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

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S1 Batch experiments

(1) Experiments on effects of acidity

0.05 g IRA900 resin was weighed and mixed with 5.0 mL working solution containing 1000 mg/L Th and 600 mg/L Ba in glass bottles. The acidities of the working solution were controlled at 0.1, 0.5, 1.0, 3.0, 5.0, 7.0 and 9.0 M HNO₃, respectively. These samples were placed in a water bath shaker for 3 h, with the temperature controlled at 25°C and the shaking frequency controlled at 120 rpm.

(2) Experiments on adsorption kinetics

0.05 g IRA900 resin was weighed and mixed with 5.0 mL working solution containing 1000 or 500 mg/L Th in glass bottles, which was acidified with 7.5 M HNO₃. The contact times were controlled in 5, 10, 20, 30, 45, 60, 90, 120, 180, 240, 300, 360, 480, 960, 1200 and 1440 min, respectively. These samples were placed in a water bath shaker, with the temperature controlled at 25°C and the shaking frequency controlled at 120 rpm.

(3) Experiments on adsorption isotherms

0.05 g IRA900 resin was weighed and mixed with 5.0 mL working solution in glass bottles. The acidity of the working solution was 7.5 M HNO₃. The thorium concentration was controlled at 51, 94, 180, 470, 730, 800, 1000, 1500, 2000 and 2400 mg/L, respectively. These samples were placed in a water bath shaker for 960 min, with the temperature controlled at 25°C and the shaking frequency controlled at 120 rpm.

(4) Experiments on adsorption thermodynamic

0.05 g IRA900 resin was weighed and mixed with 5.0 mL working solution containing 1000 mg/L Th and 7.5 M HNO₃ in glass bottles. These samples were placed in a water bath
shaker for 960 min with the shanking frequency controlled at 120 rpm. The temperature values were controlled at 25, 35, 45, 55 and 65℃, respectively.

S2 Introduction of the mathematic models used

(1) The pseudo-first order kinetic model (PFO) and pseudo-second order kinetic model (PSO) are usually used to determine the rate-controlling step and investigate the adsorption mechanism. Generally, the PFO corresponds to physical adsorption, while the PSO corresponds to chemical adsorption. Two models are expressed by the following equations:

\[
\text{PFO: } \quad Q_t = Q_e (1 - e^{-k_1 t}) \quad \text{(S-1)}
\]

\[
\text{PSO: } \quad Q_t = \frac{tQ^2}{k^2 + Q^2 t} \quad \text{(S-2)}
\]

Where \( Q_t \) (mg/g) is the adsorption amount at time \( t \) (min). \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g/(mg·min)) denote the kinetic constants for the PFO model and PSO model, respectively, related to the adsorption rate.

(2) The intra-particle diffusion model (IPD) is usually used to investigate the diffusion process. The IPD assumes that the diffusion resistance of the liquid film can be ignored or only works in a short period of time during the initial adsorption stage; The diffusion direction is random, and the concentration of adsorbate does not change with the position of particles; The internal diffusion coefficient is constant and does not change with the adsorption time and adsorption position. The IPD can be expressed by the following equation:

\[
Q_t = K_r t^{0.5} + C \quad \text{(S-3)}
\]

Where \( K_r \) (mg/g/min\(^{0.5}\)) is the kinetic constant of the IPD model, which is related to the diffusion
speed; $C$ (mg/g) is a constant related to the thickness of the boundary layer or the diffusion resistance. If the value of $C$ is large, the intra-particle diffusion effect is low.

The IPD is a three-stage model. The first linear adsorption stage is related to surface diffusion. The second stage is the process of intra-particle diffusion. The third stage is the dynamic equilibrium process of adsorption and desorption.

(3) The Langmuir isotherm model, Freundlich isotherm model and Redlich-Peterson (R-P) model were adopted to describe the adsorption isotherm of IRA900. The Langmuir isotherm model assumes the active sites on the surface of adsorbents are homogeneous, all the active sites have the same adsorption energy, and the distribution of adsorbate is monolayer-adsorption. The Freundlich model is an empirical adsorption model presuming that the adsorption process belongs to multilayer adsorption. The empirical $n$ stands for the non-linearity between the metal concentration of solution and the adsorption. “$n>1$” corresponds to “chemical process”, while “$n<1$” denotes “physical adsorption”. The R-P model is also an empirical model with three parameters. The accuracy of the R-P model is equal to or higher than that of the other two isotherm models. When the R-P model constant $b$ equals to 1, the equation transforms into the Langmuir model. The three models can be expressed by the following equations:

