Adsorption and Separation of Sr(II) and Y(III) by Extraction Chromatography Using HDEHP-impregnated Adsorbent

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Abstract

To separate Y (III) and Sr(II) from a Sr(II)-Y(III) mixed solution, a silica-based (HDEHP+Oct)/SiO$_2$-P adsorbent was prepared by successive impregnation and fixing the bis(2-ethylhexyl)phosphate (HDEHP) and its molecule modifier 1-octanol into the macroporous SiO$_2$-P support with a mean diameter of 50 μm. The adsorption and separation of Y(III) and Sr(II) from HNO$_3$ or HCl solutions onto the adsorbent were investigated by batch and column methods. The adsorbent showed a higher adsorption affinity to Y(III) than Sr(II). The adsorption of Y(III) decreased as the acidity of the solution increased. The adsorption of Y(III) could be expressed by the Langmuir adsorption model and was governed by chemisorption. In column experiments, using a column packed with (HDEHP+Oct)/SiO$_2$-P adsorbent, Sr(II) and Y(III) were eluted by HNO$_3$ or HCl solution, respectively. The separation of Y(III) from Sr(II)-Y(III) mixed solution was achieved successfully.

Keywords: Yttrium, Strontium, Separation, Extraction Chromatography, Bis(2-ethylhexyl)phosphate

1. Introduction

To ensure a sustainable development of nuclear energy in the future, the generic objective of partitioning and transmutation strategies for spent nuclear fuel is to improve nuclear waste management by minimizing nuclear waste mass, reducing the heat load and the quantity of potential radiotoxic isotopes to be disposed finally in a geological repository. The partitioning of high-level liquid waste (HLLW) produced from the PUREX processing of spent nuclear fuel is thought to be a favorable method from the viewpoints of minimizing long-term radiological risk and radioactive waste accumulation$^1$.

In the utilization of large amounts of $^{90}$Sr separated from HLLW (~1.1 kg/t tHU, 45 GWd/t), $^{90}$Y, a daughter nuclide of $^{90}$Sr ($T_{1/2} = 28.8$ y), is expected to separate from the $^{90}$Sr-$^{90}$Y group; $^{90}$Y is an important radionuclide known for its therapeutic application in the medical field. It is a pure beta-emitter with no associated gamma rays and decays to stable daughter nuclide $^{90}$Zr. This radioisotope is particularly useful owing to its emitted a hard beta emission ($E_{max} = 2.28$ MeV), which can penetrate soft tissues up to 1 cm while it has a short half-life ($T_{1/2} = 64.1$ h)$^{5,6}$. For these reasons, $^{90}$Y has recently been clinically used for internal radiation therapy$^6$. In the nuclear decay process, $^{90}$Y is generated from the beta decay of $^{90}$Sr, and a regular production of $^{90}$Y from a purified $^{90}$Sr solution is possible as $^{90}$Y is generated from the decay line of $^{90}$Sr/$^{90}$Y as shown below:

\[
^{90}\text{Sr} \xrightarrow{\beta^- \left(0.54\text{MeV}\right)}^{90}\text{Y} \xrightarrow{\beta^- \left(2.28\text{MeV}\right)}^{90}\text{Zr} \text{ (stable)}
\]

Therefore, it can be considered that $^{90}$Y needs to be separated and purified from $^{90}$Y-$^{90}$Sr mixtures before being used for radiotherapy. For therapeutic application in nuclear medicine, the basic requirements for $^{90}$Y-$^{90}$Sr separation are a high yield of the daughter radionuclide $^{90}$Y in minimal volumes and high radionuclidic purity with low breakthrough of the parent $^{90}$Sr.

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For this purpose, there have been numerous chemical separation methods of separation of $^{90}Y$ from $^{90}Y, ^{90}Sr$ groups, such as precipitation\(^7\), solvent extraction\(^8\)\(^\sim\)\(^1\)\(^1\)\(^1\), ion exchange\(^2\)\(^2\), use of liquid membranes\(^3\)\(^3\), electrochemical separation\(^4\)\(^4\) and extraction chromatography\(^5\)\(^5\) in literatures.

