1. Introduction

The spent fuel used in nuclear power plants contains uranium and plutonium. These nuclides are reusable as nuclear fuel, thus they are separated and recovered by reprocessing. The various other nuclides generated as a result of fissions and neutron captures (e.g., Cs-137, Sr-90, Pd-107, and Am-241) are also present in the spent fuel. These nuclides are separated from uranium and plutonium by reprocessing, and they are discharged as high-level liquid waste (HLLW). In Japan, the PUREX method is used to reprocess spent fuels. The PUREX method is a process in which finely sheared spent fuel is dissolved in HNO₃ and continuously extracted with a solvent to separate uranium, plutonium, and other elements. Thus, the HLLW is the HNO₃ solution including so many kinds of nuclides. HLLW is vitrified as a way to immobilize the radioactive nuclides; subsequently, the vitrified HLLW is geologically disposed after cooling time of 30–50 years. However, radioactive cesium, barium, strontium, and yttrium contained in the vitrified HLLW generate a lot of heat as a consequence of their radioactive decay; in fact, the heat generated by these radionuclides accounts for 80% of the heat generated by the vitrified HLLW. Therefore, removing these exothermic nuclides from the HLLW is assumed to contribute to the efficient disposal of the vitrified HLLW.

Y-90 is one of the exothermic nuclides present in HLLW, and so is its daughter nuclide Sr-90. Y-90 has a short half-life of approximately 64 hours, and Y-90 emits a strong β-ray of 2.28 MeV, when it decays to the stable Zr-90. Therefore, Y-90 has recently been used as a radiopharmaceutical antitumor agent, and it is expected to exhibit high therapeutic activity. The radioactive decay of Y-90 can be represented by the following equation:

\[
{ }^{90}Y \rightarrow { }^{90}Zr + { }^{0}\beta + E_{\beta} = 2.28\text{ MeV}
\]
\[
{^{90}\text{Sr}} \rightarrow {^{90}\text{Y}} \rightarrow {^{90}\text{Zr\,(stable)}},
\]

Since Sr-90 and Y-90 are in a secular radioactive equilibrium, Y-90 can be easily obtained by milking Y-90 from the Sr-90 solution separated from the HLLW. Therefore, Sr-90 needs to be separated from the HLLW to obtain a stable source of Y-90.

Various methods for the separation of Sr ions from aqueous solutions have been studied \(^{7–15}\). In the methods that rely on porous materials, the Sr ion has been shown to be separable from aqueous solution via adsorption of the ion onto arsenate-modified mesoporous titania \(^7\), sodium-modified mesoporous titanium dioxide \(^8\), or expanded perlite \(^9\). Methods that rely on fibers, like alginate fibers \(^10\), hexagonal tungsten oxide \(^11\), or sodium vanadate \(^12\), have also been studied, and evidence indicated that they afford the adsorption of the Sr ion. Moreover, functionalized silica microspheres prepared by poly methacrylic acid or amidoxime groups and functionalized algal/polyethyleneimine beads by amidoxime have also been observed to be able to adsorb the Sr ion \(^13\).

The method consisting of the continuous separation of Sr by extraction chromatography has also been investigated. In the case of extraction chromatography, an adsorbent with the extractant immobilized onto a macroporous silica/polymer composite carrier (SiO\(_2\)-P) was used. SiO\(_2\)-P, an inorganic–organic hybrid material, was prepared by polymerizing a styrene-divinylbenzene copolymer on a spherical macroporous SiO\(_2\) particle as base material. SiO\(_2\)-P exhibits some advantageous characteristics, like mechanical strength as well as high acid resistance; moreover, it affords an easy separation of solids from liquids by filtration. Especially, it has higher radiation resistance than other carriers and is suitable for use in radioactive substances. It will eventually reduce the amount of impregnated extractant and should be discarded as radioactive waste. However, it is considered that metal ions can be eluted by contacting with a solution under conditions of low affinity, and it can be used multiple times. In previously published studies, silica-based adsorbents impregnated with 4,4',(5')-di-(tert-butyl-cyclohexano)-18-crown-6 (DBuCH18C6) or 2,6-bis(5,6-di(iso-butyl)-1,2,4-triazine-3-yl)pyridine (BDIBTP) were used \(^{14,15}\). However, in these studies, Ba ions were separated from HLLW alongside Sr ions during the same process, as a consequence of the similar chemical properties of Ba and Sr ions. In order to employ HLLW-separated Sr ions for medical purposes, however, Sr ions need to be separated from Ba ions, because the latter have an adverse effect of damage for bones as impurities of radiopharmaceutical. Therefore, after carrying out the process whereby Sr ions are separated from HLLW, Ba ions should be removed from the mixed solution of Ba and Sr ions. Ba ions are assumed to be separable using the difference in the intensity of the adsorption of Ba and Sr ions onto the impregnated extractant.

