

Improved Adsorption and Separation of Palladium(II) and Platinum(IV) in Strong Hydrochloric Acid Solutions Using Thiocyanate-Retaining Tannin Gel

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ABSTRACT: A tannin gel (TG) synthesized from condensed tannin molecules has a remarkable ability to adsorb various metal ions in aqueous solutions. In the present study, we have investigated the adsorption behaviors of palladium and platinum ions, Pd(II) and Pt(IV), in strong HCl solutions using the thiocyanate-retaining tannin gel (SCN-TG) prepared by adsorption of thiocyanate ion (SCN⁻) onto the TG in acidic thiocyanate solutions as reported previously (Ind Eng Chem Res 2011, 50, 12366). Although the adsorption rate of Pt(IV) is slow compared

to that of Pd(II), the SCN-TG was able to adsorb both Pd(II) and Pt(IV) in a 1 M HCl solution, where the TG can never adsorb them. Besides, we have succeeded in the selective adsorption of Pd(II) from the mixture solution of Pd(II) and Pt(IV) at a temperature somewhat lower than room temperature using the SCN-TG. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: adsorption; gels; metal–polymer complexes; tannin; thiocyanate ion

INTRODUCTION

Precious metals, such as palladium (Pd) and platinum (Pt), are utilized in various electrical devices and catalysts because of their physical and chemical properties and have been in great demand recently despite their small recoverable reserves. For this reason, the recovery of precious metals from electronic and catalyst scraps is highly important from the viewpoint of resource management and security. In the recycling of precious metals from such scraps, hydrometallurgical techniques, including cementation, solvent extraction, ion exchange, and adsorption, play a crucial role.^{1,2} Solvent extraction is an established technique for the metal recovery and is useful only for large-scale operations at high metal ion concentrations. In contrast, adsorption can be applied to the precious metal recovery even from low concentration sources with relatively simple processes. Particularly, biosorption has attracted considerable interest to recover precious metal ions from aqueous solutions, because biosorbents are inexpensive and environmentally friendly.^{3–5} We

have also developed a novel biosorbent prepared from condensed tannin molecules by crosslinking with formaldehyde: the tannin is an inexpensive and ubiquitous natural polymer extracted from leaves and barks of plants and has many hydroxy groups as shown in Figure 1.⁶ The resultant tannin gel (TG) has a significant ability to adsorb precious metal ions^{7–11} as well as toxic ions.^{12–17} Such tannin-based materials have also been developed by many other researchers.^{18–36}

In our previous studies,⁹ we clarified that the adsorption of precious metal ions takes place through the formation of the ligand-substituted metal–tannin complex. In acidic chloride solutions, the adsorption of metal ions onto the TG is significantly affected by pH and chloride ion concentrations: for example, the Pd(II) adsorption amount onto the TG decreases with increasing HCl concentration, where the hydroxy groups in the TG compete mainly with chloride ions for complexation with Pd(II).⁷ According to HSAB theory, the complexation ability between the tannin and soft metal ions, such as precious metal ions, is considered not strong enough because of the hard O-donor of the hydroxy groups in the TG.³⁷ Compared to the hydroxy group, an amino group has higher affinity for soft metal ions, because the nitrogen atom is softer than the oxygen atom. In fact, we succeeded in enhancing the adsorbability for Pd(II) and Pt(IV) by the amine modification of the TG.^{38,39} Unfortunately, however, their adsorption amounts significantly decrease with

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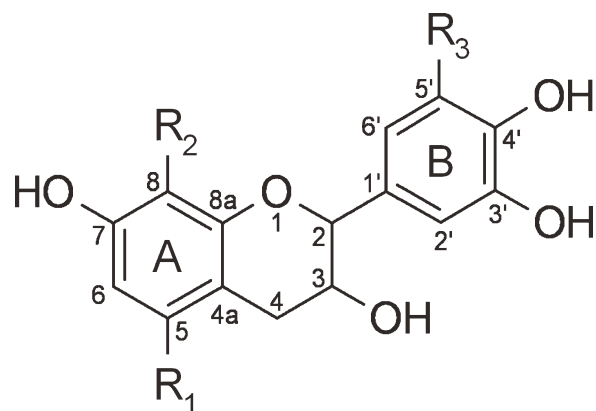


