Extraction and Separation of Uranium (VI) and Thorium (IV) Using Tri-n-dodecylamine Impregnated Resins

E. Metwally, A. Sh. Saleh, and H. A. El-Naggar

Nuclear Chemistry Department, Radioisotopes Production and Radiation Sources Division, Hot Laboratories Center, Atomic Energy Authority, P.O. Box 13759, Cairo, Egypt

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Extraction of U(VI) and Th(IV) from chloride and nitrate solutions with tri-n-dodecylamine impregnated on Amberlite XAD4, was investigated. The distribution of U(VI) and Th(IV) was studied at different concentrations of acid, salting-out agent, extractant, aqueous metal ion and other parameters. Absorption spectral studies have been investigated for uranium species in both aqueous HCl solution and the resin phase. From these studies, it is suggested that the tetrachloro complex of U(VI) is formed in the extraction of uranium (VI) from hydrochloric acid solutions by TDA impregnated resin. Stripping of the extracted U(VI) and Th(IV) was assayed with HCl and HNO₃. Finally, the separation of uranium from thorium and fission products in HCl media was achieved.

1. INTRODUCTION

There is a growing need for uranium and thorium, the main radioactive elements, for nuclear fuel production. Disposal of industrial waste effluents containing uranium and thorium has serious hazard impacts on the environment. Therefore, recovery of these two elements from aqueous waste solutions is preferable for economical and ecological reasons.

Solvent impregnated resin (SIR) is a good alternative to solvent extraction and ion exchange techniques for metal separation and recovery. They combine the advantages of solvent extraction systems such as fast mass transfer rates, high distribution and selectivity factors, with the advantages of solid ion-exchange technology such as simplicity of equipment and operation and applicability for processing very dilute solutions. For these reasons, SIRs have been widely used in metal recovery and separation in the nuclear industry. Hydro metallurgical applications for the separation of rare earth elements, platinum group metals, gold, and base metals. SIRs are suitable also for preconcentration and separation of trace metal ions for analytical purposes.

Solvent extraction with high molecular weight amines provides a useful method for recovery of actinides. Preparation of a new type of metal ion selective resin based on phosphoric acid functionality and its application on the separation of Mo and V ions have been reported, where the metal ion selective resin was prepared by immobilizing D₂EHPA onto the surface of porous Amberlite XAD4 resin. The recovery of Pd, Pt, and Rh from batches of industrial metal refinery effluents containing large amounts of Ni, Cu, and Fe ions and relatively small amounts of the expensive Pt, Pd, and Rh ions has been investigated with silica-based poly amine anion exchangers. However, the studies on recovery and separation of actinides with amine impregnated resins are few. The present work aimed to investigate the extraction of uranium (VI) and thorium (IV) from chloride and nitrate media with tri-n-dodecylamine (TDA) impregnated resin, to throw light on the extraction mechanism and to compare it with that in solvent extraction systems. The separation of uranium from thorium and fission products with the TDA impregnated resin was studied as well.

2. EXPERIMENTAL

Reagents: Reagent grade TDA (> 95% purity, Merck) was used as extractant without further purification. Amberlite XAD4 resin (Rohm and Hass) was used as a macroporous polymeric support. It is made of styrene-divinylbenzene copolymer with a specific surface area of 750 m²/g, an average pore diameter of 40 Å, and a particle size of 20–50 mesh. The resin was washed with distilled water and acetone several times in turn, and dried at 50°C. Stock solutions of U(VI) and Th(IV) (∼10⁻³ M) were prepared by dissolving UO₂Cl₂, 2H₂O and Th (NO₃)₄, 4H₂O (Prolabo) in distilled water, respectively. Concentrated HCl (1–2 mL) was added to 100 mL solutions of U(VI) and Th(IV) to suppress hydrolysis. ¹⁵²,¹⁵⁴Eu, ⁵¹Cr, ⁶⁰Co, ⁶⁵Zn, and ¹³⁴Cs were obtained by neutron irradiation of appropriate target materials in the ERR-1 reactor in Egypt. All chemicals used were of analytical grade.

