

Preparation and characterization of a mesoporous polycrown impregnated silica and its adsorption for palladium from highly acid medium

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Abstract A polycrown loaded silica composite material named Polycrown/SiO₂-P was firstly prepared by impregnating and immobilizing polycrown into porous silica and was characterized by scanning electron microscope (SEM), and Fourier transformed infrared (FT-IR) spectroscopy, nitrogen adsorption and desorption isotherms. Polycrown/SiO₂-P was tested with regard to adsorption performance. Interestingly, Polycrown/SiO₂-P preferred Pd(II) than alkali metals, alkaline-earth metals and actinides. Pd(II) adsorption with Polycrown/SiO₂-P as functions of HNO₃ concentration, contact time, initial Pd(II) concentration, temperature were thus investigated. The results showed the optimal adsorption acidity was determined as 5.0 M nitric acid, proving good acidity-resistant. Pseudo-second-order kinetics model fitted adsorption well indicating chemical adsorption. The isotherm adsorption equilibrium was well described by Langmuir isotherm model with maximum adsorption capacity of 14.30 mg/g. Pd(II) adsorption increased with temperature increased. The positive ΔH° and ΔS° , and the negative ΔG° indicated the adsorption was endothermic, entropy increase and spontaneous in nature. Pd(II) loaded Polycrown/SiO₂-P was characterized by XPS. Further, the adsorption efficiency of recovered Polycrown/SiO₂-P retained up ~93.7% after five ad-desorption cycles. Polycrown/SiO₂-P was promising to separate Pd(II) from highly acid medium.

Keywords Pd(II) · Silica-based material · Highly acid medium · Selective adsorption · Desorption

1 Introduction

Palladium, one of platinum group, is a precious metal. Because of specific ductibility, malleability, and inertness, palladium is widely used in fields of industries such as: jewelry and ornament [1], electronics [2], telephone circuits [3], heat and corrosion resistance apparatus [4], catalysts [5, 6], and dental alloys [7]. The increasing demand stimulates recovery of palladium from the second resources as the low palladium concentration in terrestrial crust [8]. A commercial light water reactor at a burn-up of 33 GWd/t produces the burnt spent nuclear fuel with *ca.* 1 kg palladium. By 2030 spent nuclear fuel could supply up to 1000 t palladium worldwide. Fission palladium is comprised of isotopes 104 (17 wt%), 105 (29 wt%), 106 (21 wt%), 107 (17 wt%), 108 (12 wt%), and 110 (4 wt%). Among them, Pd-107 is the only radioactive isotope with a half-life of 6.5×10^6 years [9]. In addition, palladium separation is helpful to the final follow-up treatment for the spent nuclear fuel of high radioactivity risk. Therefore palladium deserves recovery from the spent nuclear fuel. Notably, palladium made in this way is finally concentrated in high level radioactive liquid waste of 3.0–6.0 M nitric acid, leading a big challenge for separation.

First generation supramolecular crown has unique affinity toward metal ions. 15-Crown-5 commonly complexes sodium cation while complexes other metal ions once modification. *N*-phenylaza-15-crown-5 recognizes Fe having potential as a selective electrode [10]. Monoaza-15-crown-5 containing an optically active aminobenzoxazinone moiety responds to Mg, Ca, Ba, Sr, Cd and

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particularly responds to Hg and Pb [11]. Benzo-15-crown-5 is capable to detect uranyl [12] and naphthaleneacetamide modifying benzo-15-crown-5 can become Mg-responsive fluorescent chemosensor [13]. Thus 15-crown-5 via proper modification has reason to complex Pd. Moreover, polymers including polymeric crowns have special characters such as high resistance to chemicals, to temperature, and to radiolysis [14]. It has been utilized for selective separating lead [15], neodymium [16], uranium [15], barium [17], etc.

Authors have devoted to metals separation from high level radioactive liquid waste by preparing various silica-based materials [18–20], most of which possessed outstanding acid resistance. The made (Calix[4]+MODB)/SiO₂-P has cesium distribution coefficient of over 10 even nitric acid concentration beyond 6.0 M [21]. (DtBuCH18C6+TBP)/SiO₂-P can selectively adsorb strontium from La(III), Y(III), Na(I), K(I), Cs(I), Ru(III), Mo(VI) and Pd(II) under 2.0 M HNO₃ [22]. Base on above materials, authors developed an advanced partitioning technology SPEC (strontium/cesium partitioning from high level radioactive liquid waste by extraction chromatography) process. Cs(I) and Sr(II) can be successfully separated from high HNO₃ concentration medium [23].