Figure 1 Estimated chemical structure of condensed tannin molecule: $R_1 = \text{OH}$ and $R_2 = \text{H}$, phloroglucinolic; $R_1 = R_2 = \text{H}$, resorcinolic; $R_1 = \text{H}$ and $R_2 = \text{OH}$, pyrogallolic; $R_3 = \text{H}$, catecholic; $R_3 = \text{OH}$, pyrogallolic.⁶

increasing HCl concentration up to molar levels, because most Pd(II) and Pt(IV) exist as PdCl_4^{2-} and PtCl_6^{2-} , respectively, which are highly unfavorable for the formation of the ligand-substituted metal-tannin complexes, even after the amine modification of the TG.

Thiocyanate ion (SCN^-) is well-known as a soft ligand and can strongly coordinate with soft metal ions compared to hard ligands such as chloride ion.⁴⁰ This suggests that if SCN^- can be introduced into the TG in some way, precious metal ions could be adsorbed even in such strong HCl solutions through the ligand-substitution reaction of metal ions with SCN^- in the gel. Based on this idea, we prepared the SCN^- -retaining tannin gel (SCN-TG) by adsorption of SCN^- onto the TG in acidic thiocyanate solutions and then demonstrated that the resultant SCN-TG can adsorb Pd(II) efficiently at molar-level concentrations of HCl.⁴¹

In the present study, we have investigated the adsorption behaviors of Pd(II) and Pt(IV) onto this SCN-TG in a strong HCl solution at different temperatures. Also, we have conducted the adsorption experiments in the mixture solutions of Pd(II) and Pt(IV) at molar-level concentrations of HCl to examine the possibility of the separation of Pd(II) and Pt(IV) by using the SCN-TG.

EXPERIMENTAL

Materials

Wattle tannin powder (condensed tannin molecule) was kindly supplied by Mitsubishi Nuclear Fuel Co. (Tokyo, Japan), and all other reagents were of analytical grade. The stock solutions of palladium, platinum, and thiocyanate ion were prepared from palladium(II) chloride (Wako Pure Chemical Industries, Ltd., Osaka, Japan), hydrogen hexachloroplatina-

te(IV) hexahydrate (Wako Pure Chemical Industries, Ltd., Osaka, Japan), and sodium thiocyanate (Wako Pure Chemical Industries, Ltd., Osaka, Japan), respectively. Deionized distilled water was used in all procedures, and all reagents were used as received in the present study.

Preparation of tannin gel

The TG was prepared following section 2.1 of Ref. 9. Wattle tannin powder (28 g) was dissolved in 45 mL of 0.25 M NaOH solution, and 6 mL of 37 wt% formaldehyde solution was successively added as a cross-linker. After gelation at 353 K for 12 h, the gel obtained was grinded into small particles and sieved by the screens with mesh sizes of 125 and 250 μm . The gel particles in the fraction of 125–250 μm were washed with distilled water and 0.05 M HNO_3 solution to remove the residual chemicals and finally rinsed thoroughly with distilled water again. The washed gel particles were dried by the freeze-drying method.

Preparation of SCN^- -retaining tannin gel

The SCN-TG was prepared by soaking the TG particles in an acidic thiocyanate solution. Previously, we investigated the introduction mechanism of SCN^- into the TG in detail to determine the optimum procedure for preparing the SCN-TG and found that SCN^- can be adsorbed onto the TG through the electrostatic attraction with the protonated hydroxy groups of the TG under acidic conditions.⁴¹ From the results obtained in this previous study, we determined the optimum procedure for the SCN-TG preparation as follows. The TG particles were added to a vial containing an acidic thiocyanate solution at 2 g-gel/L on a dry basis, where the concentrations of SCN^- and HCl were $[\text{SCN}^-] = 0.01 \text{ M}$ and $[\text{HCl}] = 1 \text{ M}$, respectively. The vial was sealed and then placed in a thermostatic shaker with a sufficient shaking speed at 298 K for 72 h: under this condition, the loading amount of SCN^- was 0.6 mmol/g-dry gel.⁴¹