Preparation of impregnated resin: Impregnated resins were prepared using a dry impregnation method. An appropriate volume of 0.2 M TDA solution in n-hexane was mixed with a weighted amount of the resin for 1 hour. The diluent was then evaporated at 50°C for 24 hours. The concentration of TDA in the prepared impregnated resin was determined from the amount of HCl sorbed by shaking the impregnated resin with 0.1 M HCl, and is given as moles of TDA per Kg of dry impregnated resin.

Extraction procedure: All extraction experiments were conducted batch wise at room temperature (25 ± 2°C). Samples of 0.05 g of impregnated resin were shaken vigorously with 5 mL of aqueous solutions containing U(VI) or Th(IV) (∼10⁻⁴ M) for 24 hours, unless otherwise stated. ¹⁵²,¹⁵⁴Eu, ⁵¹Cr, ⁶⁰Co, ⁶⁵Zn, and ¹³⁴Cs were used in trace concentrations. The distribution ratio (D) and the uptake percent of metals were calculated as follows:

\[ D = \frac{[M]_e - [M]_i}{[M]_i} \times \frac{V}{m} \]
\[ \text{Uptake} \% = \frac{[M]_e - [M]_i}{[M]_i} \times 100 \]

where [M]ᵢ and [M]ₑ are the initial and the equilibrium concentrations of metal ions in the aqueous phase, respectively, V is volume of the aqueous phase, and m is weight of dry impregnated resin. The uranium and thorium concentrations were determined spectrophotometrically using a spectrophotometer (Shimadzu UV-120-02) with arsenazo III. Gamma emitter...
radioisotopes were controlled using hyper pure germanium detector connected to a multichannel analyzer (Canberra Genie 2000). The extracted uranium amine complexes were eluted from metal-loaded impregnated resins by shaking with benzene for 24 hours. The absorption spectra of these benzene solutions and the corresponding aqueous phases were obtained by a spectrophotometer (Shimadzu UV-160 A).

3. RESULTS AND DISCUSSION

3.1. Extraction of uranium from chloride media. The effect of contact time on sorption of U(VI) from 6 M HCl solution with TDA-impregnated resin is shown in Figure 1. The uranium uptake percent increases with increasing contact time till equilibrium is reached after 24 hours. The extraction of $10^{-4}$ M UO$_2$$^2+$ solution with TDA-impregnated resin was examined at different HCl concentrations. The results indicate that U(VI) extraction increases with increasing acidity and becomes quantitative at 7 M HCl. The data are shown in Figure 2. These results are in agreement with those obtained for the solvent extraction of U(VI) from HCl solution with high molecular weight amines dissolved in organic solvents.\textsuperscript{27-31} The results for the extraction of U(VI) from solutions containing 0.1 M HCl and lithium chloride at various concentrations are also presented in Figure 2. As LiCl concentration increases, the uptake percent of U(VI) increases. This probably implies that the controlling factor for the extraction process is the chloride ion concentration. Thus, it may be assumed that the increase in U(VI) extraction arises from the effect of chloride ion in the aqueous phase or from the formation of an extractable uranyl-chloro complex. Hence, it is possible to describe the present extraction reaction in the same way as reported for the solvent extraction of uranium in U(VI)-HCl-R$_3$N systems.\textsuperscript{27-31}

$$\text{UO}_2\text{Cl}_2 + m\text{R}_3\text{NH}^+\text{Cl}^- \rightarrow (\text{R}_3\text{NH})_m\text{UO}_2\text{Cl}_{2m} \quad (1)$$

where the subscript (r) denotes the resin phase.