The adsorption behavior of the Ba ion has also been studied. In particular, sodium-modified mesoporous titanium dioxide \(^8\), hydrous ferric oxide \(^16\), and expanded perlite \(^9\), which are volcanic rhyolitic rock, were observed to adsorb Ba as well as Sr ions. Since both Ba and Sr are alkaline earth metals, their chemical behaviors are similar to each other, so the adsorption behaviors of Ba and Sr ions need to be investigated in more depth to separate these metal ions from each other.

For this purpose, the impregnated adsorbents used SiO\(_2\)-P as a support were prepared in the present study. Plus, since it has been reported that sulfur-containing thiuram disulfide (TDS) derivatives form complexes with metal ions \(^{17–19}\), two types of TDS derivatives were used as an extractant for impregnated adsorbents in this study. One of them is tetra-n-butyl thiuram disulfide (TBTDS), which comprises four butyl groups in the side-chain, and the other is tetrakis(2-ethylhexyl) thiuram disulfide (T(2EH)TDS), which comprises a 2-ethylhexyl group in the side-chain. Notably, the molecular structures of TBTDS and T(2EH)TDS are depicted in Fig. 1. These extractants were impregnated into the SiO\(_2\)-P to prepare three different adsorbents. The adsorption behaviors of Ba and Sr ions onto the said adsorbents, like, for instance, the dependence on acid concentration, were investigated by the batch method.

### 2. Experimental

#### 2.1 Materials

Strontium nitrate (98.0%) was purchased from Wako.

\[
\begin{align*}
\text{(a) TBTDS} & \quad \text{N}S-SSN \quad \text{N}S-SSN \\
\text{(b) T(2EH)TDS} & \quad \text{N}S-SSN \quad \text{N}S-SSN
\end{align*}
\]

Fig. 1 Molecular structures of thiuram disulfide TDS-based extractants.
Pure Chemical Industries, Ltd. Barium nitrate (99.0%) was purchased from Kanto Chemical Co., Inc. TBTDS was obtained from Tokyo Chemical Industry Co., Ltd. T(2EH)TDS was obtained from Ouchi Shinko Chemical Industrial Co., Ltd. A solution of metal ions was prepared by adding the metal-based reagents just mentioned to HNO₃ and distilled water to achieve the desired concentrations.

2.2 Preparation of the adsorbents

The novel silica-based adsorbents dubbed (TBTDS + Dodec)/SiO₂-P, T(2EH)/SiO₂-P, and (T(2EH)TDS + Dodec)/SiO₂-P were prepared by impregnating TBTDS, T(2EH)TDS, and 1-dodecanol (Dodec) into the SiO₂-P particles, respectively. Dodec was added as a molecule modifier in addition to the extractants. Notably, as a pretreatment, the SiO₂-P particles were washed three times with about 300 cm³ of methanol to remove impurities; the particles were then dried in vacuum overnight after separation from the methanol by filtration. In detail, for the preparation of (TBTDS + Dodec)/SiO₂-P, the TBTDS and Dodec were dissolved in 200 mL of dichloromethane; subsequently, the dichloromethane solution and the washed SiO₂-P were mixed together in an eggplant flask. After impregnating TBTDS and Dodec into the SiO₂-P for several hours at room temperature using a rotary evaporator, the solvent was removed at 313 K under reduced pressure. T(2EH)TDS/SiO₂-P was prepared by the procedure just described using T(2EH)TDS and SiO₂-P, in the absence of Dodec. In addition, the same procedure was implemented to prepare (T(2EH)TDS + Dodec)/SiO₂-P using T(2EH)TDS, Dodec, and SiO₂-P. The residues obtained after the evaporation process were vacuum-dried overnight at 313 K, leading to the isolation of the three adsorbents.

