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Effect of Br^- on the Adsorption Rate of Palladium(II) Ions onto Condensed-Tannin Gel in Chloride Media

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Abstract: In chloride media, chloropalladium(II) species are adsorbed onto tannin gel particles through an inner-sphere redox reaction mechanism containing the intermediate step, formation of a ligand-substituted Pd(II)-tannin complex. In this Pd(II) adsorption process, it was observed that the adsorption rate can be increased by introducing Br^-, a softer ligand than Cl^-, into the aqueous chloride solution. The formation of mixed-ligand palladium(II) complexes accelerates the rate of ligand-substitution reactions with the hydroxyl groups of tannin gel by the trans effect. The adsorption condition can be optimized by controlling the $[Br_{tot}]/[Cl_{tot}]$ ratio, in which the predominant Pd(II) species are bromo-chloro palladium(II) complexes, the favorable species for the trans effect.

Keywords: Adsorption, palladium(II), tannin gel, trans effect

INTRODUCTION

Palladium has been recently in great demand in various industrial fields, such as catalysts, electronic devices, and chemicals. Because of the small amount of deposits, various methods have been investigated to recover palladium from the wastes, such as spent catalysts and scraps (1).

Tannin gel, synthesized from condensed tannin, which is a ubiquitous and inexpensive natural material, has been reported to have a high

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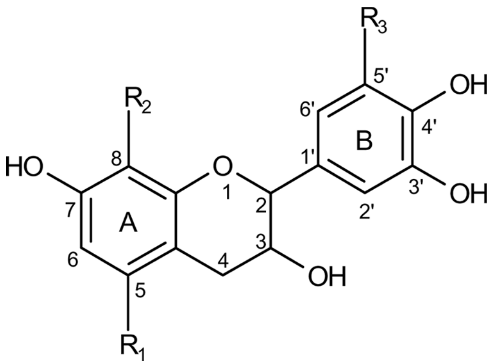


Figure 1. Chemical structure of condensed tannin: flavan-3-ol unit of condensed tannins (to A-ring: $R_1 = OH$, $R_2 = H$, phloroglucinolic; $R_1 = R_2 = H$, resorcinolic; $R_1 = H$, $R_2 = OH$, pyrogallolic. To B-ring: $R_3 = H$, catecholic; $R_3 = OH$, pyrogallolic) (8).

affinity for heavy metal ions such as Cr^{6+}, Pb^{2+}, Ag^+, and Au^{3+} (2,3,4,5). This is ascribed to polyhydroxyphenyl groups such as pyrocatechol and pyrogallol contained in the chemical structures, as shown in Fig. 1. The polyhydroxyphenyl groups of the B-ring can act as an adsorption sites for metal ions through electrostatic interaction (3), complexation (6) and redox-induced adsorption (5,7).

In our previous papers (9,10), we reported that in chloride media, Pd(II) ionic species are adsorbed as a reduced metallic form onto the tannin gel particles through an inner-sphere redox reaction mechanism: two-electron transfer from tannin gel to chloro-palladium(II) ionic species (reaction step (b) in Eq. (1)), accompanied by ligand substitution between chloro-palladium(II) ionic species and hydroxyl groups of tannin gel (reaction step (a) in Eq. (1)).

$$2R-OH + PdL_4 \overset{(a)}{\rightleftarrows} (R\text{–}\overset{H}{O})_2\, Pd_{ls}L_2 + 2L \overset{(b)}{\rightleftarrows} (R = O)_2 \bullet Pd_{re} + 2H^+ + 4L \qquad (1)$$

2R–OH: Adsorption site (hydroxyl groups of tannin gel)
R=O: Oxidized state of R–OH
L: Ligand of Pd(II) complex (Cl or H_2O)
Pd_{ls}: Pd(II) ligand-substituted by R–OH
Pd_{re}: Pd(0) reduced by R–OH

In the above Pd(II) adsorption process (Eq. (1)), the Pd(II) adsorbability onto tannin gel decreases with increasing $[Cl_{tot}]$ and Pd(II) is not readily adsorbed at [Cl_{tot}] 1 M and over, where the predominant Pd(II) species is $PdCl_4^{2-}$ (9,10). The chemical forms containing fewer Cl, such as $PdCl^+$ and $PdCl_2$, are more favorable for the adsorption onto the tannin gel particles in comparison with $PdCl_3^-$ and $PdCl_4^{2-}$, which means that low [Cl_{tot}] is an optimum condition for the Pd(II) adsorption by tannin gel particles.

