, the increase in K_d of Am(III) was insignificant after adding 5 g of DGAn during synthesis. Therefore, bulk of ZrP-DGA was synthesized by adding 5 g of DGAn to ZrP and the product obtained was employed for all other extraction studies. Figure 2 shows the XRD pattern of ZrP and ZrP-DGA. The XRD pattern of ZrP matches well with the XRD pattern of zirconium phosphate reported in literature (JCPDS 34-0127, [34]). Moreover, it can be seen that the pattern obtained after DGAn modification (ZrP-DGA) is similar to ZrP. This indicates that introduction of diglycolamic acid in ZrP does not alter the structure of ZrP to any significant extent, indicating the matrix is intact.

3.2 Kinetics of extraction

The rate of extraction of Am(III) and Eu(III) in ZrP-DGA was studied and the results are shown in Figure 3. It can be seen that the percentage of extraction of Am(III) and Eu(III) in ZrP-DGA increases with increase in the duration of equilibration and the equilibrium was established in 100 min. Therefore, for all extraction studies, equilibration was conducted for about 3 h to ensure the establishment of equilibrium. To understand the kinetics of extraction, the uptake of Am(III) and Eu(III) in ZrP-DGA was modeled with the pseudo-first order and pseudo-second order kinetics equation. It is well-recognized [35] that the rate of extraction of metal ions in solid phase can be given by the pseudo-first order and pseudo-second order

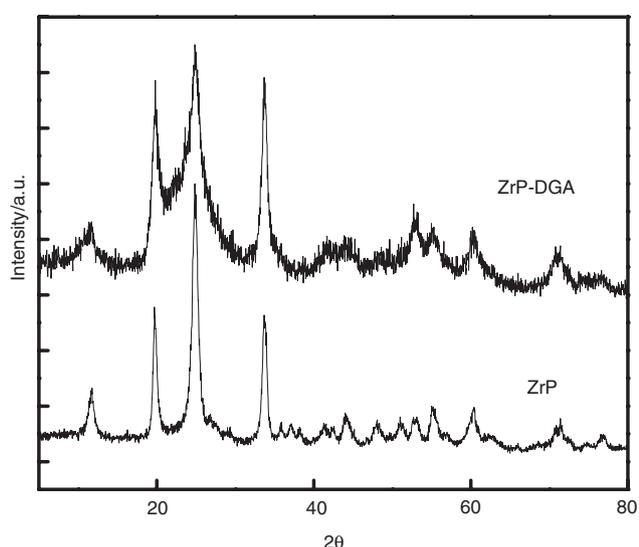


Figure 2: Powder X-Ray diffraction pattern of ZrP and ZrP-DGA. The XRD pattern of ZrP matches with std. zirconium phosphate JCPDS 34-0127.

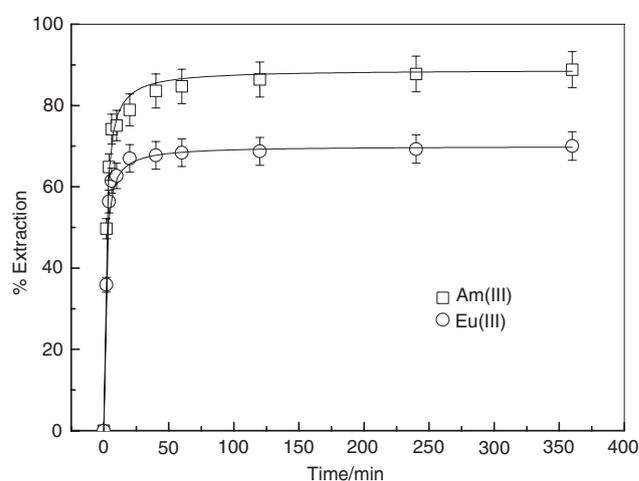


Figure 3: Variation in the percentage extraction of Am(III) and Eu(III) as a function of time, fitted using pseudo-second order rate equation. Adsorbent phase: ZrP-DGA (0.05 g), Aqueous Phase: pH 2 solution (nitric acid medium) (10 mL), spiked with ²⁴¹Am or (¹⁵²⁺¹⁵⁴)Eu tracer at 298 K.

rate equations of the form shown in equations 3 and equation 4, respectively.

$$q_t = q_e (1 - e^{-k_1 t}) \quad (3)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (4)$$

where q_t is the amount of metal ions extracted at a time t in $\text{mmol}\cdot\text{g}^{-1}$, q_e (in $\text{mmol}\cdot\text{g}^{-1}$) is the amount of metal ion extracted at equilibrium, and k_1 and k_2 are the pseudo-first order and pseudo-second order rate constants.