Adsorption experiments

All adsorption experiments in the present study were carried out in a batch system at a specific temperature, and the SCN-TG was used immediately after SCN^- loading without drying: once the SCN-TG was dried, its adsorbability decreased because of the precipitation of a thiocyanate salt on the gel surface.⁴¹ For the adsorption experiments in the single metal ion systems, the TG or the SCN-TG particles were added to HCl solutions containing Pd(II) or Pt(IV) at 1 g-gel/L, where the initial metal ion concentration, $[\text{Pd}]_{\text{ini}}$ or $[\text{Pt}]_{\text{ini}}$, was 0.0001 M. The

adsorption experiments in the Pd(II)/Pt(IV) mixture system were carried out in the same manner as described above except that the initial metal ion concentrations were $[Pd]_{ini} = 0.0001\text{ M}$ and $[Pt]_{ini} = 0.0001\text{ M}$. During the adsorption experiments, the solution in a sealed vial was vigorously shaken and sampled at different time intervals. After filtration of the gel particles, the metal ion concentrations of the sample solution were measured by an inductively coupled plasma spectrometer (ICPS-8100, Shimadzu, Kyoto, Japan). The amount of the metal ions adsorbed onto the gel was calculated by the mass balance.

In the case of the Pt(IV) adsorption, the experiments were started after the Pt(IV) speciation in the solutions reached the equilibrium state, which was confirmed by no change in the UV-vis spectra measured with a UV-vis spectrophotometer (V-550, JASCO, Tokyo, Japan), because the formation rates of the Pt(IV) complexes are very slow.⁴² Also, the Pt(IV) adsorption experiments were conducted under dark conditions, because the ligand-substitution rates of the Pt(IV) complexes have relatively high photosensitivity.⁴³⁻⁴⁵

One possible problem of the SCN-TG is that SCN^- may be released from the gel to the solution during the metal ion adsorption, because it is retained in the gel only by the electrostatic attraction. In the previous study,⁴¹ however, we confirmed that the amount of SCN^- released from the SCN-TG is negligible small during the metal ion adsorption in strong HCl solutions.

RESULTS AND DISCUSSION

Adsorption behavior of Pd(II) and Pt(IV) in single metal ion system

Enhanced adsorbability by SCN^- loading

Figure 2 shows the adsorption amounts of Pd(II) and Pt(IV) onto the SCN-TG, q , at $[HCl] = 1\text{ M}$ and 298 K , as a function of time t , where the adsorption behaviors for the TG were also shown to clarify the effect of SCN^- loading on the adsorbability of the tannin gels. The TG can never adsorb both Pd(II) and Pt(IV) at $[HCl] = 1\text{ M}$, because at such a high HCl concentration, most Pd(II) and Pt(IV) exist as $PdCl_4^{2-}$ and $PtCl_6^{2-}$, respectively, which are highly unfavorable for the ligand-substitution reaction with the TG as reported in the previous studies.^{7,9,10,39} As for the SCN-TG, on the other hand, both precious metal ions can be adsorbed: the adsorption rate of Pt(IV) is rather slow compared to that of Pd(II) because the formation rates of the Pt(IV) complexes are generally very slow.⁴² This significant improvement in the adsorbability for Pd(II) and Pt(IV) is attributed to the extremely strong complexation of the precious metal ions with SCN^- retained in the gel.