In the present work, polycrown (poly 4-[3-(3-benzo-15-crown-5)methyl-4-hydroxy-phenyl]methyl-ethyl-phenol) loaded silica composite material (Polycrown/SiO₂-P for short) was prepared. Recognition ability and high acidity resistance endowed Polycrown/SiO₂-P suitable in palladium separation from highly acid medium. Effects of experimental parameters such as nitric acid concentration, contact time, initial palladium concentration, temperature and coexistence metal on adsorption were studied. The isotherms and kinetics models were used to fit and describe adsorption. The adsorption mechanism was researched in microscopic level by XPS.

2 Materials and methods

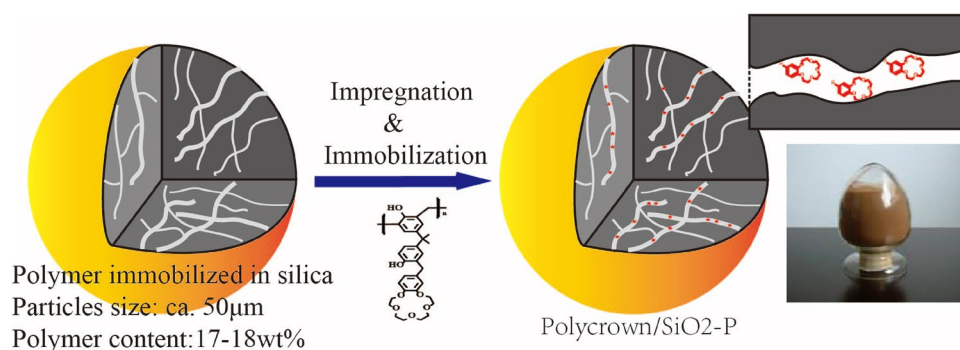
2.1 Materials

The polycrown synthesized using formic acid, bisphenol A, benzo-15-crown-5, and concentrated sulfuric acid [24] was provided by Prof. Tatsuya Suzuki, Tokyo Institute of Technology, Japan. The analytical grade chemicals of M^INO₃ (M^I=Na(I), K(I), Rb(I) and Cs(I)), M^{II}(NO₃)₂ (M^{II}=Sr(II) and Ba(II)), hydrochloric acid and 30% hydrogen peroxide were purchased from Sinopharm Chemical Reagent Co.,Ltd. 68% HNO₃ was purchased from Zhongxing Chemical Limited Company, Hangzhou, China. Palladium nitrate solution with 4.5 wt% Pd(II) was from Tanaka Noble Metal Co. Inc., Japan. Deionized water with purity of conductivity <0.5 μs/cm was used throughout. U(VI) stock solution was prepared as following. To 7.0167 g U₃O₈ in a 100 mL beaker 10 mL hydrochloric acid ($\rho=1.18 \text{ g}\cdot\text{mL}^{-1}$) and 2 mL 30% hydrogen peroxide were added. After heated to near dry, the solution was added with 10 mL hydrochloric acid ($\rho=1.18 \text{ g}\cdot\text{mL}^{-1}$) and then diluted to 1,000 mL with distilled water to make U(VI) concentration of $5.0\times 10^{-2} \text{ M}$ [25].

Polycrown/SiO₂-P was prepared according to an available method in lab in Fig. 1 [26–28]. The preparation method for Polycrown/SiO₂-P in detail is as following. The silica particles were put into a evacuated glass flask, and into the flask the following was sucked such as a mixture of monomers composed of 85 wt% of *m/p*-formyl-styrene, 15 wt% *m/p*-divinylbenzene, dioctyl phthate and methylbenzoate, initiators made of α,α -azobisisobutyronitrile (AIBN) and 1,1'-azobiscyclohexane-1-carbonitrile, and diluents consisted of 1,2,3-trichloropropane and *m*-xylene. The flask was rotated continuously for complete soaking silica particles and then filled with N₂ gas. The flask was then heated at 363 K for 20 h with a silicone oil bath. The grafted material (SiO₂-P) was obtained after wash with acetone and water and then dry overnight at 323 K.

To increase affinity of the styrene–divinylbenzene copolymer contained in SiO₂-P for polycrown molecule, SiO₂-P particles were washed in advance with methanol for three

Fig. 1 Schematic diagram of synthesizing Polycrown/SiO₂-P



times prior to synthesizing Polycrown/SiO₂-P. 1.0 g polycrown dissolved with about 150 mL dichloromethane and 9.0 g of above prepared SiO₂-P particles were mixed into a 500 mL flask and mechanically stirred for nearly 90 min at room temperature. Later, the mixture was transferred into a silicon-oil bath and kept at *ca.* 45 °C for about 180 min under stirring. After drying in vacuum at 50 °C for 24 h, the polymeric adsorption material Polycrown/SiO₂-P was obtained. Physical and chemical parameters of Polycrown/SiO₂-P were shown in Table 1.