The extraction data shown in Figure 3 was fitted into these first-order and second order rate equations by non-linear regression. The fitting constants and the statistical parameters obtained by fitting are tabulated in Table 2. It can be seen that the R^2 values are more and χ^2 is low for second order fitting (i. e. equation 4). Therefore the experimental data was fitted in to second order rate equation and displayed in Figure 3. It is interesting to note from Figure 3 that the extraction of Am(III) is more as compared to Eu(III). This result is in contrast to data reported for the extraction of these trivalent metal ions in alkyl diglycolamic acid, in solvent extraction [11] mode as well as the solid phase adsorption modes [36]. The oxygen donor ligands generally extract Eu(III) more as compared to Am(III) owing to the hard-acid and soft base (HSAB) concept [37]. However, higher extraction of Am(III) over Eu(III) obtained in ZrP-DGA is not clear at present, perhaps it could be attributed to the matrix effect of ZrP. In view of the above, the pseudo-second order rate constant (k_2) obtained for the extraction of Am(III) is more as compared to Eu(III).

3.3 Extraction of Am(III) and Eu(III)

The variation in the distribution coefficient of Am(III) and Eu(III) in ZrP-DGA as a function of pH is shown in Figure 4. The data are compared with those obtained in the extraction of Am(III) and Eu(III) by diglycolamic acid impregnated chromatographic resin [36]. In addition,

Table 2: Pseudo-first order and pseudo-second order rate constants obtained by non-linear regression of the kinetics of extraction.

Metal ion	Pseudo-first order			Pseudo-second order		
	k_1/min^{-1}	R^2	χ^2	$k_2/\text{L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$	R^2	χ^2
Am(III)	0.33 ± 0.03	0.9548	30.7	0.007 ± 0.01	0.9943	3.8
Eu(III)	0.36 ± 0.02	0.9576	31.2	0.01 ± 0.01	0.9839	7.3

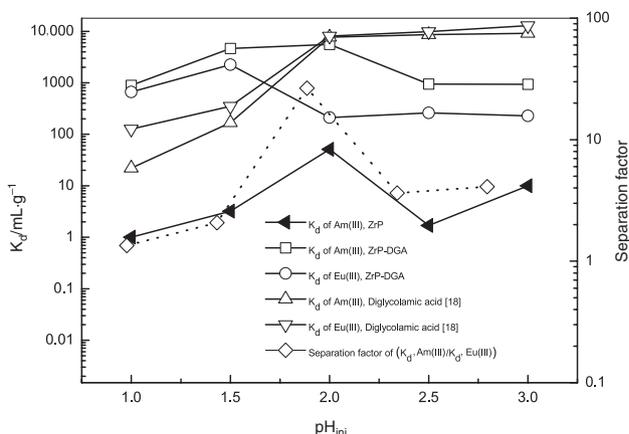


Figure 4: Variation in the distribution coefficient of Am(III) and Eu(III) as a function of initial pH of aqueous phase. Adsorbent phase: ZrP-DGA (0.05 g), Aqueous phase: Nitric acid at various pH (10 mL), spiked with ^{241}Am or $^{152+154}\text{Eu}$ tracer at 298 K. The distribution ratio of Am(III) and Eu(III) in diglycolamic acid impregnated ADS 400 resin was taken from reference [36]. The distribution values agree with $\pm 5\%$.