In the present work, a silica-based extraction adsorbent ((HDEHP+Oct)/SiO₂-P) was prepared by impregnating HDEHP extractant and a molecular modifier, 1-octanol (Oct), into a macrotetrical styrene-divinylbenzene copolymer that is immobilized in porous silica particles with a diameter of 50 μm, and then, adsorption and separation behavior of stable Sr(II)/Y(III) onto (HDEHP+Oct)/SiO₂-P adsorbent in HNO₃, HCl solution were investigated experimentally. The present article deals with the preparation of the (HDEHP+Oct)/SiO₂-P adsorbent and the characterization, adsorption equilibrium, kinetic modeling, and elution properties of Y(III) with a fixed-bed column.

2. Experimental

2.1 Preparation and characterization of (HDEHP+Oct)/SiO₂-P adsorbent

Bis(2-ethylhexyl)phosphate (HDEHP, 97%) was purchased from Sigma-Aldrich Chemical Co. and used without any further purification. The molecular structure of HDEHP was shown in Fig. 1.

![Structure formula of bis(2-ethylhexyl)phosphate (HDEHP).](image)

The silica-based polymer support (SiO₂-P) was prepared as described in the previous studies\(^6\). For simplicity, “P” in the SiO₂-P particles was abbreviated as styrene-divinylbenzene (SDB) copolymer, which was immobilized inside the macroporous SiO₂ substrate by polymerization reaction. Here, SiO₂-P particles was consisted of 82 wt% SiO₂ and 18 wt% copolymer. The physical properties of SiO₂-P were showed in Table 1. The (HDEHP+Oct)/SiO₂-P adsorbent was synthesized by loading HEDHP and 1-octanol into SiO₂-P support based on impregnation method. The HDEHP and a molecule modifier 1-octanol impregnated on SiO₂-P support ((HDEHP+Oct)/SiO₂-P) was synthesized as follows\(^5\). First, the HDEHP and octanol were dissolved in dichloromethane and then mixed with the SiO₂-P supports in a glass flask for approximately 1 h at 25 °C. After that the mixture was stirred gently for 2 h at 40 °C under reduced pressure by using a rotary evaporator in order to enhance the impregnation, and finally vacuum drying oven around 40 °C for overnight, a silica-based (HDEHP+Oct)/SiO₂-P adsorbent was obtained.

Table 1  Physical properties of SiO₂-P.

| Property               | Value   |
|------------------------|---------|
| Pore size (nm)         | 50      |
| Pore volume (cm³·g⁻¹)  | 1.1     |
| Spec. Surface area (m²·g⁻¹) | 3.6   |
| Diameter (mm)          | 40–60   |
| Matrix of copolymer    | Styrene-divinylbenzene(SDB) |

2.2 Batch experiments

The adsorption of Sr(II) and Y(III) ions onto the adsorbent was examined by batch method. Dry adsorbent (0.20 g) was mixed in a glass flask with 4.0 cm³ liquid phase up to 5 hours in a thermostatic shaking bath. The solutions contained 10 mM of Sr(II) and Y(III) in different concentrations of HNO₃, HCl solution. After the resultant mixture was separated by vacuum filtration, the concentrations of metal ions in the liquid phase were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

The adsorbed amount ($q$, mg·g⁻¹), uptake ratio (R, %), distribution coefficient ($K_a$, cm³·g⁻¹) of Y(III) was calculated as follows:

\[
d = \frac{(C_0 - C_t) \times V}{1000 \times m} \tag{2}
\]

\[
R = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{3}
\]

\[
K_a = \frac{(C_0 - C_t)}{C_e} \times \frac{V}{m} \tag{4}
\]

where, $C_0$, $C_t$ and $C_e$ denote the concentrations of metal ion before adsorption, after adsorption and after reaching an equilibrium state in the liquid phase, respectively. Also, $m$ and $V$ denote the weight of dry adsorbent in g and the volume of the liquid phase in cm³, respectively.