2.2 Instruments and spectroscopic measurements

An EYELA SB-2000 rotary evaporator was used to prepare Polycrown/SiO₂-P. A TAITEC MM-10 Model auto-thermostated water bath shaker was applied in adsorption experiment. A Varian AA 240 FS Model atomic adsorption spectroscopy with RSD less than 0.5% was used to analyze metal ion concentration. Morphology of Polycrown/SiO₂-P was observed by a scanning electron microscope (SEM) (HITACHI S-4800). Secondary electron resolutions of SEM are 1.4 nm (1 kV, deceleration mode) and 1 nm (15 kV). FT-IR spectrum was measured on a BRUKER Vector 22 FT-IR spectrometer and the background spectrum was measured on pure KBr. The resolution ratio and wavenumber accuracy of FT-IR are 1 and 0.01 cm⁻¹, respectively. Nitrogen adsorption and desorption isotherms were measured at 77 K using an ASAP 2020 M analyzer. The measurement accuracy of BET surface analyzer is 1%. Surface area was calculated by Brunauer–Emmett–Teller (BET) method, and pore volume and pore size distribution were calculated using Barret–Joyner–Halenda (BJH) model. The XPS photoelectron spectra was recorded using an ADES 400 angle-resolved photoelectron spectrometer (VG Scientific, UK) equipped with a rotatable hemispherical electron energy analyser with a Mg K α X-ray source (1253.6 eV, Specs). The XPS wide spectra was recorded

with a pass energy of 100 eV, step –1 eV and dwell time 0.1 s. The high-resolution spectra with 20 eV, step 0.1 eV and dwell time 0.1 s.

2.3 Adsorption studies

The adsorption of metal ions of the desired concentration and HNO₃ concentration on 0.25 g Polycrown/SiO₂-P was investigated batch wise in 10 mL polyethylene centrifuge tubes. After shaken at 120 rpm for the adsorption equilibrium, solid and liquid phases were separated by filtration. The metal ion concentration was determined using the Varian AA 240 FS Model atomic adsorption spectroscopy except U which was analyzed using the arsenazo III method with a 721 type spectrophotometer at 650 nm. Distribution coefficient (K_d) and the adsorption amount (q_e) were calculated by the following equations:

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{W} \quad (1)$$

$$q_e = \frac{C_0 - C_e}{W} \times V \quad (2)$$

where C_0 (mg/L) is the initial concentration, C_e (mg/L) denotes the equilibrium concentration, V (L) is solution volume and W (g) is Polycrown/SiO₂-P weight. All of the experimental data were averages of duplicate detections after deducting the tiny adsorption values of SiO₂-P, *i.e.* blank experiments.

2.4 Desorption studies

After each adsorption study, the solution was filtered to recover the spent Polycrown/SiO₂-P, which was then washed with acidic solution (0.01 M HNO₃) to remove the adsorbed Pd(II). The recovered Polycrown/SiO₂-P was thoroughly washed with water and ethanol, dried in a

Table 1 Physical and chemical parameters of Polycrown/SiO₂-P

Silica-based polymeric composite	Polycrown/SiO ₂ -P
Supramolecular recognition agent	Poly4-[3-(3-benzo-15-crown-5)methyl-4-hydroxy-phenyl]-methyl-ethyl-phenol
Mean pore size	4.20 nm
Bead diameter	<i>ca.</i> 50 μ m
Specific surface area	3.118 m ² ·g ⁻¹
Integrated pore volume	0.008 mL·g ⁻¹
Copolymer inside SiO ₂ -P support	Inert copolymer-containing compound
Appearance	Brown powdered micro-ball
Affinity for water or acidic solution	Good

vacuum, and used for further adsorption studies. During the repeated adsorption studies, Pd(II) adsorption amount (q_e) was determined. The adsorption and desorption processes were repeated up to 5 times, to further ascertain the recyclability of Polycrown/SiO₂-P.

3 Results and discussion

3.1 Characterization of Polycrown/SiO₂-P

SEM micrograph of Polycrown/SiO₂-P is shown in Fig. 2a. It could be seen that Polycrown/SiO₂-P was a sphere structure with a diameter of 50 μm .

The FT-IR spectra of Polycrown/SiO₂-P (Fig. 2b) exhibited several characteristic bands at 3453, 2925, 1627, 1511, 1462, 1074, 794 cm^{-1} , respectively assignable to hydroxyl [29], methylene band [30], polymer, phenolic hydroxyl [31], C-H methyl and methylene deformation [32], Si-O-Si bending [33], Si-O stretching [34].