The surface morphology of the adsorbents was investigated by scanning electron microscopy (SEM, HITACHI S-3100H), and the images thus recorded are reported in Fig. 2. Moreover, the thermal stabilities of the adsorbents were examined by thermal gravimetry (TG) analysis (Shimadzu DTG-60).

2.3 Batch method

The adsorption behaviors of Ba and Sr ions onto (TBTDS + Dodec)/SiO₂-P, T(2EH)TDS/SiO₂-P, and (T(2EH)TDS + Dodec)/SiO₂-P were examined implementing the batch method, focusing on acid concentration, contact time, temperature, and metal concentrations. A 0.2-g sample of the dried adsorbent and 4 cm³ of the Sr–Ba mixed aqueous solution were placed in a 13.5-cm³ glass vial, which was then shaken at 160 rpm in a thermostatic shaking bath. The acid, Sr ion

![Scanning electron microscopy images of the adsorbents.](image1)

(a) (TBTDS + Dodec)/SiO₂-P
(b) T(2EH)TDS/SiO₂-P
(c) (T(2EH)TDS + Dodec)/SiO₂-P

Fig. 2 Scanning electron microscopy images of the adsorbents.
and Ba ion concentrations in the aqueous solution were adjusted to 5 mM. After shaking the glass vial for several min to a few hour, the liquid phase was separated from the adsorbent by filtration. The concentrations of the two metal ions in the liquid phases before and after the shaking were measured by inductively coupled plasma atomic emission spectrometry (ICP–AES, Shimadzu ICPE-9000). Based on the results of the measurements, the distribution coefficient ($K_d$), uptake ratio ($R$) and the amount of metal ions adsorbed onto an adsorbent ($Q$) were calculated for each metal ion employing equations (2)–(4):

$$K_d = \frac{C_0 - C_t}{C_t} \times \frac{V}{m},$$  \hspace{1cm} (2)

$$R = \frac{C_0 - C_t}{C_0} \times 100,$$  \hspace{1cm} (3)

$$Q = (C_0 - C_t) \times \frac{V}{m},$$  \hspace{1cm} (4)

where $C_0$ is the metal ion concentration before adsorption, $C_t$ is the metal ion concentration after adsorption at time $t$, and $C_e$ is the metal ion concentration after equilibrium has been reached in the liquid phase. The concentrations are reported in ppm, $V$ is the volume of the mixed solution (cm$^3$), and $m$ is the weight of the adsorbent in g.

### 3. Results and discussion

#### 3.1 Thermal stability

The results of TG analyses conducted on the three adsorbents are reported in Fig. 3. The pre-dried adsorbents were heated at a rate of 1°C/min from 25°C to 600°C in an N$_2$ atmosphere. Thus, the changes of weight were due to thermal decomposition and evaporation because this experiment was carried out in N$_2$ atmosphere.

Based on the TG curve of SiO$_2$-P (curve (d) in Fig. 3), it can be evinced that approximately 16.0% of the whole weight of the adsorbent used for this analysis was lost in the 300°C–400°C temperature range. As SiO$_2$-P consisted of SiO$_2$ and a styrene-divinylbenzene copolymer (SDB), the weight reduction observed in the mentioned temperature range was assumed to be associated with the decomposition of SDB. As can be evinced from the TG curves (a) and (c) (for (TBTDS + Dodec)/SiO$_2$-P and (T(2EH)TDS + Dodec)/SiO$_2$-P, respectively), the relevant samples lost approximately 10% of their weights in the 100°C–130°C temperature range. Since no similar weight reductions were observed for curve (b) (for T(2EH)/SiO$_2$-P), the weight change at 100°C–130°C rendered evident by the TG curves (a) and (c) was assumed to be caused by the decomposition and/or vaporization of Dodec. Notably, weight decreases were observed in the 150°C–220°C temperature range for all three adsorbents. These weight reductions were assumed to descend from the decomposition of TDS-type extractants. Comparing the synthetic conditions and the results of TG analysis, the weight changes were close to each other. The compositions of the adsorbents as inferred from the results of TG analyses as well as the synthesis conditions are listed in Table 1.

