# Adsorption Behaviors of Palladium Ion from Nitric Acid Solution by a Silica-based Hybrid Donor Adsorbent

**Hao Wu, Naoki Oosawa, Masahiko Kubota, and Seong-Yun Kim[†]**

*Department of Quantum Science and Energy Engineering, Graduate School of Engineering, Tohoku University, Sendai 980–8579, Japan*

The adsorption behaviors of a silica-based hybrid donor adsorbent (TAMIA-EH+1-dodecanol)/SiO$_2$–P towards Pd(II) were investigated under the effect of the contact time, temperature *etc.* in simulated high-level liquid waste. The adsorption rates of Pd(II) and Re(VII) were fairly fast and could reach the equilibrium state in only 1 h compared with other co-existing metal ions. The adsorption kinetics of Pd(II) was found to fit well with the pseudo-first order model. Even though with increasing the concentration of HNO$_3$ above 1 M, the adsorption performance of (TAMIA-EH+1-dodecanol)/SiO$_2$–P decreased gradually; it still exhibited a better selectivity towards Pd(II) when [HNO$_3$] > 0.5 M. The adsorption isotherms of Pd(II) and Re(VII) were well-described by the Langmuir isotherm model, while the Freundlich isotherm model was considered to be more suitable for the adsorption of Ru(III), Zr(IV) and Mo(VI). A high temperature of an aqueous solution was not good for the effective recovery of Pd(II). The calculated thermodynamic parameters revealed that the adsorption of Pd(II) was exothermic in nature.

**Keywords** Adsorption, palladium, hybrid donor, (TAMIA-EH+1-dodecanol)/SiO$_2$–P adsorbent, high-level liquid waste

**(Received July 13, 2020; Accepted August 21, 2020; Advance Publication Released Online by J-STAGE August 28, 2020)**

## Introduction

The high-level liquid wastes (HLLW) generated from the spent nuclear fuel reprocessing process contain large amounts of fission products (FPs). These include long-lived minor actinides (MAs(III)), heat-emitting Cs(I), Sr(II), trivalent rare-earth (Lns(III)) and precious platinum group metals (PGMs) *etc.*[1] Palladium (Pd(II)), is one of most important FPs. A high concentration of Pd(II) accumulated in HLLW will finally deteriorate the quality of glasses fabricated during the vitrification process of HLLW.[2] In order to obtain a higher quality of the final vitrified products and to achieve a better vitrification process, an effective recovery and separation of Pd(II) from HLLW is very urgent in the nuclear fuel reprocessing process.[3] On the other hand, the recovered Pd(II) can further be re-used in various fields, such as catalysis, electronics, *etc.* to reduce the last growing demand due to a lack of Pd(II) in the rapid industrial development.[4]

HLLW possesses the properties of strong radioactivity, a high concentration of nitric acid, and different kinds of co-existing metal ions *etc.* Compared with traditional solvent extraction, the solid-phase extraction method is considered to be more economic, with no third-phase formation, being more workable, and having less hazardous byproducts.[5] According to the theory of hard and soft Lewis acids and bases (HSAB), the cationic Pd(II) species in nitric acid solution are classified soft Lewis acids.[6] Therefore, depending on the acidity of the aqueous phase, several kinds of soft nitrogen (N) and sulfur (S) donors containing solid-phase adsorbents are currently being widely

studied concerning the effective recovery of Pd(II).[7] However, the selective separation of Pd(II) from HLLW is still challenging. Even though the S donor is softer than the N donor, showing a stronger affinity towards Pd(II), the S donor ligands are not environmentally friendly (not fulfill CHON criterion).[8] Thus, N containing ligands are paid much attention on the practical separation process. Mehrani *et al.*, synthesized a dipyridylamine modified adsorbent and studied its separation and recovery performance of Pd(II) in nitric acid. Their results found that a relatively high uptake percentage of Pd(II) can only be well maintained when the pH value was above 2. All of the soft N donors on the adsorbent were protonated under a more acidic condition, and finally lost their complexation ability. Also, the selectivity towards Pd(II) was also not satisfied under a high concentration of other co-existing metal ions in the solution.[9] Ruhela *et al.*, prepared an amberlite XAD 16 resin anchoring a 2-acetyl pyridine group. This resin consisted of one pyridine group (soft N donor) and one acetyl group (hard O donor). The effect of the nitric acid concentration results revealed that though with increasing the concentration of nitric acid, the distribution ratio ($K_d$) of Pd(II) slightly decreased, and an appreciable $K_d$ of Pd(II) was still obtained at more than 100 in the whole HNO$_3$ concentration range up to around 10 M. The high $K_d$ value was explained as the result of both participation of the pyridine moiety and the C=O group from the acetyl group in the complexation process.[10] In order to further lower the basicity of heterocycles, Ruhela *et al.*, introduced the adsorption performance of Pd(II) by amberlite XAD 16 functionalized with the 2-acetyl amide group. Compared with the 2-acetyl pyridine group, the 2-acetyl amide group exhibited a more acid resistance ability. The $K_d$ of Pd(II) was more than 400 when the concentration of HNO$_3$ varied from 0.5 – 6 M, and Pd(II) was selectively separated from simulated HLLW under the effect of other