Low-temperature nitrogen adsorption–desorption isotherms spectra was obtained as Fig. 2c. The isotherms were

of type III as defined by IUPAC, which indicated the weak interaction between Polycrown/SiO₂-P and nitrogen molecules. The BET surface area was $3.118 \text{ m}^2 \cdot \text{g}^{-1}$ and the pore volume was $0.008 \text{ mL} \cdot \text{g}^{-1}$. Pore size distribution presented as Barret-Joyner-Halenda (BJH) plot showed the average pore diameter was *ca.* 4.0 nm.

3.2 Effect of HNO₃ concentration on adsorption

Nitric acid is almost sole medium employed in reprocessing process of nuclear spent fuel, which is dissolved by hot and concentrated nitric acid. After recovery uranium and plutonium by the famous PUREX process, palladium exists in the raffinate, the aqueous phase treated by 30% tributyl phosphate/kerosene. By protonation with the oxygen atom in Polycrown/SiO₂-P, nitric acid is considered to probably influence the complexation of Pd(II) [35, 36]. The effect of HNO₃ concentration on distribution coefficient of Pd(II) are presented in Fig. 3.

It can be seen from Fig. 3 that $K_{d(\text{Pd})}$ slightly changed as HNO₃ concentration increased from 0.4 to 2.0 M, later drastically increased to 5.0 M, then decreased

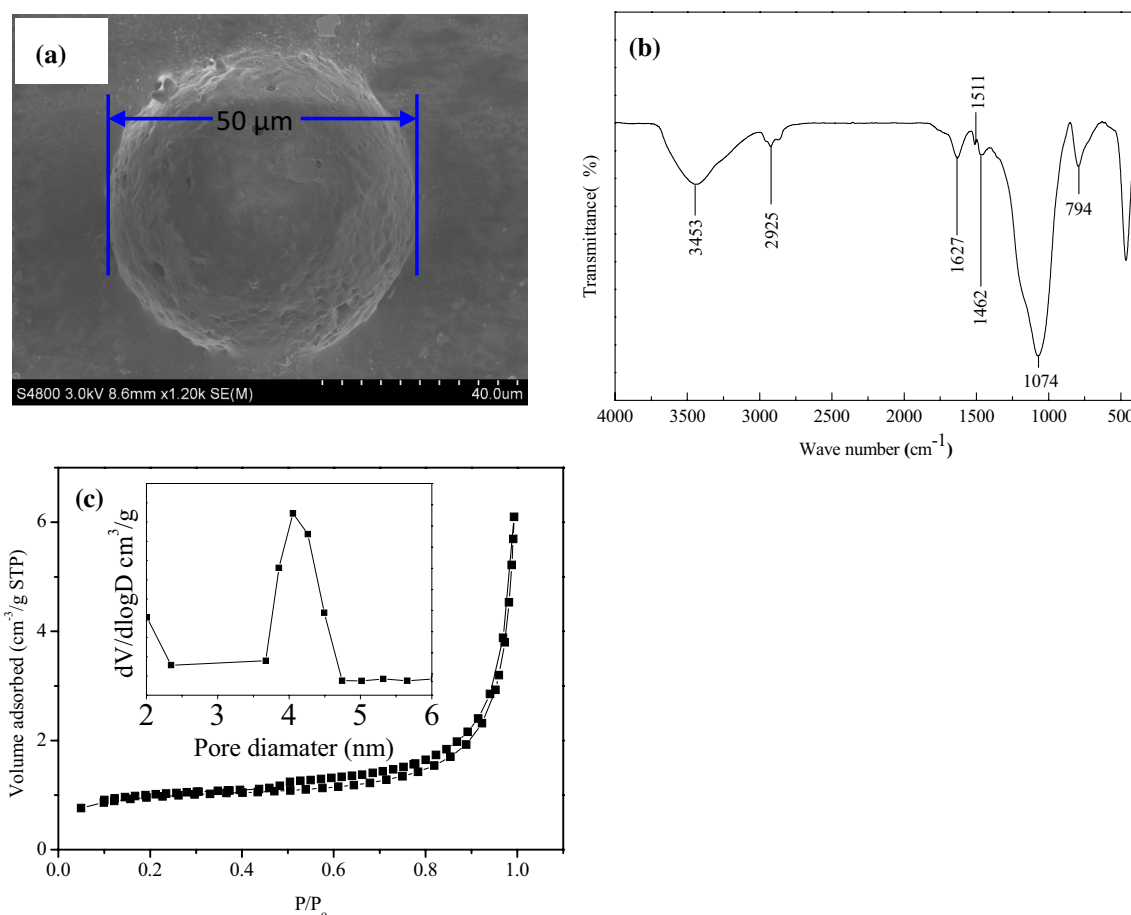


Fig. 2 a SEM images, b Fourier transform infrared spectroscopy, d nitrogen adsorption–desorption isotherms of Polycrown/SiO₂-P

