Method and mechanism for efficient radium isolation from bulk thorium based on anion exchange

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Abstract: In recent years, targeted-α-nuclide therapy (TAT) has been widely concerned in the world. As one of the few representative TAT nuclides, $^{212}\text{Pb}$ has shown good efficacy in cancer treatment; however, the amount remains scarce. Separating $^{228}\text{Ra}$ and $^{224}\text{Ra}$ from $^{232}\text{Th}$ is expected to fundamentally solve this issue. In this work, a novel and effective method for trace radium isolation from bulk thorium was proposed and verified through a systematic investigation of the adsorption behaviors of an anion exchanger denoted IRA900 toward thorium and barium/radium. Batch experiments suggested that IRA900 had unique selectivity for thorium in nitric acid solution, with almost no barium adsorbed. The thorium adsorption performance kept improving with increasing concentration of nitric acid and decreasing temperature. The IRA900 resin required about 8 h to reach adsorption equilibrium, and the estimated maximum adsorption capacity toward thorium was about 254 mg/g. The adsorption kinetics and adsorption isotherm could be well fitted by the pseudo-second-order kinetic model and the Langmuir model, respectively. Column experiments suggested that thorium could be effectively immobilized by a column packed with IRA900, while barium was directly penetrated. For desorbing the fixed thorium, 0.1 M HNO$_3$ was optimal. A final hot test demonstrated the successful radium isolation from bulk thorium, with high chemical yield and purity. The selective separation mechanism was attributed to the formation of an anionic [Th(NO$_3$)$_5$]$^-$ complex, while barium or radium existed in the cationic form in any nitric acid concentration. This work provides a promising method for separating trace radium from natural thorium, which will be significant for promoting the large-scale utilization of $^{212}\text{Pb}$.

Key words: thorium; radium; separation; anion exchange; mechanism
1 Introduction

In recent years, TAT has been widely concerned in the world, for its outstanding advantages in cancer treatment[1-4]. TAT refers to the targeted delivery of α-nuclide in tumor lesions with highly selective carriers, relying on ionizing radiation generated by α-nuclides to inflict damage to diseased tissues in a small range. Compared with traditional radiotherapy, TAT causes less damage to normal tissues and cells and can minimize pain in cancer patients during the treatment process; thus, it is considered one of the most promising technologies in future cancer treatment[5].

The core principle of TAT involves unique radionuclides. As one of the few representative TAT nuclides, $^{212}$Pb ($T_{1/2} = 10.6$ h) has shown good efficacy in treating malignant tumors[6-12]. According to numerous preclinical experimental data, the first clinical trials on $^{212}$Pb were performed in the US in 2011, achieving good results[2]. However, due to the rare resources of $^{212}$Pb, the medicinal development and clinical application of its targeted medicines have remained severely limited[13]. Currently, $^{212}$Pb is mainly derived from $^{232}$U ($T_{1/2} = 68.9$ a)[2]. The acquisition cost and technical threshold of $^{232}$U are very high due to the involvement of nuclear reactors, nuclear material control, radiation protection, separation of extremely trace elements, and even isotopes, resulting in the scarcity of $^{232}$U. Therefore, it is important to explore new routes and methods for obtaining sufficient $^{212}$Pb.

In addition to obtaining $^{212}$Pb from $^{232}$U, another route to obtaining $^{212}$Pb involves separating $^{228}$Ra and $^{224}$Ra from natural $^{232}$Th, fabricating these compounds in generators, and relying on the spontaneous decay of $^{228}$Ra and $^{224}$Ra to produce sufficient $^{212}$Pb[14-17]. In contrast to obtaining $^{212}$Pb from $^{232}$U, this route offers a low access barrier and a low cost and does not require reactors to obtain sufficient raw materials. Fig. 1 shows the decay chains of...
The key to obtaining $^{212}\text{Pb}$ through this route involves the efficient isolation of $^{228}\text{Ra}$ and $^{224}\text{Ra}$ from $^{232}\text{Th}$.