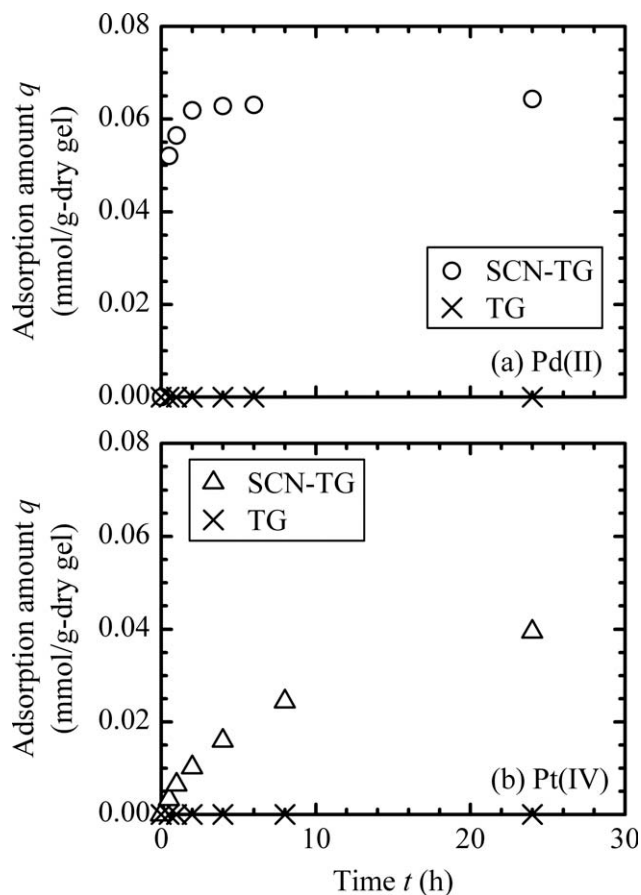


Figure 2 Adsorption amounts of Pd(II) and Pt(IV) onto the SCN-TG and the TG at $[HCl] = 1\text{ M}$ and 298 K , as a function of time: (a) Pd(II) ($[Pd]_{ini} = 0.0001\text{ M}$); (b) Pt(IV) ($[Pt]_{ini} = 0.0001\text{ M}$).

Effect of temperature

In general, temperature is one of the important factors in adsorption processes because it more or less affects the adsorption behaviors. Figure 3 shows the adsorption amounts of Pd(II) and Pt(IV) onto the SCN-TG at $[HCl] = 1\text{ M}$ and different temperatures, as a function of time. The adsorption rate of Pd(II) seemed to increase slightly with increasing temperature, because it is quite fast even at lower temperature. As for Pt(IV), on the other hand, the adsorption rate as well as the adsorption amount seemed to be improved by increasing the temperature. To evaluate the adsorption kinetics quantitatively, we employed the pseudo-second order model, because this model expression provides the well correlation of the experimental data in many cases.^{46,47} The kinetic equation for the pseudo-second order model is represented by

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (1)$$

where k_2 is the pseudo-second order rate constant and q_e is the equilibrium adsorption amount.

