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# Adsorption and separation behavior of strontium and yttrium using a silica-based CMPO adsorbent

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## Abstract

To separate Y(III) from a Sr(II)–Y(II) mixture, two silica-based adsorbents, CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P were prepared by impregnating octyl(phenyl)-*N*,*N*-diisobutylcarbamoyl methylphosphine oxide (CMPO) extractant and a molecule modifier (1-Dodecanol) into macroporous silica/polymer composite support ($SiO_2$-P). The Adsorbents showed high adsorption affinity to Y(III) and weak adsorption affinity to Sr(II) in $HNO_3$ solution. The amount of adsorbed Y(III) increased with the $HNO_3$ in the solution. The amount of adsorbed Y(III) increased with contact time and reached equilibrium within 30 min. The results showed that a pseudo-second-order kinetic model with a high correlation coefficient described the adsorption process better than other kinetic models. Successful Y(III) separation from Sr(II)–Y(III) mixture in $HNO_3$ solution was achieved.

**Keywords** CMPO-impregnated adsorbent · Strontium · Yttrium · Separation · Extraction chromatography

## Introduction

The heat-generated nuclides, $^{90}$Sr, with a half-life of approximately 28 years, exhibits high radioactivity and heat generation, and large quantities of Sr and Y isotopes (~ 1.1 kg/1 tHU, 45 GWd/t) are present in high-level liquid waste (HLLW) generated by the spent nuclear fuel reprocessing [1, 2]. Thus, selective $^{90}$Sr separation from HLLW is an important environmental issue in nuclear waste management. In our previous research, Sr(II), one of the heat-generating elements in HLLW, was separated from simulated HLLW by extraction chromatography using distilled water as eluent [1, 2].

Moreover, $^{90}$Y, a daughter nuclide of $^{90}$Sr, is a useful isotope in radiopharmaceuticals for various therapeutic applications in nuclear medicine, and it must be separated from a $^{90}$Sr–$^{90}$Y mixture for use in this field [3, 4]. In the $^{90}$Sr decay system, the majority of $^{90}$Y is generated from beta decay of $^{90}$Sr, and it has a short half-life ($T_{1/2} = 64.1$ h) to form stable daughter nuclide $^{90}$Zr, mainly at 2.28 MeV [5]. This is represented by the following reaction;

$$^{90}\mathrm{Sr} \xrightarrow[28.8\ \mathrm{years}]{\beta^-(0.54\ \mathrm{Mev})} {}^{90}\mathrm{Y} \xrightarrow[64\ \mathrm{h}]{\beta^-(2.28\ \mathrm{Mev})} {}^{90}\mathrm{Zr(stable)} \quad (1)$$

As separation and purification of $^{90}$Y from $^{90}$Sr–$^{90}$Y mixtures before use for radiotherapy are essential, numerous chemical methods for separating $^{90}$Y, including precipitation [6], solvent extraction [7, 8], ion exchange [9], and extraction chromatography [10, 11], have been studied.

An impregnation method for extraction chromatography was recently proposed, involving immobilization of organic extractants in a macroporous silica/polymer composite support ($SiO_2$-P). $SiO_2$-P is an inorganic/organic hybrid material prepared by impregnating a macroporous $SiO_2$ substrate with a copolymer. Advantages of $SiO_2$-P include strong acidity, radiation resistance, and mechanical strength, and it is easily separated from solids and liquids.

However, $^{90}$Y exists as a trivalent cation in solution; thus, it can be separated from a $^{90}$Sr–$^{90}$Y mixture using impregnated octyl(phenyl)-*N*,*N*-diisobutylcarbamoyl methylphosphine oxide (CMPO), a known extractant for trivalent cations.

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To understand the adsorption and separation behavior of Y(III), we investigated the effects of acid concentration, contact time, and temperature for two adsorbents, silica-based CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P. Moreover, it was verified that $^{90}$Y could be separated continuously from a $^{90}$Sr–$^{90}$Y mixture using a column. The adsorbents were prepared by impregnating CMPO extractant and a molecular modifier (1-dodecanol) into a macroporous silica/polymer composite support ($SiO_2$-P), exploiting its high immobilizing capacity to separate Y(III) from a Sr(II)–Y(III) mixture. This article describes the preparation of a CMPO-impregnated adsorbent; kinetic modeling and adsorption thermodynamics for Y(III) adsorption by adsorbents were studied by batch and column experiments, respectively.