The effect of hydrochloric acid concentration on sorption of U(VI) was studied at constant chloride ion concentration. The total chloride ion concentration was kept constant using lithium chloride. As shown in Figure 3, at low aqueous acidities, the uranium distribution ratio increases with increasing HCl concentration. At high aqueous acidities, the distribution ratio becomes approximately constant. This behavior has not been reported before for the extraction of actinides by amines. A possible explanation for this behavior may be as follows: at low aqueous acidities, the replacement of hydrogen ion by lithium ion results in a decrease in the distribution ratio because Li$^+$ ion has a lower hydration affinity than H$^+$ ion and consequently Li$^+$ ion has a lower salting-out effect than H$^+$ ion. At high aqueous acidities, the extraction of excess HCl which is a little from aqueous acid concentrations below 2 M\textsuperscript{23} becomes more pronounced. The competition between excess HCl and uranium for association with amine results in a decrease of the uranium distribution ratio. This decrease is compensated by the higher effect of the hydrogen ion.

The uranium distribution ratio, determined as a function of amine concentration in the resin phase, is presented in Figure...
4, where uranium distribution ratio increases slightly with amine concentration then it decreases at high amine concentrations. Blocking of resin pores by amine molecules and extracted metal complexes may be the reason for such behavior.\(^{5,32}\) The uranium concentration of the resin phase is determined as a function of initial aqueous uranium concentration at 7 M HCl. The data shown in Figure 5 represents a typical Langmuir isotherm. The U(VI) concentration of the resin phase approaches a limiting value of \(-0.04\) mol/kg. According to eq 1 the uranium to amine loading ratio was expected to amount of \(1/m\). However, the ratio was found to be much smaller than any reasonable value for \(1/m\). This suggests that some of the amine molecules within the sorbent are unavailable and do not participate in the sorption reaction owing to steric hinderance or an occlusion.\(^{5,32}\)

**Adsorption Spectral Studies:** The absorption spectra of aqueous uranyl chloride solutions (0.015 M) containing hydrochloric acid at various concentrations are presented in Figure 6a. The corresponding spectra of uranium species eluted from impregnated resin (preloaded with uranium) using benzene are presented in Figure 6b. For the spectra of aqueous uranyl chloride solutions, the following results were observed: In 1 M HCl, a band center at 415 nm is exhibited due to the uranyl ion UO\(_2\)\(^{2+}\),\(^{31}\) while in 5 M HCl, this absorption shifts to longer wavelength due to the formation of the species UO\(_2\)Cl\(^+\) and UO\(_2\)Cl\(_2\)\(^-\) and is accompanied by the characteristic absorption peaks at 402, 428, 441, 460, 467, and 492 nm, which probably arise from the presence of the complex ion UO\(_2\)Cl\(_2\)\(^-\).\(^{34,35}\) For solutions up to 9 M HCl, these peaks show a progressive increase in intensity, which indicates that UO\(_2\)Cl\(_2\)\(^-\) complex becomes more predominant. In contrast, the spectra of the organic solutions show largely the adsorption peaks characteristic to the UO\(_2\)Cl\(_4\)\(^2-\) complex, even though the spectrum of the aqueous solution at low HCl concentration does not indicate the presence of UO\(_2\)Cl\(_4\)\(^2-\) complex ion. This indicates that the extracted species is the six-coordinated uranium complex ion UO\(_2\)Cl\(_4\)\(^2-\) and the value of \(m\) in eq 1 equals 2. Hence, the extraction reaction may be written as follows:

\[
\text{UO}_2\text{Cl}_2 + 2 \text{R}_3\text{NH}^+\text{Cl}^- \rightarrow \left(\text{R}_3\text{NH}\right)_2\text{UO}_2\text{Cl}_4
\]

**3.2. Extraction of uranium from nitrate media.** Extraction of U(VI) from aqueous solutions containing various concentrations of nitric acid with TDA-impregnated resin is shown in
The uptake percent of uranium increases with increasing initial aqueous HNO$_3$ concentration, reaches a maximum at approximately 5 M HNO$_3$, and then decreases. The uptake percent does not exceed 20% in the whole range of acidity studied. Generally, the extraction reaction could possibly be described as follows:

$$\text{UO}_2(\text{NO}_3)_{2} + m \text{R}_3\text{NH}^+ \text{NO}_3^-(r) \rightarrow (\text{R}_3\text{NH})_m \text{UO}_2(\text{NO}_3)_{2+m}(r)(3)$$