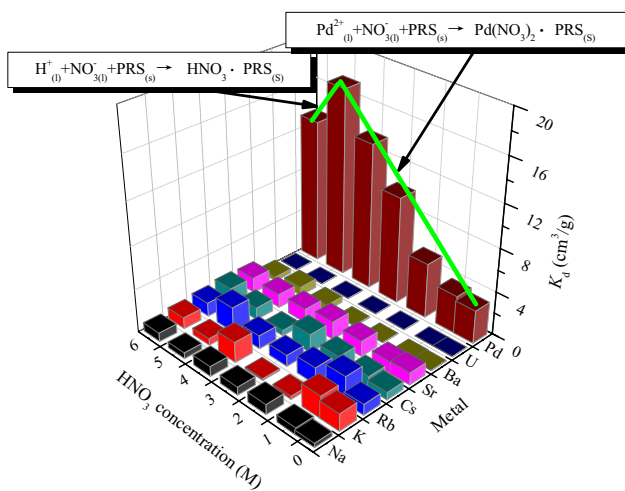


Fig. 3 Effect of HNO₃ concentration on metal ions adsorption. [Metal] = 5.0 × 10⁻³ M, contact time = 600 min and T = 298 K

significantly to 6.0 M. Main reactions of complexation and protonation were shown in Fig. 3 [25]. The optimal nitric acid concentration was determined as 5.0 M, proving good acid-resistance and making possibility for using Polycrown/SiO₂-P to separate Pd(II) from highly acid raffinate. The investigated Na(I), K(I), Rb(I), Cs(I), Sr(II), Ba(II) and U(VI) showed low *K_d* indicating those metal ions hardly interrupted Pd(II) adsorption. It is thus predicts that alkali, alkaline earth, and actinide metal ions would not be adsorbed. Such selectivity is interesting as the crown ether compounds normally selectively bind alkali or alkaline-ether metal ions and especially 15-crown-5 with cavity diameter of 0.170–0.220 nm is commonly known to fit well with potassium in monovalence with effective ionic radii of 0.138 nm [37]. Thus the selectivity of crown compounds with metal ions can't be simplified with the size match. In fact when one ion can fit within the cavity, the crown ether-metal ion coordination reacts in 1:1 ratio; and if the ion size is too different with the cavity, the crown ether has a tendency to “sandwich” or “coil” the metal ion [38]. The effective ionic radii of the divalent palladium is 0.100 nm, more coincident than K(I) and other metals. Thus palladium ion probably exclusively forms 1:1 type complex with Polycrown/SiO₂-P.

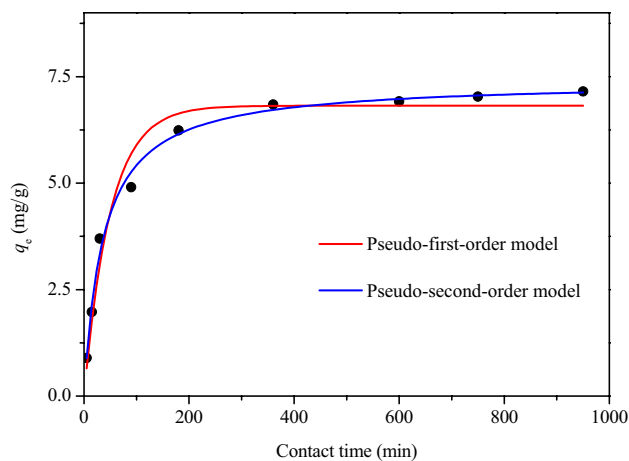


Fig. 4 Effect of contact time on Pd(II) adsorption. [Pd(II)] = 5.0 × 10⁻³ M, [HNO₃] = 5.0 M, and T = 298 K

3.3 Adsorption kinetics

The effect of contact time on Pd(II) adsorption on Polycrown/SiO₂-P is shown in Fig. 4. As could be seen, *K_d(Pd)* rapidly increased in the first 90 min, then slowly increased from 90 to 950 min. The decreasing concentration gradient attributes to the decrease in adsorption rate. In order to interpret the kinetic in detail, pseudo-first-order and pseudo-second-order were used to fit the experimental data [39]. The resultant fitness represents the corresponding mechanism [40]. The pseudo-first-order and pseudo-second-order models can be described using Eq. 2 and Eq. 3 [41].

$$q_t = q_e \times (1 - e^{-k_1 t}) \tag{3}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{4}$$

where *k₁* (min⁻¹) and *k₂* (g/(mg·min)) represent adsorption rate constants of pseudo-first-order, pseudo-second-order models, respectively; *q_t* (mg/g) is the adsorption amount at time *t* (min) and *q_e* (mg/g) is the amount at equilibrium. Kinetic parameters of two kinetic models are listed in Table 2.