For the Pd(II) recovery, however, the hydrometallurgical process is normally carried out in chloride media, which affects the adsorption rate and adsorption capacity. It is well known that in the solvent extraction of Pd(II), the addition of soft ligands, such as SCN^-, I^- and Br^-, enhances the extraction rate of Pd(II) from chloride solution (11,12).

In the present investigation, it was elucidated that the intermediate step (ligand substitution) of the above Eq. (1) plays an essential role in Pd(II) adsorption, because the ligand substitution rate can be increased by introducing Br^- ion into chloride media. Addition of Br^- ion to Pd(II) chloride solution was found to lead to the formation of bromo-chloro-palladium(II) complexes, more labile species for the ligand substitution with tannin gel than chlorocomplexes because of the trans effect. An increase of the complexation rate of Pd(II) ionic species with the hydroxyl groups of tannin gel can also induce an increase of the consecutive redox reaction rate between tannin gel and ligand-substituted Pd(II), which finally results in an increase of overall Pd(II) adsorption rate.

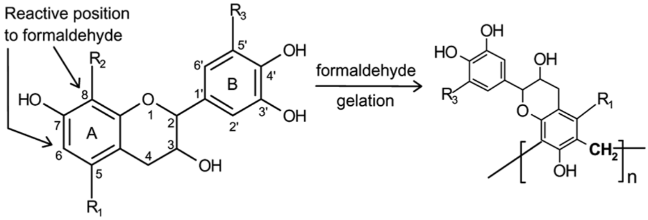
We report here the effect of Br^- addition to the Pd(II) recovery process using tannin gel in chloride media and an optimum condition of [Br_{tot}]/[Cl_{tot}] ratio for efficient Pd(II) recovery.

EXPERIMENTAL

Preparation of Tannin Gel Adsorbent

To overcome the solubility of tannin molecules and apply it as an adsorbent to the Pd(II) recovery process, it was immobilized by gelation. The C6 and C8 positions of condensed-tannin molecules are highly reactive with formaldehyde, because of the strong nucleophilicity of the A-ring, by which the condensed tannin can be gelated with the methylene bridge linkages ($-CH_2-$), as shown in Scheme 1 (13).

Wattle tannin powder (28 g), condensed-type tannin, in 45 mL of 0.25 N NaOH solution was polymerized with formaldehyde (37 wt%, 6 mL), a cross-linking agent, at 353 K for 12 hr. The macroporous tannin gel synthesized in a hermetically sealed container without solvent evaporation, was then grounded into small particles and sieved to a size of 125–250 μm in diameter. The micro-sized tannin gel particles were washed



Scheme 1. Synthesis of tannin gel adsorbent from condensed-tannin by gelation with formaldehyde.

consecutively with distilled water, 0.05 M HNO_3 and distilled water. Finally, the tannin gel particles were kept in a refrigerated storage after freeze-drying. An SEM image of the particle surface is shown in Fig. 2.

Pd(II) Adsorption Experiment

The Pd(II) (10 ppm) solutions were prepared through dissolving palladium(II) chloride ($PdCl_2$) in distilled water. The pH and ionic strength were controlled by HCl, $HClO_4$ and $NaClO_4$, respectively. [Br_{tot}], total Br concentration, and [Cl_{tot}], total Cl concentration, which were controlled by NaBr and NaCl, are essential factors to investigate the trans effect on the ligand substitution between bromo-chloro palladium(II) complexes

Figure 2. SEM image of the tannin gel particle surface.

and hydroxyl groups of tannin gel. In this study, sum of $[Br_{tot}]$ and $[Cl_{tot}]$ was kept constant and the common logarithm of the $[Br_{tot}]/[Cl_{tot}]$ ratio, $R_{BC} = \log([Br_{tot}]/[Cl_{tot}])$, was varied to estimate the optimum condition for Pd(II) adsorption.