Therefore, the nitric acid dependency may be explained as follows: at low aqueous acidities, the increase in the uptake percent arises from the effect of nitrate ion or the formation of extractable uranium-nitrato complex. Where, at high aqueous acidities, the decrease in the uptake percent is attributed to competition between nitric acid and uranium species for the association with the amine or to the formation of less readily extractable complexes. Sato$^{6}$ explained similarly the acid dependency of uranium (VI) extraction from nitric acid solutions by tri-n-octylamine dissolved in benzene. So, one should expect no decrease of the uranium uptake percent when plotted against the nitrate ion concentration at constant (low) aqueous acidities. Actually, this behavior is verified when lithium nitrate is the source of nitrate ions, as shown in Figure 7, where the uptake percent increases continuously with increasing nitrate ion concentration.

Figure 8 represents the extraction of U(VI) as a function of initial aqueous nitric acid concentration, while the total nitrate ion concentration was kept constant using lithium nitrate. The uranium distribution ratio decreases with increasing nitric acid concentration. This behavior confirms the assumption that nitric acid competes with uranium for association with the amine through the reaction:

$$\text{R}_3\text{NH}^+ \text{NO}_3^-(r) + \text{HNO}_3 \rightarrow \text{R}_3\text{NH}^+ \text{NO}_3^- \cdot \text{HNO}_3(r)(4)$$

3.3. Elution of uranium. Elution of uranium from metal preloaded impregnated resin with HCl and HNO$_3$ acids of various concentrations is presented in Figure 9. The maximum elution percent of U (VI) was attained using dilute acids, which is in agreement with results obtained by Felinto et al.$^{15}$ The hydrochloric and nitric acid dependencies of elution percent have reversible shapes to that of acid dependencies of uptake percent shown in Figures 2 and 7. It means that the extraction reactions of uranium (VI) from hydrochloric and nitric acids eqs 2 and 3 are reversible.

Two successive extraction-elution cycles were carried out on the system U(VI)-HCl-TDA/XAD4. The data are listed in Table 1. Uptake percent of the second extraction process is 10% less than that at the first extraction process. This decrease may be attributed to leakage of some amine molecules from the resin. More investigations are required to precisely describe
TABLE 1: Two Successive Extraction Elution Cycles of Uranyl Chloride from TDA-Impregnated Resin

<table>
<thead>
<tr>
<th>Extraction processes</th>
<th>Uptake %</th>
<th>Elution processes</th>
<th>Elution %</th>
</tr>
</thead>
<tbody>
<tr>
<td>First extraction</td>
<td>100</td>
<td>First elution</td>
<td>73</td>
</tr>
<tr>
<td>Second extraction</td>
<td>90</td>
<td>Second elution</td>
<td>70</td>
</tr>
</tbody>
</table>

\[ [\text{TDA}]_{(r)} = 0.96 \text{ mol/kg}, \ m = 0.05 \text{ g}, \ V = 5 \text{ mL}. \]

this behavior and its effect on the stability of the amine impregnated resins.

3.4. Extraction of thorium from chloride media. The extraction of Th(IV), \(10^{-4} \text{ M}\), from hydrochloric acid solutions with TDA-impregnated resin was experimented. The uptake percent of thorium is negligible all over the studied range of HCl concentration, as observed in the solvent extraction with high molecular weight amines.\(^{38,39}\). This behavior was reasoned, since thorium (IV) does not form anionic complexes with the chloride ion.

3.5. Extraction of thorium from nitrate media. Based on preliminary experiments of nitrate ion concentration dependency, effect of contact time on sorption of \(10^{-4} \text{ M} \) Th(IV), from nitrate media was studied at 6 M initial nitrate ion concentration. As Figure 10 indicates, equilibrium is attained after 24 hours. Therefore, a 24 hours extraction time was chosen for all the subsequent experiments.