Validity of each model could be checked by fitness of the straight lines (*R*² values). As shown, the good fitness

Table 2 Kinetic parameters of pseudo-first-order and pseudo-second-order models

Pseudo-first-order model			Pseudo-second-order model			
<i>k₁</i> (min ⁻¹)	<i>q_e</i> (mg·g ⁻¹)	<i>R</i> ²	<i>k₂</i> (g·mg ⁻¹ ·min ⁻¹)	<i>h</i> (mg·g ⁻¹ ·min ⁻¹)	<i>q_e</i> (mg·g ⁻¹)	<i>R</i> ²
0.02	6.819	0.963	0.004	0.219	7.401	0.991

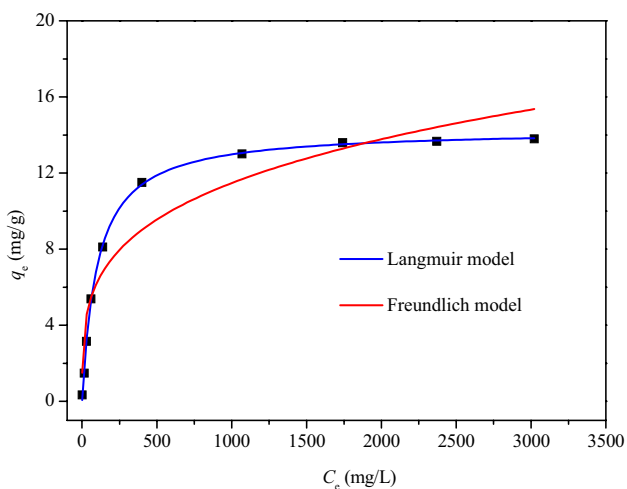


Fig. 5 Adsorption isotherms of Pd(II) uptakes on Polycrown/SiO₂-P. [Pd(II)] = 5.0 × 10⁻³ M, [HNO₃] = 5.0 M, T = 298 K, and contact time = 600 min

(R² = 0.991) with pseudo-second-order model and the close experimental (7.155 mg·g⁻¹) and theoretical q_e (7.401 mg·g⁻¹) jointly confirmed validity of pseudo-second-order model, which suggested that chemical adsorption was the ruling way. Pd(II) and Polycrown/SiO₂-P shared electrons when adsorption happened. The initial adsorption rates (h) was calculated as 0.215 mg·g⁻¹·min⁻¹ using $h = k_2 q_e^2$.

3.4 Adsorption isotherm

To understand adsorption better, Pd(II) uptakes at different initial concentrations were investigated and the result was shown in Fig. 5. It was found that Pd(II) uptake firstly increased with increasing equilibrium concentration, and kept at constant beyond the equilibrium concentration of ca. 500 mg/L. Langmuir and Freundlich [42], were utilized to simulate adsorption data. Langmuir model (shown in Eq. 4) presupposes homogeneous and equal energy sites on adsorbent, which present an ideal adsorption behavior. Freundlich model (shown in Eq. 5) is an empirical equation with the assumption of heterogeneous surfaces on adsorbent.

$$q_e = \frac{aq_m C_e}{1 + aC_e} \tag{5}$$

$$q_e = KC_e^{1/n} \tag{6}$$

Table 3 Isotherm parameters of Langmuir and Freundlich models

Langmuir model			Freundlich model		
q _m (mg·g ⁻¹)	a (L·mg ⁻¹)	R ²	K (mg·g ⁻¹)	n	R ²
14.301	0.010	0.999	1.853	3.789	0.911

