



Adsorption and separation behavior of palladium(II) on a silica-based hybrid donor adsorbent from simulated high-level liquid waste

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Abstract

Adsorption and separation performances of a microporous silica-based (DAMIA-EH + TOA)/SiO₂-P adsorbent towards Pd(II) were systematically investigated under the effect of contact time, temperature, concentration of nitric acid, chromatography etc. in a simulated high-level liquid waste containing 14 kinds of representative co-existing metal ions. Successful recovery of around 97.95% Pd(II) was achieved under the elution with 0.01 M Tu (pH = 2) solution in column experiment.

Keywords Separation · Palladium · Chromatography · Simulated high-level liquid waste

Introduction

The high-level liquid waste (HLLW) coming from the reprocessing of spent nuclear fuel consists of several waste liquids, the main, in terms of radioactivity and volume, being the raffinate of the solvent extraction process [1]. As a result, large amounts of nonvolatile fission products (FPs), actinides, and trace amounts of uranium and plutonium, together with corrosion products are contained in HLLW [2]. Due to its high corrosiveness, high concentration of nitric acid, generation of decay heat, high rates of radioactivity and related generation of hydrogen, storage and disposal of HLLW requires strict control and complicated management from the perspective of environmental protection. Palladium, as one of main FPs, is not extracted with U and Pu in the solvent extraction process of PUREX and finally remains in HLLW [3]. High concentration of Pd(II) in the HLLW raises problems during the raffinate solution has to be concentrated and solidified prior to its interim storage and final disposal. When Pd(II) is accumulated, it will form separate phases in the borosilicate glass matrix, not chemically incorporated in the final glass. Sedimentation of these dispersed phases in the absence of convective mixing in the melt leads to the formation of a layer with increased viscosity (up to a factor of

4) and electric conductivity (up to a factor of 100), possibly causing a short circuit and temperature gradients, and finally resulting deterioration in the stability of the glasses, discontinuous operation of the vitrification process and heterogeneous molten glass formation (lowering the quality of the final product) in waste vitrification process [4]. In order to decrease the volume of vitrified glass units to be disposed and to achieve better stability of the vitrification process and higher quality of the final product, effective recovery and separation of Pd(II) from HLLW is very important.

Many methods have been adopted in the treatment and disposal of HLLW. Extraction chromatography as one of the most effective one, can decrease the formation of third phase; operate with smaller elution volumes, adjustable flow rates; minimize the accumulation of secondary waste, etc. [5]. In extraction chromatography, a certain extractant is impregnated either alone or in combination with a suitable diluent into an inert support, to prepare a solid sorbent capable of selectively removing metal ions from HLLW. Based on the Hard–Soft Acid–Base (HSAB) theory by Pearson, palladium(II) is classified as soft acid, showing affinity to soft bases with atoms S and N [6]. Thiodiglycolamide (TDGA) and its derivatives act as classic S donor chelating agent, have been widely studied in the separation of Pd(II) in acid solution [7]. Xu et al. [8] reported the adsorption behaviors of Pd(II) onto a silica-based (Crea + 1-dodecane)/SiO₂-P extraction resin from simulated HLLW, their results found (Crea + 1-dodecane)/SiO₂-P extraction resin exhibited good adsorption selectivity for Pd(II) over the other fission products in HNO₃ solution, the distribution coefficient (K_d)

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of Pd(II) was more than 10^4 even the concentration of HNO_3 reached 5 M. Even though S donor ligands showed superior separation performances towards Pd(II) in acid solution, the unstable and unfriendly (not fulfill CHON criteria) S group is still a problem for the effective recovery of Pd(II) in HLLW. Earlier it has been reported that S donor ligands namely DHS etc. undergo oxidation in strong nitric acid medium [9]. Ruhela et al. [10] studied the extraction of Pd(II) from simulated HLLW in T(2EH)TDGA/n-dodecane solvent system. It was found that K_d of Pd(II) decreased from 1000 to less than 30 when the adsorbed does reached 0.5 MGy. And the degradation phenomenon of T(2EH)TDGA was caused by the cleavage of amide bond, thioether bond and carboxyl linkage of amide. On the other hand, utilizing N donor ligand has also been considered as one of the possible methods to separate Pd(II) in HLLW, though water solubility caused by protonation in highly acidic condition is frustrating. Amberlite XAD-16 adsorbent functionalized with 2-acteyl pyridine by coupling it with 2-chloro pyridine has been synthesized in Ruhela et al. [11] group. Their results showed with an increase of acidity, N atom got gradually protonated and consequently there was a huge decrease in K_d of Pd(II). Mehrani et al. [12] prepared a chemical dipyrindylamine-modified nano-porous silicas as a novel adsorbents for the pre-concentration and recovery of Pd(II). It was observed that the highest recovery for Pd(II) was obtained at neutral pH area. When the pH was lowered to 2, the extraction percentage of Pd(II) decreased to only 20%. As we known, soft N donor can maintain the selectivity towards Pd(II), hard O donor such as amide oxygen donor can lower the basicity of the N donor and then could be utilized in more acidic condition [13]. Therefore, to develop a ligand merging both soft N donor and hard O donor without S donor may become a feasible ligand to be utilized in the practical separation of Pd(II) from HLLW.

