

Adsorption Recovery of Rhodium(III) in Acidic Chloride Solutions by Amine-Modified Tannin Gel

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ABSTRACT: A tannin gel (TG), synthesized from condensed tannin molecules, has the remarkable ability to adsorb various metal ions in aqueous solutions. In the present study, the adsorption behavior of rhodium ion [Rh(III)] in acidic chloride solutions was investigated using an amine-modified tannin gel (ATG) prepared by the ammonia treatment of a TG. The ATG was able to adsorb Rh(III) in strong hydrochloric acid solutions, whereas the TG failed to adsorb it. This is because the amino group in the ATG can form a stable complex with Rh(III) compared to the hydroxy group. With increasing chloride ion concentration, the adsorption amount of Rh(III) onto the ATG decreased somewhat, while

the number of chloride ligands in the Rh(III) complex was expected to increase. This suggests that the Rh(III) complexes with fewer chloride ligands are more favorable for adsorption onto the ATG. Also, the Rh(III) adsorbability of the ATG decreased significantly with decreasing initial pH because of the protonation of the hydroxy and amino groups in the ATG. The results obtained here indicate that in the Rh(III) adsorption onto the ATG, the solution pH is more influential than the chloride ion concentration. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: adsorption; gels; metal–polymer complexes

INTRODUCTION

The recovery of precious metals from electronic and catalyst scraps is highly important from the viewpoint of resource management and security because these materials have been in great demand recently, despite their small recoverable reserves. In the recycling of precious metals from such scraps, hydrometallurgical techniques play a major role.^{1,2} Solvent extraction is one of the most established techniques for metal recovery, and it is especially useful for large-scale operations at high metal-ion concentrations. In contrast, adsorption can be applied to precious metal recovery even from low-concentration sources with relatively simple processes. Particularly, biosorption has attracted considerable interest in the recovery of 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: tannin is an inexpensive and ubiquitous natural polymer extracted from the leaves and bark of plants, and it 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} and toxic ions.^{12–17}

Such tannin-based materials have also been developed by many other researchers.^{18–38}

It is known that the recovery of rhodium (Rh) is usually difficult compared to that of other precious metals, such as palladium (Pd) and platinum (Pt).³⁹ Indeed, we found that the TG can hardly adsorb Rh(III) in acidic chloride solutions, whereas it can adsorb Pd(II) and Pt(IV) under the same conditions.¹⁰ The adsorption of precious metal ions onto TG takes place through the formation of a ligand-substituted metal–tannin complex.⁹ In acidic chloride solutions, the adsorption of metal ions onto TG is strongly affected by the pH and chloride ion concentrations: for example, the Pd(II) adsorbability is very low in strong hydrochloric acid solutions, where the hydroxy groups of the TG compete mainly with chloride ions for complexation with Pd(II).⁷ According to HSAB theory, the complexes between the tannin and soft metal ions, such as precious metal ions, are not strong enough because of the hard O donor of the hydroxy groups in the TG.⁴⁰ Compared to the hydroxy group, an amino group has a higher affinity for precious metal ions because the nitrogen atom is somewhat softer than the oxygen atom. On the basis of this idea, we conducted an ammonia treatment of the TG to introduce amino groups into it and found that the resultant amine-modified tannin gel (ATG) has much better adsorabilities for Pd(II) and Pt(IV) in acidic chloride solutions.^{41,42}

In the present study, therefore, we have investigated the possibility of the Rh(III) adsorption in acidic chloride solutions using the ATG. The Rh(III)

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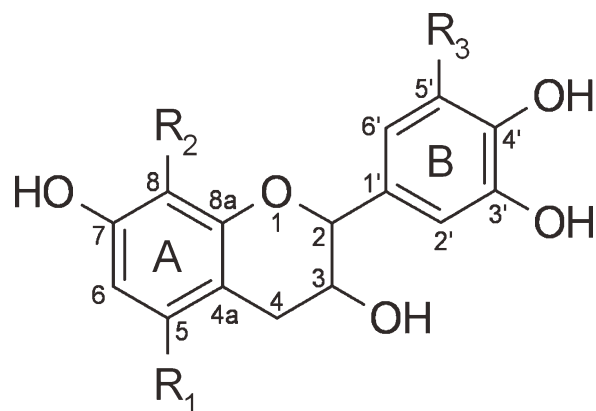