#### 3.2 Effect of HNO$_3$ concentration

In the process of separation ions, the concentration of acid

| Adsorbent                  | SiO$_2$-P [%] | 1-Dodecanol [%] | Extractant [%] |
|----------------------------|---------------|------------------|----------------|
| (TBTDS + Dodec)/SiO$_2$-P  | 57.9          | 9.7              | 32.4           |
| Synthetic conditions       | 60.5          | 9.3              | 30.2           |
| TG analysis                |               |                  |                |
| T(2EH)TDS/SiO$_2$-P        | 64.3          | –                | 35.7           |
| Synthetic conditions       | 65.9          | –                | 34.1           |
| TG analysis                |               |                  |                |
| (T(2EH)TDS + Dodec)/SiO$_2$-P | 58.0          | 9.7              | 32.3           |
| Synthetic conditions       | 61.2          | 9.0              | 29.8           |
| TG analysis                |               |                  |                |
is very important factor for metal ions. The effects of the concentration of HNO₃ on the adsorption of Ba and Sr ions onto the three adsorbents were investigated by the batch method using Sr–Ba mixed aqueous solutions characterized by different HNO₃ concentrations in the 0.001–1 M range. The results of these experiments are reported in Fig. 4. The graph in this figure reflects the relationship between the calculated Kₑ values of metal ions and initial HNO₃ concentrations for each of the adsorbents.

For all three adsorbents, a weak adsorption of the Sr ion was observed under the experimental conditions. Only in the range of low HNO₃ concentration up to at least 0.1 M, the adsorbents showed weak adsorption of both the Ba ion and the Sr ion. However, at 0.5 M concentration of HNO₃, T(2EH)/SiO₂-P adsorbed the Ba ion, and (TBTDS + Dodec)/SiO₂-P exhibited stronger adsorption of the Ba ion than T(2EH)/SiO₂-P. In addition, at 1 M concentration of HNO₃, (T(2EH)TDS + Dodec)/SiO₂-P exhibited adsorption capability of the Ba ion, and the adsorption of Ba onto (TBTDS + Dodec)/SiO₂-P and T(2EH)/SiO₂-P increased with the HNO₃ concentration.

The mechanism of the reaction in liquid-liquid extraction between TBTDS and divalent metal ions was proposed previously. The said mechanism can be expressed by equations (5) and (6):

\[ \text{TDS} \rightarrow 2\text{dtc}^- , \]  
\[ \text{dtc}^- + M(\text{dtc})_2 \rightarrow M(\text{dtc})_2(\text{dtc}^-) , \]  

Specifically, the disulfide bond of TBTDS is broken, leading to the generation of dithiocarbamate (dtc). Afterwards, the thus generated dtc forms a complex with a divalent metal ion. Although in the study wherein the described mechanism was introduced the divalent metal ion utilized was Ni(II), the same mechanism is assumed to be applicable to the case of Ba, since the latter is also divalent metal ion. Another difference between the previously published study and the present one is that the disassembly reaction between TBTDS and the divalent metal ion was promoted by Laser light irradiation in the previously published paper, while in the present experimental system, the nitrate ion is assumed to act as nucleophile and promote the decomposition of the disulfide bond. Therefore, it is considered that the decomposition of the disulfide bond was increasingly promoted as the acid concentration increased.

Based on the described results, all three adsorbents were concluded to be able to separate Ba ions from Sr ions in 1 M HNO₃ solution. Although the rationale for the difference in reactivity with dtc between Ba and Sr ions has not been clarified, it is assumed that it has to do with the stability of the dtc complex with ionic Sr being lower than that with ionic Ba. Since it was confirmed that the affinity of Sr and the adsorbents were weak, subsequent experimental results describe about adsorption of Ba.

3.3 Effect of the contact time

The effect of the contact time on the adsorption of the Ba ion onto the three adsorbents was investigated implementing the batch method at different shaking times. The results of these experiments are summarized in Fig. 5. Indeed, the data in this figure reflect the relationship between the uptake ratio R of Ba ions and the shaking time for each of the adsorbents.