In this paper, to seek the possibility of Pd(II) removal from HLLW, a hybrid N and O donor ligand, 2,2'-[(2-ethylhexyl)imino]bis[*N,N*-bis(2-ethylhexyl)acetamide] (DAMIA-EH) was selected as the extractant [14, 15]. Tri-*n*-octylamine (TOA) was added as synergist. DAMIA-EH and TOA were

impregnated and immobilized into the pores of a microporous silica ($\text{SiO}_2\text{-P}$, "P" refers to the styrene–divinylbenzene copolymer) particles with a mean diameter of 50 μm (mean pore size of 50 nm) by wet vacuum immersion method to give the (DAMIA-EH + TOA)/ $\text{SiO}_2\text{-P}$ adsorbent [16–20]. Its adsorption properties concerning effect of adsorption speed, effect of HNO_3 concentration, effect of temperature, extraction chromatography etc. towards Pd(II) will be evaluated in simulated HLLW.

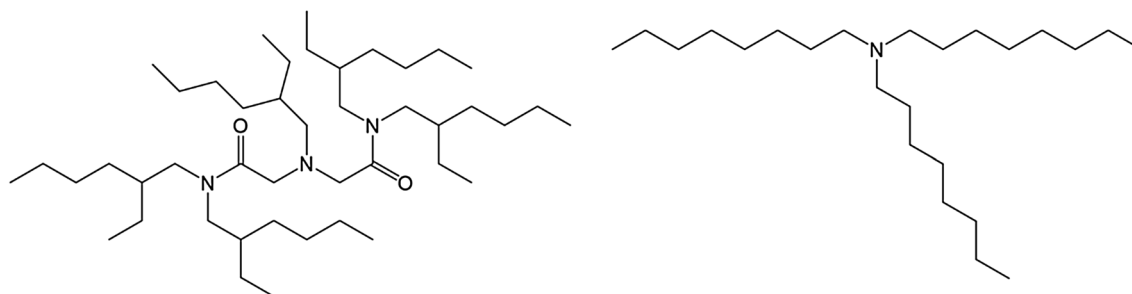
Experimental

Materials

All chemical reagents used in this research, such as nitric acid (HNO_3), diethylene triamine pentaacetic acid (DTPA), thiourea (Tu), palladium (II) nitrate ($\text{Pd}(\text{NO}_3)_2$) solution with 10 wt% of Pd(II) in 10 wt% nitric acid (99.99% trace metals basis), ruthenium(III) nitrosyl nitrate ($\text{Ru}(\text{NO})(\text{NO}_3)_x(\text{OH})_y$, $x + y = 3$) with 1.4 wt% of Ru(III) in dilute nitric acid, rhodium(III) nitrate solution ($\text{Rh}(\text{NO}_3)_3$) with ~10 wt% of Rh(III) in > 5 wt% etc. were all chemical pure from Wako Pure Chemical Industries, Inc. and Aladdin Industrial, Inc. The extractant DAMIA-EH (chemical structure is shown in Scheme 1) was purchased from Chemicrea Inc and used directly without further purification. All aqueous solutions were prepared by deionized water with a specific resistance of 18.3 $\text{M}\Omega\text{ cm}$ or greater.

Preparation of (DAMIA-EH + TOA)/ $\text{SiO}_2\text{-P}$ adsorbent

The relevant synthesis procedures were described briefly as follows: $\text{SiO}_2\text{-P}$ particles were firstly washed three time (each time 1 h) by methanol to remove the industrial residuals in their pores and then dried in vacuum for 24 h [21]. Equal quality of 10 g DAMIA-EH and TOA were placed in a beaker and dissolved using 300 mL dichloromethane (CH_2Cl_2) as diluent. 20 g of weighed $\text{SiO}_2\text{-P}$ particles were slowly added into the solution. The mixture was transferred