Fig. 1 Decay chains of $^{232}\text{Th}$ and $^{232}\text{U}$[1]

Reports on radium isolation from thorium remain limited in the world. Specifically, the main reason is that the isotopes of radium are all $\alpha$-decay nuclides with strong radioactivity, making experimental studies difficult and dangerous. Reported thorium/radium separation methods are classified into three kinds: co-precipitation[18], adsorption[19-21], and liquid–liquid extraction[14, 22]. The co-precipitation method involves simultaneously adding sulfuric acid and barium ions to thorium solution[18], with trace radium separated as Ba/RaSO$_4$ precipitate. Although this method has shown to be effective, it greatly increases the difficulty of subsequent dissolution and the further purification of radium. In the liquid–liquid extraction method[14], the di-(2-ethylhexyl) phosphate (HDEHP) extractant was used and dissolved in the diluent. HDEHP has shown high selectivity to thorium, but little affinity to radium, allowing it to be used for the efficient isolation of radium from thorium. However, this method may produce significant amounts of organic waste. In addition, due to the water solubility of HDEHP, the separation of thorium and radium will not be complete, and a small
amount of extractant will coexist in the radium product[14]. Adsorption methods are more
convenient and efficient in comparison, contributing to the greatest number of reports. Cation
exchange resins are frequently used in the adsorption method to separate radium from thorium.
For example, Daniel et al.[19] reported on the isolation of $^{225}\text{Ra}$ from irradiated $^{232}\text{Th}$ targets
in sulfuric acid media using a cation exchange resin. Tara et al.[20] reported on the successful
isolation of $^{225}\text{Ac}$ and $^{223,224,225}\text{Ra}$ from irradiated thorium targets using a combination of
cation exchange resins with other adsorbents. In our recent work[1], we reported on the
separation of $^{226}\text{Ra}$ from $^{232}\text{Th}$ in the medium of HNO$_3$ using a special silica-supported cation
exchange resin with excellent separation performance. Although the cation exchange resin
could be used for the separation of thorium and radium, the separation coefficient between
thorium and radium was relatively low, less than 120 in the medium of 0.1 M HNO$_3$[1].
Considering the enormous mass difference between thorium and radium in the natural
thorium decay chain ($\geq 10^8$:1), using cation exchange resin to isolate trace $^{228}\text{Ra}$ and $^{224}\text{Ra}$
from natural thorium remains difficult. Other than cation exchange resins, extraction resins
loaded with HDEHP have also been reported for separation[15]. However, the water solubility
of HDEHP was not fundamentally addressed in these extraction resins.

In this work, we reported a novel and effective method for the isolation of $^{228}\text{Ra}$ and
$^{224}\text{Ra}$ from bulk thorium through a systematic investigation of the adsorption behaviors and
mechanisms of an anion exchanger denoted IRA900 toward thorium and radium in the nitric
acid solution. Compared with methods using cation exchange resins, this method showed a
higher separation factor and efficiency. Compared with extraction and adsorption methods
using HDEHP extractant, this method avoided the use of sparingly soluble extractant and a
large amount of diluent, leading to a reduction in the amount of produced organic water and
waste. In addition, thorium species distribution in nitric acid was calculated and exhibited for the first time, successfully laying a theoretical foundation for this type of separation. This work offers a promising method for the isolation of $^{228}$Ra and $^{224}$Ra from bulk $^{232}$Th, rendering it significant for promoting the large-scale utilization of $^{212}$Pb.

2 Experimental methods

2.1 Materials and reagents

The IRA900 resin, the 732 resin, the thorium tetranitrate (AR, 98%), and the barium dinitrate (AR, 99%) were purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Concentrated nitric acid (65–68 wt%) was provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The $^{226}$Ra standard solution was purchased from China Isotope & Radiation Co., Ltd. (Beijing, China). The ultrapure water with a resistivity of 18.2 MΩ was used to prepare solutions. The IRA900 resin is a strong base anion exchange resin, of which the body involves the styrene–divinylbenzene copolymer, and the functional group involves quaternary amine ($\text{R}^+\text{N}^+(\text{CH}_3)_3$). The 732 resin is a cation exchange resin, of which the body involves the styrene–divinylbenzene copolymer, and the functional groups involves sulfonic group ($\text{R}-\text{SO}_3^-$). The IRA900 and 732 resin were pretreated with 1.0 M HNO$_3$ and were dried before use. Other reagents were used directly.

2.2 Characterization

The IRA900 resin samples before and after adsorption were scanned by a scanning electron microscope with an energy-dispersive spectrometer (SEM-EDS, Tesscan Mira Lms, Czech) to obtain the surface morphology and element composition. The functional groups were assessed by a Fourier-transform infrared spectrometer (FT-IR, Shimadzu IR Tracer 100,
Japan), and KBr (SP) was employed for tablet pressing and sample preparation. The porosity and specific surface area were assessed by a Brunauer–Emmett–Teller specific surface area and porosity analyzer (BET, ASAP 2460, Micromeritics, USA) with nitrogen adsorption and desorption.