Figure 1 Estimated chemical structure of the condensed tannin molecule: $R_1 = \text{OH}$ and $R_2 = \text{H}$, phloroglucinolic; $R_1 = R_2 = \text{H}$, resorcinolic; $R_1 = \text{H}$ and $R_2 = \text{OH}$, pyrogallolic; $R_3 = \text{H}$, catecholic; $R_3 = \text{OH}$, pyrogallolic.⁶

adsorption onto the ATG in hydrochloric acid at various concentrations has been examined and compared to that onto the TG to demonstrate the effect of the amine modification on the adsorbability for Rh(III). Also, Rh(III) adsorption experiments at various pHs and chloride ion concentrations have been conducted to scrutinize its adsorption mechanism in acidic chloride solutions.

EXPERIMENTAL

Materials

Wattle tannin powder (condensed tannin molecules) was kindly supplied by Mitsubishi Nuclear Fuel Co., Ltd., and all other reagents were of analytical grade. The stock solution of Rh(III) was prepared from rhodium(III) chloride trihydrate (Wako Pure Chemical Industries, Ltd., Japan). Deionized distilled water was used in all of the procedures, and all of the reagents were used as received in the present study.

Preparation of TG and ATG

The TG was prepared according to a procedure from our previous work.⁹ Wattle tannin powder (28 g) was dissolved in 45 mL of a 0.25 M NaOH solution, and 6 mL of 37 wt% formaldehyde solution was successively added as a crosslinker. After gelation at 353 K for 12 h, the obtained gel was ground into small particles and sieved by the screens with mesh sizes of 125 and 250 μm . The gel particles in a 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 ATG was prepared according to a procedure from our previous reports.^{41,42} The freeze-dried TG particles were added to a vial containing 10 wt% aqueous ammonia at 50 g-gel/L. The vial was well sealed and then placed in a thermostatic shaker with

a sufficient shaking speed at 333 K. After 12 h, the ATG particles were washed with 1 M HCl solution until the gel particles contained no ammonium ions, which can be retained in the gel through electrostatic interaction with the deprotonated hydroxy groups of tannin.

In the previous study,⁴¹ we conducted the elemental analyses of the TG and the ATG to examine the amount of amino groups in the ATG and found that their nitrogen contents are about 0.4 and 3%, respectively. Because of the complicated chemical structure of the tannin extract, it is very difficult to discuss the elemental analysis data. Wattle tannin extract consists of two major types of flavanoid units, that is, resorcinol A and pyrogallol B rings (ca. 70%) and resorcinol A and catechol B rings (ca. 25%), and two minor types of flavanoid units (ca. 5%), phloroglucinol A and pyrogallol B rings and phloroglucinol A and catechol B rings (see Fig. 1).^{18,43} In addition, only the flavanoids with the pyrogallol type B ring can be modified by ammonia treatment, whereas the rest of the flavanoids never react with ammonia.⁴⁴ On the basis of these results, the nitrogen content in the ATG, about 3%, was found to be close to the estimated maximum of the nitrogen content. Also, we previously measured the solid-state CP/MAS ^{13}C -NMR spectra of the TG and the ATG and confirmed that the hydroxy group at the C-4' position in the pyrogallol B ring is substituted by the amino groups through the ammonia treatment.⁴²

Adsorption experiments

All adsorption experiments in the present study were carried out in a batch system at a specific temperature. The TG or the ATG particles (1.0 g, dry basis) were added to 50 mL of Rh(III) solutions at hydrochloric acid concentrations of 0.1–5.0 M, where the initial Rh(III) concentration ($[\text{Rh}]_{\text{ini}}$) was 100 ppm. The solution in a sealed vial was vigorously shaken in a water bath at 313 K and sampled at different time intervals. After the filtration of the gel particles, the Rh(III) concentration of the sample solution was measured by an inductively coupled plasma spectrometer (ICPS-8100, Shimadzu, Japan). The amount of Rh(III) adsorbed onto the gel was calculated by the mass balance. Likewise, the Rh(III) adsorption behavior for the ATG was examined at different initial pHs and total chloride ion concentrations ($[\text{Cl}_{\text{tot}}]$), where the initial pH, $[\text{Cl}_{\text{tot}}]$, and ionic strength of the solutions were adjusted with HCl, HClO_4 , NaCl, and NaClO_4 .