the extraction data is also compared with the extraction of Am(III) observed in ZrP (without modification). It can be seen that the distribution trend obtained in diglycolamic acid impregnated resin (ADS 400) increased with increase of pH, as expected for the carboxylic acid functional moiety. The distribution coefficient of Am(III) observed in ZrP is much lower than those observed in ZrP-DGA. A maximum distribution coefficient of $\sim 50 \text{ mL}\cdot\text{g}^{-1}$ is observed for the extraction of Am(III) in ZrP at pH 2. The Eu(III) distribution values in ZrP were much lower than Am(III) (not shown in Figure 4 for clarity). In contrast to these observations, the distribution coefficient of Am(III) in ZrP-DGA increases with increase of pH of aqueous phase, reaches a maximum K_d value at pH 2 followed by decrease in K_d values. In case of Eu(III) extraction, the maximum K_d value is obtained at pH 1.5. The reason for the increase in the distribution coefficient of these trivalents in ZrP-DGA could be due to the presence of diglycolamic acid on the surface of ZrP-DGA. Since, the diglycolamic acid contains a couple of carbonyl groups and an etheric oxygen atom, it is expected to exhibit high extraction of trivalent lanthanides and actinides from dilute nitric acid medium. The initial increase in the distribution coefficient of Am(III) and Eu(III) with increase of pH could be due to the increase in the dissociation of carboxylic acid present on the surface of ZrP (see Figure 1). However the fall in the distribution coefficient observed after reaching maximum is not clear at present. In addition, the K_d value of Am(III) is more in ZrP-DGA as compared to Eu(III) at all pH values investigated in the present study. This observation is in

contrast to the extraction trend reported for the extraction of Am(III) and Eu(III) in diglycolamic acid impregnated chromatographic resin [36] (see Figure 4). In addition, the extraction trend obtained using diglycolamic acid through solvent extraction mode [11] (not shown in the plot) resembles the extraction trend obtained in diglycolamic acid impregnated resin. Since the difference between diglycolamic acid extractant impregnated resin and ZrP-DGA is only the solid phase, the study indicates that the matrix ZrP seems to play a profound role in altering the selectivity of these trivalent metal ions. More studies are needed in this direction to bring out the importance of matrix ZrP and insights of extraction.

Figure 4 also shows the separation factor ($K_{d,Am(III)}/K_{d,Eu(III)}$) of Am(III) over Eu(III) obtained at different pH values. It can be seen that the separation factor increases with increase of pH, reaches a maximum value at pH 2, followed by decrease. It is important to note that a separation factor of ~ 25 can be obtained for the separation of Am(III) over Eu(III) at pH 2, without the need of any external complexing reagents, which is usually required for such separations.

3.4 Extraction isotherm

Figure 5 shows the variation in the amount of Eu(III) extracted in ZrP-DGA ($\text{mg}\cdot\text{g}^{-1}$) as a function of amount of Eu(III) present in aqueous phase ($\text{mg}\cdot\text{L}^{-1}$). The extraction of Eu(III) in ZrP-DGA was carried out from pH 2 solution. It can be seen that the amount of Eu(III) extracted

in ZrP-DGA increases with increase in the amount of Eu(III) present in aqueous phase. The experimental data obtained were fitted to Langmuir [38] or Freundlich [39] adsorption isotherms of the form given by equation 5 and 6, respectively.

$$q_{\text{sor}} = \frac{K_L b q_{\text{sol}}}{1 + K_L q_{\text{sol}}} \quad (5)$$

$$q_{\text{sor}} = K_F [q_{\text{sol}}]^\beta \quad (6)$$

where q_{sol} is the amount of Eu(III) present in aqueous phase at equilibrium (in $\text{mg}\cdot\text{L}^{-1}$), q_{sor} is the amount of metal ion loaded in ZrP-DGA at equilibrium (in $\text{mg}\cdot\text{g}^{-1}$), K_L (in $\text{L}\cdot\text{mg}^{-1}$) and K_F (in $\text{L}\cdot\text{mg}^{-1}$) are the Langmuir and Freundlich constants, b is the apparent extraction capacity (in $\text{mg}\cdot\text{g}^{-1}$) and β ($0 < \beta < 1$) is a measure of heterogeneity of the sorbent [40]. The Langmuir and Freundlich constants are related to the energy of adsorption and therefore they are regarded as the measure of affinity [41] of Eu(III) ions towards ZrP-DGA. When $\beta = 1$, the adsorbent is said to be homogeneous and all the adsorption sites are indistinguishable with respect to energy of adsorption. From Langmuir adsorption isotherm (equation 5), it can be shown that $q_{\text{sor}} \rightarrow b$ at high concentration of metal ions in aqueous phase, that is at high q_{sol} values. Non-linear regression of the experimental data using equation 5 and 6 are shown in Figure 5. The regression coefficients and χ^2 values are shown in Figure 5. From Langmuir fitting, the apparent extraction capacity of Eu(III) in ZrP-DGA was determined to be $72 \text{ mg}\cdot\text{g}^{-1}$ at pH 2.

