Improvement of Pd(II) Adsorption Performance of Condensed-tannin Gel by Amine Modification

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Condensed-tannin gel adsorbent has been modified through the ammonia treatment to introduce amino groups, which have higher affinity for soft metal ions than hydroxy groups, within the gel structure. This modification resulted in the drastic enhancement of Pd(II) adsorbability in chloride media.

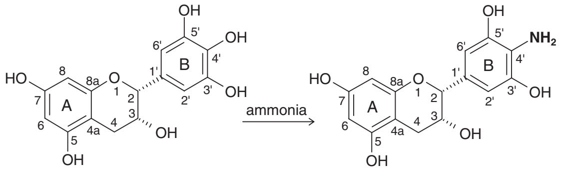
Condensed-tannin gel has been recognized as a ubiquitous and inexpensive natural polymeric-adsorbent for the removal of heavy metal ions (Cr^{6+} and Pb^{2+}) and Se^{4+}, as well as the recovery of precious metal ions (Au^{3+} and Pd^{2+}).[1] In the Pd(II) adsorption, the kinetic and the spectroscopic results provide strong evidence for the formation of ligand-substituted Pd(II)–tannin complex ($R{\cdot}PdL_m$), which is an intermediate during the following reduction-induced adsorption process in chloride media.[1g]

$$R + PdCl_n{}^{2-n} \rightleftharpoons R{\cdot}PdL_m + (4-m)L \rightleftharpoons R'{\cdot}Pd_{re} + 4L + 2H^+ \quad (1)$$

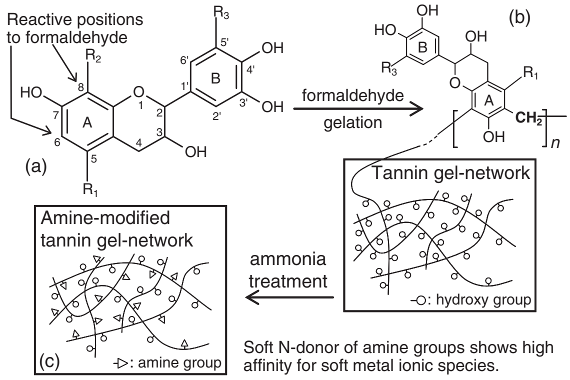
where L denotes the ligand of the Pd(II) complex (Cl or H_2O), the hydroxy groups of the tannin gel with favorable redox potential, R, is oxidized to R′, and Pd(II) is adsorbed as a reduced metallic Pd(0), Pd_{re}, through an inner-sphere redox mechanism.

However, the Pd(II) adsorption onto the tannin gel is affected significantly by pH and pCl: the Pd(II) adsorbability is low at high [HCl], where the redox potential is unfavorable and –OH groups of tannin compete mainly with Cl^- for complexing with Pd(II).[1f] Because of the hard O-donor of tannin, the Pd(II)–tannin complex is not expected to be strong according to the Pearson principle, or HSAB theory.[2] Compared with hydroxy groups, amino groups have higher affinity and selectivity for soft metal ions,[3,4] because the nitrogen atom is a softer base than the oxygen atom, and generally forms a stronger bond with soft acidic precious metal ions such as Pd(II).

It was reported that (−)-epigallocatechin (EGC), a component of the condensed-tannin extract, has a deodorizing activity against amines, such as methylamine, ethylamine, and ammonia, and the reaction product of EGC with ammonia is 4′-amino-4′-deoxy-(−)-epigallocatechin: in this reaction, the C-4′ hydroxy group of EGC is replaced by the amino group, as shown in Scheme 1.[5] Although the mechanism of the above-mentioned ammonia reaction is still unclear, we can expect that the tannin gel with monomeric units similar to EGC can be modified through ammonia treatment, which would result in the conversion to amine-modified tannin gel (ATG), as shown in Scheme 2. From the viewpoint of HSAB theory, the ATG, which has amino groups as well as hydroxy groups within the three-dimensional gel-network structure, is expected to function as a better adsorbent for precious metal ions with respect to kinetics and stability, compared to nonmodified tannin gel (TG).



Scheme 1. Reaction of (−)-epigallocatechin with ammonia to produce amine-modified 4′-amino-4′-deoxy-(−)-epigallocatechin.[5]



Scheme 2. Synthesis of the tannin gel adsorbent (b) from condensed-tannin, flavan-3-ol unit of condensed-tannins (a), and the ATG containing amine groups within its gel-network (c).

For the amine modification, the freeze-dried tannin gel particles (125–250 μm), prepared from Wattle tannin as described in the previous paper,[1g] were soaked in an aqueous ammonia solution at 50 g-gel L^{-1}. All amine modification experiments were carried out in well-sealed glass bottles placed in a thermostatic shaker with sufficient shaking speed. The ATG particles prepared were then washed with 1 M HCl solution until the gel particles contained no ammonium ion, which can be retained in the gel-network through the electrostatic interaction with the deprotonated hydroxy groups of tannin.[6] Absence of the ammonium ion within the prepared ATG was confirmed by the indophenol method. Unlike the ammonium ions, the amino groups incorporated into the tannin gel are never removed and can act as new adsorption sites in hydrochloric acid systems. Finally, the ATG samples were washed with distilled water and kept in refrigerated storage after freeze-drying.