[†] To whom correspondence should be addressed.
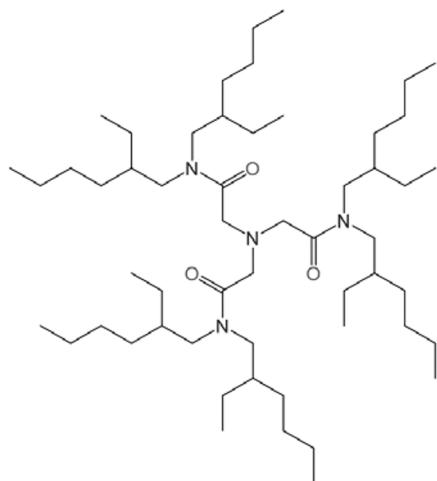E-mail: sonyun.kimu.d7@tohoku.ac.jp

Fig. 1   Molecular structure of TAMIA-EH.



Fig. 2   SEM image of synthesized (TAMIA-EH+1-dodecanol)/ SiO$_2$–P adsorbent.

co-existing metal ions.[11]   Based on the experimental results, it provided us a hint that by introducing a hard O donor into a soft ligand, the adsorbent could not only be used in a more acidic condition, but also could maintain a good selectivity.[12]

2,2′,2″-Nitrilotris[$N$,$N$-bis(2-ethylhexyl)acetamide] (TAMIA-EH), acts as a new chelating agent derived from nitrilotriacetamide (NTAamide), which includes a nitrogen atom that forms the center of the backbone and three amide units surrounding the central skeleton.   It is expected to exhibit a good separation performance towards Pd(II) in simulated HLLW.[13]   Therefore, the objective in this research is try to synthesized a novel hybrid soft N and hard O donor silica-based adsorbent by impregnating the TAMIA-EH agent into the pores of the silica support.   Its adsorption behaviors towards Pd(II) will be investigated as an effect of contact, and an effect of nitric acid concentration *etc.*

## Experimental

### Reagents

All chemicals used in this research, such as palladium(II) nitrate (Pd(NO$_3$)$_2$), ruthenium(III) nitrosyl nitrate (Ru(NO)-(NO$_3$)$_x$(OH)$_y$,   $x + y = 3$),   rhodium(III)   nitrate   (Rh(NO$_3$)$_3$), zirconium oxynitrate, 2-hydrate (ZrO(NO$_3$)$_2$·2H$_2$O), hexaammonium heptamolybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O), rhenium oxide(VII) (Re$_2$O$_7$) and other metal nitrates *etc.*, were employed as commercially received from Aladdin Industrial, Inc. or Wako Pure Chemical Industries, Inc. without any further purification. The chelating agent TAMIA-EH (chemical structure is shown in Fig. 1) was purchased from Chemicrea Inc. and used directly without further purification.   1-Dodecanol with a purity of 99% was used as a molecule modifier by a hydrogen bond to increase the chemical stability of the adsorbent.[14]   A stock solution containing 15 types (Pd(II), Ru(III), Rh(III), Zr(IV), Mo(VI), Re(VII), Cs(I), Sr(II), Ba(II), La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III)) of 50 mM metal nitrates were used.   All working solutions were prepared by diluting a stock solution into deionized water with a specific resistance of 18.3 MΩ·cm or greater.   The acidity of an aqueous solution was adjusted by diluting concentrated nitric acid.   Microporous silica (SiO$_2$–P, "P" refers to the styrene-divinylbenzene copolymer) with a mean diameter of 50 μm and a mean pore size of 50 nm was used as the support.

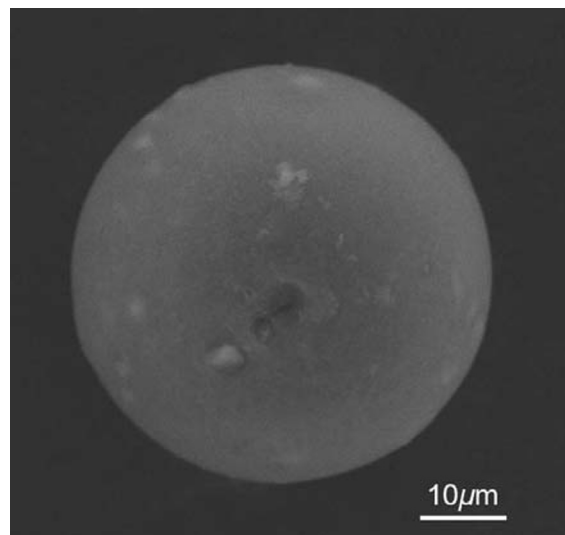### Preparation of (TAMIA-EH+1-dodecanol)/SiO$_2$–P adsorbent