Scheme 1 Chemical structure of 2,2'-[(2-ethylhexyl)imino]bis[*N,N*-bis(2-ethylhexyl) acetamide] (DAMIA-EH) (Left) and trioctylamine (TOA) (Right)

to a round-bottomed flask and rotated mechanically for 1 h at room temperature. With increasing the temperature of water bath to 318 K, the CH_2Cl_2 solution was gradually evaporated under reduced pressure to immobilize DAMIA-EH and TOA into the pores of $\text{SiO}_2\text{-P}$. After drying for further 24 h in vacuum at 323 K, the light-yellow silica-based (DAMIA-EH + TOA)/ $\text{SiO}_2\text{-P}$ adsorbent was obtained [22]. The surface morphology of synthesized (DAMIA-EH + TOA)/ $\text{SiO}_2\text{-P}$ was characterized by scanning electron microscopy (SEM, Hitachi S-3100H) as shown in Fig. 1 to prove the successfully impregnate DAMIA-EH and TOA into the pores of $\text{SiO}_2\text{-P}$.

Batch adsorption experiments

Adsorption behaviors, such as effect of adsorption speed, effect of concentration of HNO_3 , effect of temperature etc. towards Pd(II) by (DAMIA-EH + TOA)/ $\text{SiO}_2\text{-P}$ adsorbent was firstly studied in simulated HLLW. The solutions used in batch experiments were all prepared in 2 M HNO_3 , containing 14 types of different kinds of co-existing metal ions, such as Cs(I), Sr(II), Ba(II), Ru(III), Rh(III) etc. and the concentration of each metal ion was prepared as 5 mM. Firstly, a weighed amount of (DAMIA-EH + TOA)/ $\text{SiO}_2\text{-P}$ adsorbent 0.2 g as a solid phase was combined with 4 mL of solution in a 13.5 mL glass vial with a plastic cap. Then, the mixture was stirred vigorously at 160 rpm in a water bath, followed by a solid and aqueous phase separation by using syringe and water membrane filter with the average pore size of 0.2 μm . The concentration of Cs(I) remained in solution was analyzed by atomic absorption photometer (AAS, Shimadzu AA-6200). The concentration of other metal ions was detected by inductively coupled plasma

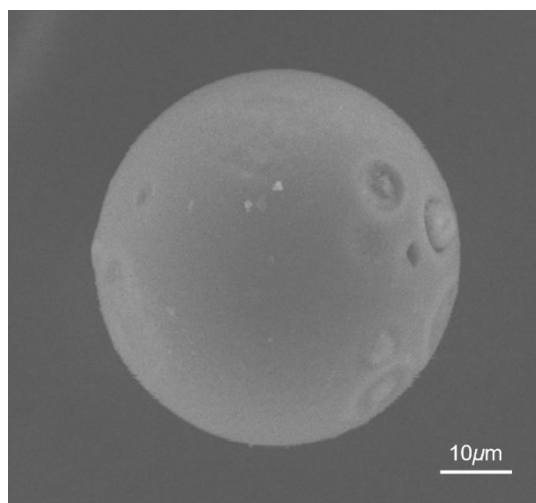


Fig. 1 A typical SEM of synthesized (DAMIA-EH + TOA)/ $\text{SiO}_2\text{-P}$ adsorbent

atomic emission spectrometer (ICP-AES, Shimadzu ICPS-7510), and the experiments were triplicate and the average values were recorded. The adsorption percentage (E , %), distribution coefficient (K_d , cm^3/g), separation factor (SF) and adsorbed amount (q , mmol/g) were decided by the following equations [23]:

$$E = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (2)$$

$$SF_{A/B} = K_{dA}/K_{dB} \quad (3)$$

$$q = (C_0 - C_t) \times \frac{V}{m} \quad (4)$$

where C_0 , C_t , C_e are the concentration of each metal ion in the aqueous phase (mM) at the initial, certain time and equilibrium state, respectively. m and V indicate the mass of dry (DAMIA-EH + TOA)/ $\text{SiO}_2\text{-P}$ adsorbent (g) and the volume of the aqueous phase (mL), respectively. A and B mean different metal ions.

Dynamic chromatography adsorption

Prior to the separation experiments, 5 g of dry (DAMIA-EH + TOA)/ $\text{SiO}_2\text{-P}$ adsorbent was slowly added in a glass column with 10 mm diameter and 170 mm height by wet packing method. A constant temperature outside the column was set to 298 K in the loading and elution process by circulating the thermo-stated water through an EYELA model water jacket [24]. The flow rate of feed solution was controlled as 0.5 mL/min. after 5 mL, 2 M HNO_3 solution containing 5 mM of 14 types of different kinds of co-existing metal ions, such as Cs(I), Sr(II), Ba(II), Ru(III), Rh(III) etc. passed through the column, the certain volumes of 50 mL, 2 M HNO_3 solution, 30 mL, 0.01 M Tu (pH = 2) solution, 30 mL, 0.01 M DTPA solution as eluents were subsequently pumped into the column. The effluent flowed out from column was collected with fraction of 5 cm^3 aliquot by a DC-1500 model auto fractional collector (EYELA). The concentration of Cs(I) was measured by AAS, others were measured by ICP-AES.

