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Separation of Y(III) and Sr(II) from acid solutions by extraction chromatography using HDEHP-impregnated adsorbent and its medical application

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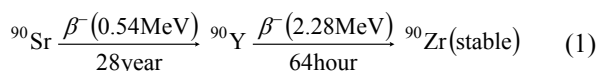
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The selective separation and recovery of Y (III) from Sr(II) were investigated using a macroporous silica/polymer composite (SiO₂-P) supported bis(2-ethylhexyl)phosphate (HDEHP) and 1-dodecanol (dodec) impregnated adsorbent (HDEHP+dodec)/SiO₂-P. The adsorption and separation of Y(III) and Sr(II) in HNO₃ and 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 addition, the adsorption thermodynamic parameters of Y(III) were calculated using the van't Hoff equation, and the reaction was found to be exothermic. In column experiments, a relatively satisfactory chromatographic separation of Y(III) from a Sr(II)-Y(III) mixed solution was obtained using the adsorbent packed column.

Keywords: yttrium, strontium, HDEHP impregnated resin, extraction chromatography

1. Introduction

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 ⁹⁰Sr separated from HLLW (~1.1 kg/1 tHU, 45 GWd/t), ⁹⁰Y, a daughter nuclide of ⁹⁰Sr ($T_{1/2} = 28.8$ y), is expected to separate from the ⁹⁰Sr-⁹⁰Y group; ⁹⁰Y 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 ⁹⁰Zr. This radioisotope is particularly useful owing to its emitted beta particles, which have a maximum energy of 2.28 MeV and a short half-life ($T_{1/2} = 64.1$ h). For these reasons, ⁹⁰Y has recently been clinically used for internal radiation therapy [2]. In the nuclear decay process, ⁹⁰Y is generated from the beta decay of ⁹⁰Sr, and the decay line of ⁹⁰Sr/⁹⁰Y is shown below:



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

with low breakthrough of the parent ⁹⁰Sr. For this purpose, numerous chemical separation methods have been reported for the separation of ⁹⁰Y from ⁹⁰Y-⁹⁰Sr mixtures, such as precipitation [3], solvent extraction [4], ion exchange [5], use of liquid membranes [6], and extraction chromatography [7].

In this study, we have attempted to load the bis(2-ethylhexyl)phosphate (HDEHP) extractant and a molecular modifier, 1-dodecanol (dodec), into macroporous silica/styrene-divinylbenzene copolymer composite particles (SiO₂-P), named as (HDEHP+dodec)/SiO₂-P, for the separation of Y(III) from a Sr(II)-Y(III) mixed solution. The present article deals with the preparation of the HDEHP-loaded adsorbent and the characterization, adsorption equilibrium, kinetic modeling, and elution properties of Y(III) with a fixed-bed column.

2. Experimental

The (HDEHP+dodec)/SiO₂-P adsorbent was synthesized by loading HEDHP and dodec into SiO₂-P support based on impregnation method [7]. Dissolved HDEHP and dodec in dichloromethane were mixed with the washed with methanol and dried SiO₂-P, and the solvent was removed by evaporation under reduced-pressure. After drying in a vacuum, the adsorbent was obtained. The compositions of the adsorbent under the preparation conditions were HEDHP: 25 wt%, dodec: 25 wt%, and SiO₂-P: 50 wt%.

The adsorption of Sr(II) and Y(III) ions onto the adsorbent was examined by batch method. Dry

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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 or HCl. 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) of Y(III) was calculated as follows:

$$q = \frac{(C_0 - C_t) \times V}{1000 \times m} \quad (2)$$

where C_0 is the initial concentration of Y(III) and C_t is the concentration after a certain time in the liquid phase (mg·L⁻¹). V is the initial solution volume (mL), and m is the mass of dry adsorbent (g), or this can be expressed as the uptake ratio (R , %)

$$R = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (3)$$

The distribution coefficient (K_d , cm³·g⁻¹) of Y(III) between an aqueous and a solid phase was obtained from the following equation:

$$K_d = \frac{(C_0 - C_e)}{C_e} \times \frac{V}{m} \quad (4)$$

where C_e is the concentration at equilibrium (mg·L⁻¹).