The synthesis procedures of (TAMIA-EH+1-dodecanol)/ SiO$_2$–P adsorbent were similar to as reported previously.[15] Firstly, the inner pores of SiO$_2$–P particles were completely cleaned by mixing with methanol (MeOH) in a plastic bottle and shaken vigorously at room temperature until the color of the filtrate became transparent.   The washed SiO$_2$–P particles were stored in a vacuum at 313 K.   Next, equal qualities of 10 g TAMIA-EH and 1-dodecanol were weighed and placed in a 500 mL beaker and diluted by adding 300 mL of dichloromethane (CH$_2$Cl$_2$).   Subsequently, the above solution was poured into a flask which contained 20 g of dried SiO$_2$–P particles, and then transferred to a rotary evaporator.   CH$_2$Cl$_2$ was slowly evaporated at 318 K under reduced pressure to immobilize TAMIA-EH and 1-dodecanol into the pores of SiO$_2$–P particles.   After drying in a vacuum at 338 K for more than 24 h to further remove the remaining CH$_2$Cl$_2$ in the pores, the silica-based (TAMIA-EH+1-dodecanol)/SiO$_2$–P adsorbent could be obtained as a light-yellow powder.   In order to clarify whether all of the functional reagents were impregnated into the pores of the SiO$_2$–P particles, the surface morphology of the prepared adsorbent was characterized by scanning electron microscopy (SEM, Hitachi S-3100H), as shown in Fig. 2.   A smooth surface of prepared adsorbent indicated successful impregnation.

### Batch adsorption experiments

The adsorption behaviors of (TAMIA-EH+1-dodecanol)/ SiO$_2$–P adsorbent towards 15 types of selected metal ions in nitric acid solution were systematically investigated.     In experiments about the effect of the contact time, effect of the adsorption temperature, the aqueous solutions used were prepared by diluting the stock solution 10 times to 5 mM of each metal ion with a fixed concentration of nitric acid in the aqueous solutions adjusted as 2 M.   In experiments concerning the effect of the concentration of nitric acid, the concentration of each metal ion was diluted as 5 mM at the concentration range of nitric acid varying over 0.1 – 5 M.   Experiments of the adsorption   capacity   of   (TAMIA-EH+1-dodecanol)/SiO$_2$–P adsorbent were conducted under the concentration of HNO$_3$ in aqueous solution being maintained at 2 M, while the concentration of representative metal ions varied over 1 – 100 mM.
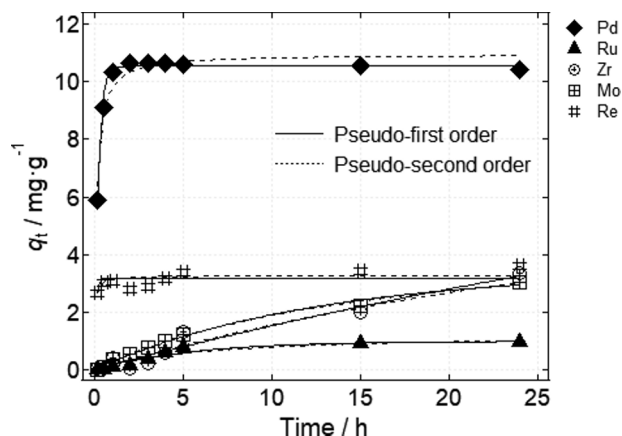
Fig. 3 Non-linear pseudo-first order and Pseudo-second order model fitting for Pd(II), Ru(III), Re(VII), Zr(IV), Mo(VI) adsorbed onto (TAMIA-EH+1-dodecanol)/SiO₂-P. [Metal], 5 mM; [HNO₃], 2 M; phase ratio, 0.2 g/4 mL; shaking speed, 160 rpm; shaking time, 10 min – 24 h; temperature, 298 K.

Table 1    Fitted parameters of non-linear pseudo-first order and Pseudo-second order model for Pd(II), Ru(III), Re(VII), Zr(IV), Mo(VI) adsorbed onto (TAMIA-EH+1-dodecanol)/SiO₂–P at 298 K

| Metal ion | Pseudo-first order model | | | Pseudo-second order model | | |
|---|---|---|---|---|---|---|
| | $q_e$/ mg g$^{-1}$ | $k_1$/h | $R^2$ | $q_e$/ mg g$^{-1}$ | $k_2$/g (mg h)$^{-1}$ | $R^2$ |
| Pd$^{2+}$ | 10.533 | 4.577 | 0.993 | 10.951 | 0.753 | 0.938 |
| Ru$^{3+}$ | 0.988 | 0.184 | 0.925 | 1.274 | 0.126 | 0.905 |
| Zr$^{4+}$ | 4.889 | 0.043 | 0.947 | 6.922 | 3.438 | 0.951 |
| Mo$^{6+}$ | 3.423 | 0.081 | 0.988 | 4.997 | 0.012 | 0.992 |
| Re$^{7+}$ | 3.494 | 8.711 | 0.932 | 3.514 | 5.436 | 0.944 |