Results and discussion

Effect of contact time

To investigate the adsorption kinetics of (DAMIA-EH+TOA)/SiO₂-P towards Pd(II), the effect of contact time on adsorption performance was carried out in the presence of 2 M HNO₃ solution through batch method. The results for adsorption speed were illustrated as shown in Fig. 2. It was found that the adsorption kinetics of Pd(II) and Re(VII) were fairly fast, the adsorption equilibrium can be attained within only 10 min. With increasing the contact time, the uptake amount of Pd(II) and Re(VII) onto (DAMIA-EH+TOA)/SiO₂-P was increased to 90.93% and 58.09%, respectively, comparatively higher than other alkali metals (Cs(I)), alkaline earth metals (Sr(II), Ba(II)) and rare earth metals (La(III), Ce(III) etc.) [25]. It revealed that the co-existing metal ions contained in simulated HLLW would not affect the uptake selectivity towards Pd(II) onto (DAMIA-EH+TOA)/SiO₂-P adsorbent. Due to (DAMIA-EH+TOA)/SiO₂-P containing both soft N and hard O donors, the strong uptake performance of Pd(II) and Re(VII) resulted from the efficient complexing ability with N donor in DAMIA-EH. The weak uptake performance towards other co-existing La(III), Ce(III) etc. derived from the amide group (hard O donors) [26]. Moreover, the adsorption kinetics of Ru(III) was previously reported to be slow in many cases. In contrast, in the present study, the adsorption equilibrium of Ru(III) was attained in around 5 h. This can be attributed to the high surface reactivity and the large surface area of the porous silica [27].

To analyze the adsorption kinetics of representative metal ions by (DAMIA-EH+TOA)/SiO₂-P, the linear

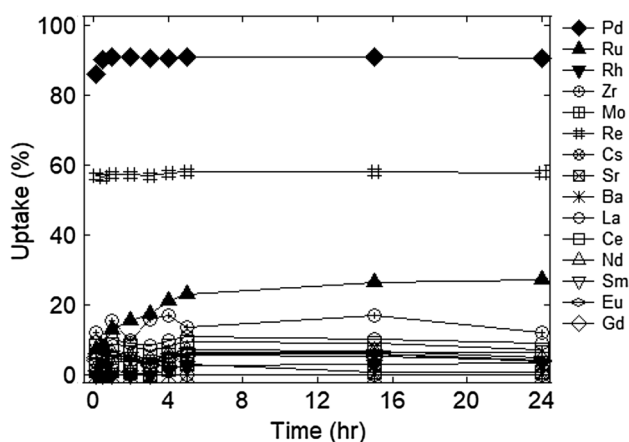


Fig. 2 Dependence of the tested 15 types of metal ions on contact time in 2 M HNO₃ solution. [Metal]=5 mM; Phase ratio=0.2 g/4 mL; Shaking speed: 160 rpm; Shaking time=10 min–24 h; Temperature: 298 K

Pseudo-second order kinetic model was applied to the experimental data. And it was described as shown in Eq. 5 [28]:

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

where q_e and q_t (in mg/g) are adsorption capacity of the metal ions at equilibrium and certain time t , respectively. k_2 represents the rate constant of the second order at the equilibrium state (g/(mg h)).

The kinetic data of t/q_t versus t for Pd(II), Re(VII), Ru(III) adsorption were plotted as depicted in Fig. 3. The kinetic parameters including the calculated adsorption amount ($q_{e, \text{calc}}$), rate constant (k_2), correlation coefficient (R^2) were calculated from the plots and summarized as listed in Table 1. The results showed the R^2 of Pd(II), Ru(III), Re(VII) were more than 0.99, indicating the use of linear Pseudo-second model was feasible for the predicating the adsorption process. And it can be predicted the adsorption behavior of Pd(II), Ru(III), Re(VII) onto (DAMIA-EH+TOA)/SiO₂-P by chemisorption and the complexation reaction between metal ions with ligands was the rate controlling step of the adsorption process [29].