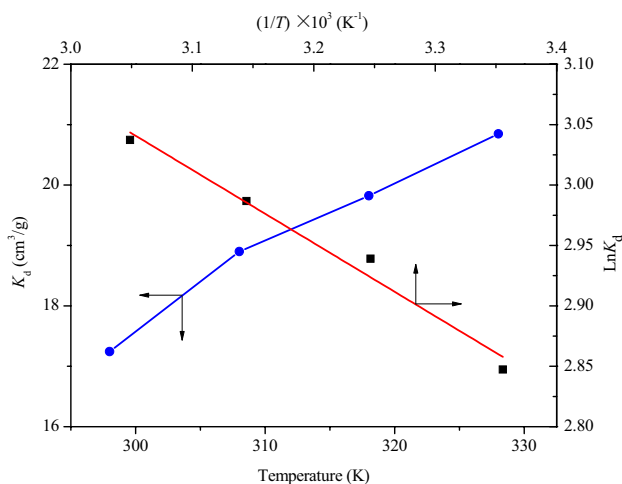


Fig. 6 Effect of temperature on Pd(II) adsorption and lnK_d vs. 1/T. [Pd(II)] = 5.0 × 10⁻³ M, [HNO₃] = 5.0 M, and contact time = 600 min

where C_e is the aquatic concentration (mg·L⁻¹) of Pd(II) at equilibrium; q_e is the equilibrium uptake (mg·g⁻¹); q_m is the maximum adsorption capacity (mg·g⁻¹); a is the Langmuir constant related to the affinity between adsorbate and adsorbent (L·mg⁻¹), and K is Freundlich isotherm constant (mg·g⁻¹), n is adsorption intensity. The parameters calculated from the plots of C_e/q_e vs. C_e and lnq_e vs. lnC_e are listed in Table 3.

The Freundlich plots had a lower regression coefficient suggesting a restriction on the use of Freundlich isotherm. The Langmuir model with R² of 0.983 showed a better fitness and Q_m given by the Langmuir model was 14.30 mg·g⁻¹, consistent with the experimental value of 13.79 mg·g⁻¹ at 5.0 M HNO₃. The Langmuir model was thus determined to describe the Pd(II) adsorption process as a monolayer adsorption. We would like comparing the maximum adsorption capacity of 14.30 mg·g⁻¹ at 5.0 M HNO₃ with other adsorbents, but as far as we known, data about the adsorbent performance at acidity greater than 1.0 M is rare.

The separation factor (R_L, R_L = 1/(1 + aC₀)), a dimensionless constant, can be used to explain the essential characteristics of a Langmuir isotherm. R_L values can be related to the equilibrium isotherm as follows: unfavorable, R_L > 1; linear, R_L = 1; favorable 0 < R_L < 1; and irreversible, R_L = 0 [43, 44]. According to studied concentrations, all calculated R_L values (0.018–0.882) were found to lie in between 0 and 1, proving a favorable adsorption process.

3.5 Thermodynamics

Effect of the temperature on Pd(II) adsorption is shown in Fig. 6. As could be seen, increasing the adsorption temperature from 298 to 328 K resulted in a significant

Table 4 Thermodynamic parameters of adsorption of Pd(II) onto Polycrown/SiO₂-P

ΔS° (J·mol ⁻¹ ·K ⁻¹)	ΔH° (kJ·mol ⁻¹)	ΔG° (kJ·mol ⁻¹)			
		298 K	308 K	318 K	328 K
27.270	5.032	-3.068	-3.406	-3.642	-3.895

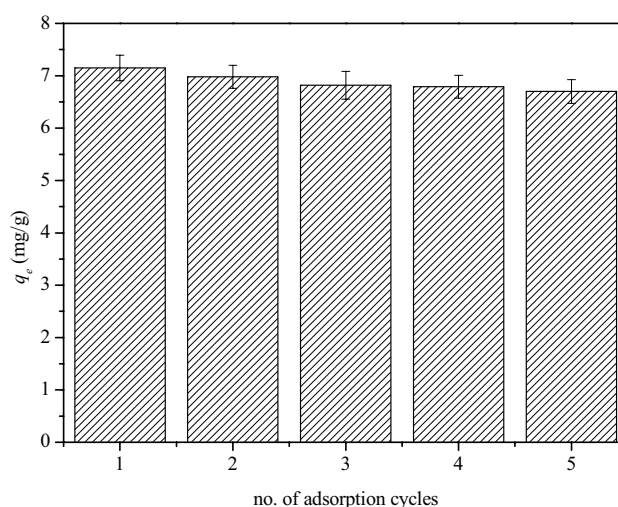
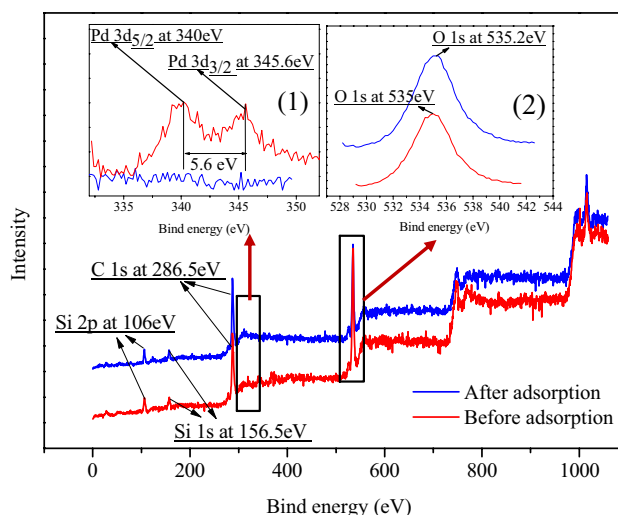
increase in K_d from 17.24 to 20.84, denoting an endothermic nature. A linear plot of $\ln K_d$ vs. $1/T$ was constructed. Thermodynamic parameters including the change in enthalpy (ΔH°), free energy (ΔG°) and entropy (ΔS°) were calculated using the Arrhenius law $\ln K_d/dT = \Delta H^\circ/RT^2$ and Gibbs free energy $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and were shown in Table 4. The positive value (5.032 kJ·mol⁻¹) of ΔH° means an endothermic process. One possible explanation for the endothermic process was that the solvated Pd(II) needed energy to strip the hydration shell before adsorption. The positive value (27.270 J·mol⁻¹·K⁻¹) of ΔS° represented that Polycrown/SiO₂-P had affinity toward Pd(II). The negative values of ΔG° (-3.068 kJ·mol⁻¹ at 298 K, -3.406 kJ·mol⁻¹ at 308 K, -3.642 kJ·mol⁻¹ at 318 K, and -3.895 kJ·mol⁻¹ at 328 K) confirmed the adsorption was spontaneous.