Next, each sample was prepared by mixing 0.2 g of the adsorbent (as the solid phase) and 4 mL of the above prepared solution in a 13.5-mL glass vial with a stopper. The mixture was mechanically stirred at 160 rpm in a water bath, followed phase separation by using a syringe and filter. The concentration of Cs remaining in the solution was detected by an atomic absorption photometer (AAS, Shimazu AA-6200) at a wavelength of 363.5 nm using an acetylene flame. The concentrations of other metal ions were analyzed by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimazu ICPS-7510). All of the experimental samples were measured three times continuously and the average values were recorded. The adsorption percentage ($E$, %), distribution coefficient ($K_d$, cm$^3$/g) and the adsorbed amount ($q$, mmol/g) were defined according to the following equations:[16]

$$E = 100 \times (C_0 - C_t)/C_0, \qquad (1)$$

$$K_d = [(C_0 - C_e)V]/[C_e \cdot m], \qquad (2)$$

$$q = (C_0 - C_t)V/m, \qquad (3)$$

where, $C_0$ (mM) denotes the concentration of each metal ion at the initial state; $C_t$ (mM) denotes the concentration of each metal ion at certain time; $C_e$ (mM) denotes the concentration of each metal ion at equilibrium state; $m$ (g) indicates the mass of dry (TAMIA-EH+1-dodecanol)/SiO₂-P adsorbent; $V$ (mL) indicates the volume of the aqueous phase.

## Results and Discussion

### Effect of contact time

Studies concerning the effect of the adsorption rate were firstly carried out in the presence of a 2 M HNO₃ solution at 298 K. The experimental results were summarized as shown in Fig. 3. As can be seen the adsorption rate of (TAMIA-EH+1-dodecanol)/SiO₂-P towards Pd(II) and Re(VII) was relatively fast at the first beginning and could reach equilibrium state in just 1 h, while the adsorption rates of Zr(IV), Mo(VI) were comparatively slow which still could not attained the equilibrium state even after shaking for 24 h. In the case of Ru(III), its

adsorption rate was often reported to be slow in many previous studies.[17] As a comparison, the adsorption equilibrium of Ru(III) in this study was attained in around 5 h, which can be explained as the high surface reactivity and the large surface area inside porous silica support. On the other hand, the uptake percentage of Pd(II) in a 2 M HNO₃ solution was calculated as to be 90.77%, much higher than Re(VII), Zr(IV), Mo(VI), Ru(III). The selectivity in such a highly acidic condition was attributed to the co-working effect of soft N donors and hard O donors on the TAMIA-EH chelating agent.[18] Next, in order to clarify the mechanism of the adsorption kinetics, obtained experimental data for the representative metal ions were further fitted by using a pseudo-first order and a pseudo-second order model. Their expressions were described as follows:[19]

$$q_t = q_e(1 - e^{-k_1 t}), \qquad (4)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t'}, \qquad (5)$$

where, $q_e$ (mg/g) refers the amount of metal ions adsorbed onto the surface of (TAMIA-EH+1-dodecanol)/SiO₂-P adsorbent at equilibrium state; $q_t$ (mg/g) refers the amount of metal ions adsorbed onto the surface of (TAMIA-EH+1-dodecanol)/SiO₂-P adsorbent at any time $t$; $k_1$ (h$^{-1}$) means the rate constant of the first order at the equilibrium state; $k_2$ (g/(mg·h)) means the rate constant of the second order at the equilibrium state.

The fitting results of $q_t$ against $t$ were plotted as shown in Fig. 3 and summarized in Table 1. In a pseudo-first order model, the $q_e$ value of Pd(II) obtained from the experiment data and from the fitting results were found to be 10.665 and 10.533 mg/g, respectively. The proximity of the above two parameters and high regression coefficient (>0.99) indicated the experimental data to be in a good accordance with the pseudo-first order model. For instance, the adsorption process was controlled by a chemical adsorption process, which can be explained as Pd(II) in an aqueous solution diffused to the external surface of the adsorbent and then captured immediately by TAMIA-EH.[20]