2.3 Batch experiments

The IRA 900 resin (0.05 ± 0.0005 g) was weighed and added to multiple small glass bottles. Subsequently, each bottle was added to 20 mL working solution, which contained certain concentrations of thorium, barium, and nitric acid, and then was sealed with a Teflon lid. Barium served as a radium surrogate due to similar chemical properties[23]. These glass bottles were placed in a water bath shaker and subjected to oscillation at a frequency of 160 rpm at a temperature of 25°C. After a period of time, the glass bottles were removed, and then the solution was separated from IRA900 using a microporous filter membrane. The thorium and barium concentrations were measured with an inductively coupled plasma emission spectrometer (ICP-AES, Ultima Expert, Japan). Based on the concentration changes before and after adsorption, the adsorption efficiency $A$ (%), the adsorption amount $Q$ (mg/g), the distribution coefficient $K_d$ (mL/g), and the separation factor $SF$ were calculated using the following formulas[24]:

$$A = \left( \frac{C_0 - C_t}{C_0} \right) \times 100,$$

$$Q = \left( \frac{C_0 - C_t}{C_t} \right) \times \frac{V}{m},$$

$$K_d = \left( \frac{C_0 - C_t}{C_t} \right) \times \frac{V}{mC_e},$$

$$SF_{Th/Ba} = K_d^{Th} / K_d^{Ba},$$

where $C_0$ (mg/L) and $C_e$ (mg/L) denote the initial and equilibrium metal concentrations,
respectively, $C_t$ (mg/L) is the metal concentration at time $t$ (h), and $V$ (mL) and $m$ (g) represent the solution volume and adsorbent mass, respectively.

The effects of HNO$_3$ concentration, contact time, equilibrium concentration, and ambient temperature on the separation behaviors of the IRA900 resin were investigated by controlling the variables. On the basis, the data were further fitted using typical mathematical adsorption models[25], including the pseudo-first-order kinetic model (PFO), the pseudo-second-order kinetic model (PSO), the intra-particle diffusion model (IPD), the Langmuir model, and the Freundlich model. Details regarding the batch experiments and an introduction of these mathematical models are described in the Supplementary Materials (SM).

2.4 Column experiments

A certain amount of IRA900 resin was added to a glass column (dimensions: $h \times \phi = 20 \times 1$ cm) equipped with sieve plates at both ends, where the resin volume in the wet state was half of the column volume. Ultrapure water was pumped to remove any bubbles in the resin column and ensure that the liquid level always remained 1–2 cm higher than the resin height. The solution was pumped from the upper side to the bottom of the column by a peristatic pump, and then collected by a fraction collector. In this part, the flow rate and desorption condition were optimized, and Th/Ba and Th/Ra separation were performed based on the optimized parameters. Because $^{228}$Ra ($T_{1/2} = 5.75$ a) and $^{224}$Ra ($T_{1/2} = 3.66$ d) had short half-lives and high specific activities, $^{226}$Ra ($T_{1/2} = 1600$ a) with a long half-life was used as a tracer nuclide to facilitate measurements and confirm the separation effect in practical applications, and the mass ratio of $^{232}$Th to $^{226}$Ra reached $1.64 \times 10^7 : 1$ in the hot test. More details are provided in the SM, including the $^{226}$Ra measurement method.
2.5 Calculations

Calculations to determine the amounts of $^{228}\text{Ra}$ and $^{224}\text{Ra}$ produced by thorium were based on the half-lives of the nuclides in the decay chain of $^{232}\text{Th}$, as shown in Fig. 1, using the following equations:

$$A_n(t) = \lambda_n \cdot N_1^0 \left( C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t} + C_3 e^{-\lambda_3 t} + \cdots + C_n e^{-\lambda_n t} \right).$$  \hspace{1cm} (5)

In Equation (5)

$$C_n = \frac{\lambda_1 \lambda_2 \cdots \lambda_{n-1}}{(\lambda_1 - \lambda_2)(\lambda_2 - \lambda_3)\cdots(\lambda_{n-1} - \lambda_n)},$$  \hspace{1cm} (6)

$$\lambda_n = \frac{\ln 2}{T_{1/2}^n},$$  \hspace{1cm} (7)

where $A_n(t)$ (Bq) represents the activity of the $n^{th}$ member of the decay chain at time $t$ (a), $\lambda_n$ (s$^{-1}$) and $T_{1/2}^n$ (s) represent the decay constant and half-life of the $n^{th}$ member of the decay chain, respectively, and $N_1^0$ denotes the initial number of atoms of the first member of the decay chain.