All adsorption experiments (Pd 10 ppm, 50 mL) were carried out in a batchwise system whose temperature was kept at 333 K in temperature-controlled bath. After sampling for the initial Pd(II) concentration, the tannin gel particles (1 g/L) were added to the Pd(II) solution. During the adsorption experiment, the solution was shook at enough speed to be well-mixed and sampled at different time intervals. The concentration of samples was measured by inductivity coupled plasma spectrometer (ICPS-8100, Shimadzu).

RESULTS AND DISCUSSION

The chemical form of Pd(II) ionic species in the mixed-ligand system of Cl^- and Br^- is one of important clues to understand the effect of Br^- addition on Pd(II) adsorption in chloride media. Figure 3 shows the distribution of bromo-chloro-palladium(II) ionic species determined as a function of R_{BC} ($= \log([Br_{tot}]/[Cl_{tot}])$) at Pd 10 ppm and $[Cl_{tot}] + [Br_{tot}] = 1$ M, using the stability constants of Pd(II) complexes coordinated with Cl and Br (Table 1).

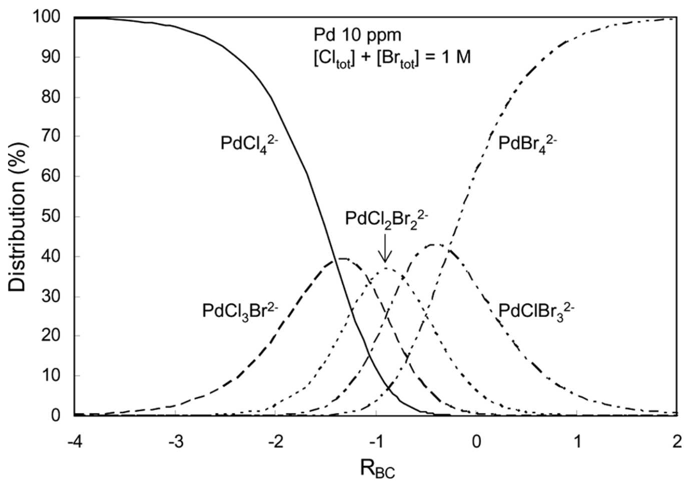


Figure 3. Distribution of bromo-chloro-palladium(II) ionic species, $PdCl_{4-n}Br_n^{2-}$ (n = 0, 1, 2, 3, 4), determined as a function of R_{BC} at Pd 10 ppm and $[Cl_{tot}] + [Br_{tot}] = 1$ M.

Table 1. Stability constants of bromo-chloro palladium(II) complexes, $PdCl_{4\text{-}n}Br_n^{2-}$, in aqueous solution. β_n is an overall stability constant at equilibrium (14).

$PdCl_4^{2-} + nBr \rightleftarrows PdCl_{4-n}Br_n^{2-} + nCl^-(n = 1,\ 2,\ 3,\ 4)$
$\beta_1 = 10^{1.4}$
$\beta_2 = 10^{2.46}$
$\beta_3 = 10^{3.18}$
$\beta_4 = 10^{3.45}$

As shown in Fig. 3, the distribution of Pd(II) ionic species can be varied with a small amount of Br^-, because it has a higher affinity to soft acidic Pd(II) ions than Cl^-. It is assumed that the Pd(II) adsorbability onto tannin gel particles depends on the Pd(II) speciation affected by R_{BC} value, because the adsorbabilities of Pd(II) species are expected to differ from each other due to their different chemical structure.