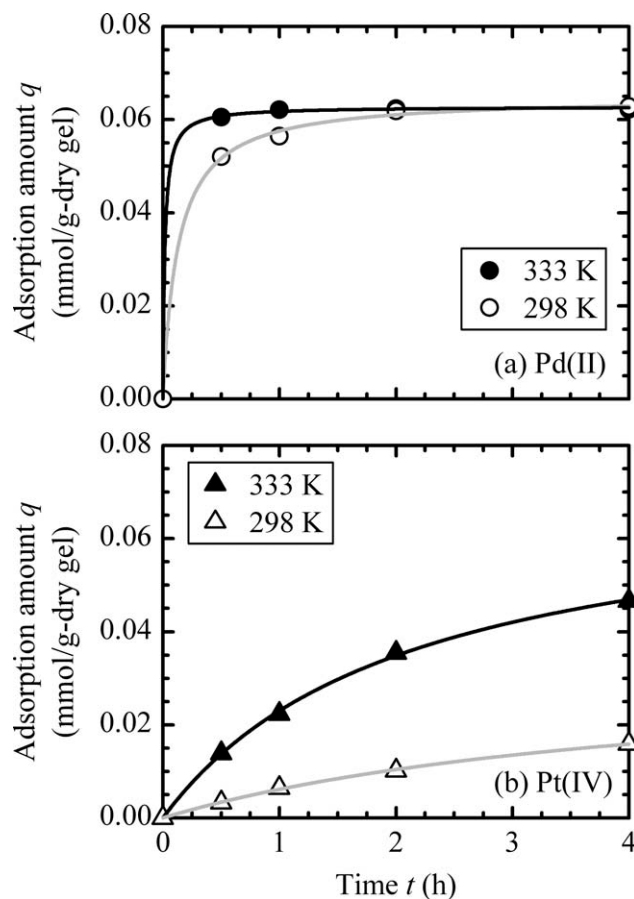


Figure 3 Adsorption amounts of Pd(II) and Pt(IV) onto the SCN-TG at $[HCl] = 1 M$ and different temperatures, as a function of time: (a) Pd(II) ($[Pd]_{ini} = 0.0001 M$); (b) Pt(IV) ($[Pt]_{ini} = 0.0001 M$). The black and gray lines represent fits of the pseudo-second order kinetic model to the experimental data.

Integrating Eq. (1) with the boundary conditions, $t = 0$ to $t = t$ and $q = 0$ to $q = q$, gives

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t \quad (2)$$

Above equation can be written as:

$$q = q_e \left(1 - \frac{1}{1 + k_2 q_e t} \right) \quad (3)$$

We then fitted Eq. (3) to the experimental results to estimate the values of k_2 and q_e as shown in Figure 3. Also, the resultant values and the correlation coefficients R^2 are summarized in Table I. The extremely high values of R^2 demonstrate that the pseudo-second order model adequately describes the adsorption data shown in Figure 3. The rate constant k_2 for the Pd(II) adsorption significantly increases with increasing temperature, while the equilibrium adsorption amount q_e is almost unchanged. As for

TABLE I
Pseudo-Second Order Rate Constants k_2 , Equilibrium Adsorption Amounts q_e , and Correlation Coefficients R^2 for Pd(II) and Pt(IV) Adsorption onto the SCN-TG at $T = 298$ and $333 K$

Ion	T (K)	k_2 (g-dry gel/ mmol h)	q_e (mmol/ g-dry gel)	R^2
Pd(II)	298	120	0.0650	0.9996
	333	948	0.0628	0.9999
Pt(IV)	298	6.69	0.0335	0.9996
	333	6.62	0.0716	0.9996

See also Figure 3.

Pt(IV), the values of k_2 at 298 and 333 K, which are much smaller than those for Pd(II), are similar to each other, whereas q_e greatly increased with increasing temperature.

Adsorption behavior of Pd(II) and Pt(IV) in their mixture solution

Effect of temperature

As is clear from the results in Figures 2 and 3, the adsorbability of Pd(II) onto the SCN-TG is much higher than that of Pt(IV). This implies the possibility that the SCN-TG can adsorb Pd(II) selectively from the mixture solution of Pd(II) and Pt(IV) at molar-level concentrations of HCl. Figure 4 shows the adsorption behaviors of Pd(II) and Pt(IV) onto the SCN-TG in their mixture solution, where $[HCl] = 1 M$ and at different temperatures. At 298 K, the SCN-TG immediately adsorbed Pd(II) from the Pd(II)/Pt(IV) mixture solution, while it adsorbed Pt(IV) slightly and gradually. At 333 K, not only Pd(II) but also Pt(IV) was appreciably adsorbed onto the SCN-TG, compared to that at 298 K. These results suggest that the SCN-TG can roughly separate Pd(II) from the Pd(II)/Pt(IV) mixture solution at 298 K, but adsorbs both Pd(II) and Pt(IV) simultaneously at 333 K, because the adsorbability of Pt(IV) onto the SCN-TG significantly increases with increasing temperature, as also seen in Figure 3(b).