No adsorption of the Ba ion onto (TBTDS + Dodec)/SiO₂-P and T(2EH)/SiO₂-P was observed up to 1 hours after the start of shaking; moreover, no such adsorption was observed onto (T(2EH)TDS + Dodec)/SiO₂-P up to 2 hours after the start of shaking. However, after 1 hours, the uptake ratios onto (TBTDS + Dodec)/SiO₂-P and T(2EH)/SiO₂-P increased with the shaking time, reaching a value close to 100% after 5 hours. In the case of (T(2EH)TDS + Dodec)/SiO₂-P, the uptake ratio onto (T(2EH)/TDS + Dodec)/SiO₂-P of the Ba ion increased with the shaking time once the 2 hours mark was passed, reaching a value close to 100% after 5 hours. Therefore, the adsorption reaction was assumed not to start immediately after the adsorbent and metal ion solution were placed in contact with each other because the adsorption of the Ba ion by dtc can only take place after the decomposition reaction of TDS described by equation (5) occurs.

![Fig. 4] Effect of HNO₃ concentration on the value of the distribution coefficient (Kₑ) for the Ba and Sr ions onto the adsorbents. (initial metal concentration: 5 mM, contact time: 5 hours, temperature: 298 K)
Effect of the temperature

The effect of the temperature on the adsorption of Ba ion onto the three adsorbents was investigated by changing the temperature of the shaking bath. The results of the relevant experiments are reported in Fig. 6. The data in this figure reflect the relationship existing between $\ln(K_d)$ and the reciprocal of the absolute temperature for each of the adsorbents.

The thermodynamic properties of the adsorption reaction were evaluated based on these results. Specifically, the changes in Gibbs free energy, standard enthalpy, and standard entropy were calculated using the Van’t Hoff’s equation:

$$\Delta H = \Delta H^0 - T\Delta S^0$$  

$$\Delta G = -RT\ln(K_d)$$  

where $\Delta G^0$ is the change in Gibbs free energy (kJ mol$^{-1}$), $\Delta H^0$ is the change in standard enthalpy (kJ mol$^{-1}$), and $\Delta S^0$ is the change in standard entropy (J K$^{-1}$ mol$^{-1}$). $K_d$ is the parameter defined in equation (2). $T$ is the temperature (K). $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$).

Here, for each applied temperature, the $\Delta H^0$ and $\Delta S^0$ values were calculated by using equation (7), and the $\Delta G^0$ values were calculated by using equation (8). The results of these calculations are listed in Table 2. The $\Delta H^0$ values were positive, which means that the adsorption of the Ba ion onto the TDS impregnated adsorbents was an endothermic reaction. The $\Delta S^0$ values were also positive for the three adsorbents, and the calculated $\Delta G^0$ values were negative at all temperatures. Indeed, reactions proceed spontaneously when the values of $\Delta H^0$ and $\Delta S^0$ are positive and $\Delta G^0$ is negative.

The effect of temperature is an important factor for the design of separation processes. Thus, it is necessary to set the optimal temperature conditions. From the results of this experiment, it was clarified that the reaction is likely to proceed on higher temperatures within the range of experimental conditions, and necessary and important characteristics were obtained in process design.

Adsorption isotherms

The isotherms of the processes whereby the Ba ion is adsorbed onto the three adsorbents were recorded for solutions containing different concentrations of Ba ions, so as to investigate the maximum adsorption amount and the adsorption process. In Fig. 7 and Fig. 8 are reported the plots of the adsorbed amount of Ba ion onto the adsorbents versus the concentration of the Ba ion in solution phase at equilibrium.

The characteristics of the adsorption isotherm are important
to understand the surface conditions of the adsorbent and the interaction between adsorbate and adsorbent. The relationship between the concentration of the adsorbate in solution and the amount of adsorbate on the adsorbent at equilibrium is represented by the adsorption isotherm. Furthermore, the maximum adsorption capacity of the absorbents could be calculated as the theoretical adsorption isotherm model parameter, and the parameter is one of the essential factors to determine the amount of adsorbent required in the adsorption process.

As part of the present investigation, two isotherm models, the Freundlich equation and the Langmuir equation, were utilized to fit the obtained isotherms. The Langmuir equation is applicable when the thickness of the adsorption site corresponds to a single layer of about one molecule in size. The Freundlich equation is the empirical formula expressing the adsorption equilibrium. This equation usually applies when adsorption sites are distributed heterogeneously and no single layer. The Langmuir and Freundlich models are expressed by the following equations:

**Langmuir equation:**

\[
Q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \text{(non-linear),} \tag{8}
\]

\[
\frac{C_e}{Q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad \text{(linear),} \tag{9}
\]