To investigate the influence of $[Br_{tot}]$ on Pd(II) adsorption onto tannin gel in chloride media, the R_{BC} value was controlled as -2, -0.95, -0.37 and 3 at pH 2, $[Cl_{tot}] + [Br_{tot}] = 1$ M. The time history of Pd(II) adsorption is shown in Fig. 4, along with the result of a control

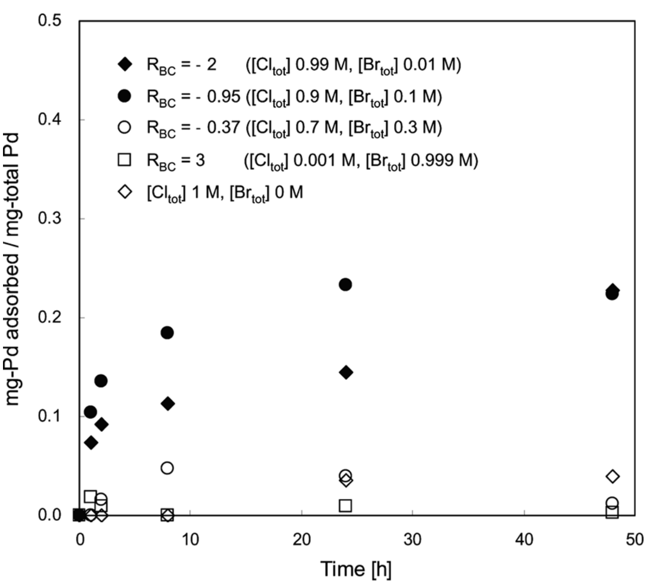


Figure 4. Pd (II) adsorption behavior at Pd 10 ppm, tannin gel particles 1 g/L, pH 2, ionic strength 1, 333 K and various R_{BC} ($[Cl_{tot}] + [Br_{tot}] = 1$ M).

test obtained at $[Br_{tot}] = 0\,M$. The Pd(II) adsorption rate was enhanced in the mixed-ligand system of Cl^- and Br^-, especially at R_{BC} -0.95 where the predominant Pd(II) species is $PdCl_2Br_2^{2-}$ as shown in Fig. 3. However, in the single-ligand system where only single-ligand Pd(II) complex, $PdCl_4^{2-}$ (at $[Cl_{tot}]$ 1 M, $[Br_{tot}]$ 0 M) or $PdBr_4^{2-}$ (at R_{BC} 3), exists in solution, Pd(II) was little adsorbed with a low adsorption rate.

The enhanced adsorption rate in the mixed-ligand system can be explained by the trans-effect of bromo-chloro palladium(II) complexes on the ligand-substitution step of Eq. (1). In the square-planar structure of mixed-ligand Pd(II) complexes, the Cl ligands coordinated in trans position of Br ligand, are more easily replaced with the hydroxyl groups of tannin gel than any ligand of single-ligand Pd(II) complexes such as $PdCl_4^{2-}$ and $PdBr_4^{2-}$. $PdCl_2Br_2^{2-}$ is assumed to have the highest reactivity because this species can take cis-conformation.

In addition, it is also suggested that this result is one of the important evidences that support the inner-sphere redox mechanism (Eq. (1)). In the case of outer-sphere mechanism which occurs by collision of the reactants, the diffusion, electric charge and inert complex are important, while coordination, bridging, and labile complex are important in the inner-sphere mechanism. Therefore, the synergistically facilitated ligand-substitution rate by the trans effect can also accelerate the consecutive inner-sphere redox reaction between tannin gel and ligand-substituted Pd(II) (reaction step (b) in Eq. (1)), which finally results in an increased rate of overall Pd(II) adsorption.

The result of Fig. 4 suggests that in the Pd(II) recovery process using tannin gel, the addition of a small amount of bromide into chloride media causes the bromo-chloro palladium(II) complexes to form, by which the adsorption rate can be increased drastically under the condition optimized by R_{BC} value.