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. 10 cm³ of the Sr(II)-Y(III) mixed solution was fed into the column by tube pump 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. Batch adsorption behavior

To investigate the adsorption mechanism, the rate constants for the adsorption of Y(III) onto the (HDEHP+dodec)/SiO₂-P adsorbent were calculated using the equation of a pseudo-second order mechanism [8] from the results in **Figure 1**. This adsorption model assumes that the adsorption rate is controlled by chemisorption and that the adsorption capacity is proportional to the number of active sites on the adsorbent. The adsorption model is shown as follows

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

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 **Figure 1**, plots of t/q_t vs. t provide two relatively good straight lines for the tested Y(III), indicating that the results fit well with the

pseudo-second order model and the rate-controlling step of this adsorption process is governed by chemisorption. From the analysis, the q_e values for Y(III) were determined to be 17.2 and 15.8 mg·g⁻¹. These calculated q_e were found to be similar to the experimental values of 16.6 and 15.4 mg·g⁻¹, respectively.

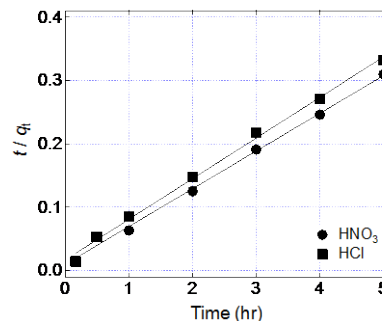


Figure 1. Plot of the pseudo-second order model for Y(III) adsorption onto (HDEHP+dodec)/SiO₂-P adsorbent. V/m : 20 cm³; [Y(III)]: 10 mM; 25°C.

To understand the effect of the acid concentration, the adsorption of the Sr(II) and Y(III) onto the adsorbent for acid solution concentrations in the range 0.001 to 5 M ($M = \text{mol} \cdot \text{dm}^{-3}$) was investigated at 25°C.

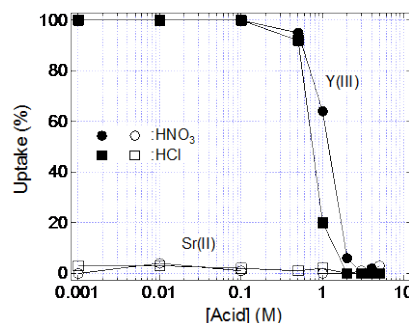


Figure 2. Effect of acid concentration on uptake of Sr(II) and Y(III) onto (HDEHP+dodec)/SiO₂-P adsorbent. V/m : 20 cm³; [Sr(II), Y(III)]: 10 mM; 25°C.

As shown in **Figure 2**, the 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 and HCl solutions increased. From the literatures on studies on the solvent extraction of rare-earth elements from acidic solution, deprotonation of dialkylphosphinic acids was necessary to extract the trivalent ions [9]. Therefore, an increase of acidity was considered to interfere the adsorption.

The high adsorption affinity for Y(III) indicates that selective separation of Y(III) from a Sr(II)-Y(III) mixture by the (HDEHP+dodec)/SiO₂-P is possible in low-acid solution.

3.2. Equilibrium adsorption isotherm models

Besides the adsorption behavior, the liquid phase is important in determining the maximum adsorption capacity (q_{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+dodec)/SiO₂-P in HNO₃ and 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 [10].