Table 1 Thermodynamic data of thorium and barium used for calculation

<table>
<thead>
<tr>
<th>Products</th>
<th>Chemical Equations</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ba(NO}_3\text{)}]^+$</td>
<td>$\text{Ba}^{2+} + \text{NO}_3^- = [\text{BaNO}_3]^+$</td>
<td>0.92$^a$</td>
</tr>
<tr>
<td>$[\text{Th(NO}_3\text{)}]^3+$</td>
<td>$\text{Th} + \text{NO}_3^- = [\text{Th(NO}_3\text{)}]^3+$</td>
<td>0.78$^b$</td>
</tr>
<tr>
<td>$[\text{Th(NO}_3\text{)}]^2+$</td>
<td>$\text{Th} + 2\text{NO}_3^- = [\text{Th(NO}_3\text{)}]^2+$</td>
<td>1.11$^b$</td>
</tr>
<tr>
<td>$[\text{Th(NO}_3\text{)}]^-$</td>
<td>$\text{Th} + 3\text{NO}_3^- = [\text{Th(NO}_3\text{)}]^-$</td>
<td>1.00$^b$</td>
</tr>
<tr>
<td>$\text{Th(NO}_3\text{)}^4$</td>
<td>$\text{Th} + 4\text{NO}_3^- = \text{Th(NO}_3\text{)}^4$</td>
<td>0.74$^b$</td>
</tr>
<tr>
<td>$[\text{Th(NO}_3\text{)}]^-$</td>
<td>$\text{Th(NO}_3\text{)}^4 + \text{NO}_3^- = [\text{Th(NO}_3\text{)}]^-$</td>
<td>−0.80$^b$</td>
</tr>
<tr>
<td>$[\text{Th(NO}_3\text{)}]^2$</td>
<td>$\text{Th(NO}_3\text{)}^4 + 2\text{NO}_3^- = [\text{Th(NO}_3\text{)}]^2$</td>
<td>−1.70$^b$</td>
</tr>
</tbody>
</table>

$^a$ Obtained from the lnt.dat database in the PHREEQC software[26].

$^b$ Obtained from the work of J. Danon[27].

The thorium and barium species distribution were calculated by PHREEQC software, and thorium and barium concentrations were set as 1000 and 600 mg/L, respectively, with the
temperature set as 25°C. Table 1 lists the thermodynamic data used for calculation.

3 Results and discussion

3.1 Amounts of $^{228}$Ra and $^{224}$Ra produced by $^{232}$Th

To determine the amount of radium in natural $^{232}$Th, the activities of $^{228}$Ra and $^{224}$Ra with increasing time were calculated for 100 t of thorium, based on their half-lives. As shown in Fig. 2, the activities of $^{228}$Ra and $^{224}$Ra quickly increased with increasing time over the first 15 years, reaching equilibrium after about 50 years. In the equilibrium state, the activities of $^{228}$Ra and $^{224}$Ra both reached 109 Ci (1 Ci = $3.7 \times 10^{10}$ Bq). Even after the first year, the activities of $^{228}$Ra and $^{224}$Ra produced by $^{232}$-Th could still reach 12.5 and 2.0 Ci, respectively. The amount of $^{212}$Pb produced by these radium isotopes was expected to exceed 20 Ci or more if extracted at a suitable interval within 1 year. Therefore, extracting sufficient $^{228}$Ra and $^{224}$Ra from natural thorium would be theoretically possible.

3.2 Characterization

The IRA 900 resin was first examined by FT-IR spectroscopy to assess its chemical structure and functional groups. As shown in Fig. 3, the broad and strong peak in 3433 cm$^{-1}$

Fig. 2 Activities of $^{228}$Ra and $^{224}$Ra produced by 100 t of $^{232}$Th with increasing time

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resulted from the stretching vibrations of -OH of the adsorbed water molecules[28]; the peaks at 2968 and 2931 cm$^{-1}$ were the characteristic peaks of –CH$_3$ and –CH$_2$–, respectively[29]; the strong peak at 1624 cm$^{-1}$ was the characteristic peak of the conjugated alkene double bonds on the aromatic rings[30]; the peaks at 760 and 670 cm$^{-1}$ were attributed to the bending vibrations of the C–H bond. Except for the above peaks, the characteristic peak of NO$_3^-$ was also observed at 1380 cm$^{-1}$[31], suggesting that the IRA900 resin was successfully transformed into nitrate-type, with NO$_3^-$ anions as the counter ions. The shoulder peak at 1350 cm$^{-1}$ was attributed to the stretching vibrations of C–N[32, 33], but no strong peaks were found around 1429 cm$^{-1}$ (resulting from the bending vibrations of N–H)[34], suggesting that the amine groups carried by the IRA900 resin were the quaternary amine.