## Experimental

### Materials

$Sr(NO_3)_2$ (98%) and $SrCl_2$ (95%) for experiments were obtained from Wako Pure Chemical Industries, Ltd. $Y(NO_3)_3 \cdot 6H_2O$ (99.99%) and $YCl_3 \cdot 6H_2O$ (99.99%) were obtained from Kanto Chemical Co.

### Preparation of adsorbent

In this study, two silica-based adsorbents, CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P were prepared. CMPO/$SiO_2$-P was prepared by impregnating CMPO extractant into $SiO_2$-P, and (CMPO + Dodec)/$SiO_2$-P was prepared by impregnating CMPO extractant and 1-Dodecanol as a molecule modifier into $SiO_2$-P.

The $SiO_2$-P particles were washed thrice with about 300 cm$^3$ methanol and dried in a vacuum for approximately 1 day. CMPO (18 g) extractant was dissolved in 200 cm$^3$ dichloromethane, which was used as a diluent, with and without 1-Dodecanol (6 g) as a molecule modifier. The washed $SiO_2$-P [36 g (with 1-dodecanol) or 42 g (without)] and dichloromethane were mixed, and the diluent was removed with rotary evaporator. The residue was dried under vacuum overnight at 313 K, and 60 g of the two adsorbents, CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P were obtained [12].

### Batch method

In the batch method, the adsorption behaviors of Sr(II) and Y(III) ions onto CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P were examined. Dry adsorbent (0.2 g) was mixed with 4 cm$^3$ liquid phase solution in a 13.5 cm$^3$ glass vial under several contact times in a thermostatic shaking bath at 160 rpm. This solution contained 10 mM (M = mol dm$^{-3}$) of Sr(II) and Y(III) ions with different concentrations of $HNO_3$ or HCl. Following phase separation of the mixture by filtration, the metal ions concentrations in the liquid phase were determined by inductively coupled plasma-atomic emission spectrometer (ICP-AES, Shimadzu ICPE-9000). The distribution coefficients ($K_d$, cm$^3$ g$^{-1}$) and uptake ratios ($R$, %) of Sr(II) and Y(III) ions were calculated as follows:

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \tag{2}$$

$$R = \frac{C_0 - C_t}{C_0} \times 100 \tag{3}$$

where $C_0$, $C_t$ and $C_e$ are the metal ion concentrations before adsorption, after adsorption at time $t$, and after reaching equilibrium in the liquid phase in ppm, respectively. $m$ is the weight of dry adsorbent in g and $V$ is the volume of the liquid phase in cm$^3$.

### Column method

The columns ware prepared by packing approximately 4 g CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P adsorbents into glass column (8 mm inner diameter × 120 mm length). Several elutions were passed through the column for the adsorption experiment. $HNO_3$ solution (2 M) containing 5 mM Sr(II) and Y(III) was fed into the column. $HNO_3$ solution (2 M) without metal ions was fed into the column continuously as washing solution. $H_2O$ was also fed into the column continuously. The solutions were fed into the column at a flow rate of 0.3 cm$^3$/min with a metering pump, and the column was maintained at 298 K with a thermostatic water jacket. Simultaneously, outflowing solution from the column was collected with a fraction collector in 2.5 ml per a tube. The concentration of metal ions in the fractions were determined by ICP-AES. Additionally, a pH meter (HORIBA pH meter D-52) was used to measure the pH of the fractions.

## Results and discussion

### Effect of acid concentration

The effect of the acid concentration was determined by a batch method. The result with CMPO/$SiO_2$-P is shown in Fig. 1 and that with (CMPO + Dodec)/$SiO_2$-P is shown in Fig. 2. Y(III) showed a high adsorption affinity for CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P, and this increased with the $HNO_3$ concentration. However, Y(III) showed weak adsorption on both adsorbents in HCl solution. Sr(II) showed weak adsorption on CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P in $HNO_3$ and HCl solutions.