In the single metal ion systems (Fig. 3), as well as the Pd(II)/Pt(IV) mixture system (Fig. 4), the adsorbability of Pt(IV) is significantly decreased with decreasing temperature, while that of Pd(II) is less affected. This indicates that the Pt(IV) adsorption onto the SCN-TG from the Pd(II)/Pt(IV) mixture solution may be inhibited more effectively by lowering the temperature below 298 K, resulting in the improvement in the selective adsorption of Pd(II). Figure 5 shows the adsorption behaviors of Pd(II) and Pt(IV) onto the SCN-TG from their mixture solution at $[HCl] = 1 M$ and 283 K. As expected, the Pt(IV) adsorption was fairly inhibited until ~ 4 h, while the Pd(II) adsorption rate was comparable to

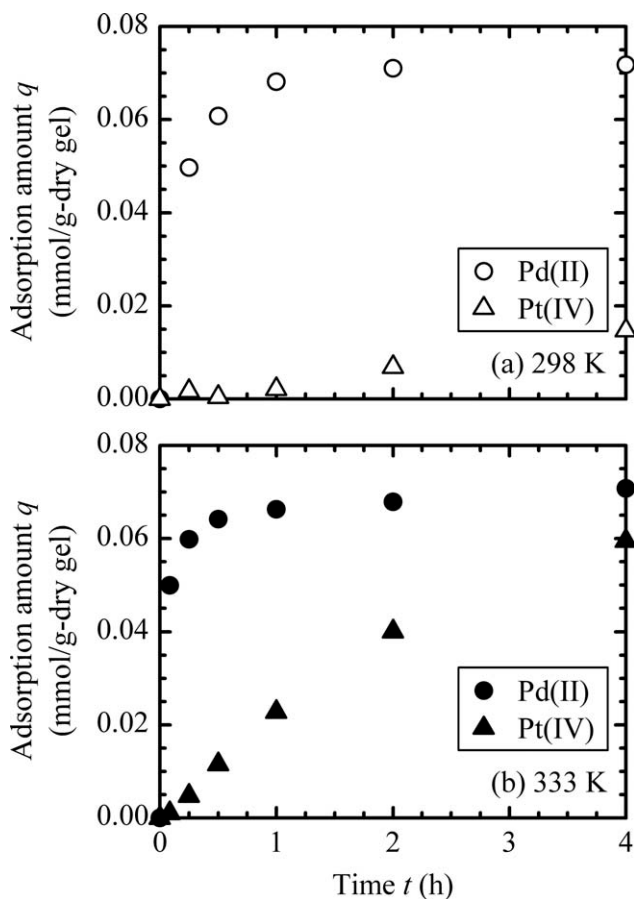


Figure 4 Adsorption amounts of Pd(II) and Pt(IV) onto the SCN-TG in their mixture solution at $[Pd]_{ini} = 0.0001 M$, $[Pt]_{ini} = 0.0001 M$, $[HCl] = 1 M$, and different temperatures, as a function of time: (a) 298 K; (b) 333 K.

those at higher temperatures, demonstrating that the selective adsorption of Pd(II) onto the SCN-TG can be improved at a temperature somewhat lower than room temperature.

Effect of HCl concentration

In hydrometallurgical recovery processes of precious metals, very strong acid is usually used to leach out the precious metal ions from scraps. To examine the feasibility of the SCN-TG for the separation of Pd(II) and Pt(IV) at such strongly acidic conditions, we also performed the adsorption experiments in the Pd(II)/Pt(IV) mixture system at $[HCl] = 5 M$ and 298 K. The resultant adsorption behaviors of Pd(II) and Pt(IV) onto the SCN-TG are shown in Figure 6. Although Pt(IV) was slightly and gradually adsorbed onto the SCN-TG, the SCN-TG preferentially and quickly adsorbed Pd(II), as in the case of $[HCl] = 1 M$ [compared to Fig. 4(a)]: previously, we investigated the Pd(II) adsorption behaviors onto the SCN-TG in the single ion system at $[HCl] = 1-5 M$ and also found that the Pd(II) adsorbability of the