![FT-IR spectrum](https://doi.org/10.26434/chemrxiv-2024-3c9cq)

**Fig. 3** FT-IR spectrum of the IRA900 resin and the resin loaded with thorium.

The IRA900 resin was further examined by the BET method. As shown in **Fig. 4(a)**, the N$_2$ adsorption/desorption isotherms of IRA900 showed almost no hysteresis loop. **Fig. 4(b)** presents the pore size distribution of the resin, which showed that the pore size mainly concentrated around 53 nm, with few micropores and small mesopores, which were responsible for no hysteresis loops observed in **Fig. 4(a)**. The pores in the IRA900 resin
mainly consisted of macropores, which conformed to the characteristics of macro-porous resins. According to the calculations, the BET specific surface area, the pore volume and the average pore diameter of the IRA900 resin were 17.2 m$^2$/g, 0.15 cm$^3$/g, and 54.3 nm, respectively. These data demonstrated that IRA900 was a macro-porous resin with insufficient pores.

**Fig. 4** BET measurement results of IRA900. (a) N$_2$ adsorption and desorption isotherms; (b) Pore size distribution.

**Fig. 5** SEM-EDS scanning results of the IRA900 resin.
Fig. 5 shows the surface morphologies and element distribution of the IRA900 resin, which possessed a regular spherical form, and the diameter was estimated 200–700 μm. The elements of carbon, oxygen, and nitrogen were uniformly distributed on the surface, and no barium or thorium was observed, suggesting that the IRA900 resin consisted of carbon, hydrogen, oxygen, and Nitrogen. In addition, the atomic ratio of nitrogen to oxygen was 1.82:3 (>1:3), indicating the presence of amine groups except for NO$_3^-$ as the counter ions.

3.3 Batch experiments

The adsorption behaviors of IRA900 towards barium and thorium were first studied by varying the nitric acid concentrations. As exhibited in Fig. 6(a), the distribution coefficient of IRA900 toward thorium gradually increased with increasing nitric acid concentration, while the distribution coefficient toward barium was quite low at all acidities and close to 0. These results suggested that IRA900 could only adsorb thorium and showed almost no affinity to barium in the nitric acid solution, indicating an excellent separation factor for thorium and barium. As comparison, the adsorption behaviors of the 732 resin were also exhibited, which was observed to adsorb thorium and barium simultaneously. Hence, compared with traditional cation exchange resins, the anion exchange resin IRA900 showed significant advantages for Ba/Th separation. Because IRA900 showed no adsorption toward barium, barium was unnecessary to consider for the subsequent experiments. In addition, 7.5 M HNO$_3$ was selected to avoid excessive acidity.

The adsorption kinetics of IRA900 toward thorium were subsequently studied by changing the contact times between the adsorbent and solution, and the experimental results are exhibited in Fig. 6(b). For a thorium concentration of 500 mg/L, IRA900 required
approximately 480 min (= 8 h) to get the adsorption equilibrium, while for a thorium concentration of 1000 mg/L, IRA900 required 960 min (= 16 h) to get the adsorption equilibrium. In general, the adsorption speed of IRA900 was slow, which could be ascribed to its large particle size and small specific surface area, as shown in Fig. 4 and 5. A large particle size indicated that more time was required for adsorbate diffusion, and a small specific surface area indicated that the active sites were difficult to expose[35].

To further determine the rate-controlling step, PFO and PSO models were adopted to describe the kinetic data, and the fitting results are exhibited in Fig. 6(c) and Table 2. According to the correlation coefficient ($R^2$), the PSO model fit the kinetic data better than the PFO models, and the estimated adsorption amounts were closer to the actual values, indicating that the thorium adsorption process was dominated by chemical reactions[36-38]. The kinetic data was also fitted by the IPD model, and the results were exhibited in Fig. 6(d). The adsorption process of the IRA900 resin could be divided into three linear adsorption processes, suggesting that the intra-particle diffusion played an important role in the adsorption process[31]. The first linear adsorption stage marked in black was attributed to the adsorption of thorium on the external surface or in the macropores. The adsorption speed was the fastest during this period. At the second linear adsorption stage marked in blue, the adsorption speed started to slow down, which corresponded to the diffusion into the mesopores and micropores. The third linear stage was the equilibrium stage, suggesting that adsorption was mostly finished. The obtained parameters of the IPD model are shown in Table 3, where $K_2$ for 1000 mg/L was larger than for 500 mg/L, suggesting a more rapid diffusion rate, which was considered relative to the concentration gradient.
Fig. 6 Thorium and barium adsorption behaviors of IRA900: (a) Effects of HNO₃ concentration on the distribution coefficients of IRA900 toward thorium and barium ([Th⁴⁺] = 1000 mg/L, [Ba²⁺] = 600 mg/L, S/L = 0.05g / 5 mL); (b) Effects of contact time on the thorium adsorption amounts ([HNO₃] = 7.5 M, S/L = 0.05g / 5 mL); (c) Effects of equilibrium concentration of thorium on the equilibrium adsorption amount ([HNO₃] = 7.5 M, t = 16 h, S/L = 0.05g / 5 mL); (d) Effects of ambient temperature on the thorium adsorption efficiencies
\([\text{HNO}_3] = 7.5 \text{ M}, [\text{Th}^{4+}] = 1000 \text{ mg/L}, t = 16 \text{ h}, S/L = 0.05 \text{g} / 5 \text{ mL})\).