3.5 Effect of lanthanides

Significant quantities of lanthanides are formed as fission products in the nuclear fuel [42]. These lanthanides coexist along with Am(III) since the chemical behavior of these trivalent lanthanides are similar to Am(III) [43]. The quantity of lanthanides present in the feed solution could vary from $50 \text{ mg}\cdot\text{L}^{-1}$ to $1000 \text{ mg}\cdot\text{L}^{-1}$ depending upon the type of fuel employed in a nuclear reactor and burn-up achieved. However, the concentration of alpha emitting Am(III) ($\sim 10 \text{ mg}\cdot\text{L}^{-1}$ to $20 \text{ mg}\cdot\text{L}^{-1}$) present in the fuel is very small as compared to the total quantity of lanthanides. Since the concentration of nitric acid in the feed solution for lanthanide-actinide separation could vary from 0.001 M to 0.1 M, as discussed above (in Section 1), it is necessary to study the effect of the lanthanides on the distribution coefficient of Am(III) in ZrP-DGA at pH 2. For this purpose, the distribution coefficient of Am(III) was measured as a function

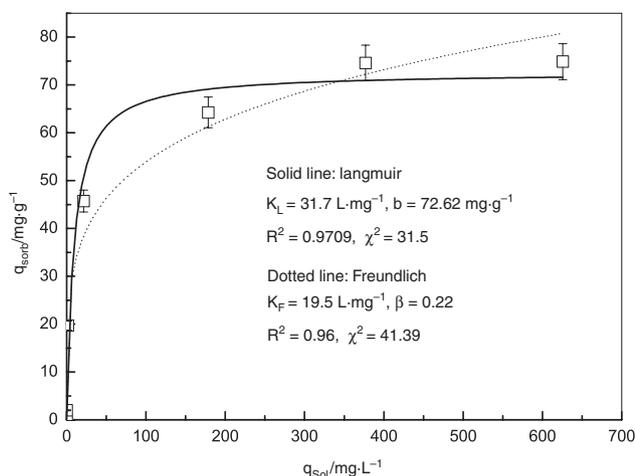


Figure 5: Langmuir and Freundlich adsorption isotherms for the extraction of Eu(III) in ZrP-DGA. Adsorbent phase: ZrP-DGA (0.05 g), Aqueous Phase: Europium nitrate in nitric acid medium at pH 2 (10 mL), spiked with $(^{152}+^{154})\text{Eu}$ tracer at 298 K.

of Eu(III) concentration present in aqueous phase, and Eu(III) was considered as a lanthanide representative in this case. The quantity of Eu(III) present in aqueous phase was varied from $10 \text{ mg}\cdot\text{L}^{-1}$ to $1000 \text{ mg}\cdot\text{L}^{-1}$, where as the quantity of Am(III) was fixed at $10 \text{ mg}\cdot\text{L}^{-1}$ in the feed solution. The results are shown in Figure 6. It can be seen the distribution coefficient of Am(III) is not altered to any significant extent, when the quantity of Eu(III) was varied from $10 \text{ mg}\cdot\text{L}^{-1}$ to $100 \text{ mg}\cdot\text{L}^{-1}$. Thereafter, the K_d of Am(III) decreased with increase in the quantity of Eu(III) in aqueous phase. The study, thus, shows that the extraction of Am(III) in ZrP-DGA is unaffected by the presence of Eu(III) to the extent of $100 \text{ mg}\cdot\text{L}^{-1}$.