For determining the optimized ammonia treatment that gives the maximum amount of the introduced amino groups, several parameters, that is, the ammonia concentration, the treatment time, and temperature, were varied over the range of 1–25 wt %, 0.5–96 h, and 298–333 K, respectively. To estimate the amount of the amino groups in the ATG samples, we con-

Table 1. Elemental analyses of the tannin molecule (TM), the tannin gel (TG), and the ATGs prepared in 10 wt % aqueous ammonia at 333 K for different treatment times

Sample	Treatment time/h	C/%	H/%	N/%	O/%
TM	—	55.63	4.87	0.45	37.35
TG	—	57.86	5.21	0.44	35.83
ATG-1	0.5	58.45	4.58	2.40	34.08
ATG-2	1	58.39	4.21	2.85	34.54
ATG-3	6	58.92	4.37	3.17	31.35
ATG-4	12	57.93	4.13	3.10	33.84
ATG-5	24	57.96	4.30	3.13	33.95
ATG-6	96	57.53	4.09	3.02	34.27

ducted elemental analysis (MT-5, Yanaco for C, H, N; VTF-900, Leco for O) and found that the ammonia treatment can introduce ca. 3% of nitrogen into the tannin gel. For instance, the elemental analysis data for the different treatment times at 10 wt % aqueous ammonia and 333 K are summarized in Table 1, where the results of the tannin molecule (TM) and the TG are also listed. As expected, the nitrogen content increases with increasing treatment time, and reaches ca. 3% after 6 h. On the other hand, the introduction rate of nitrogen into the gel increased with the ammonia concentration or the treatment temperature, whereas these treatment conditions hardly influenced the maximum nitrogen content in the present study. It should be noted that the oxygen content decreases as the nitrogen content increases as in Table 1, which implies that the hydroxy groups of the tannin gel are replaced by the amino groups during the ammonia treatment.

Due to the complicated chemical structure and the composition of the tannin extract, it is difficult to discuss the elemental analysis data. Wattle tannin extract consists of the 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%), as well as the two minor types (ca. 5%), phloroglucinol A and pyrogallol B rings and phloroglucinol A and catechol B rings.[7,8] In addition, only the flavanoids with the pyrogallol type B-ring, which has the vicinal trihydroxyphenyl group, can be modified by the ammonia treatment (Scheme 1), while the rest of the flavanoids with the catechol type B-ring never react with ammonia.[5] Based on these facts, we considered that the estimated value of the maximum nitrogen content in the ATG, ca. 3%, is reasonable.

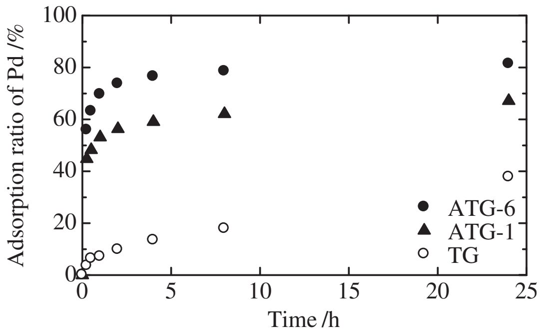


Figure 1. Adsorption ratios of Pd(II) by ATG-1 (2.40% of nitrogen), ATG-6 (3.02% of nitrogen), and TG at Pd 100 ppm, [HCl] = 0.01 M, and 298 K with adsorbent 1 g L^{-1}, as a function of time.

The prepared ATG with the soft amino groups is expected to exhibit an improved adsorption performance for the soft acidic Pd(II) ionic species compared with the TG. The Pd(II) adsorption experiments in aqueous chloride solutions were conducted in a batch system, and the adsorption ratio, $\{([\mathrm{Pd}]_{\mathrm{ini}} - [\mathrm{Pd}]_{\mathrm{obs}})/[\mathrm{Pd}]_{\mathrm{ini}}\} \times 100$, was calculated by mass balance using the initial and the observed Pd(II) concentrations, $[\mathrm{Pd}]_{\mathrm{ini}}$ and $[\mathrm{Pd}]_{\mathrm{obs}}$, determined by inductively coupled plasma spectrometry (ICPS-8100, Shimadzu). The adsorbability of Pd(II) (100 ppm) onto the ATGs (1 g L^{-1}) was investigated at 298 K and [HCl] = 0.01 M, and compared with the result obtained using the TG under the same condition. Figure 1 shows the adsorption ratios of Pd(II) by the two types of the ATGs (ATG-1 and ATG-6 in Table 1) and the TG, as a function of time. Both the ATGs exhibited a significant increase in the Pd(II) adsorbability compared to the TG. Additionally, the enhanced adsorbabilities are different between the ATGs of different nitrogen contents. Not only the adsorption rate but also the adsorption amount can be improved by the amine modification. This is because the high affinity of the amino groups to the Pd(II) ionic species results in a relatively stable metal–amine complex on the ATG in the intermediate step of eq 1.

The ATG prepared by the ammonia treatment of the tannin gel has potential as a novel adsorbent for recovery, removal, and separation of metal ions through complexation and/or the electrostatic interaction. Pd(II) employed in the present study is a good example of soft acidic metal ions, which have a high affinity for soft amine bases and can be separated easily from less soft ones. Furthermore, the redox potential of the ATG, which may be different from that of the original TG, is worthy of detailed investigation and will provide an important information for the more efficient recovery system.

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