**Table 2** Parameters obtained by fitting the kinetic data with the PFO and PSO models

<table>
<thead>
<tr>
<th>Thorium concentration (mg/L)</th>
<th>(Q_e \text{ (exp)} ) (mg/g)</th>
<th>PFO</th>
<th>PSO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(k_1 ) (min(^{-1}))</td>
<td>(R^2)</td>
</tr>
<tr>
<td>500</td>
<td>38.3</td>
<td>34.5</td>
<td>0.022</td>
</tr>
<tr>
<td>1000</td>
<td>73.3</td>
<td>64.9</td>
<td>0.0134</td>
</tr>
</tbody>
</table>

**Table 3** Parameters obtained by fitting the kinetic data with the IPD model

<table>
<thead>
<tr>
<th>Concentration</th>
<th>(K_1)</th>
<th>(K_2)</th>
<th>(K_3)</th>
<th>(C_1)</th>
<th>(C_2)</th>
<th>(C_3)</th>
<th>(R_1^2)</th>
<th>(R_2^2)</th>
<th>(R_3^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 mg/L</td>
<td>2.63</td>
<td>0.977</td>
<td>0.122</td>
<td>3.82</td>
<td>1.56</td>
<td>33.8</td>
<td>0.940</td>
<td>0.943</td>
<td>0.857</td>
</tr>
<tr>
<td>1000 mg/L</td>
<td>5.20</td>
<td>1.42</td>
<td>0.302</td>
<td>-2.11</td>
<td>31.5</td>
<td>62.1</td>
<td>0.981</td>
<td>0.978</td>
<td>0.911</td>
</tr>
</tbody>
</table>

Next, the adsorption isotherm of IRA900 toward thorium was investigated by changing the initial thorium concentrations. As shown in Fig. 6(e), the equilibrium adsorption amount of thorium rapidly climbed with the rising equilibrium concentration, and then slowly changed and was constant. The maximum adsorption amount of IRA900 toward thorium was observed \(\geq 146 \text{ mg/g}\). The Freundlich model, Langmuir model and R-P model were used to fit the adsorption isotherm, of which the fitting parameters are listed in Table 4. The R-P model demonstrated the largest \(R^2\), reaching 0.998, indicating that the R-P model described the isotherm very well. However, the R-P model was an empirical model without any special meaning[35]. Except for the R-P model, the Langmuir model also fit the data well, with \(R^2\) reaching 0.991, while that of the Freundlich model only could reach 0.971. Therefore, we concluded that thorium adsorption by IRA900 was based on a monolayer adsorption
mechanism[39, 40]. In addition, the Langmuir model provided the estimated maximum adsorption amount $Q_m$, which reached 254 mg/g.

Following the investigation on the adsorption isotherm, the effect of temperature on the adsorption performance of thorium was investigated by varying the ambient temperature in a 7.5 M HNO$_3$ medium, and the results were exhibited in Fig. 6(f). Generally, the adsorption efficiency of thorium decreased with increasing temperature. Two factors could lead to these results. One was that thorium adsorption by IRA900 was exothermic, and higher temperatures suppressed adsorption. Another factor was that the chemical structure of IRA900 could not withstand high temperatures, and some functional groups were removed. Therefore, Ba/Th separation could be suitably conducted at room temperature and even lower temperatures.

### Table 4 Parameters obtained by fitting the adsorption isotherm data

<table>
<thead>
<tr>
<th>Langmuir model</th>
<th>Freundlich model</th>
<th>R-P model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_m$</td>
<td>$K_L$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>254</td>
<td>0.0016</td>
<td>0.991</td>
</tr>
<tr>
<td>$K_F$</td>
<td>$n$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>2.00</td>
<td>1.56</td>
<td>0.971</td>
</tr>
<tr>
<td>$K_R$</td>
<td>$a$</td>
<td>$b$</td>
</tr>
<tr>
<td>0.316</td>
<td>1.10×10$^{-6}$</td>
<td>2.01</td>
</tr>
</tbody>
</table>

### 3.4 Column experiments

Compared with static adsorption, dynamic adsorption has shown higher removal efficiency for target adsorbates, with most separation activities conducted in columns. To optimize the separation conditions, the effect of flow speeds on the removal performance of IRA900 toward thorium was first investigated in this section, because the IRA900 resin had a slow adsorption speed. As shown in Fig. 7(a), the flow speed had significant impacts on the removal performance of IRA900. With increasing flow speed, the thorium concentration in the effluent quickly increased, which meant that the packed columns fixed fewer thorium...
cations at higher flow speeds. Notably, compared with 0.9 and 0.5 mL/min, 0.3 mL/min was more suitable for thorium capture. Therefore, 0.3 mL/min (≈ 0.038 BV/min) was adopted in the following column experiments.