3.6 Reusability

As shown in Fig. 7, $K_{d(Pd)}$ slightly decreased from 7.15 mg·g⁻¹ to 6.05 mg·g⁻¹ during cycles from 1 to 5 in sequence. For another, the adsorption capability remained at considerable ~93.7% for the 5th cycle. This indicated that the chemisorption activity of Polycrown/SiO₂-P was still high even after 5 regenerations. The adsorption/desorption cycle data also indicate that the effective composition in Polycrown/SiO₂-P are regenerated without losing adsorption activity (recycling), and further proved the ability for reuse. As an adsorbent, Polycrown/SiO₂-P was very expensive compared with the low-cost activated carbon [45]. But the novel properties of Polycrown/SiO₂-P such as high acidity resistance, mechanical strength, high adsorption efficiency, easy desorption and repeated usability provide a reason to be a novel adsorbent in Pd(II) recovery from acid solution.

3.7 XPS analyses

The action between Pd(II) and Polycrown/SiO₂-P in electron was analyzed by XPS and the result was shown in Fig. 8. In wide spectra before and after adsorption, 106 eV and 156.6 eV were denoted as Si 2p and Si 1 s peaks. 286.5 eV was assigned as C 1 s peak. O 1 s peaks were observed around 535 eV. The embedded Fig. 8(1) showed magnified spectra in the range from 335 to 350 eV. The

**Fig. 7** Pd(II) adsorption ability with Polycrown/SiO₂-P at each cycle**Fig. 8** XPS spectra of Polycrown/SiO₂-P before and after Pd(II) adsorption

spectra after adsorption showed two obvious peaks at 340 and 345.6 eV with the difference of 5.6 eV. Two peaks were defined as Pd 3d_{5/2} and Pd 3d_{3/2}. The embedded Fig. 8(2) offered O 1 s spectra in which O 1 s before adsorption was at 535 eV and O 1 s after adsorption was at 535.2 eV [46]. This little difference of 0.2 eV was because the binding energy change for one palladium atom was averaged by five oxygen atoms.

4 Conclusion

For effective separation of Pd(II) from highly acid medium, the inorganic–organic composite silica-based material

Polycrown/SiO₂-P was successfully prepared. The adsorption results indicated that Polycrown/SiO₂-P had ability to separate Pd(II) from the aqueous solution containing Na(I), K(I), Rb(I), Cs(I), Sr(I), Ba(II) and U(VI). The adsorption process depended on contact time, HNO₃ concentration and slightly on temperature. The optimal acidity of HNO₃ concentration was determined as 5.0 M. The pseudo-second-order kinetics fitted the adsorption well, suggesting that chemical adsorption was the rate-limiting step. Positive ΔH° and ΔS° , and negative ΔG° demonstrated an adsorption of endothermic, freedom increase, and spontaneous nature. XPS proved the effective adsorption of Polycrown/SiO₂-P toward Pd(II). The experimental results demonstrate Polycrown/SiO₂-P is promising in partitioning of Pd(II) from acid medium of 5.0 M HNO₃.

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