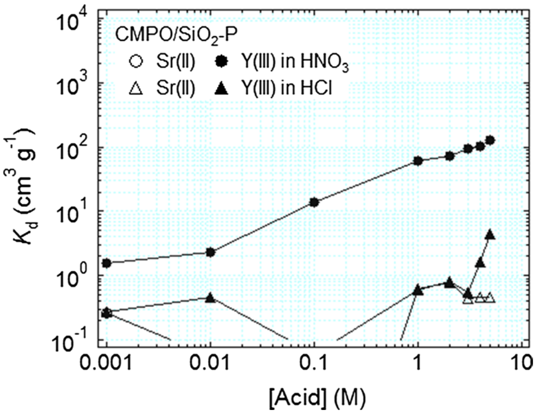

**Fig. 1** Effects of acid concentration on CMPO/$SiO_2$-P adsorbent

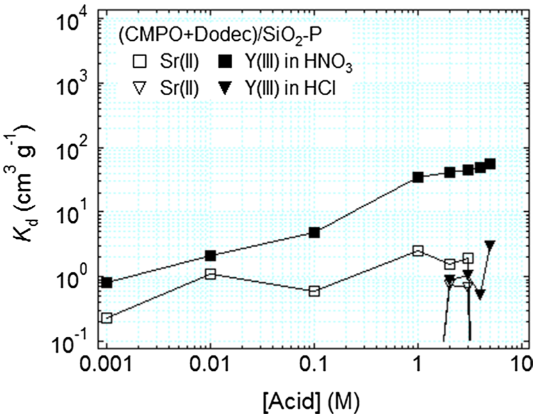

**Fig. 2** Effects of acid concentration on (CMPO + Dodec)/$SiO_2$-P adsorbent

CMPO has good selectively for the adsorption of trivalent Rare Earth (RE) and MA(III) [13]. It is believed that Y(III), which is trivalent RE, forms a complex with $NO_3^-$ and impregnated CMPO. The proposed complex formation is as follows:

$$Y^{3+} + 3HNO_3 \leftrightarrow Y(NO_3)_3 + 3H^+ \tag{4}$$

$$\begin{aligned} &Y^{3+} + 3HNO_3 + nCMPO/SiO_2 - P \\ &\leftrightarrow Y(NO_3)_3(CMPO/SiO_2 - P) + 3H^+ \end{aligned} \tag{5}$$

$$\begin{aligned} &Y^{3+} + 3HNO_3 + n(CMPO + Dodec)/SiO_2 - P \\ &\leftrightarrow Y(NO_3)_3((CMPO + Dodec)/SiO_2 - P) + 3H^+ \end{aligned} \tag{6}$$

According to Eqs. (4)–(6), as the $NO_3^-$ concentration increase, the chemical equilibrium shift to the right and $Y(NO_3)_3$ increases. In conjunction with this, $Y(NO_3)_3$(CMPO/$SiO_2$-P) and $Y(NO_3)_3$((CMPO + Dodec)/$SiO_2$-P) increase. Consequentry, Y(III) showed strong adsorption in high $HNO_3$ concentration.

From another viewpoint, $K_d$ for (CMPO + Dodec)/$SiO_2$-P is lower than for CMPO/$SiO_2$-P. It was considered that (CMPO + Dodec)/$SiO_2$-P contains 1-dodecanol and CMPO in the same microporous structure. Therefore, it is thought that 1-dodecanol inhibits the chelate complex formation between Y(III) and CMPO due to its geometrical arrangement and/or its hydrophobicity.

As it was verified that Y(III) exhibited weak adsorption on both adsorbents in HCl, the remaining batch experiments were performed in $HNO_3$.