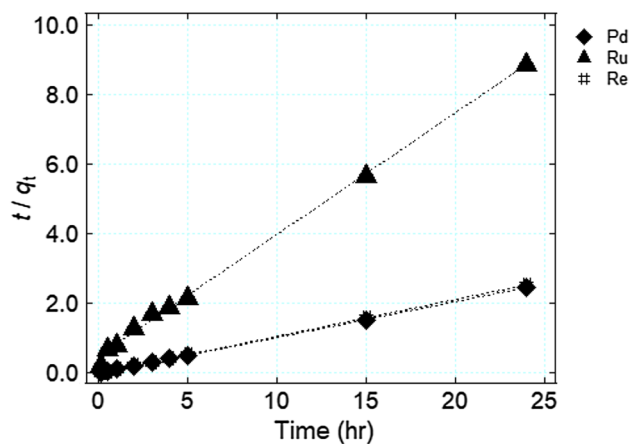


Fig. 3 Linear Pseudo-second order kinetic fitting results for representative metal ions (Pd(II), Ru(III), Re(VII)) adsorption onto (DAMIA-EH+TOA)/SiO₂-P adsorbent

Table 1 Fitted parameters of linear Pseudo-second order kinetic model for representative metal ions adsorption onto (DAMIA-EH+TOA)/SiO₂-P adsorbent at 298 K

	K_2 (g/mg h)	Calculated q_e (mg/g)	Experimentl q_e (mg/g)	R^2
Pd ²⁺	26.937	10.653	10.694	0.9999
Ru ³⁺	0.267	2.851	2.703	0.9983
Re ⁷⁺	11.972	10.695	10.648	0.9999

Effect of HNO₃ concentration

In the adsorption process, the complexation reactions of N donors in DAMIA-EH with metal ions and HNO₃ were considered as two competition reactions. As a result, the association of DAMIA-EH and HNO₃ may decrease the complexation of tested metal ions with DAMIA-EH, causing the decreasing of adsorption ability of metal ions onto (DAMIA-EH + TOA)/SiO₂-P adsorbent [30]. However, DAMIA-EH was classified as a hybrid N and O donor ligand, through introduction of O donors into DAMIA-EH, the adsorbent was expected to be used in more acidic condition.

Therefore, the influence of HNO₃ concentration on the sorption of 15 types of metal ions has been studied under an initial metal concentration of 5 mM in a wide HNO₃ concentration varying from 0.1 to 5 M at 298 K. Figure 4 presented with an increase in the HNO₃ concentration, the K_d of Pd(II) decreased gradually from 2159.04 cm³/g in 0.1 M HNO₃ to 12.09 cm³/g in 5 M HNO₃. The K_d of Re(VII) decreased gradually from 1355.56 cm³/g in 0.1 M HNO₃ to 1.86 cm³/g in 5 M HNO₃. The decrease of K_d values of Pd(II) can be explained as the competition reactions between protonation of soft N donors and complexation of metal ions. While in the case of Re(VII), it was attributed to the increasing amounts of NO₃⁻ with increasing the [HNO₃] [31]. The higher K_d of Pd(II) indicated that (DAMIA-EH + TOA)/SiO₂-P adsorbent showed a better preference to Pd(II) than Re(VII). For Ru(III), the K_d slightly increased to 6.82 when the HNO₃ concentration reached 2 M, and then decreased gradually to 1.67 in 5 M HNO₃, which meant the 2 M HNO₃ was an optimum acidity for the adsorption of Ru(III). Meanwhile, the adsorption performance towards other metal ions showed relatively weak adsorption. These results indicated that (DAMIA-EH + TOA)/SiO₂-P adsorbent had an excellent adsorption

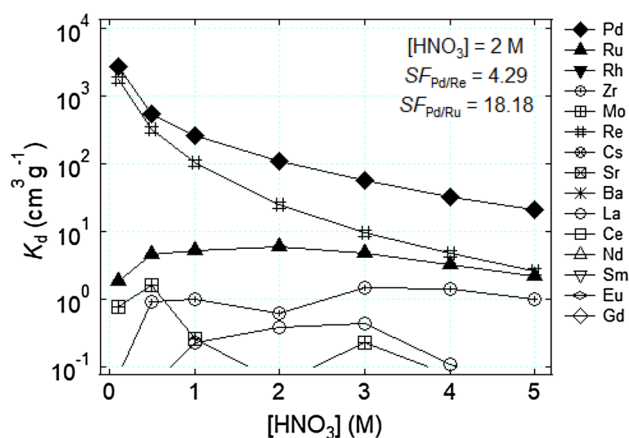


Fig. 4 Dependence of the tested 15 types of metal ions on HNO₃ concentration. [Metal]=5 mM; [HNO₃]=0.1–5 M; Phase ratio=0.2 g/4 mL; Shaking speed: 160 rpm; Shaking time: 5 h; Temperature: 298 K

and high selectively for Pd(II) over other metal ions through introduction of O donors, the acidity resistance of (DAMIA-EH+TOA)/SiO₂-P adsorbent was enhanced and was expected to be feasible in the separation of Pd(II) from HLLW [32].