Langmuir:

$$\text{Non-linear form} \quad q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad \text{Linear form} \quad \frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{b \cdot q_{\max}} \quad (6)$$

Freundlich:

$$\text{Non-linear form} \quad q_e = K_f C_e^{(1/n_f)} \quad \text{Linear form} \quad \log q_e = \log K_f + \frac{1}{n_f} \log C_e \quad (7)$$

Dubinin-Radushkevich:

$$\text{Non-linear form} \quad q_e = \ln q_{\max} - \exp(-\beta \varepsilon^2) \quad \text{Linear form} \quad \ln q_e = \ln q_{\max} - \beta \varepsilon^2 \quad (8)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (9) \quad E = \frac{1}{\sqrt{2\beta}} \quad (10)$$

where, b , $1/n_f$, K_f and β are the Langmuir constant ($\text{L} \cdot \text{mmol}^{-1}$), the Freundlich isotherm exponent constant related to the adsorption intensity, the Freundlich constant ($\text{mmol} \cdot \text{g}^{-1}$) and the Dubinin-Radushkevich constant ($\text{mol}^2 \cdot \text{kJ}^{-2}$), respectively. R , T and E represent the gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), temperature (K) and the mean adsorption energy ($\text{kJ} \cdot \text{mol}^{-1}$).

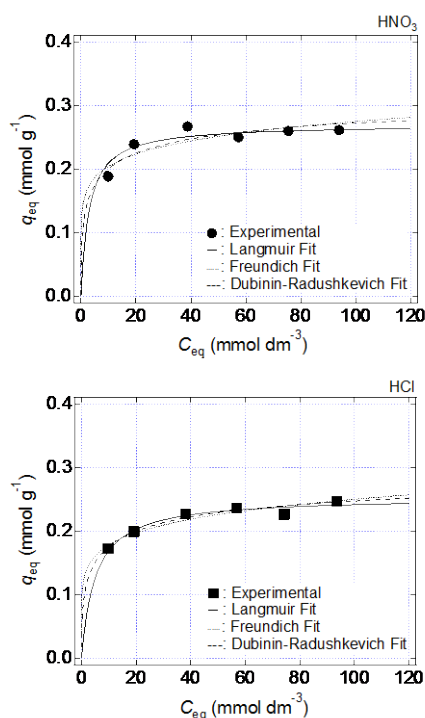


Figure 3. Non-linear isotherm plots of Y(III) on (HDEHP+dodec)/SiO₂-P adsorbent.

Figure 3 shows Y(III) adsorption data for the adsorbent and the non-linear fits, and the calculated parameters are summarized in **Table 1**. The isotherms were obtained for a wide range of Y(III) concentrations in the initial mixture with 0.5 M HNO₃ or HCl at 25 °C.

The equilibrium adsorbed amounts of Y(III) approached a constant value with increasing concentration.

The maximum adsorption amounts are 0.27 and 0.25 $\text{mmol} \cdot \text{g}^{-1}$ for HNO₃ 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.

Table 1. Isotherm parameters for the adsorption of Y(III).

Models		HNO ₃	HCl
Langmuir	q_{\max}	0.270	0.254
	b	0.346	0.200
	R^2	1.00	1.00
Freundlich	K_f	0.152	0.127
	$1/n_f$	0.129	0.147
	R^2	0.73	0.92
Dubinin-Radushkevich	q_{\max}	0.305	0.281
	K	-0.00320	-0.00358
	E	12.5	11.8
	R^2	0.80	0.95

3.3. Effect of temperature on Y(III) adsorption

To understand the temperature effect, the adsorption of Y(III) onto (HDEHP+dodec)/SiO₂-P adsorbent in 0.5 M HNO₃ and HCl solution were investigated at different temperature. The corresponding plots of $\ln K_d$ versus $1/T$ provide were depicted in **Figure 4**. The $\ln K_d$ value showed significant decrease with the increase of temperature, reflecting that adsorption process were exothermic reaction and the adsorption of Y(III) was decreased by temperature elevation.