The condition of $[Cl_{tot}] + [Br_{tot}] = 1\,M$ is suitable and sufficiently high to verify the trans effect in Pd(II) adsorption mechanism and to confirm which species is the most labile for the ligand-substitution among the species of $PdCl_nBr_{4-n}^{2-}$ (n = 0, 1, 2, 3, 4) without hydrated species. However, the adsorption amount at $[Cl_{tot}] + [Br_{tot}] = 1\,M$ where a large amount of free Cl^- or Br^- ions exists in aqueous solution, is still relatively small because those free ligands compete with the hydroxyl groups of tannin gel for the ligand-substitution of Pd(II) complexes.

In addition to the above results, the relationship between R_{BC} value and adsorption rate under different condition of $[Cl_{tot}] + [Br_{tot}] = 0.1\,M$ where the competing reaction has less effect than that at $[Cl_{tot}] + [Br_{tot}] = 1\,M$, was investigated over the R_{BC} range of -2 to 2.

As shown in Fig. 5, the Pd(II) adsorption behavior influenced by R_{BC} value shows a tendency similar to the result of Fig. 4: the Pd(II)

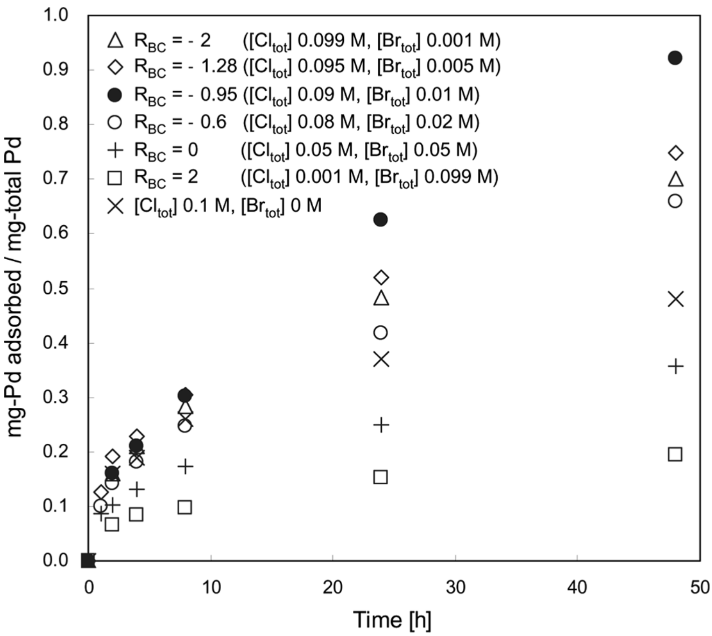


Figure 5. Pd (II) adsorption behavior at Pd 10 ppm, tannin gel particles 1 g/L, pH 2, ionic strength 0.11, 333 K and various R_{BC} ([Cl_{tot}] + [Br_{tot}] = 0.1 M).

adsorption rate can be increased by adding small amount of Br^- into chloride media, which also implies the enhanced Pd(II) adsorption efficiency in the mixed-ligand system of Cl^- and Br^-, especially at R_{BC} -0.95, in comparison to the single-ligand sytem.

It is difficult to discuss the distribution of Pd(II) species at [Cl_{tot}] + [Br_{tot}] = 0.1 M because H_2O is involved as a ligand in the formation of Pd(II) complexes at low [Cl_{tot}] + [Br_{tot}]. Although the still unclear equilibrium state of hydrated bromo-chloro palladium(II) species ($PdCl_xBr_y(H2O)_z^{2-x-y}$, $x + y + z = 4$) might make it difficult to understand which species is the most labile, however, even at low [Cl_{tot}] + [Br_{tot}], the trans-effect of mixed-ligand complexes can also influence the Pd(II) adsorption rate in the ligand-substitution step of Eq. (1), which results in the increase of adsorption rate.

Both results of Figs. 4 and 5 suggest that the R_{BC} value can be an indicator for the optimum condition in Pd(II) recovery processes utilizing the mixed-ligand system of Cl^- and Br^-, which is around -1 under the condition of this study.