Since the other lanthanides also coexist with Eu(III) in the feed solution, the distribution coefficient of lanthanum to dysprosium in ZrP-DGA was measured at pH 2 and the results are shown in Figure 7. It can be seen that the distribution coefficient increases from lanthanum to dysprosium. However, the distribution coefficient of Dy(III) ($\sim 3300 \text{ mL}\cdot\text{g}^{-1}$) (Figure 7) at pH 2 is lower than that of Am(III) ($\sim 6000 \text{ mL}\cdot\text{g}^{-1}$) under similar conditions (Figure 4). This indicates that Am(III) can be extracted efficiently even in the presence of Dy(III).

3.6 Recovery and recycling

From the Figure 4, it was learnt that the distribution coefficient of Am(III) and Eu(III) was very low at nitric acid concentration (lower than 0.1 M). Therefore, 0.5 M nitric acid solution can be used for the recovery of Am(III) and

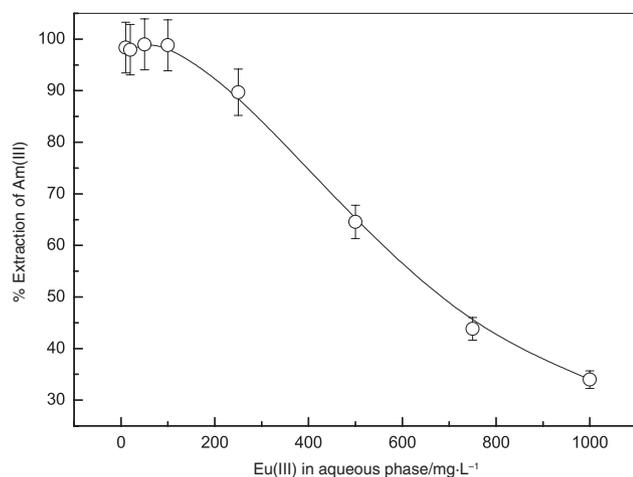


Figure 6: Variation in the distribution coefficient of Am(III) as a function of concentration of Eu(III) in aqueous phase at pH 2. Adsorbent phase: ZrP-DGA (0.05 g), Aqueous phase: Eu(III) nitrate in nitric acid medium at pH 2 (10 mL), spiked with ^{241}Am tracer at 298 K.

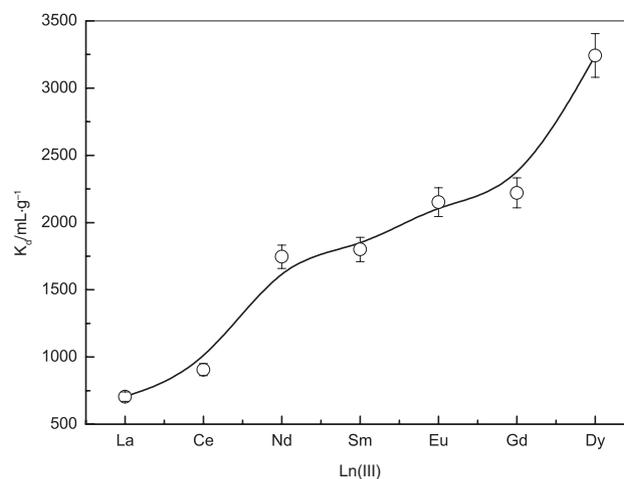


Figure 7: Distribution co-efficient of various lanthanides in ZrP-DGA at pH 2 at 298 K. Adsorbent phase: ZrP-DGA (0.05 g), Aqueous phase: lanthanide nitrate ($250 \text{ mg}\cdot\text{L}^{-1}$) in nitric acid medium at pH 2 (10 mL). The initial and final concentration of lanthanides was measured using ICP-MS.

Eu(III) from the loaded ZrP-DGA. In this context, the initial extraction of Am(III) and Eu(III) in ZrP-DGA was carried out at pH 2 and the aqueous phase was separated. Then, the loaded ZrP-DGA was contacted with 0.5 M nitric acid. The radioactivity of ^{241}Am and $^{(152+154)}\text{Eu}$ present in the aqueous phase was determined. The recovery of Am(III) and Eu(III) in the first contact was more than 90% and near quantitative recovery ($>99\%$) of Am(III) and Eu(III) was achieved in three contacts of the loaded ZrP-DGA with 0.5 M nitric acid.