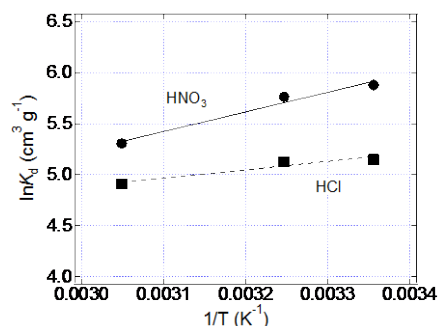


Figure 4. Effect of solution temperature on the K_d value of Y(III) adsorption on adsorbents.

Table 2. Thermodynamic parameters for Y(III) adsorption onto the (HDEHP+dodec)/SiO₂-P adsorbent

	HNO ₃	HCl
ΔH^0 ($\text{kJ} \cdot \text{mol}^{-1}$)	-16.0	-6.81
ΔS^0 ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	-0.00442	0.0202
R^2	0.972	0.929
Temp (K)	$-\Delta G^0$ ($\text{kJ} \cdot \text{mol}^{-1}$)	$-\Delta G^0$ ($\text{kJ} \cdot \text{mol}^{-1}$)
298	-14.7	-12.8
303	-14.6	-13.0
323	-14.5	-13.4

In order to gain insight into the thermodynamic nature of the adsorption process, several thermodynamic parameters for the adsorption system were calculated [11] and summarized in **Table 2**. In Table 2, the obtained the negative values of ΔG^0 for the

(HDEHP+dodec)/SiO₂-P adsorbent indicate spontaneous adsorption. ΔH^0 was negative for the adsorbent, which indicates that the adsorption processes are endothermic. Furthermore, the negative values of ΔS^0 indicate increasing randomness in the solid/solution interface during the adsorption process.

3.4. Column separation

The efficient separation of Y(III) from Sr(II) by means of extraction chromatography using the (HDEHP+dodec)/SiO₂-P is expected from the large difference in their uptake shown in Figure 2. For the separation of Y(III) and Sr(II), the elution curves in the effluent are illustrated in Figure 5.

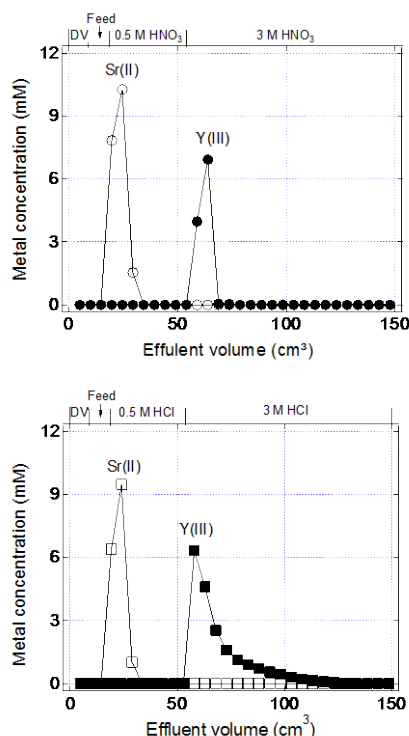


Figure 5. Column separation results of Sr(II) and Y(III) from 0.5 M HNO₃, HCl solution using the (HDEHP+dodec)/SiO₂-P adsorbent.

As shown in the figure, Sr(II) showed a very weak adsorption by the adsorbent and broke through the column along with 0.5 M HNO₃ and 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 HNO₃ and 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% (HNO₃) and 96.2 wt% (HCl). Satisfactory partitioning and recovery of Y(III) from the Sr-Y group with the (HDEHP+dodec)/SiO₂-P was thus achieved.

4. Conclusion

It was found that the adsorbent showed a strong adsorption affinity to Y(III) and a weak adsorption ability with Sr(II) under experimental conditions.

Kinetic data were successfully modeled using pseudo-second-order kinetics. This adsorption process could be expressed by the Langmuir model, and is governed by chemisorption. In the extraction chromatography experiments, the separation of Y(III) from a Sr(II)-Y(III) mixed solution was achieved successfully.

Acknowledgements

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