Figure 11 represents the extraction of Th(IV) from aqueous solutions containing various concentrations of nitric acid. The uptake percent of thorium increases with increasing nitric acid concentration, reaching a maximum of \(\approx 25\%\) at approximately 6 M HNO\(_3\) and then decreases. This behavior was observed for the extraction of Th(IV) with high molecular weight amines.\(^{39,40}\) and could be interpreted as follows: at low aqueous acidities the increase in the uptake percent arises from the effect of nitrate ion in the aqueous phase or the formation of extractable thorium nitrate complexes; while at high aqueous acidities the decrease in the uptake percent is attributed either to competition between nitric acid and thorium complexes for association with amine or to the formation of less readily extractable thorium complexes. The results of the extraction of thorium from aqueous solutions containing 0.2 M nitric acid and lithium nitrate at various concentrations are shown in Figure 11. Replacement of nitric acid in the aqueous phase by lithium nitrate (except the amount of acid needed for the amine salt formation) checks the above mentioned decrease in the thorium percentage uptake at high aqueous acidities. The reason for this check may be the removal of nitric acid which competes with thorium complexes for association with the amine. On the other hand, when a part of nitric acid was replaced by lithium nitrate, thorium distribution ratio increased considerably, as shown in Figure 12. Thus at constant nitrate ion and TDA

![Figure 10](image1)

![Figure 11](image2)

![Figure 12](image3)
concentrations, the distribution ratio decreases with increasing acidity. This phenomenon is also probably associated with the formation of the acid species R3NHNO3 in the resin phase. A similar behavior was observed for solvent extraction of cerium (III) by TDA.41

The amine dependency of thorium (IV) extraction was studied at constant nitric acid and nitrate ion concentrations. As shown in Figure 13, thorium distribution ratio, D, increases slightly with increasing TDA concentration from 0.48 to 0.96 mol/kg followed by a steep increase till extraction of thorium becomes nearly quantitative. The amine dependency could not properly describe the present extraction equilibrium, probably due to complicating factors originating from blocking of resin pores32 by amine molecules, amine aggregates and amine metal complex mixed associates which may be formed in the resin phase.

Figure 14 represents thorium concentration of the resin phase as a function of initial aqueous thorium concentration. Sorption behavior represents a typical Langmuir isotherm. The amounts of Th (IV) sorbed by the resin increase with increasing aqueous thorium concentration and approaches limiting values of 0.05 and 0.07 mol/kg with sorbents of 0.96 and 1.32 mol/kg, respectively. The thorium to amine loading ratio is too small to reasonably indicate their stoichiometric ratio in the extracted species. The reason for this complication may be the existence of unavailable TDA molecules within the sorbent, which do not participate in the sorption reaction due to steric hindrance or occlusion.32

3.6. Elution of thorium (IV). Figure 15 shows the effect of initial aqueous concentrations of HCl and HNO3 on the percent of thorium eluted from TDA-impregnated resin preloaded with Th(IV). As would be expected, hydrochloric acid is much more efficient than nitric acid for thorium elution. The maximum elution percent attained with nitric acid was 66% using 0.01 M HNO3. Approximately the same elution percent was attained, when distilled water was used as an eluent. Quantitative recovery of thorium is possible only with dilute HCl solution.

The trend of nitric acid dependency of thorium elution, shown in Figure 15, is nearly the reverse of that of thorium extraction. (See Figure 11 which indicates that thorium extraction is a reversible process.) The successive extraction elution cycles were performed to study the regeneration of the TDA-impregnated resin after being loaded with thorium. The conditions and results obtained are given in Table 2. Results indicate that the extraction process is reversible and TDA-impregnated resin can be regenerated and reused efficiently.