Adsorption capacity and isotherm

The adsorption capacity and isotherm of representative metal ions such as Pd(II), Re(VII), Ru(III) onto (DAMIA-EH + TOA)/SiO₂-P adsorbent at 298 K were studied by plotting the amount of metal ions adsorbed versus the equilibrium concentration as show in Fig. 5. Adsorption amount of Pd(II) increased gradually with increasing the initial concentration of Pd(II) in the aqueous phase, and then gradually reached to a stable state as it further increased, which meant the adsorption of Pd(II) onto (DAMIA-EH + TOA)/SiO₂-P reached saturated. While the adsorption of Re(VII) and Ru(III) still have not approached a stable state. In order to further study the adsorption isotherm of metal ions onto (DAMIA-EH + TOA)/SiO₂-P, Langmuir and Freundlich isotherm models described as follows were selected to analyze the obtained experimental data. Langmuir isotherm model applies to the adsorption reaction is a monolayer adsorption with constant adsorption energy. Freundlich isotherm model assumes to multilayer adsorption. The expressions of these models were described as follows [33]:

$$Q_{eq} = \frac{Q_{max}K_L C_{eq}}{(1 + K_L C_{eq})} \quad (6)$$

$$Q_{eq} = K_F C_{eq}^{1/n} \quad (7)$$

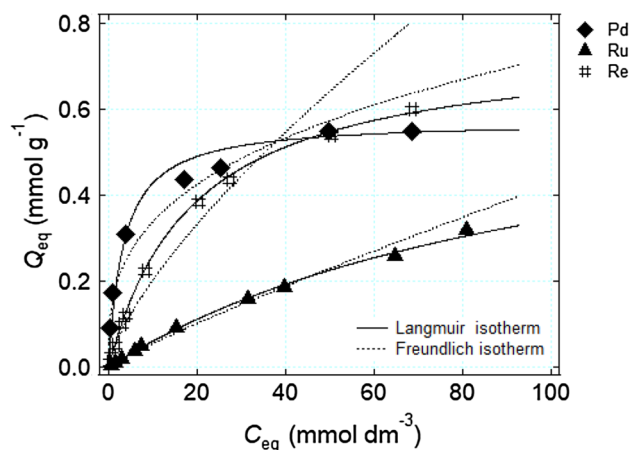


Fig. 5 Non-Linear Langmuir and Freundlich isotherm fitting for ions adsorption onto (DAMIA-EH+TOA)/SiO₂-P adsorbent. [Metal]=1–100 mM; [HNO₃]=2 M; Phase ratio=0.2 g/4 mL; Shaking speed: 160 rpm; Shaking time: 5 h; Temperature: 298 K

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

Non-linear theoretical fitting details of Pd(II), Re(VII), Ru(III) were shown in Fig. 5 and summarized Table 2. The R^2 of Pd(II), Re(VII), Ru(III) obtained suggested that the Langmuir isotherm model was well fitted with the experimental data, indicating the adsorption process was identified as a monolayer adsorption [34]. The Q_{max} values of Pd(II), Ru(III) and Re(VII) were estimated to be 0.573, 0.714, and 0.757 mmol/g, respectively.

Effect of temperature

The effect of temperature on the adsorption performance of tested 15 types metal ions onto (DAMIA-EH + TOA)/SiO₂-P adsorbent in 2 M HNO₃ was studied. Based on experimental results shown in Fig. 6a, it was found that except Pd(II), Re(VII), Ru(III), the adsorption abilities of other metal ions still remained in a relatively low level ($K_d < 1$). Furthermore, the plots of $\ln K_d$ versus $1/T$ only gave the fitting lines of Pd(II), Re(VII), Ru(III) as shown in Fig. 6b. With increasing the T, the adsorption ability towards Pd(II) and Re(VII) onto (DAMIA-EH + TOA)/SiO₂-Pd(II) decreased gradually, while the adsorption towards Ru(III) slightly increased, which meant the high temperature was not benefit for the effective adsorption towards Pd(II). In order to further clarify the effect of T in more details, van't Hoff equation (as shown below) was used to calculate the thermodynamic parameters [35]. ΔH° and ΔS° were provided as the slope and intercept of the fitting lines in Fig. 6, and the theoretical fitting results were summarized as shown in Table 3.

$$\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ T \quad (9)$$

where R is the universal gas constant (8.314 J/(K mol)), K_d is distribution coefficient. ΔG° , ΔH° , ΔS° are the standard