RESULTS AND DISCUSSION

Enhanced adsorbability by amine modification

To clarify the effect of the amine modification on the Rh(III) adsorbability of the TG, the adsorption

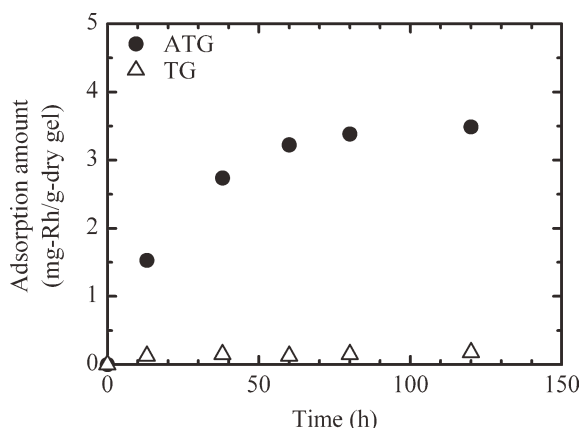


Figure 2 Adsorption amounts of Rh(III) onto the TG and the ATG at $[Rh]_{ini} = 100$ ppm, $[HCl] = 0.1$ M, and 313 K as a function of time.

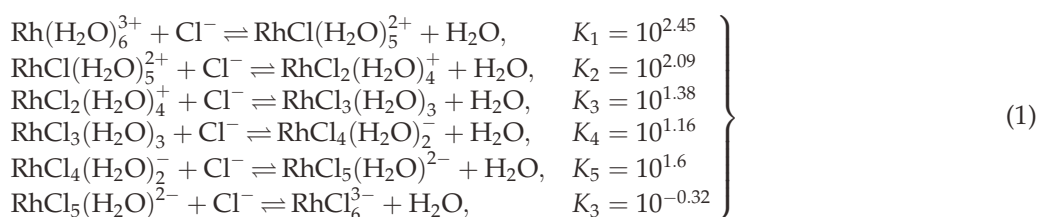
behavior of Rh(III) onto the ATG at $[HCl] = 0.1$ M was compared to that onto the TG, as shown in Figure 2. The TG hardly adsorbed Rh(III), as was also observed in the previous work.¹⁰ In contrast, the ATG adsorbed Rh(III) under the same conditions, and the adsorption amount reached its equilibrium value at around 100 h: this demonstrates that the Rh(III) adsorbability of the TG can be improved dramatically by amine modification. As mentioned in the Introduction, the affinity of the amino group for precious metal ions is higher than that of the hydroxy group, according to HSAB theory.⁴⁰ This results in the formation of a fairly stable Rh(III)–tannin complex on the ATG compared to the TG.

Accordingly, the adsorbability of Rh(III) onto the ATG was much better than that onto the TG.

Figure 3 shows the Rh(III) adsorption behavior onto the ATG at $[HCl] = 0.1$ – 5.0 M. Although the adsorption amount of Rh(III) onto the ATG decreased with increasing $[HCl]$, the ATG was able to adsorb Rh(III) even at $[HCl] = 5.0$ M, where almost no Rh(III) was adsorbed onto the TG (data not shown). Our previous studies demonstrated that the adsorption behaviors of other precious metal ions onto tannin gels were significantly affected by the concentrations of both hydrogen and chloride ions.^{8,9,42} To clarify the adsorption mechanism of Rh(III) onto the ATG, therefore, we separately investigated their influence on the Rh(III) adsorption behavior, as discussed in the following sections.

Rh(III) complexes in acidic chloride solutions

In general, metal ions in acidic chloride solutions form different types of complexes depending on the concentrations of the hydrogen and chloride ions. As for Rh(III) in solutions at pH values below 3, the following seven complexes are formed depending only on the chloride concentration:³⁹ $Rh(H_2O)_6^{3+}$, $RhCl(H_2O)_5^{2+}$, $RhCl_2(H_2O)_4^+$, $RhCl_3(H_2O)_3$, $RhCl_4(H_2O)_2^-$, $RhCl_5(H_2O)^{2-}$, and $RhCl_6^{3-}$. Because the type of the metal-ion complex greatly affects its adsorption behavior, we calculated the mole fractions of the chloroaqua complexes of Rh(III) as a function of $[Cl_{tot}]$ using the following stability constants:^{39,45}