2.3 Column experiments

The separation of metal ions with the adsorbent was
evaluated using a column experiment for chromatographic separation. Dry adsorbent (4.0 g) was packed into a glass column, and the experiment was performed at 25 °C by circulating thermostatic water through the column jacket. A feed solution (10 cm³, 5 mM of Sr(II) or Y(III), 0.5 M HNO₃, HCl) was passed through the column at flow rate 0.5 cm³·min⁻¹. Subsequently, 30 cm³ of wash solution and 100 cm³ of eluent were also supplied. The effluent from the column was collected by fraction collector and the concentration of metal ions in each fraction were analyzed by ICP-AES.

3. Results and discussion

3.1 Characterization of adsorbent

The SEM image of (HDEHP+Oct)/SiO₂-P adsorbent is shown in Fig. 2, in which the spherical porous structure with a diameter of 50 μm was confirmed.

![SEM image of silica-based (HDEHP+Oct)/SiO₂-P adsorbent.](image)

The thermal stability of (HDEHP+Oct)/SiO₂-P adsorbent was evaluated by TG-DTA analyses within the temperature range: 25–600 °C. The preparation conditions and estimated weight percents of compositions were summarized in Table 2. As can be seen, the SDB polymer was successfully immobilized inside the SiO₂ substrate, and the solvents were loaded into the pore of SiO₂-P completely.

Table 2 Composition of SiO₂-P and (HDEHP+Oct)/SiO₂-P.

| Conditions of synthesis | SiO₂ (wt%) | SDB (wt%) | Solvents (wt%) |
|-------------------------|------------|-----------|----------------|
| SiO₂-P                  | 81.6       | 18.4      | -              |
| (HDEHP+Oct)/SiO₂-P      | 48.5       | 10.9      | 40.6           |

Table 2 Composition of SiO₂-P and (HDEHP+Oct)/SiO₂-P.

| Thermal analysis        | SiO₂-P      |          |       |
|-------------------------|-------------|----------|-------|
|                         | 82          | 18       | -     |
| (HDEHP+Oct)/SiO₂-P      | 48.3        | 10.9     | 40.8  |

3.2 Batch adsorption behavior

To understand the effect of the HNO₃, HCl concentration, the adsorption of the Sr(II) and Y(III) towards (HDEHP+Oct)/SiO₂-P adsorbent in the HNO₃, HCl solution concentrations in the range 0.001 to 5 M (M = mol·dm⁻³) were investigated at 25 °C.

The results for the equilibrium experiments are illustrated in Fig. 3. Adsorbent showed a strong adsorption affinity to Y(III) and a weak adsorption to Sr(II). On the other hand, the uptake ratios of Y(III) decreased as the acidity of HNO₃, HCl solutions increased. The high adsorption affinity for Y(III) indicates that selective separation of Y(III) from a Sr(II)-Y(III) mixed solution by the (HDEHP+Oct)/SiO₂-P is possible in under 0.5 M solution.

![Effect of acid concentration on uptake of Sr(II) and Y(III) onto (HDEHP+Oct)/SiO₂-P adsorbent.](image)

To investigate the adsorption mechanism, the results for adsorption rates are illustrated in Fig. 4. The effect of contact time on adsorption capacity of Y(III) for (HDEHP+Oct)/SiO₂-P adsorbent was examined in the presence of 0.5 M HNO₃, HCl solution through batch method.

The pseudo-second order kinetic expression for the adsorption system was developed by Ho ⁷. This adsorption model assumes that the adsorption rate is controlled by chemical adsorption and the adsorption capacity is proportional to the number of active sites on the adsorbent. To investigate the kinetic data of the adsorption, the rate constants for the adsorption of Y(III) onto (HDEHP+Oct)/SiO₂-P adsorbent were determined by the equation of a pseudo-second order.