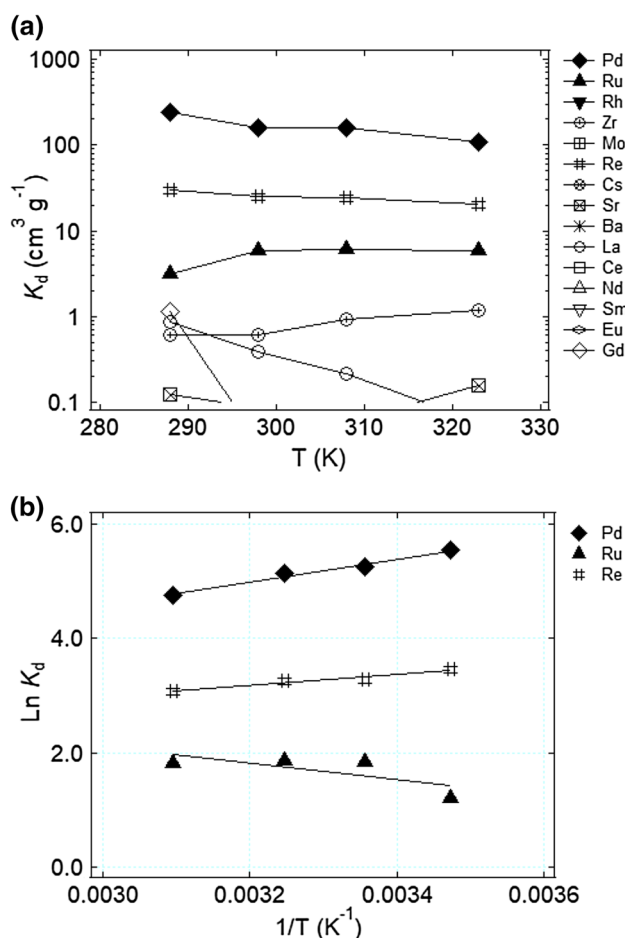


Fig. 6 a Effect of temperature on the adsorption percentage of 15 types of tested metal ions onto (DAMIA-EH + TOA)/SiO₂-P; b Relationship between $\ln K_d$ versus $1/T$ for the adsorption of Pd(II), Ru(III), Re(VII). [Metal]=5 mM; [HNO₃]=2 M; Phase ratio=0.2 g/4 mL; Shaking speed: 160 rpm; Shaking time: 5 h; Temperature: 288–323 K

changes in Gibbs free energy (J/mol), enthalpy (J/mol), entropy (J/(K mol)), respectively.

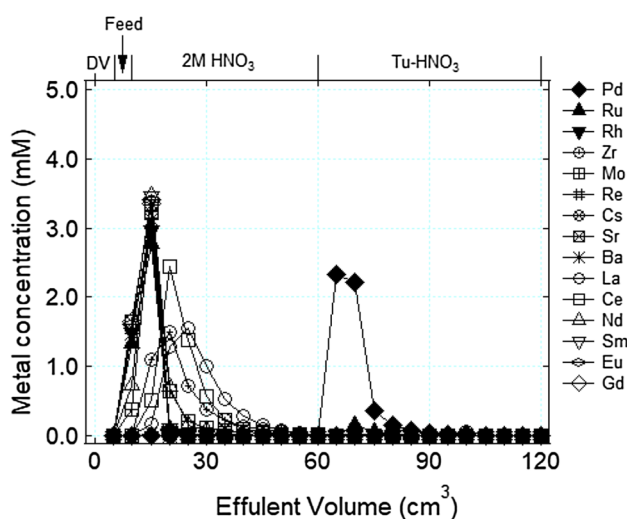
Based on the results, it was found that all the ΔG° values were negative, indicating the adsorption process was spontaneous and thermodynamically favorable. The corresponding thermodynamic parameters ΔH° of Pd(II), Re(VII) adsorption onto (DAMIA-EH + TOA)/SiO₂-P were calculated as -16.625 and -7.796 kJ/mol, respectively. The negative value of ΔH° indicated that Pd(II), Re(VII) adsorption was

Table 2 Fitted parameters of Non-Linear Langmuir and Freundlich isotherm models for ions adsorption onto (DAMIA-EH + TOA)/SiO₂-P adsorbent at 298 K

Metal ion	Langmuir model parameters			Freundlich model parameters		
	Q_{max} (mmol/g)	K_L (L/mmol)	R^2	K_F (mmol/g)	$1/n_f$	R^2
Pd ²⁺	0.573	0.295	0.990	0.159	0.328	0.958
Ru ³⁺	0.714	0.009	0.997	0.007	0.890	0.955
Re ⁷⁺	0.757	0.052	0.990	0.039	0.716	0.955