CONCLUSION

In Pd (II) adsorption onto tannin gel particles, which proceeds through the inner-sphere redox mechanism, the enhancement of adsorption rate was achieved by introducing Br^- into chloride media. The addition of Br^- leads the bromo-chloro palladium(II) complexes to form in aqueous solution and the rate of ligand-substitution between bromo-chloro palladium(II) complexes and hydroxyl groups of tannin gel is accelerated, which can be explained by the trans-effect. The adsorption condition can be optimized by controlling the $[Br_{tot}]/[Cl_{tot}]$ ratio so that the mixed-ligand palladium(II) complexes, labile for the ligand-substitution reaction with the hydroxyl groups, can form.

By utilizing such characteristics of tannin gel adsorbent and considering the distribution of bromo-chloro palladium(II) complexes, it is expected that they can be applied to recover Pd(II) efficiently and simply with low cost.

REFERENCES

1. Shibata, J.; Okuda, A. (2002) Recycling technology of precious metals. *Shigen-to-Sozai*, *118*: 1. (in Japanese)
2. Nakano, Y.; Takeshita, K.; Tsutsumi, T. (2001) Adsorption mechanism of hexavalent chromium by redox within condensed-tannin gel. *Water Res.*, *35* (2): 496.
3. Zhan, X.; Miyazaki, A.; Nakano, Y. (2001) Mechanisms of lead removal from aqueous solutions using a novel tannin gel adsorbent synthesized from natural condensed tannin. *J. Chem. Eng. Jpn.*, *34* (10): 1204.
4. Nakano, Y.; Miyazaki, A.; Yamazaki, K. (2001) Recovery of silver from metal scraps by gel/liquid extraction. 6th World Congress of Chemical Engineering, Melbourne, Australia, CD-ROM.
5. Ogata, T.; Nakano, Y. (2005) Mechanisms of gold recovery from aqueous solutions using a novel tannin gel adsorbent synthesized from natural condensed tannin. *Water Res.*, *39*: 4281.
6. Beauvais, R.A.; Alexandratos, S.D. (1998) Polymer-supported reagents for the selective complexation of metal ions: an overview. *React. Funct. Polym.*, *36*: 113.
7. Hendrickson, H.P.; Kaufman, A.D.; Lunte, C.E. (1994) Electrochemistry of catechol-containing flavonoids. *J. Pharm. Biomed. Anal.*, *12*: 325.
8. Hemingway, R.W. (1984) *Chemistry and significance of condensed tannins*; Plenum Press: New York.
9. Kim, Y.H.; Nakano, Y. (2005) Adsorption mechanism of palladium by redox within condensed-tannin gel. *Water Res.*, *39*: 1324.
10. Kim, Y.-H.; Nakano, Y. (2007) Kinetic analysis of palladium(II) adsorption process on condensed-tannin gel based on redox reaction models. *Water Res.*, *41* (14): 3043.

11. Al-Bazi, S.J.; Freiser, H. (1986) Trans-effect in extraction kinetics: palladium extraction by 7-(1-vinyl-3, 3, 5, 5-tetramethylhexyl)-8-quinolinol. *Solv. Extr. Ion. Exch.*, *4* (6): 1121.
12. Anticó, E.; Hidalgo, M.; Masana, A.; Salvadó, V.; Valiente, M. (1996) SCN^- effect on the palladium(II) transfer in two and three phases systems using triphenylphosphine sulfide as a carrier. *React. Funct. Polym.*, *28*: 103.
13. Pizzi, A.; Tekely, P. (1995) Mechanism of polyphenolic tannin resin hardening by hexamethylenetetramine: CP-MAS 13C-NMR. *J. Appl. Polym. Sci.*, *56*: 1645.
14. Feldberg, S.; Klotz, P.; Newman, L. (1972) Computer evaluation of equilibrium constants from spectrophotometric data. *Inorg. Chem.*, *11* (12): 2860.