### Effect of the concentration of nitric acid

Adsorption experiments regarding the effect of the HNO₃ concentration on the (TAMIA-EH+1-dodecanol)/SiO₂-P adsorbent towards Pd(II) and other 14 types cp-existing metal ions were conducted in 0.1 – 5 M, with the results as shown in Fig. 4. (TAMIA-EH+1-dodecanol)/SiO₂-P adsorbent exhibited almost no or very weak adsorption ability towards the metal ions such as Cs(I), Sr(II), Ba(II), La(III), Ce(III) etc., while it showed very good adsorption towards Pd(II). The uptake percentage of Pd(II) increased to 90.27% as the acidity increased when
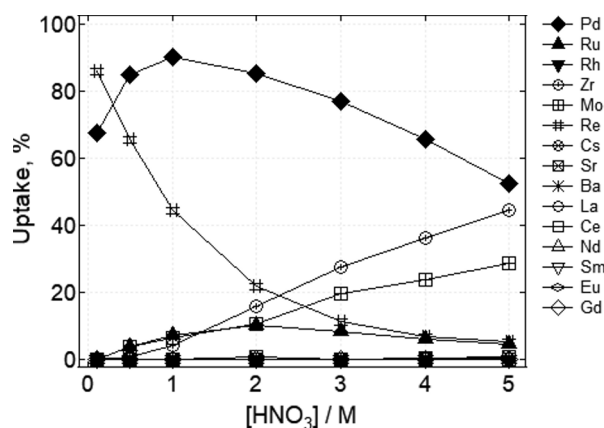
Fig. 4   Effect of the concentration of nitric acid for the adsorption of 15 types of tested metal ions onto (TAMIA-EH+1-dodecanol)/SiO2–P. [Metal], 5 mM; [HNO3], 0.1 – 5 M; phase ratio, 0.2 g/4 mL; shaking speed, 160 rpm; shaking time, 5 h; temperature, 298 K.



Fig. 5   Non-linear Langmuir and Freundlich isotherm fitting for Pd(II), Ru(III), Re(VII), Zr(IV), Mo(VI) adsorbed onto (TAMIA-EH+1-dodecanol)/SiO2–P. [Metal], 1 – 10 mM; [HNO3], 2 M; phase ratio, 0.2 g/4 mL; shaking speed, 160 rpm; shaking time, 5 h; temperature, 298 K.

[HNO3] < 1 M, indicating the participation of $NO_3^-$ in the adsorption process of Pd(II).   With further increasing the concentration of HNO3, the uptake percentage of Pd(II) gradually decreased which can be explained as the proton in large amounts causing competition with the Pd(II) complexation behavior.[21]   Ru(III), as one of the important members in PGMs; a similar adsorption tendency with Pd(II) was observed, but its uptake percentage was relatively low (less than 10%), attributed to the stronger affinity of (TAMIA-EH+1-dodecanol)/SiO2–P towards Pd(II) than Ru(III).   In the case of Zr(IV) and Mo(VI), with an increase in [HNO3], the uptake percentage increased gradually, and especially in the case of Zr(IV) it almost reached the same value with Pd(II) when [HNO3] = 5 M.   Also, this phenomenon could be explained as hard O donors in TAMIA-EH becoming more dominant than gradually protonated soft N donors at higher acidity areas.   Concerning Re(VII), its uptake percentage decreased drastically due to increasing amounts of $NO_3^-$ along with increasing [HNO3].[22]   Moreover, a possible extraction reaction of representative cations was described, as shown in Eq. (6).[23]   In a word, even though (TAMIA-EH+1-dodecanol)/SiO2–P as a hybrid donor adsorbent exhibited adsorption behaviors towards many different metal ions, due to the effect of three amide units and the central amino group, (TAMIA-EH+1-dodecanol)/SiO2–P adsorbent was still expected to exhibit good selectivity towards Pd(II) in the HNO3 range above 0.5 M.[24]

$$mH^+ + M^{n+}_{aq} + nNO_3^-{}_{aq} + L \rightleftharpoons M(NO_3^-)_n \cdot mHL, \qquad (6)$$
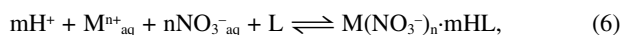
where M and L were metal ions and TAMIA-EH, respectively.

*Adsorption isotherm*

The commonly used Langmuir and Freundlich isotherm models were adopted to study the adsorption isotherm by varying the initial concentration of representative metal ions in the solution from 1 – 100 mM, and the experimental results were summarized as shown in Fig. 5.   At the beginning, with increasing the concentrations of Pd(II) and Re(VII), the adsorption amounts increased quickly.   With further increasing their concentration, it was found the adsorption amounts gradually approached to equilibrium, for instance being saturated.   The equations of the above two models were descried as below.[25]
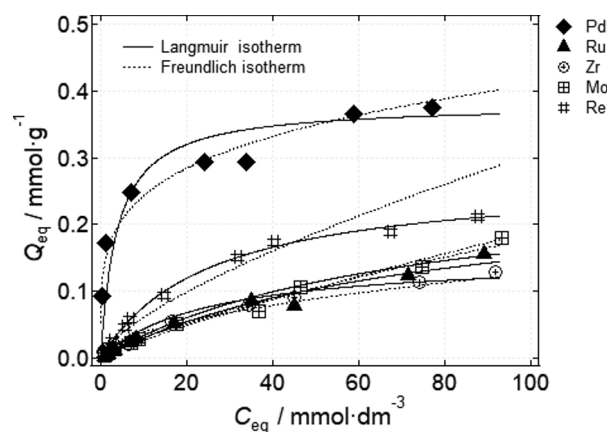
$$Q_{eq} = \frac{Q_{max}K_L C_{eq}}{(1 + K_L C_{eq})}, \qquad (7)$$