In order to recycle the adsorbent after stripping, the adsorbent was washed with distilled water after stripping and the distribution coefficient of Am(III) was measured again at pH 2. A K_d value of $\sim 6000 \text{ mL}\cdot\text{g}^{-1}$ was obtained in this case, which compares well with the distribution coefficient of Am(III) determined before recycling. This procedure was repeated five times and the distribution coefficient of Am(III) was found to be comparable with the initial K_d value of Am(III) before recycling. Therefore, the study indicates the possibility of recovering the loaded Am(III) and Eu(III) from ZrP-DGA and shows the potential for recycling.

4 Conclusion

The surface of zirconium phosphate was modified to diglycolic acid moiety by reacting zirconium phosphate with diglycolic anhydride. The resultant modified adsorbent, ZrP-DGA, was evaluated for the extraction of Am(III) and Eu(III) from dilute nitric acid medium. A maximum

distribution coefficient of $\sim 6000 \text{ mL}\cdot\text{g}^{-1}$ for Am(III) at pH 2 and $\sim 2000 \text{ mL}\cdot\text{g}^{-1}$ for Eu(III) at pH 1.5 was obtained. A separation factor of ~ 25 was obtained for Am(III) over Eu(III) at pH 2. The study showed the possibility of separating Am(III) from Eu(III) without the need of any aqueous complexing reagent, which is usually employed for lanthanide-actinide separation. Rapid extraction of Am(III) and Eu(III) in the initial stages of equilibration followed by the establishment of equilibrium occurred in 100 min. The distribution coefficient of Am(III) was unaltered to any significant extent even in the presence of large amount of Eu(III) ($\sim 100 \text{ mg}\cdot\text{L}^{-1}$) present in the feed solution at pH 2. The apparent extraction capacity of ZrP-DGA was determined to be $\sim 70 \text{ mg}\cdot\text{g}^{-1}$ from Langmuir adsorption isotherm. Quantitative recovery of Am(III) and Eu(III) from the loaded ZrP-DGA was achieved in three contacts with 0.5 M nitric acid and ZrP-DGA can be recycled back for extraction. In contrast to the conventional oxygen donors, the distribution coefficient of Am(III) was higher than Eu(III) at all pH values investigated in the present study indicating the role of ZrP in altering the selectivity. More studies are needed in this direction to understand the role of matrix in the extraction of trivalent metal ions.