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

where \(q_t\) and \(q_e\) are the amounts of Y(III) adsorbed at time \(t\) (hr) or at equilibrium (mg g⁻¹) and \(k_2\) is the pseudo-second-order rate constant for adsorption (g·mg⁻¹·h⁻¹).

As shown in Fig. 5, plots of \(t/q_t\) versus \(t\) provide a good straight line and the correlation coefficient \(R^2\) is calculated to be 1.00, indicating that the results are fitted well with the pseudo-second order model and the rate-controlling step of this
adsorption process is governed by the chemisorption process.

From the slopes of the straight lines, the values of \( q_e \) for Y(III) at equilibrium are determined to be 0.200 and 0.192 mg g\(^{-1}\) for HNO\(_3\) and HCl. These calculated \( q_e \) values are found to be similar to the experimental values of 0.200 and 0.196 mg g\(^{-1}\) for HNO\(_3\) and HCl respectively.

![Graph](image1.png)

**Fig. 4** Relationship between adsorption capacity of Y(III) and contact time onto (HDEHP-Oct)/SiO\(_2\)-P adsorbent at 298 K. *Vim*: 20 cm\(^3\)/g; [Y(III)]: 10 mM; [HNO\(_3\), HCl]: 0.5 M; 25 °C.

![Graph](image2.png)

**Fig. 5** Plot of the pseudo-second order model for Y(III) adsorption onto (HDEHP-Oct)/SiO\(_2\)-P adsorbent. *Vim*: 20 cm\(^3\); [Y(III)]: 10 mM; 25 °C.

### 3.3 Equilibrium adsorption isotherm models

Besides the adsorption behavior, the liquid phase is important in determining the maximum adsorption capacity (\( q_{\text{max}} \), mmol·g\(^{-1}\)), which is an important parameter in the adsorption process. Adsorption equilibrium data is important in clarifying the adsorption of Y(III) on the (HDEHP-Oct)/SiO\(_2\)-P adsorbent in HNO\(_3\) or HCl solutions. In this study, three important isotherm models are selected to fit the experimental data, which are the Langmuir, Freundlich and Dubinin-Radushkevich isotherm models\(^{(19)}\). The mathematical equations of the models are listed in Table 3.

| Table 3 The isotherm model equations used for analysis of adsorption data. |
|-----------------------------------------------|
| **Non-linear form** | **Linear form** |
| Langmuir model | \( q_e = q_{\text{max}}/(1 + bC_e) \) |
| Freundlich model | \( \log q_e = \log K_f + (1/n_f) \log C_e \) |
| Dubinin-Radushkevich model | \( q_e = q_{\text{max}} \exp(-\beta C_e^{1/2}) \) |

\( q_e \): the adsorbed amount at the equilibrium state (mmol·g\(^{-1}\))

\( q_{\text{max}} \): the maximum adsorbed amount (mmol·g\(^{-1}\))

\( C_e \): the equilibrium concentration of metal ion in the aqueous phases (mmol·dm\(^{-3}\))

\( b \): the Langmuir constant (L·mmol\(^{-1}\))

\( K_f \): the Freundlich constant (mmol·g\(^{-1}\))

\( 1/n_f \): the Freundlich isotherm exponent constant related to the adsorption intensity

\( \beta \): the Dubinin-Radushkevich constant (mol\(^2\)·kJ\(^{-2}\))

\( R \): the gas constant (8.314 J·mol\(^{-1}\)·K\(^{-1}\))

\( T \): the absolute temperature (K)

The constant \( \beta \) gives the mean adsorption energy \( E \) (kJ·mol\(^{-1}\)) as

\[
E = \frac{1}{\sqrt{2\beta}}
\]  

**Figure 6** shows Y(III) adsorption data for the adsorbent and the non-linear fits, and the calculated parameters are summarized in Table 4.