$$Q_{eq} = K_F C_{eq}^{1/n}, \qquad (8)$$

where, $C_{eq}$ (mmol/L) is the equilibrium concentration; $Q_{eq}$ (mmol/g) is the amount of metal ions adsorbed at equilibrium state; $Q_{max}$ (mmol/g) is the theoretical maximum of metal adsorbed; $K_L$ (L/mmol) and $K_F$ (mmol/g) are the Langmuir and Freundlich constant, respectively; $1/n$ is the Freundlich isotherm exponent constant.

Equations (7) and (8) were fitted to the obtained experimental data by a non-linear regression analysis, and the fitted curves are plotted in Fig. 5.   The calculated constants are listed in Table 2.   The correlation coefficients between the regressed values and the experimental data were used to evaluate the fitting results.   Therefore, it was found that Pd(II) and Re(VII) adsorption onto (TAMIA-EH+1-dodecanol)/SiO2–P would be best fitted with Langmuir isotherm models with a high correlation coefficients (>0.98).   It can be visualized as one-on-one single-layer adsorption of Pd(II) or Re(VII) onto (TAMIA-EH+1-dodecanol)/SiO2–P.[26]   The experimental $Q_{max}$ of Pd(II) was 0.3747 mM/g, which had good consistency with the fitted $Q_{max}$ (0.38 mM/g).   On the other hand, in the case of Ru(III), Zr(IV) and Mo(VI), a Freundlich isotherm model seemed to be more suitable, indicating that the adsorption process occurred on a heterogeneous surface.

*Effect of adsorption temperature*

In order to understand the effect of temperature on the adsorption process of (TAMIA-EH+1-dodecanol)/SiO2–P towards representative metal ions and to further clarify the thermodynamic parameters, van't Hoff equations, described as follows, were selected:[27]

$$\text{Ln } K_d = -\Delta H^0/(R \cdot T) + \Delta S^0/R, \qquad (9)$$

$$\Delta G^0 = \Delta H^0 - \Delta S^0 \cdot T, \qquad (10)$$

where, $K_d$ is distribution coefficient; $\Delta G^0$, $\Delta H^0$, $\Delta S^0$ are the standard changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol), entropy (J/(K·mol)), respectively; $R$ is the universal gas constant

(8.314 J/(K·mol)).

The experimental data were depicted by plotting Ln $K_d$ against $1/T$, as shown in Fig. 6. It was found that with increasing the temperature in the solution, the adsorption ability of (TAMIA-EH+1-dodecanol)/SiO$_2$-P towards Pd(II), Re(VII) and Ru(III) decreased gradually, which revealed that high temperature was not beneficial for adsorption of the above three elements. While the adsorption performances towards Zr(IV) and Mo(VI) were enhanced in a higher temperature area, the thermodynamic parameters, such as $\Delta H^0$ and $\Delta S^0$, can be obtained respectively from the slope and intercept in Eq. (9). $\Delta G^0$ at different temperature can be calculated from Eq. (10) on the basis of the values of $\Delta H^0$ and $\Delta S^0$. The results are summarized as shown in Table 3. The negative value of $\Delta H^0$ for Pd(II), Re(VII) and Ru(III) (−1.911, −3.92 and −33.16 kJ/mol, respectively) indicated that the adsorption process was exothermic in nature, while the positive values of $\Delta H^0$ for Zr(IV) and Mo(VI) (104.45, 73.75 kJ/mol, respectively) revealed that the adsorption process was endothermic. On the other hand, all of the calculated $\Delta G^0$ values were negative in the whole temperature range, verifying that the metal ions adsorption occurred spontaneously and was thermodynamically favorable.[28]

## Conclusions

The adsorption behaviors of a silica-based hybrid O and N donor adsorbent (TAMIA-EH+1-dodecanol)/SiO$_2$-P towards Pd(II) under the effect of the adsorption rate, adsorption temperature, concentration of nitric acid *etc.* in simulated HLLW was systematically investigated. The adsorption rate of Pd(II) was fairly fast, and could reach the equilibrium state within only 1 h. The adsorption kinetics was found be in a good accordance with the pseudo-first order model, indicating a chemical adsorption process. When [HNO$_3$] < 1 M, with increasing the concentration of HNO$_3$ in the aqueous phase, the uptake percentage of Pd(II) gradually increased due to the involvement of NO$_3^-$. When [HNO$_3$] > 1 M, the uptake percentage gradually decreased, which can be explained as a competition reaction between (TAMIA-EH+1-dodecanol)/SiO$_2$-P with protons and metal ions. When the [HNO$_3$] = 0.5 – 5 M, (TAMIA-EH+1-dodecanol)/SiO$_2$-P exhibited a better selectivity towards Pd(II) than other co-existing metal ions. The adsorption isotherm of Pd(II) fitted well with the Langmuir isotherm model, which meant that the mono-layer adsorption was dominant. On the other hand, with an increase in temperature, the adsorption of Pd(II) became less effective, revealing that the relatively high temperature was not benefitial for Pd(II) adsorption. The calculated results of $\Delta H^0$, $\Delta G^0$ and $\Delta S^0$ proved that the adsorption process of Pd(II) was endothermic and occurred spontaneously. Based on the results introduced in this research, further improvement of the adsorption system to obtain better selectivity towards Pd(II) with less interference from other co-existing metal ions should be considered.