**Freundlich equation:**

\[
Q_e = K_F C_e^\frac{1}{n} \quad \text{(non-linear),} \tag{10}
\]

\[
\log(Q_e) = \log(q_m) + \frac{1}{n} \log(C_e) \quad \text{(linear),} \tag{11}
\]

where \(C_e\) (mol dm\(^{-3}\)) is the equilibrium concentrations of the Ba ion in the aqueous solution, \(Q_e\) (mol g\(^{-1}\)) is the amount of Ba ions adsorbed onto the adsorbent, \(q_m\) (mol g\(^{-1}\)) is the maximum adsorption capacity of the Ba ion, \(K_L\) (dm\(^3\) mol\(^{-1}\)) is the Langmuir constant, \(K_F\) (mol g\(^{-1}\)) and \(1/n\) are the Freundlich constants, and \(1/n\) is a parameter related to the intensity of the adsorption.

These isotherm models were applied to the experimental data obtained for the two adsorbents T(2EH)TDS/SiO\(_2\)-P and (T(2EH)TDS + Dodec)/SiO\(_2\)-P as a way to investigate the adsorption mechanism. The parameters thus calculated employing the adsorption models are listed in Table 3. The correlation coefficients for the two adsorbents were best closely 1.0 in the Langmuir model, so the adsorption processes of the Ba ion onto the two adsorbents appear to be single layer adsorptions in nature. The maximum adsorption capacity of the Ba ion according to the Langmuir model had values of 0.38 mmol/g for T(2EH)TDS/SiO\(_2\)-P and 0.32 mmol/g for (T(2EH)TDS + Dodec)/SiO\(_2\)-P.

On the other hand, in the case of TBTDS, almost 100% of the Ba ions were adsorbed onto the (TBTDS + Dodec)/SiO\(_2\)-P under all metal concentration conditions in this experiment. This observation was assumed to descend from a large increase in the number of apparent adsorption sites due to the increase in dtc concentration resulting from the decomposition of TBTDS, which was considered to undergo decomposition more easily than T(2EH)TDS. The isotherm models were also used to fit the experimental data collected for (TBTDS + Dodec)/SiO\(_2\)-P, and the values of the parameters thus calculated are also reported in Table 3. The calculated correlation coefficient had a value of 0.96 for
Freundlich model and one of 0.66 for the Langmuir model. Therefore, the adsorption process appeared to be multi-layer rather than single layer in nature for (TBTDS + Dodec)/SiO₂-P. However, the relationship was S-shaped rather than linear. The theoretical isotherms obtained applying each of the models for the TBTDS adsorbent are reported in Fig. 7, and those for the T(2EH)TDS adsorbents are reported in Fig. 8. Notably, the theoretical isotherms obtained applying the Langmuir model are reported as dotted lines whereas those obtained applying the Freundlich model are reported as dashed lines. In Fig. 8, the shapes of the experimental isotherms showed convex upwards, and this were well fitted to the Langmuir model. On the other hand, the experimental isotherm reported in Fig. 7 is S-shaped, but it should be noted that the range on the horizontal axis is different from the others. The fact that the experimental isotherm is S-shaped means that the adsorption process has the features of an adsorption onto a microporous or mesoporous material, in other words, adsorption into a materials characterized by smaller pores than a microporous material.

It can be seen that the reaction ratio between the metal ion and T(2EH)TDS is 1:1.5 from equations (5) and (6). Plus, from Table 1, the amount of T(2EH)TDS impregnated the 1 g of T(2EH)TDS/SiO₂-P and (T(2EH)TDS/SiO₂-P) adsorbents were 0.341 g and 0.298 g respectively, and they were equal to 0.54 mmol and 0.47 mmol. The qₘ value of T(2EH)TDS/SiO₂-P and (T(2EH)TDS/SiO₂-P) were 0.38 mmol/g and 0.32 mmol/g respectively, and these reaction ratios were 1:1.47 and 1:41 respectively. Therefore, these qₘ values are close to the calculated values and are considered reasonable.

The isotherm shape of TBTDS/SiO₂-P was different from the others, and the qₘ value was considerably larger than the others. The reason of these difference was not clarified but may be the difference of decomposition. Since the qₘ value was quite large, it is considered that the reason is that the decomposition of TBTDS proceeded further, and the number of apparent adsorption sites increased significantly.