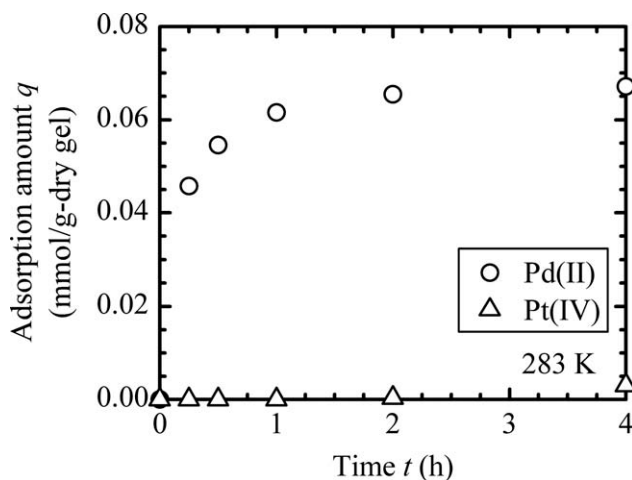


Figure 5 Adsorption amounts of Pd(II) and Pt(IV) onto the SCN-TG in their mixture solution at $[Pd]_{ini} = 0.0001 M$, $[Pt]_{ini} = 0.0001 M$, $[HCl] = 1 M$, and 283 K.

SCN-TG barely decreases with increasing HCl concentration.⁴¹ This indicates that the SCN-TG can be used for at least the rough separation of Pd(II) from the Pd(II)/Pt(IV) mixture solution even at such a high HCl concentration.

CONCLUSION

In the present study, we have investigated the adsorption behaviors of Pt(II) and Pd(IV) in strong HCl solutions at different temperatures using the SCN-TG and then drawn the following conclusions.

1. Although the adsorption rate of Pt(IV) is rather slow compared to that of Pd(II), the SCN-TG can adsorb both Pd(II) and Pt(IV) in a 1 M HCl solution at 298 K, where the TG can never adsorb them.

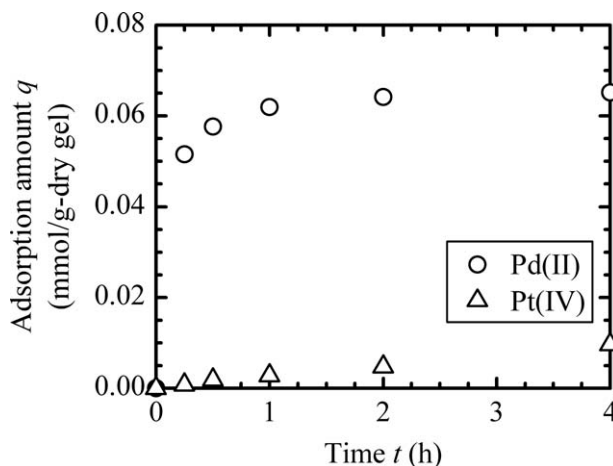


Figure 6 Adsorption amounts of Pd(II) and Pt(IV) onto the SCN-TG in their mixture solution at $[Pd]_{ini} = 0.0001 M$, $[Pt]_{ini} = 0.0001 M$, $[HCl] = 5 M$, and 298 K.

2. The adsorbability of Pt(IV) increase considerably with increasing temperature, while that of Pd(II) is less affected by temperature.
3. Pd(II) can be selectively adsorbed onto the SCN-TG from the mixture solution of Pd(II) and Pt(IV) at 1 M HCl and 283 K, while not only Pd(II) but also Pt(IV) is more or less adsorbed at higher temperatures.
4. The SCN-TG can be used for the rough separation of Pd(II) from the Pd(II)/Pt(IV) mixture solution even at 5 M.

Y.-H.K. and S.Y. designed and performed the experiments; S.M., Y.-H.K., S.Y., and T.O. analyzed the data; S.M. and Y.N. supervised the project; S.M. and T.O. prepared the manuscript.

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