## References

1. S. E. Vinokurov, S. A. Kulikova, and B. F. Myasoedov, *Nucl. Eng. Technol.*, **2019**, *51*, 755.
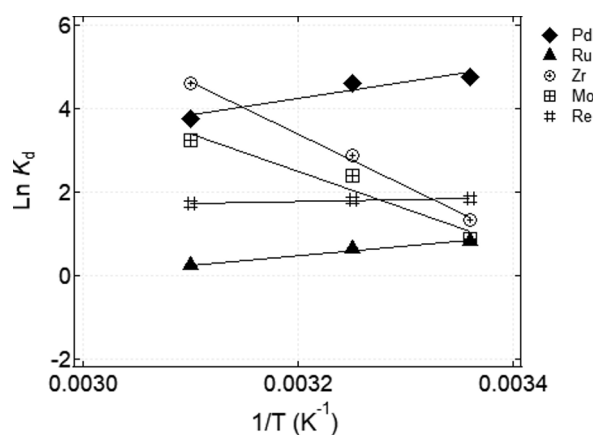2. R. Ruhela, A. K. Singh, B. S. Tomarb, and R. C. Hublia, *RSC Adv.*, **2014**, *4*, 24344.

Fig. 6   Effect of temperature for the adsorption of Pd(II), Ru(III), Re(VII), Zr(IV), Mo(VI) onto (TAMIA-EH+1-dodecanol)/SiO$_2$-P. [Metal], 5 mM; [HNO$_3$], 2 M; phase ratio, 0.2 g/4 mL; shaking speed, 160 rpm; shaking time, 5 h; temperature, 298 – 323 K.

Table 2   Fitted parameters of non-linear Langmuir and Freundlich isotherm models for Pd(II), Ru(III), Re(VII), Zr(IV), Mo(VI) adsorbed onto (TAMIA-EH+1-dodecanol)/SiO$_2$-P at 298 K

| Metal ion | Langmuir model parameters | | | Freundlich model parameters | | |
|---|---|---|---|---|---|---|
| | $Q_{max}/$ mmol g$^{-1}$ | $K_L/$ L mmol$^{-1}$ | $R^2$ | $K_F/$ mmol g$^{-1}$ | $1/n_f$ | $R^2$ |
| Pd$^{2+}$ | 0.380 | 0.266 | 0.986 | 0.145 | 0.255 | 0.956 |
| Ru$^{3+}$ | 0.264 | 0.013 | 0.850 | 0.004 | 0.847 | 0.982 |
| Zr$^{4+}$ | 0.152 | 0.041 | 0.897 | 0.012 | 0.514 | 0.966 |
| Mo$^{6+}$ | 0.275 | 0.014 | 0.790 | 0.005 | 0.767 | 0.996 |
| Re$^{7+}$ | 0.271 | 0.040 | 0.996 | 0.012 | 0.699 | 0.975 |

Table 3   Summary of calculated values of the thermodynamic parameters

| Temperature/ K | $\Delta G_0$/kJ mol$^{-1}$ | | | $\Delta H^0$/kJ mol$^{-1}$ | | | $\Delta S^0$/J mol$^{-1}$ K$^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | Pd$^{2+}$ | Ru$^{3+}$ | Zr$^{4+}$ | Pd$^{2+}$ | Ru$^{3+}$ | Zr$^{4+}$ | Pd$^{2+}$ | Ru$^{3+}$ | Zr$^{4+}$ |
| 298 | −12.07 | −2.09 | −3.44 | −33.16 | −1.911 | 104.45 | −0.071 | −0.057 | 0.362 |
| 308 | −11.36 | −1.52 | −7.07 | | | | | | |
| 323 | −10.30 | −0.67 | −12.50 | | | | | | |
| | Mo$^{6+}$ | Re$^{7+}$ | | Mo$^{6+}$ | Re$^{7+}$ | | Mo$^{6+}$ | Re$^{7+}$ | |
| 298 | −2.67 | −4.61 | | 73.75 | −3.92 | | 0.256 | 0.002 | |
| 308 | −5.23 | −4.63 | | | | | | | |
| 323 | −9.08 | −4.66 | | | | | | | |

3.  R. Ruhela, B. S. Tomar, J. N. Sharma, T. K. Seshagiri, V. C. Adya, R. C. Hubli, and A. K. Suri, *Sep. Sci. Technol.*, **2013**, *48*, 1049.