4. Conclusions

In order to separate the Ba ions from the Sr ions in HNO₃ solution, TDS-type extractant immobilized adsorbents, (TBTDS + Dodec)/SiO₂-P, T(2EH)TDS/SiO₂-P, and (T(2EH)TDS + Dodec)/SiO₂-P were prepared via impregnation of the extractant into SiO₂-P. The Ba ion adsorption behaviors of the three adsorbents were investigated implementing a batch method.

The three adsorbents showed no Sr ion adsorption capability under the applied experimental conditions. By contrast, the Ba ion was well adsorbed onto the adsorbents in solutions containing HNO₃ at concentration higher than 0.5 M. Furthermore, the difference in adsorption capability between the Sr and Ba ions was more pronounced at an HNO₃ concentration of 1.0 M than at lower concentrations of the said acid. The results of experiments conducted to investigate the effect of the contact time indicated that it took several hours for the adsorption of the metal ions to begin. Moreover, (TBTDS + Dodec)/SiO₂-P and T(2EH)/SiO₂-P reached a status of adsorption equilibrium within 4 hours, while the same status was reached only after 10 hours in the case of (T(2EH)TDS + Dodec)/SiO₂-P. The time lag between the start of the experiment and the start of the Ba ion adsorption was attributed to the metal ion reacting with dtc, which was initially absent in the adsorbents, as it is the product of TDS decomposition. Based on the results of the experiments conducted to probe the effect of the temperature, it was suggested that the Ba ion adsorption reactions were endothermic and proceeded spontaneously under the applied experimental conditions. The experimental Ba ion adsorption isotherms were such that those of (T(2EH)TDS)/SiO₂-P and (T(2EH)TDS + Dodec)/SiO₂-P were well fitted by the Langmuir model. Thus, for these two absorbents, the process of Ba ion adsorption appeared to consist of a single layer adsorption. In addition, the experimental Ba ion adsorption isotherm of (TBTDS + Dodec)/SiO₂-P was S-shaped, suggesting that the process consisted of a metal ion being adsorbed onto a microporous or mesoporous material.

Based on the described results, it was suggested that the TBTDS or T(2EH)TDS impregnated adsorbents have adequate capability to separate the Ba ion from Sr ion in 1 M HNO₃ solution.