Different eluents were used to desorb thorium in the columns under the same conditions. As shown in Fig. 7(b), the elusion peaks were observed for two types of eluents. However, a low concentration of nitric acid of 0.1 HNO₃ was more suitable to desorb thorium than a high concentration of nitric acid of 1.0 M HNO₃, which produced a sharp elution peak. These results coincided with those obtained in Fig. 6(a), which suggested that high concentrations of nitric acid contributed to thorium adsorption by the IRA900 resin. Therefore, the following separation experiments both employed 0.1 M HNO₃ as the eluent.

![Fig. 7](https://example.com/figure7.png)

**Fig. 7** Breakthrough curves of IRA900 at different flow speeds (a) and elusion curves using different concentrations of nitric acid as eluents (b) (column dimension $h \times \phi = 20 \text{ cm} \times 1 \text{ cm}, V_{\text{resin (wet)}} \approx 7.8 \text{ mL}, [\text{Th}^{4+}] = 1020 \text{ mg/L}$.)

The separation experiments were started with 20 mL working solution which simultaneously contained thorium and barium. Subsequently, 20 mL of 7.5 M HNO₃ and 50 mL of 0.1 M HNO₃ were also successively pumped. The separation results are shown in Fig. 8(a). Barium almost directly flowed through the column and was not captured by the packed
column, while thorium was fixed first and then desorbed by 0.1 M HNO₃. Thorium and barium were completely separated from each other, as reflected by two individual concentration peaks.

Finally, barium was replaced with $^{226}$Ra to verify the separation effect in practical occasions. Here, $^{226}$Ra served as the tracer nuclide of $^{228}$Ra and $^{224}$Ra, of which the daughter nuclide $^{222}$Rn was collected and measured to determine the activity. The separation results are shown in Fig. 8(b), which suggested that thorium and radium were completely and easily separated from each other. According to the calculations, the chemical yield of $^{226}$Ra almost reached 100%, and the decontamination factor of thorium exceeded $10^5$. These results demonstrated that this method could be used for the extraction of $^{228}$Ra and $^{224}$Ra from natural $^{232}$Th, which was of great significance for the future preparation and application of TAT nuclide $^{212}$Pb.

**Fig. 8** Isolation of barium or radium from thorium using a column packed with IRA900 resin:

(a) Barium isolation from thorium (column dimension $h \times \phi = 20 \text{ cm} \times 1 \text{ cm}$, $V_{\text{resin}} \approx 7.8 \text{ mL}$, $v \approx 0.3 \text{ mL/min}$, $[\text{Th}^{4+}] = 960 \text{ mg/L}$, $[\text{Ba}^{2+}] = 420 \text{ mg/L}$); (b) Radium isolation from thorium (column dimension $h \times \phi = 20 \text{ cm} \times 1 \text{ cm}$, $V_{\text{resin}} \approx 7.8 \text{ mL}$, $v \approx 0.3 \text{ mL/min}$, $[\text{Th}^{4+}] = 1500 \text{ mg/L}$, $[\text{Ra}^{2+}] = 3340 \text{ Bq/L}$)
3.5 Adsorption and separation mechanisms

The IRA900 resin samples before and after the adsorption of thorium and barium were examined by SEM-EDS, and the results are shown in Fig. 5 and Fig. 9. Barium was not found on the surface of IRA900 before and after adsorption, suggesting that barium could not be adsorbed, which was consistent with the results obtained in the batch and column experiments. Compared with the IRA900 resin sample before adsorption, the atomic percent of thorium, nitrogen, and oxygen all increased after adsorption, while that of carbon decreased. These results suggested that the thorium cations and the nitrate anions were simultaneously adsorbed by the IRA900 resin. Because the IRA900 resin was pretreated with nitric acid in advance and the strong base anion exchange resin could only adsorb anions, the thorium cations possibly coordinated with the nitrate anions and transformed into anionic complexes.

Fig. 9 SEM-EDS scanning results of IRA900 after adsorption.