The resultant values are shown in Figure 4, where the water molecules were omitted for clarity. The mole fractions of the Rh(III) complexes change considerably according to $[Cl_{tot}]$. The predominant species of the Rh(III) complex at lower $[Cl_{tot}]$ values are Rh^{3+} , $RhCl^{2+}$, and $RhCl_2^+$, whereas those at higher $[Cl_{tot}]$ values are $RhCl_5^{2-}$ and $RhCl_6^{3-}$, indicating that the number of chloride ligands in the Rh(III) complex increases with increasing $[Cl_{tot}]$.

Effect of Cl^- concentration on Rh(III) adsorption

The adsorption behavior of Rh(III) onto the ATG at different values of $[Cl_{tot}]$ is shown in Figure 5, where

the initial pH was 2 and the ionic strength was 1. The adsorption amount of Rh(III) onto the ATG somewhat decreased with increasing $[Cl_{tot}]$. As mentioned in the previous section, the number of chloride ligands in the Rh(III) complex increases with increasing $[Cl_{tot}]$ (see Fig. 4), suggesting that the Rh(III) complexes with fewer chloride ligands are more favorable for adsorption onto the ATG through the ligand-substitution reaction. The same tendency was found in the adsorption behaviors of Pd(II) and Pt(IV) onto an ATG, although their adsorption amounts decreased more drastically with increasing $[Cl_{tot}]$.⁴²

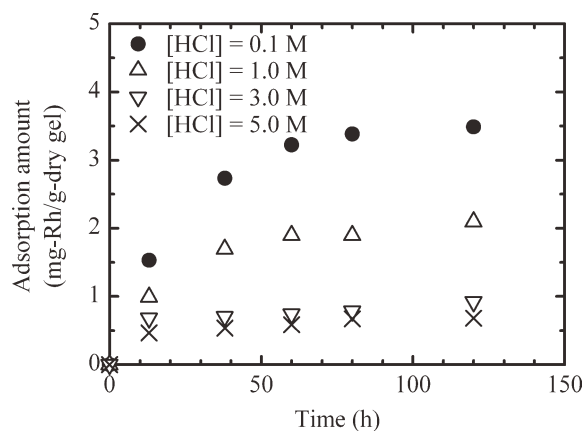


Figure 3 Adsorption amounts of Rh(III) onto the ATG at $[\text{Rh}]_{\text{ini}} = 100$ ppm, 313 K, and different values of $[\text{HCl}]$ as a function of time.

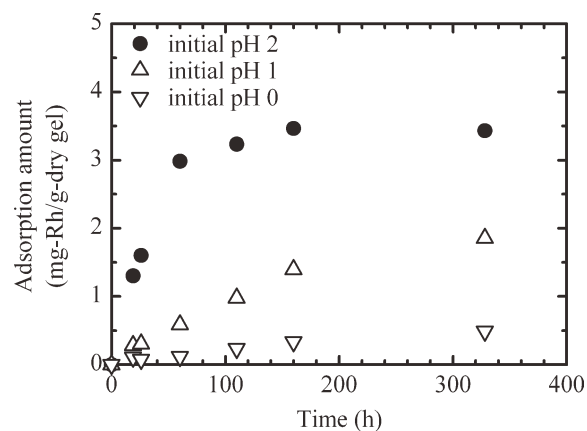


Figure 6 Adsorption amounts of Rh(III) onto ATG at $[\text{Rh}]_{\text{ini}} = 100$ ppm, $[\text{Cl}_{\text{tot}}] = 0.01$ M, 313 K, ionic strength 1, and different initial pHs as a function of time.