## Effect of contact time

The effect of contact time in $HNO_3$ solution was assessed by a batch method. Figure 3, shows plots of time versus $Q_t$ fitted to the pseudo-second-order kinetic model, described later. The Y(III) uptake on CMPO/$SiO_2$-P increased with the contact time and reached equilibrium within 30 min. However, the Y(III) uptake on (CMPO + Dodec)/$SiO_2$-P reaches equilibrium almost immediately. Additionally, the uptake ratios on CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P at equilibrium were approximately 56% and 69% respectively, at 298 K.

According to a report by Ho and Mckay [14], a pseudo-second-order kinetic model for this adsorption system was developed. This assumes that the adsorption rate is controlled by chemical adsorption and that 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 of Y(III) adsorption on CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P were determined by the pseudo-second-order equation:

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{t}{Q_e} \tag{7}$$

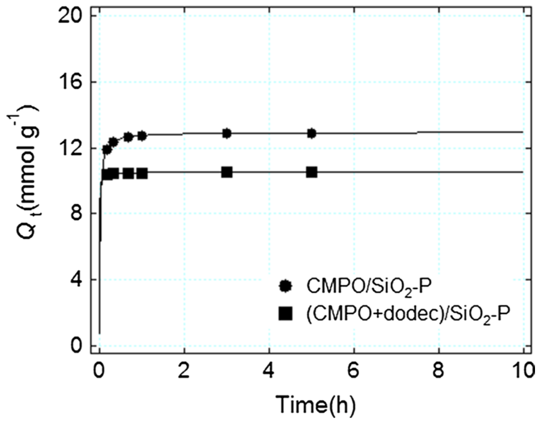

**Fig. 3** Effects of contact time on CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P adsorbents

where $Q_t$ and $Q_e$ are the amounts of Y(III) adsorbed at time $t$ and at equilibrium (mg $g^{-1}$), respectively, and $k$ is the rate constant of the pseudo-second-order adsorption (g $mg^{-1}$ $h^{-1}$).

Plots of $t/Q_t$ versus $t$, shown in Fig. 4, show straight lines with high correlation coefficients ($R^2$) of nearly 1. This indicated that the results fitted well with the pseudo-second-order model. Thus, chemisorption governs the rate-controlling step of this adsorption. The values of $Q_e$ and $k$ are determined as 13 mg $g^{-1}$ and 4.9 g $mg^{-1}$ $h^{-1}$ for CMPO/$SiO_2$-P and 11 mg $g^{-1}$ and 37 g $mg^{-1}$ $h^{-1}$ for (CMPO + Dodec)/$SiO_2$-P from the slopes of the straight lines. These results for $Q_e$ were similar to the experimental values of 13 mg $g^{-1}$ (CMPO/$SiO_2$-P, 5 h) and 11 mg $g^{-1}$ ((CMPO + Dodec)/$SiO_2$-P, 5 h) at 298 K.

## Effects of temperature

The effect of temperature in $HNO_3$ solution was evaluated by batch method. To investigate the thermodynamic nature of the adsorption on CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P, several thermodynamic parameters were calculated using the Van't Hoff equation, as shown below:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{8}$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{9}$$

where $\Delta G^0$ is the change in Gibbs free energy (kJ $mol^{-1}$), which is the fundamental criterion of spontaneity; $\Delta H^0$ is the change in standard enthalpy (kJ $mol^{-1}$). $\Delta S^0$ is the change in standard entropy (J $K^{-1}$ $mol^{-1}$). $R$ is the gas constant (8.314 J $mol^{-1}$ $K^{-1}$), $T$ is the temperature (K); and $K_d$ is the distribution coefficient at an equilibrium defined in Eq. (2).