3.7. General application to metal separation. The results obtained in the single metal experiments indicate that the extractabilities of uranium (VI) and thorium (IV) from nitric acid media are similarly low. On the other hand, U(VI) could be extracted quantitatively from HCl acid of concentration > 6 M, whereas Th(IV) extraction is negligible in the whole range.

\[\text{Figure 13. Effect of TDA concentration on extraction of Th(IV) from nitrate media (0.2 M HNO}_3 + \text{LiNO}_3).\]

\[\text{Figure 14. Effect of initial aqueous Th}^{4+} \text{concentration on amount of Th}^{4+} \text{sorbed from 0.2 M HNO}_3 + 5.8 \text{ M LiNO}_3 \text{solution with TDA-impregnated resin; } [\text{TDA}]_o; \text{ in the unit of mol/kg.}\]

\[\text{Figure 15. Effect of HCl or HNO}_3 \text{concentration on elution of Th(IV) loaded on TDA-impregnated resin; } [\text{Th}^{4+}]_{\text{initial}} = 5 \times 10^{-2} \text{ mol/kg, } m = 0.05 \text{ g, } V = 5 \text{ mL, } [\text{TDA}]_o = 0.96 \text{ mol/kg.}\]
TABLE 2: Successive Extraction-Elution Cycles of Thorium (IV) Nitrate on TDA-Impregnated Resin

<table>
<thead>
<tr>
<th>Extraction processes</th>
<th>Uptake %</th>
<th>Elution processes</th>
<th>Elution %</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Th]_{initial} = 10^{-3} M</td>
<td>94</td>
<td>using distilled</td>
<td>66</td>
</tr>
<tr>
<td>[HNO₃] = 0.2 M</td>
<td>95</td>
<td>water</td>
<td>73</td>
</tr>
<tr>
<td>[LiNO₃] = 5.8 M</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

First extraction
Second extraction

[TDA]₀ = 0.96 mol/kg, m = 0.05 g, V = 5 mL.

studied of HCl concentration. This latter observation suggests the possibility of separating uranium and thorium from hydrochloric acid medium by TDA-impregnated resin. Therefore, solution mixture of ~10⁻⁴ M initial concentration of both U(VI) and Th(IV) cations were extracted with 0.96 mol/kg TDA-impregnated resin from HCl solution of various concentrations. Results obtained are shown in Table 3 which indicates that the two cations can be well separated from each other, especially at high HCl concentration where the uranium uptake percent is quantitative and thorium uptake is generally zero.

Available data are sufficient to suggest that separation of actinides and fission products can be at least as good in HCl-tri-alkyl amine system as in Purex. Therefore, the HCl-impregnated resin system was investigated for separation of uranium from some fission products and some related elements.

TABLE 3: Separation of U(VI) and Th(IV) from HCl Solutions Using TDA-Impregnated Resin

<table>
<thead>
<tr>
<th>[HCl], M</th>
<th>Uptake % of U(VI)</th>
<th>Uptake % of Th(IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>34</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>78</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>94</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>99</td>
<td>0.0</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>0.0</td>
</tr>
</tbody>
</table>

[TDA]₀ = 0.96 mol/kg, m = 0.05 g, V = 5 mL.

A mixture solution of ~10⁻⁴ M U(VI) and tracer Cs(I), Co(II), Zn(II), Cr(III), and Eu(III) ions was extracted by 0.1 g of 0.96 mol/kg TDA-impregnated resin at various HCl acid concentrations. The results are shown in Figure 16. The extraction of the elements is approximately close to that predicted from known anionic chlorocomplexing studies. The variations in the uptake percent of the investigated elements suggest several alternatives for their separation as groups and from each other. For example, uranium (VI) can be separated from Cs(I), Co(II), Cr(III), and Eu(III) by sorption onto TDA-impregnated resin at 4 M HCl and from Zn(II) by stripping into 1 M HCl. Also, Co(II) and Zn(II) can be well separated from each other at 1–4 M HCl. While, Zn(II) is almost quantitatively extracted by the TDA-impregnated resin, where Co(II) remains almost completely in the residual bulk solution. Figure 17 represents a flowsheet diagram for separation of U(VI), Eu(III), Cr(III), Co(II), Zn(II), and Cs(I).

To be concluded that solvent extraction impregnated resin as a recent technique promises a wide applicability for separation and removal of different trace elements. Where U(VI) and Th(IV) are successfully extracted with great extent using tri-n-dodecylamine impregnated resin from aqueous media.

REFERENCES


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