References

- Mckay, H. A. C., Miles, J. H., Swanson, J. L.: The PUREX process. In: W. W. Schulz, J. D. Navratil, K. P. Bender, (Eds.) Science and Technology of Tributyl Phosphate. Vol.III CRC Press, Boca Raton, FL (1990).
- Safety and environmental aspects of partitioning and transmutation of actinides and fission products, IAEA-TECDOC-783. Proceedings of a Technical Committee meeting held in Vienna, 29 November-2 December (1993).
- Assessment of partitioning processes for transmutation of actinides, IAEA TECDOC CD series, IAEA-TECDOC-CD-1648 (2010).
- Baetsle, L. H.: A comparative systems-analysis approach on fuel cycles with partitioning and transmutation. The Fourth International Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation. 45 (1996).
- Raj, K., Prasad, K. K., Bansal, N. K.: Radioactive waste management practices in India. Nucl. Eng. Des. **236**, 914 (2006).
- Saaty, T. L., Gholamnezhad, H.: High-level nuclear waste management: analysis of options. Environ. Plan. B. **9**, 181 (1982).
- Michael, D. L., Phillip, L. B., Jeffrey, C. E.: Hazardous waste management. 2nd Ed., Waveland Press, INC, Long Grove, Illinois (2010).
- Stephane, G., Abdelouas, A., Louise, J. C., Ebert, W. L., Ferrand, K., Geisler, T., Harrison, M. T, Inagaki, Y., Mitsui, S., Mueller, K. T., Marra, J. C.: An international initiative on long-term behavior of high-level nuclear waste glass. Mater. Tod. **16**, 243 (2013).
- Modolo, G., Vijgen, H., Serrano, P. D., Christiansen, B., Malmbeck, R., Sorel, C., Baron, P.: DIAMEX counter-current extraction process for recovery of trivalent actinides from simulated high active concentrate. Sep. Sci. Technol. **42**, 439 (2007).
- Antony, M. P., Kumaresan, R., Suneesh, A. S., Rajeswari, S., Robertselvan, B., Sukumaran, V., Manivannan, R., Syamala, K. V., Venkatesan, K. A., Srinivasan, T. G., Vasudeva Rao, P. R.: Development of a CMPO based extraction process for partitioning of minor actinides and demonstration with genuine fast reactor fuel solution (155 GWd/Te). Radiochim. Acta **99**, 207 (2011).
- Suneesh, A. S., Venkatesan, K. A., Syamala, K. V., Antony, M. P., Vasudeva Rao, P. R.: Mutual separation of americium (III) and europium (III) using glycolamic acid and thioglycolamic acid. Radiochim. Acta **100**, 425 (2012).
- Suneesh, A. S., Kumaresan, R., Rajeswari, S., Prasant Kumar Nayak, Syamala, K. V., Venkatesan, K. A., Antony, M. P., Vasudeva Rao, P. R.: Development and demonstration of americium (III)-europium (III) separation using diglycolamic acid. Sep. Sci. Tech. **48**, 1998 (2013).
- Nayak, P. K., Kumaresan, R., Venkatesan, K. A., Antony, M. P., Vasudeva Rao, P. R.: A new method for partitioning of trivalent actinides from high-level liquid waste. Sep. Sci. Tech. **48**, 1409 (2013).
- Yang, D., Zheng, Z., Liu, H., Zhu, H., Ke, X., Xu, Y., Wu, D., Sun, Y.: Layered titanate nanofibers as efficient adsorbents for removal of toxic radioactive and heavy metal ions from water. J. Phy. Chem.C. **112**, 16275 (2008).
- Ebner, A. D., Ritter, J. A., Navratil, J. D.: Adsorption of cesium, strontium, and cobalt ions on magnetite and a magnetite-silica composite. I & EC research. **40**, 1615 (2001).
- Donald, I. W.: Waste immobilization in glass and ceramic based hosts: radioactive, toxic and hazardous wastes. John Wiley & Sons, West Sussex, United Kingdom (2010).
- Beall, George, H., Hermann, L. R.: Highly refractory glass-ceramics suitable for incorporating radioactive wastes. U.S. Patent No. 4,314, 909 (9 Feb. 1982).
- Tuthill, E. J., Weth, G. G., Emma, L. C., Strickland, G., Hatch, L. P.: Phosphate glass process for disposal of high level radioactive wastes. Ind. Eng. Chem. Proc. Des. Dev. **6**, 314 (1967).
- Clearfield, A., Thakur, D. S.: Zirconium and titanium phosphates as catalysts: a review. Appl. Catal. **26**, 1 (1986).
- Clearfield A.: Recent advances in metal phosphonate chemistry. Curr. Opin. Solid State Mater. Sci. **1**, 268 (1996).
- Clearfield, A., Diaz, A.: Zirconium Phosphate nano particles and their extraordinary properties. Tailor. Organ. Inorgan. Mater. **1**, 44 (2015).
- Mimura, H., Lehto, J., Harjula, R.: Selective removal of cesium from simulated high-level liquid wastes by insoluble ferrocyanides. J. Nucl. Sci. Technol. **34**, 607 (1997).
- Moon, J. K., Kim, K. W., Jung, C. H., Shul, Y. G., Lee, E. H.: Preparation of organic-inorganic composite adsorbent beads for removal of radionuclides and heavy metal ions. J. Radioanal. Nucl. Chem. **246**, 299 (2000).
- Osmanlioglu, A. E.: Treatment of radioactive liquid waste by sorption on natural zeolite in Turkey. J. Hazard. Mater. **137**, 332 (2006).
- Chakraborty, R., Bhattacharaya, K., Chattopadhyay, P.: Nanostructured zirconium phosphate as ion exchanger: synthesis, size dependent property and analytical application in radiochemical separation. Appl. Radiat. Isot. **85**, 34, (2014).