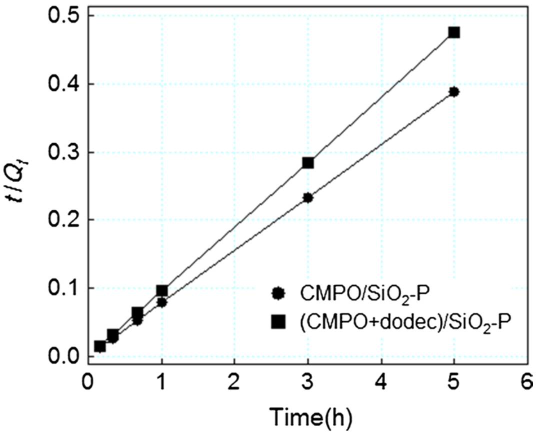

**Fig. 4** Pseudo-second-order kinetic fitting for Y(III) adsorption on CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P adsorbents

Plots of ln($K_d$) versus 1/$T$, shown in Fig. 5, show straight lines with correlation coefficients ($R^2$) of 1. The values of $\Delta H^0$ and $\Delta S^0$ were determined from the slope and intercept of the linear variation, and $\Delta G^0$ was calculated for each temperature. Table 1 summarizes these values. As $\Delta H^0$ and $\Delta S^0$ were negative for both adsorbents, the adsorption processes were exothermic, and the reaction progresses at a lower temperature with both adsorbent. Furthermore, since the $\Delta G^0$ values were negative under all conditions, Y(III) adsorption on CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P was spontaneous under the experimental condition.

## Column separation

Figures 6 and 7 show the results for separating Y(III) from Sr(II)–Y(III) by extraction chromatography using CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P. Sr(II) flowed out from the adsorbent-packed column immediately without adsorbing while feeding $HNO_3$ solution. However, Y(III) hardly flowed out while feeding $HNO_3$ solution. Subsequently, when $H_2O$ began to feed into the column, the adsorbed Y(III) on the adsorbent eluted from the column. No elution

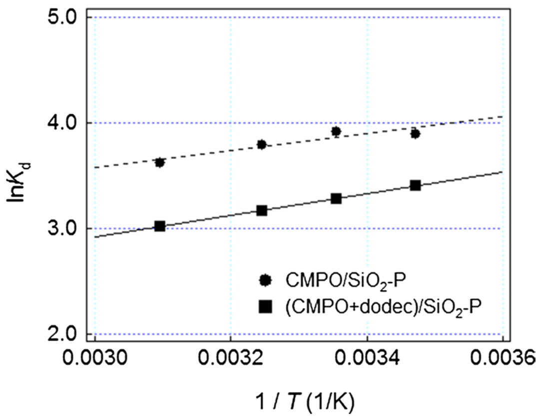

**Fig. 5** Effects of temperature onto CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P adsorbents

**Table 1** Thermodynamic parameters for the Y(III) adsorption on CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P adsorbents

| | CMPO/$SiO_2$-P | (CMPO + Dodec)/$SiO_2$-P |
|---|---|---|
| $\Delta S^0$ [kJ $K^{-1}$ $mol^{-1}$] | $-1.4 \times 10^{-3}$ | $1.0 \times 10^{-2}$ |
| $\Delta H^0$ [kJ $mol^{-1}$] | − 8.6 | − 6.6 |
| $\Delta G^0$ [kJ $mol^{-1}$] | | |
| 288.15(K) | − 8.1 | − 9.5 |
| 298.15(K) | − 8.1 | − 9.6 |
| 308.15(K) | − 8.1 | − 9.7 |
| 223.15(K) | − 8.1 | − 9.8 |