4.  N. Iyer, R. Ruhela, A. Das, M. Yadav, A. K. Singh, and J. K. Chakravartty, *Sep. Sci. Technol.*, **2016**, *51*, 1971.

5.  A. Żwir-Ferenc and M. Biziuk, *Polish J. Environ. Stud.*, **2006**, *15*, 677.

6.  A.-Y. Zhang, L. Xu, and G. M. Lei, *New J. Chem.*, **2016**, *40*, 6374.

7.  A.-Y. Zhang, Y. P. Zhu, and Z. F. Chai, *J. Chem. Eng. Data*, **2012**, *57*, 1267.

8.  H. H. Dam, D. N. Reinhoudt, and W. Verboom, *Chem. Soc. Rev.*, **2007**, *36*, 367.

9.  K. Mehrani, A. Mehrani, M. M. Amini, O. Sadeghi, and N. Tavassoli, *Microchim. Acta*, **2011**, *173*, 521.

10. R. Ruhela, K. K. Singh, B. S. Tomar, J. N. Sharma, M. Kumar, R. C. Hubli, and A. K. Suri, *Sep. Purif. Technol.*, **2012**, *99*, 36.

11. R. Ruhela, K. Singh, B. S. Tomar, T. K. Shesagiri, M. Kumar, R. C. Hubli, and A. K. Suri, *Ind. Eng. Chem. Res.*, **2013**, *52*, 5400.

12. L. Y. Yuan, L. Zhu, C. L. Xiao, Q. Y. Wu, N. Zhang, J. P. Yu, Z. F. Chai, and W. Q. Shi, *ACS Appl. Mater. Interfaces*, **2017**, *9*, 3774.

13. Y. Sasaki, Y. Tsubata, Y. Kitatsuji, Y. Sugo, N. Shirasu, Y. Morita, and T. Kimura, *Solvent Extr. Ion Exch.*, **2013**, *31*, 401.

14. Z. Chen, Y. Wu, and Y. Z. Wei, *Energy Procedia*, **2013**, *39*, 319.

15. A. Y. Zhang, W. J. Xue, and X. C. Dong, *J. Chem. Eng.*

16. S. Y. Ning, S. C. Zhang, W. Zhang, J. Zhou, S. Y. Wang, X. P. Wang, and Y. Z. Wei, *Hydrometallurgy*, **2020**, *191*, 105207.

17. Z. W. Zheng, T. Arai, and K. Takao, *ACS Sustainable Chem. Eng.*, **2019**, *7*, 9750.

18. C. L. Xiao, C. Z. Wang, L. Y. Yuan, B. Li, H. He, S. A. Wang, Y. L. Zhao, Z. F. Chai, and W. Q. Shi, *Inorg. Chem.*, **2014**, *53*, 1712.

19. J. P Simonin, *Chem. Eng. J.*, **2016**, *300*, 254

20. J. X. Lin and L. Wang, *Front. Environ. Sci. Eng. China*, **2009**, *3*, 320.

21. T. S. Grimes, C. R. Heathman, S. Jansone-Popova, A. S. Ivanov, S. Roy, V. S. Bryantsev, and P. R. Zalupski, *Inorg. Chem.*, **2018**, *57*, 1373.

22. Y. Sasaki, M. Ozawa, T. Kimura, and K. Ohashi, *Solvent Extr. Ion Exch.*, **2009**, *27*, 378.

23. H. Huang, S. D. Ding, D. P. Su, N. Liu, J. R. Wang, M. L. Tan, and J. N. Fei, *Sep. Purif. Technol.*, **2014**, *138*, 65.

24. Z. P. Wang, J. R. Wang, S.-D. Ding, Y. Liu, L. R. Zhang, L. J. Song, Z. L. Chen, X. Y. Yang, and X. Y. Wang, *Sep. Purif. Technol.*, **2019**, *210*, 107.

25. S. Gokilaa, T. Gomathia, P. N. Sudhaa, and S. Anil, *Int. J. Biol. Macromol.*, **2017**, *104*, 1459.

26. Mu. Naushad, T. Ahamad, Z. A. AlOthman, and A. H. Al-Muhtaseb, *J. Mol. Liq.*, **2019**, *279*, 1.

27. A. Khayambashi, X. L. Wang, and Y. Z. Wei, *Hydrometallurgy*, **2016**, *164*, 90.

28. Z. Fallah, H. N. Isfahani, M. Tajbakhsh, H. Tashakkorian, and A. Amouei, *Cellulose*, **2018**, *25*, 639.

Data, **2016**, *61*, 3303.