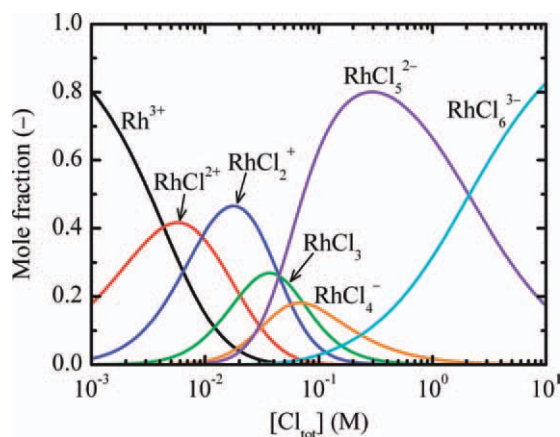


Figure 4 Mole fractions of Rh(III) chloroaqua complexes in aqueous solutions at $\text{pH} < 3$ as a function of $[\text{Cl}_{\text{tot}}]$. Water molecules were omitted for clarity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

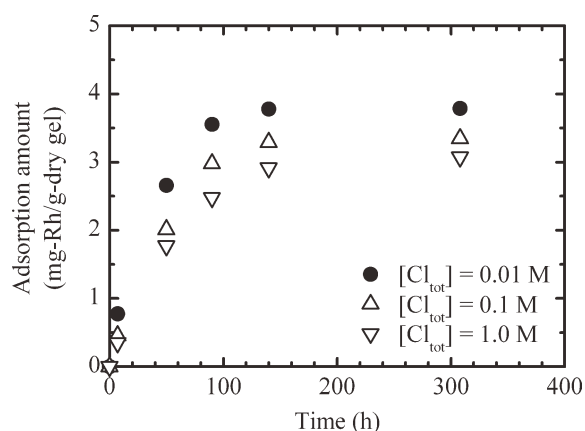


Figure 5 Adsorption amounts of Rh(III) onto the ATG at $[\text{Rh}]_{\text{ini}} = 100$ ppm, initial pH 2, 313 K, ionic strength 1, and different values of $[\text{Cl}_{\text{tot}}]$ as a function of time.

Effect of pH on Rh(III) adsorption

The adsorption amounts of Rh(III) onto the ATG at $[\text{Cl}_{\text{tot}}] = 0.01$ M, ionic strength 1, and different initial pHs are shown in Figure 6 as a function of time. With decreasing initial pH, the Rh(III) adsorption amount onto the ATG significantly decreased. Although the adsorption amount also decreased with increasing $[\text{Cl}_{\text{tot}}]$, as shown in Figure 5, the initial pH was much more influential in the Rh(III) adsorption onto the ATG. As mentioned previously, the mole fractions of the Rh(III) complexes are independent of the solution pH. This indicates that there must have been other factors causing the pH dependence of the Rh(III) adsorption onto the ATG. In a previous study,¹⁶ we investigated the pH dependence of the zeta potential of the ATG and found that the protonation of the hydroxy and amino groups in the ATG proceeds with decreasing solution pH, which leads to a decrease in the complexation ability with precious metal ions. Additionally, the predominant Rh(III) complexes at $[\text{Cl}_{\text{tot}}] = 0.01$ M are RhCl^{2+} and RhCl_2^+ , which are unfavorable for adsorption onto the ATG at lower pHs because of the electrostatic repulsion between these cationic complexes and the protonated hydroxy and amino groups. For these reasons, the Rh(III) adsorption amount onto the ATG decreased markedly with decreasing initial pH.

CONCLUSIONS

We investigated the adsorption behavior of Rh(III) onto the ATG in acidic chloride solutions and then reached the following conclusions.

1. The ATG can adsorb Rh(III) in strong hydrochloric acid solutions, where the TG can hardly adsorb it. This is because the amino groups in the ATG can form a much more stable complex

with the precious metal ions compared to the hydroxy groups.

2. With increasing $[Cl_{tot}]$, the adsorption amount of Rh(III) onto the ATG somewhat decreases, and the number of chloride ligands in the Rh(III) complex is expected to increase. This indicates that the Rh(III) complexes with fewer chloride ligands are more favorable for adsorption onto the ATG.
3. The adsorbability of the ATG for Rh(III) decreases with decreasing initial pH because the protonation of the hydroxy and amino groups in the ATG proceeds.
4. In the Rh(III) adsorption onto the ATG, the initial pH is much more influential than the chloride ion concentration under the conditions investigated in the present study.

Considering that the tannin is an inexpensive and environmentally friendly polymer, we regard the ATG as a promising adsorbent for the recovery of Rh(III) from acidic chloride solutions. To use the ATG in the recovery process of precious metals, however, the adsorption properties of the ATG in their mixture solutions should be also investigated, which we will do in the near future.

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