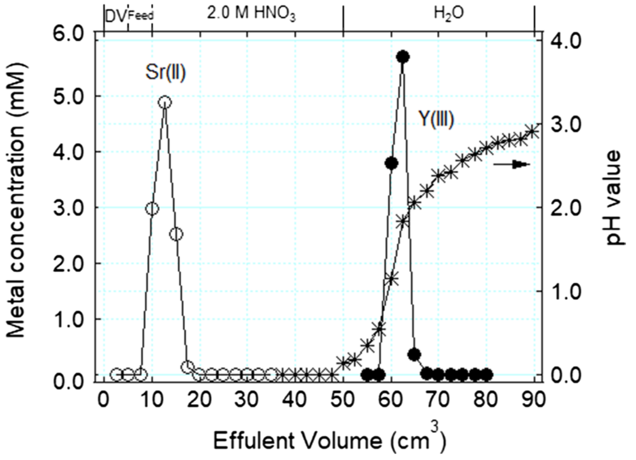

**Fig. 6** Column separation results for Sr(II) and Y(III) using $HNO_3$ solution with the CMPO/$SiO_2$-P adsorbent

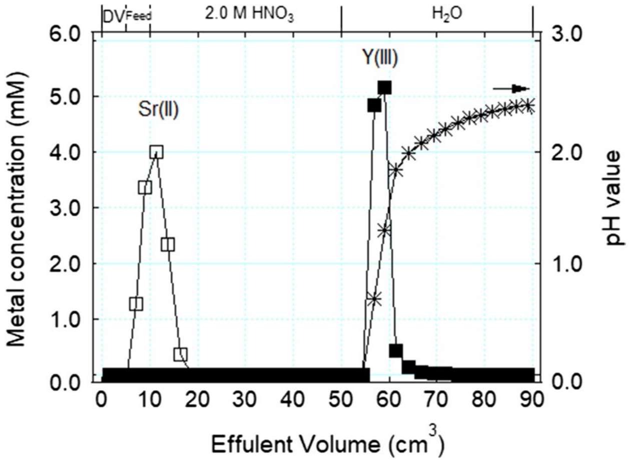

**Fig. 7** Column separation results for Sr(II) and Y(III) using $HNO_3$ solution with the (CMPO + Dodec)/$SiO_2$-P adsorbent

tailing was observed in the elution curves, and the elution band was narrow, indicating that the elution kinetics of CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P with Y(III) were rapid. Concerning the material balance, the chemical yield of Y(III) was calculated as about 100 wt%. Satisfactory separation and recovery of Y(III) from a Sr(II)–Y(II) mixture with CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P were achieved.

## Conclusions

In this study, to separate Y(III) from a Sr(II)–Y(III) mixture, the silica-based CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P adsorbents were prepared by impregnating CMPO extractant and a molecule modifier into the macroporous $SiO_2$-P support. The adsorption behavior of Sr(II) and Y(III) on both adsorbents was investigated by a batch method under various conditions involving different concentrations of acids ($HNO_3$ or HCl), contact times, and temperatures.

Regaring the effect of the acid concentration, the adsorbents showed a high adsorption affinity with Y(III) and weak adsorption affinity with Sr(II) in $HNO_3$ solution. Additionally, as the $HNO_3$ concentration increases, Y(III) showed strong adsorption on CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P. $K_d$ reached approximately 100 when using CMPO/$SiO_2$-P in 5 M $HNO_3$. However, Y(III) showed weak adsorption on both adsorbents in HCl. Sr(II) showed weak adsorption under all conditions. Concerning the effect of contact time, the Y(III) uptake on CMPO/$SiO_2$-P reached equilibrium within 30 min and that on (CMPO + Dodec)/$SiO_2$-P reached equilibrium immediately. Additionally, the uptake ratios on CMPO/$SiO_2$-P and (CMPO + Dodec)/$SiO_2$-P at an equilibrium were approximately 56% and 69%, respectively, at 298 K. This indicated that Y(III) adsorption on CMPO adsorbents fitted well with the pseudo-second-order model with a high correlation coefficient. The calculated $Q_e$ values were similar to the experimental values of 13 mg $g^{-1}$ (CMPO/$SiO_2$-P) and 11 mg $g^{-1}$ ((CMPO + Dodec)/$SiO_2$-P). Regarding the effect of temperatue, $\Delta H^0$ was − 8.6 for CMPO/$SiO_2$-P and − 6.6 for (CMPO + Dodec)/$SiO_2$-P. Therefor, Y(III) adsorption on CMPO adsorbents was spontaneous. Using the column method, successful separation of Y(III) from a Sr(II)–Y(III) mixture was achieved using both adsorbents in 2 M $HNO_3$ and $H_2O$ with a satisfactory recovery rate (almost 100%).

The above results show that both adsorbents have sufficient capacity to separate Y(III) from a Sr(II)–Y(III) mixture. However, it is considered that CMPO/$SiO_2$-P is better from the viewpoint of $K_d$ and the saturated adsorption amount because it works with a higher $^{90}$Y concentration.

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