To further confirm the above results and assumptions, the thorium and barium species
distributions in the nitric acid solution were calculated based on their reported stability constant. As shown in Fig. 10(a), when the concentration of HNO₃ was less than 1.0 M, the dominant species of thorium were Th⁴⁺ and [Th(NO₃)₃]⁺. When the concentration of HNO₃ ranged from 1.0 to 4.0 M, multiple types of thorium species coexisted in the system. When the concentration of HNO₃ was greater than 5.0 M, the dominant thorium species became Th(NO₃)₄ and [Th(NO₃)₃]⁻. Among these thorium species, only the percentages of Th(NO₃)₄ and [Th(NO₃)₃]⁻ increased with increasing concentration of HNO₃ and finally reached the highest value. In the 7.5 M HNO₃ solution, anionic [Th(NO₃)₃]⁻ complexes occupied about 34% of the total thorium species, which was considered the species adsorbed by the IRA900 resin.

In all concentrations of HNO₃ solutions, the percentages of [Th(NO₃)₆]²⁻ were quite low. Barium only had two types of species, including Ba²⁺ and [BaNO₃]⁺, as shown in Fig. 10(b), and both were cationic forms. Because the anion exchange resins had no affinity to cations, the IRA900 resin did not adsorb barium in the nitric acid solution.

**Fig. 10** Species distribution of thorium (a) and barium (b) in the medium of nitric acid ([Th⁴⁺] = 1000 mg/L, [Ba²⁺] = 600 mg/L)

The selective adsorption and desorption of thorium by the IRA 900 resin are illustrated in

**Fig. 11.** The thorium cations compounded with the nitrate anions and transformed into anionic
[Th(NO\(_3\))\(_5\)]\(^-\) complexes. The IRA900 resin combined with the anionic [Th(NO\(_3\))\(_5\)]\(^-\) complexes, while the other thorium species transformed into [Th(NO\(_3\))\(_5\)]\(^-\) via chemical equilibrium shifting, and finally were adsorbed completely by the IRA900 resin under dynamic conditions. By contrast, all barium species consisted of cationic forms, causing barium to directly penetrate the column without any limitations. After the selective adsorption of thorium, low concentrations of HNO\(_3\) as the eluent contributed to the decomposition of anionic [Th(NO\(_3\))\(_5\)]\(^-\) complexes and transformation into cationic species, which led to thorium desorption. Finally, thorium and barium were separated from each other.

\[
\begin{align*}
\text{Th}^{4+} + \text{R}_4\text{N}^+ \cdot \text{NO}_3^- &\leftrightarrow [\text{Th(NO}_3\text{)}_5^-] \\
\text{R}_4\text{N}^+ \cdot [\text{Th(NO}_3\text{)}_5^-] &\leftrightarrow \text{R}_4\text{N}^+ \cdot \text{NO}_3^- + [\text{Th(NO}_3\text{)}_5^+ + (4-x)\text{NO}_3^-]
\end{align*}
\]

**Fig. 11** Adsorption and desorption processes of IRA900 for thorium.

### 4 Conclusions

In this work, the adsorption behavior of IRA900 toward thorium and barium/radium was systematically and carefully studied in batch and column experiments, and the selective separation mechanism by IRA900 was deeply discussed. The experimental results suggested that the resin had extremely high selectivity for thorium compared with barium in the nitric acid solution, making separation simple and convenient. With increasing concentration of nitric acid, the thorium adsorption performance was greatly improved. The selective separation performance by the IRA900 resin could be attributed to the formation of anionic...
Thorium complexes, namely, \([\text{Th(NO}_3\text{)}_5]^−\), under high nitric acid concentrations, while barium or radium existed as cationic forms in the same system. Compared with the methods using cation exchange resins, this method had a higher separation factor. Compared with the extraction method and the adsorption method using HDEHP extractant, this method avoided the use of slightly soluble extractants and large amounts of diluent, thus leading to reduced production of organic water and waste. This work raised and verified a novel and highly efficient method for isolating trace \(^{228}\text{Ra}\) and \(^{224}\text{Ra}\) from natural \(^{232}\text{Th}\) in the system of nitric acid, offering great promise in the future preparation of TAT nuclide \(^{212}\text{Pb}\).

However, traditional resin IRA900 exhibited a slow adsorption speed, which will have to be substantially improved. In addition, radium may be co-separated with other daughter nuclides such as \(^{228}\text{Ac}\), \(^{212}\text{Bi}\), and \(^{212}\text{Po}\). Hence, in future work, we will focus on the separation of \(^{212}\text{Pb}\) and \(^{212}\text{Bi}\) from solutions containing \(^{228}\text{Ra}\), \(^{228}\text{Ac}\), \(^{228}\text{Th}\), \(^{224}\text{Ra}\), \(^{212}\text{Pb}\), and \(^{212}\text{Bi}\) and finally realize their extraction and application.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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