Table 3 Calculated values of the thermodynamic parameters for the adsorption of representative metal ions onto (DAMIA-EH + TOA)/SiO₂-P adsorbent

Temp (K)	ΔG° (kJ/mol)			ΔH° (kJ/mol)			ΔS° (kJ/mol)		
	Pd ²⁺	Ru ³⁺	Re ⁷⁺	Pd ²⁺	Ru ³⁺	Re ⁷⁺	Pd ²⁺	Ru ³⁺	Re ⁷⁺
288	-13.24	-3.39	-8.24	-16.625	12.087	-7.796	-0.012	0.054	0.002
298	-13.16	-3.93	-8.25						
308	-13.01	-4.46	-8.27						
323	-12.83	-5.27	-8.29						

**Fig. 7** Chromatographic separation of the tested 15 types of metal ions through (DAMIA-EH + TOA)/SiO₂-P column at 298 K**Table 4** Recovery yield of representative metal ions

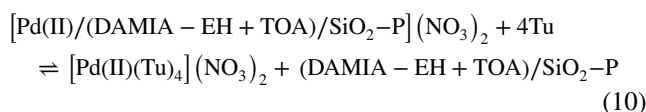
Elements	Recovery yield (%)
Pd	97.95
Ru	93.24
Re	0.39
Zr	90.64
Mo	96.76
Other	100 ± 5

exothermic, while the positive values of ΔH° for Ru(III) revealed its adsorption process was endothermic. The negative ΔS° of Pd(II) can be explained as a result of stable arrangement onto (DAMIA-EH + TOA)/SiO₂-P [36].

Chromatography separation experiment

The chromatographic separation results were illustrated in Fig. 7, and the recovery yield of representative metal ions were summarized in Table 4. As can be seen, with the feed solution was supplemented, the alkali metals (Cs(I)), alkaline earth metals (Sr(II), Ba(II)) and rare earth metal (La(III), Ce(III), Nd(III) etc.), Mo(VI), Zr(IV) etc. showed almost no adsorption ability and was quickly flowed out with

2 M HNO₃, which was consistent with the results from batch adsorption experiments. While Pd(II) and Re(VII) were still strongly adsorbed inside the column. Next, 0.01 M Tu (pH = 2) solution was employed to separate the adsorbed Pd(II) from Re(VII) in (DAMIA-EH + TOA)/SiO₂-P adsorbent. The concentration of Pd(II) in effluent was found to be quickly increased with the flowing in of 0.01 M Tu (pH = 2) solution. The phenomenon shown in Fig. 7 can be seen as the sharp elution peak of Pd(II). It can reveal the disassociation speed was also very rapid, which will be benefit in the practical utilization. After measuring by ICP-AES, it was calculated that about 97.95% of Pd(II) was recovered due to the stronger affinity of S donor in Tu (S = C functional group) than N donor in DAMIA-EH. From previous studies, four Tu molecules formed a 1:4 complex with one Pd(II) ion, the mechanism of complexation behavior between Tu and Pd(II) can be described as the following equation in details [37]:



Conclusions

The adsorption behaviors of a hybrid soft N and hard O donor (DAMIA-EH + TOA)/SiO₂-P adsorbent towards Pd(II) in simulated HLLW solution containing 14 kinds of co-existing metal ions was investigated. The results found that the adsorption speed was fairly fast and the equilibrium state can be reached at only 10 min. With increasing the concentration of HNO₃, the adsorption ability towards Pd(II) decreased gradually. K_d of Pd(II) decreased gradually from 2159.04 cm³/g in 0.1 M HNO₃ to 12.09 cm³/g in 5 M HNO₃. Such a decrease was explained as the competition reactions between protonation and complexation behaviors of N donors. The results also revealed that (DAMIA-EH + TOA)/SiO₂-P had a good selectivity of Pd(II) in a wide HNO₃ range from 0.1 to 5 M compared with other co-existing metal ions. The experimental data fitted well with Langmuir isotherm model, indicating the adsorption process was identified as a monolayer adsorption. Furthermore, with

an increase in the temperature of solution, the adsorption performance of Pd(II) slightly decreased, which meant the adsorption process was high temperature unfavorable. The values of calculated thermodynamic parameters revealed that the adsorption process of Pd(II) was spontaneous and exothermic. The chromatography separation experiment of Pd(II) was successfully completed under elution with 0.01 M Tu (pH = 2) solution, and about 97.95% of Pd(II) was selectively recovered. The results introduced above revealed that the utilization of a hybrid donor (DAMIA-EH + TOA)/SiO₂-P adsorbent to directly separate Pd(II) from simulated HLLW was feasible.

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