| Adsorbent                        | Langmuir model | Freundlich model |
|----------------------------------|----------------|-----------------|
|                                 | qₘ (mmol/g)    | Kₗ (l/mol)      | R² | K₉ (mmol/g) | 1/μ | R² |
| (TBTDS + Dodec)/SiO₂-P           | –              | –               | 0.66 | 4.4         | 0.79 | 0.96 |
| T(2EH)TDS/SiO₂-P                | 0.38           | 3.7             | 1.00 | –           | –   | 0.84 |
| (T(2EH)TDS + Dodec)/SiO₂-P      | 0.32           | 2.0             | 1.00 | –           | –   | 0.85 |
References
1) T. Ito and S. Y. Kim, *J. Radioanal. Nucl. Chem.*, **316**, 1165–1172, (2018).
2) Y. Wu, S. Y. Kim, D. Tozawa, T. Ito, T. Tada, K. Hitomi, E. Kuraoka, H. Yamazaki and K. Ishii, *J. Radioanal. Nucl. Chem.*, **293**, 13–20, (2012).
3) Y. Ando and H. Takano, *JAERI Research 99–004*, (1999) (in Japanese).
4) G. P. Wright, J. W. Marsh, M. K. Varma, M. G. Doherty, D. L. Bartlett and M. H. Chung, *Ann. Surg. Oncol.*, **24**, 906–913, (2017).
5) F. Lansigan, C. A. Costa, B. I. Zaki, S. P. Yen, E. S. Winer, H. Ryan, D. Findley, S. R. Metzler, L. Shaw, B. Toaso, T. A. MacKenzie, Y. Chen and A. W. Beaven, *Clin. Cancer Res.*, **25**, 6073–6079, (2019).
6) S. D. Puvvada, J. M. Guillén-Rodríguez, J. Yan, L. Inclán, K. Heard, X. I. Rivera, F. Anwer, D. Mahadevan, J. H. Schatz and D. O. Persky, *Oncology*, **94**, 274–280, (2018).
7) I. Mironyuk, T. Tatarchuk, H. Vasylyeva, V. M. Gun’ko and I. Mykytyn, *J. Mol. Liq.*, **282**, 587–597, (2019).
8) I. Mironyuk, I. Mykytyn, H. Vasylyeva and K. Savka, *J. Mol. Liq.*, **316**, 113840, (2020).
9) M. T. Mostaedi, A. Ghaemi, H. Ghassabzadeh and M. G. Maragheh, *Can. J. Chem. Eng.*, **89**, 1247–1254, (2011).
10) D. Dechojarassri, S. Omote, K. Nishida, T. Omura, H. Yamaguchi, T. Furuike and H. Tamura, *J. Hazard. Mater.*, **355**, 154–161, (2018).
11) X. Li, W. Mu, B. Liu, W. Zhong, H. Wei, Y. Jian, Z. Zhong, S. Luo and S. Li, *J. Radioanal. Nucl. Chem.*, **298**, 47–53, (2013).
12) S. Sarina, A. Bo, D. Liu, H. Liu, D. Yang, C. Zhou, N. Maes, S. Komarneni and H. Zhu, *Chem. Mater.*, **26**, 4788–4795, (2014).
13) Y. Wei, M. Rakhatkzyz, K. A. M. Salih, K. Wang, M. F. Hamza and E. Guibal, *Chem. Eng. J.*, **402**, 125220, (2020).
14) S. Y. Kim, Y. Xu, T. Ito, Y. Wu, T. Tada, K. Hitomi, E. Kuraoka and K. Ishii, *J. Radioanal. Nucl. Chem.*, **295**, 1043–1050, (2013).
15) A. Zhang, W. Xue and Z. Chai, *AIChE.*, **58**, 3517–3525, (2012).
16) S. P. Mishra and D. Tiwary, *Appl. Radiat. Isot.*, **51**, 359–366, (1999).
17) H. Contreras and H. Cortés, *Inorg. Nucl. Chem. Lett.*, **6**, 225–229, (1970).
18) M. J. Gismera, D. Hueso, J. R. Procopio and M. T. Sevilla, *Anal. Chim. Acta.*, **524**, 347–353, (2004).
19) O. Bergendorff and C. Hansson, *J. Agric. Food Chem.*, **50**, 1092–1096, (2002).
20) Y. Xu, S. Y. Kim, T. Ito, K. Hitomi, E. Kuraoka, S. Usuda and K. Ishii, *J. Radioanal. Nucl. Chem.*, **299**, 149–155, (2014).
21) Y. Wu, S. Y. Kim, D. Tozawa, T. Ito, T. Tada, K. Hitomi, E. Kuraoka, H. Yamazaki and K. Ishii, *J. Nucl. Sci. Technol.*, **49:3**, 320–327, (2012).
22) T. Kawamura, T. Ito and S. Y. Kim, *J. Radioanal. Nucl. Chem.*, **320**, 9–14, (2019).
23) H. Wu, M. Kubota, N. Osawa and S. K. Kim, *J. Ion Exch.*, **32**, 8–14, (2021).
24) H. M. H. Gad, Y. F. Lasheen and T. S. E. Zakla, *Radiochemistry*, **55**, 589–595, (2013).
25) O. Celebia, A. Kilikli and H. N. Erten, *J. Hazard. Mater.*, **168**, 695–703, (2009).
26) W. Mu, S. Du, Q. Yu, X. Li, H. Wei and Y. Yang, *Dalton Trans.*, **47**, 8375–8381, (2018).
27) Y. V. Ivanov, V. F. Plyusnin, V. P. Grivin and S. V. Larionov, *Chem. Phys. Lett.*, **310**, 252–258, (1999).
28) T. Shahwan and H. N. Erten, *J. Radioanal. Nucl. Chem.*, **260**, 43–48, (2004).
29) Y. Wei, K. A. M. Salih, S. Lu, M. F. Hamza, T. Fujita, T. Vincent and E. Guibal, *Molecules*, **24**, 3893, (2019).
30) K. Y. Foo and B. H. Hameed, *Chem. Eng. J.*, **156**, 2–10, (2010).
31) M. A. A. Ghouti and D. A. Da’ana, *J. Hazard. Mater.*, **393**, 122383, (2020).
32) V. J. Inglezakis, S. G. Pouloupolos and H. Kazemian, *Micropor. Mesopor. Mater.*, **272**, 166–176, (2018).