26. Lento, J., Harjula, R.: Separation of cesium from nuclear waste solutions with hexacyanoferrate (II) s and ammonium phosphomolybdate. *Sol. Ext. Ion. Exch.* **5**, 343 (1987).
27. Anthony, R. G., Philip, C. V., Dosch, R. G.: Selective adsorption and ion exchange of metal cations and anions with silico-titanates and layered titanates. *Waste Manag.* **13**, 503 (1993).
28. Zouad, S., Jeanjean, J., Loos-Neskovic, C., Fedoroff, M., Piffard, Y.: Sorption of strontium and lanthanum on polyantimonic acid and two phosphatoantimonic acids. *J. Radioanal. Nucl. Chem.* **182**, 193 (1994).
29. Rout, A., Karmakar, S., Venkatesan, K. A., Srinivasan, T. G., Vasudeva Rao, P. R.: Room temperature ionic liquid diluent for the mutual separation of europium (III) from americium (III). *Sep. Purif. Technol.* **81**, 109 (2011).
30. Suneesh, A. S., Syamala, K. V., Venkatesan, K. A., Antony, M. P., Vasudeva Rao, P. R.: Diglycolamic acid modified silica gel for the separation of hazardous trivalent metal ions from aqueous solution. *J. Coll. Interf. Sci.* **438**, 55 (2015).
31. Luca, V., Tejada, J. J., Vega, D., Arrachart, G., Rey, C.: Zirconium (IV)–Benzene phosphonate coordination polymers: lanthanide and actinide extraction and thermal properties. *Inorgan. Chem.* **55**, 7928 (2016).
32. Florek, J., Giret, S., Juere, E., Lariviere, D., Kleitz, F.: Functionalization of mesoporous materials for lanthanide and actinide extraction. *Dalton Trans.* **45**, 14832 (2016).
33. Siddiqui, W. A., Khan, S. A.: Synthesis, characterization and ion-exchange properties of a new and novel ‘organic–inorganic’ hybrid cation-exchanger: poly (methyl methacrylate) Zr (IV) phosphate. *Coll. Surf. A* **295**, 193 (2007).
34. Genoveva, G. R., Enrique, O. R., Teresita, R. G., Eduardo, O. R.: The influence of agitation speed on the morphology and size particle synthesis of Zr (HPO₄)₂·H₂O from Mexican sand. *J. Mineral. Mater. Character. Eng.* **12**, 39 (2007).
35. Reddad, Z., Gerente, C., Andres, Y., Le Cloirec, P.: Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environ. Sci. Technol.* **36**, 2067 (2002).
36. Suneesh, A. S., Syamala, K. V., Venkatesan, K. A., Antony, M. P., Vasudeva Rao, P. R.: Chromatographic separation of americium (III) from europium (III) using alkyl diglycolamic acid. *Sep. Sci. Tech.* **50**, 1213 (2015).
37. Roy, L. E., Nicholas, J. B., Leigh, R. M.: Theoretical insights into covalency driven f element separations. *Dalton Trans.* **42**, 2636 (2013).
38. Foo, K. Y., Hameed, B. H.: Insights into the modeling of adsorption isotherm systems. *Chem. Eng. J.* **156**, 2 (2010).
39. Umpleby, R. J., Sarah C. B., Miguel, B., John K. B., Ripal N. S., Shimizu, K.D.: Application of the Freundlich adsorption isotherm in the characterization of molecularly imprinted polymers. *Analyt. Chim. Acta* **435**, 35 (2001).
40. Sposito, G.: Derivation of the Freundlich equation for ion exchange reactions in soils. *Soil Sci. Soc. Am. J.* **44**, 652 (1980).
41. Ajmal, M., Rao, R. A. K., Ahmad, R., Ahmad, J.: Adsorption studies on Citrus reticulata (fruit peel of orange): removal and recovery of Ni (II) from electroplating wastewater. *J. Hazard. Mat.* **79**, 117 (2000).
42. Venkatesan, K. A., Kumaresan, R., Antony, M. P., Kumar, T., Srinivasan, T. G., Vasudeva Rao, P. R.: Characterization of high active waste (155 GWd/Te) arising from fast reactor fuel reprocessing. *Radiochim. Acta* **100**, 843 (2012).
43. Choppin, G. R.: Comparison of the solution chemistry of the actinides and lanthanides. *J. Less. Common Met.* **93**, 323 (1983).