| Table 4 Isotherm parameters for the adsorption of Y(III). |
|-----------------------|-----------------------|
| Models | [HNO\(_3\)] | HCl |
| Langmuir | \( q_{\text{max}} \) | 0.329 | 0.348 |
| | \( b \) | 0.193 | 0.152 |
| | \( R^2 \) | 1.0 | 1.0 |
| Freundlich | \( K_f \) | 0.126 | 0.113 |
| | \( 1/n_f \) | 0.213 | 0.248 |
| | \( R^2 \) | 0.83 | 0.82 |
| Dubinin-Radushkevich | \( q_{\text{max}} \) | 0.398 | 0.431 |
| | \( \beta \) | -0.0053 | -0.0062 |
| | \( E \) | 9.737 | 9.013 |
| | \( R^2 \) | 0.90 | 0.89 |

The isotherms were obtained for a wide range of Y(III) concentrations in the initial mixture with 0.5 M HNO\(_3\) or HCl at 25 °C. The equilibrium adsorbed amounts of Y(III) approached a constant value with increasing concentration.
The maximum adsorption amounts are 0.329 and 0.348 mmol·g\(^{-1}\) for HNO\(_3\) and HCl, respectively. The \(R^2\) values of these straight lines indicate that these adsorption processes could be expressed by the Langmuir monomolecular layer adsorption mode.

### 3.4. Column separation

The efficient separation of Y(III) from Sr(II) by means of extraction chromatography using the (HDEHP+Oct)/SiO\(_2\)-P adsorbent is expected from the large difference in their uptake shown in Fig. 3. For the mutual separation experiment between Y(III) and Sr(II), the elution curves in the effluent are illustrated in Fig. 7.

As can be seen in the figure, Sr(II) showed a very weak adsorption by the adsorbent and broke through the column along with 0.5 M HNO\(_3\) or HCl solution. The adsorption behavior of Sr(II) during column separation is similar to that in the batch experiment. Subsequently, with a supplement of 3 M HNO\(_3\) or HCl solution to the column, the Y(III), which strongly adsorbed onto the adsorbent, was finally eluted out. In terms of the mass balance, the recovery of Y(III) was calculated as 100 wt% (HNO\(_3\)) and 96.2 wt% (HCl). Satisfactory partitioning and recovery of Y(III) from the Sr(II)-Y(III) mixed solution with the (HDEHP+Oct)/SiO\(_2\)-P adsorbent was thus achieved.

**Figure 8** shows the sequence and procedure for producing Y(III) via extraction chromatography.

### 4. Conclusion

To separate Y(III) from Sr(II)-Y(III) group solution, a silica-based (HDEHP+Oct)/SiO\(_2\)-P adsorbent was prepared by impregnating HDEHP (bis(2-ethylhexyl)phosphate) extractant and a molecular modifier, 1-octanol (Oct), into the macroporous SiO\(_2\)-P support with a mean diameter of 50 \(\mu\)m.

Adsorption behavior of Sr(II) and Y(III) onto
(HDEHP+Oct)/SiO2-P adsorbent were investigated by batch method under various different contact time, HNO3, HCl concentration and phase ratio at 298 K, and further separation behavior by extraction chromatography was studied by column method.

**Fig. 8 Preparation of Y(III) from Sr(II)/Y(III) solution by the HDEHP/SiO2-P adsorbent.**

It was found that the adsorbent showed high adsorption affinity to Y(III) and weak adsorption ability to Sr(II) under the experimental conditions. Adsorption of Y(III) reached equilibrium state within 3 hours and adsorption results of Y(III) are fitted well with the pseudo-second order model and the rate-controlling step of this adsorption process is governed by the chemisorption process. This adsorption process could be expressed by Langmuir monomolecular layer adsorption mode. Using a (HDEHP+Oct)/SiO2-P adsorbent packed column, Sr(II) and Y(III) were eluted by HNO3 or HCl solution, respectively. A successful separation of Y(III) from Sr(II)-Y(III) mixed solution was achieved.

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