**Langmuir model:**

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$  \hspace{1cm} (S-4)

**Freundlich model:**

$$Q_e = K_F C_e^{1/n}$$  \hspace{1cm} (S-5)

**R-P model:**

$$Q_e = \frac{K_R C_e}{1 + a C_e^b}$$  \hspace{1cm} (S-6)

Where $Q_m$ (mg/g) is the maximum adsorption amounts of adsorbents, $K_L$ (L/mg) represents the Langmuir constant related to the adsorption energy, $K_F$ (L/g) is the Freundlich constant
related to the adsorption capacity, $1/n$ is the heterogeneity factor, and $K_R$, $a$ and $b$ are the Redlich-Peterson constants, respectively.

**S3 Column experiments**

(1) Breakthrough curve for thorium at different flow speeds

About 7.8 mL IRA900 resin (wet state) was packed in the glass column. The flow speeds were adjusted to $0.30 \pm 0.02$, $0.50 \pm 0.03$ and $0.90 \pm 0.05$ mL/min by pumping the ultrapure water. Next, 50 mL 7.5 M HNO$_3$ was fed to adjust the column environment, followed by the working solution containing 1000 mg/L Th and 7.5 M HNO$_3$. The collection time was set properly for each tube collecting 10 mL effluent.

(2) Investigation on the optimum eluent for thorium desorption

About 7.8 mL IRA900 resin was packed in the glass column. The flow speed was adjusted to $0.30 \pm 0.02$ mL/min by pumping the ultrapure water. After that, 50 mL 7.5 M HNO$_3$ was fed to adjust the column environment, and then 20 mL working solution containing 1000 mg/L thorium was also fed. Next, 50 mL 0.1 M or 1.0 M HNO$_3$ was pumped as eluent. The collection time was set properly for each tube collecting 5 mL effluent.

(3) Separation of Ba$^{2+}$ from Th$^{4+}$

About 7.8 mL IRA900 resin was packed in the glass column. The flow speed was adjusted to $0.30 \pm 0.02$ mL/min by pumping the ultrapure water. After that, 50 mL 7.5 M HNO$_3$ was fed to adjust the column environment, and then 20 mL working solution containing 960 mg/L thorium and 420 mg/L barium was also fed. Next, 20 mL 7.5 M HNO$_3$ and 50 mL 0.1 M HNO$_3$ were fed successively. The collection time was set properly for each tube collecting 5 mL
(4) Separation of radium from thorium

About 7.8 mL IRA900 resin was packed in the glass column. The flow speed was adjusted to 0.30 ± 0.02 mL/min by pumping the ultrapure water. After that, 50 mL 7.5 M HNO₃ was fed to adjust the column environment, and then 20 mL working solution containing 1500 mg/L $^{232}$Th and 3340 Bq/L $^{226}$Ra (Specific activity = $3.66 \times 10^{10}$ Bq/g) was fed. Next, 20 mL 7.5 M HNO₃ and 50 mL 0.1 M HNO₃ were pumped in successively. The collection time was set properly for each tube collecting 5 mL effluent. Here, the concentration ratio of thorium to radium was $1.64 \times 10^7 : 1$.

**S4 Measurement of $^{226}$Ra**

Firstly, the solution containing $^{226}$Ra was placed in a diffuser. The radon in the diffuser was discharged with a vacuum pump, which lasted for 10-15 min. The diffuser was then sealed for 24 h. Next, the scintillation chamber was also vacuumed with a vacuum pump, and the radon in the diffuser was introduced into the scintillation by means of the pressure difference. The activity of radon was measured by an analyzer designed for radon and thorium specially. Based on the counting rate, the activity of $^{226}$Ra was calculated using the following formula:

$$C = \frac{K(I_m - I_b)}{1 - e^{-\lambda t}} - C_b) / V$$

(9)

Where $C$ (Bq/L) and $C_b$ (Bq/L) represent the activity concentration of $^{226}$Ra in sample solution and blank solution, respectively; $K$ (Bq/cpm) represents the $K$ value of the scintillation chamber; $I_m$ (cpm) and $I_0$ (cpm) are the measured mean counting rate for samples and background, respectively; $\lambda$ is the decay constant of $^{222}$Rn; $V$ (mL) is the sample volume used.
for analysis.

Here, the $^{220}\text{Rn} (T_{1/2} = 55.6 \text{ s})$ produced by the $^{232}\text{Th}$ in the sample was neglected due to the extremely short half-life.