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AMINE-MODIFIED TANNIN GEL FOR EFFICIENT Pd(II) RECOVERY FROM AQUEOUS SOLUTION

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Abstract: Condensed-tannin gel has been investigated as a metal adsorbent for the recovery of precious metals from industrial wastes because of the presence of polyhydroxyphenyl groups in their structure. In order to enhance the adsorption properties of condensed-tannin gel, which shows very low adsorption rate and ability to adsorb only at low acidic condition, amine groups have been chemically introduced. Condensed-tannin gel was subjected to aqueous ammonia treatment for the introduction of new amine functional groups into the gel structure. The treatment conditions were optimized for maximum amine incorporation with the help of elemental analysis experiment. SEM photograph represented porous structure of the gel which assures effective mass-transfer performance. A comparison of adsorption kinetics of amine-modified tannin gel (ATG) with those of original tannin gel (TG) showed that ATG is more efficient for the uptake of Palladium(II) from acid solutions.

Keywords: tannin gel, amine-modified tannin gel, Pd(II) recovery, precious metal recovery.

Introduction

Natural condensed-tannins extracted from plants have an intriguing property of high affinity to metal ions that leads scientists to investigate the potential use of this biodegradable and environment friendly compound to remove toxic metal ions (Pb^{2+}, Cr^{6+}, etc) from waste water and recover precious metals (Ag^{+}, Au^{3+}, Pd^{2+}, Pt^{4+}, etc) from industrial wastes [1-6]. Much attempt has already been taken to give the natural tannin compounds proper chemical form in order to overcome their solubility and use in industrial metal recovery process [7,8]. To use these compounds as an adsorbent in hydrometallurgical process, gel phase materials are prepared using formaldehyde as a cross-linker in basic condition. The polyhydroxyphenyl groups of the B-rings of tannin gel (TG) serve as reactive sites for the adsorption process [9,10]. However, tannin gel (TG) showed very low rate and ability to adsorb precious metal ions only at low acidic conditions [11,12]. This restricts the use of tannin gel in industrial recovery process, where highly concentrated acid is used to leach metals out from their wastes. From this perspective, it is necessary to develop some more effective adsorbents able to cope with the real industrial-waste environment. To the best of our knowledge, hardly any effort has been given to modify tannin compounds for the purpose of metal recovery. To develop more efficient and selective recovery, yet biodegradable and environment friendly, we have proposed to incorporate primary amine groups into tannin gel because the amine groups have high affinity and selectivity for precious metal ions based on the approach of hard and soft acids and bases (HSAB)[13]. According to this theory the nitrogen atom of amine groups is relatively softer than oxygen atom and is generally more strongly bound to soft precious metal ions such as Pd(II). Kida *et al.* [14] used (-)-epigallocatechin (EGC), a type of flavanol having trihydroxyphenyl-type B rings, as a model compound for the ammonia reaction and showed that the hydroxyl group of EGC at the C-4 position can be replaced by the

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amino group that is shown in figure 1. Consequently, it is likely to assume that tannin gel bearing monomeric units similar to the EGC can be modified by the treatment with ammonia. This paper describes for the first time how best to introduce the amine groups into tannin gel by ammonia treatment.

The newly prepared ATG in hand, we have furthermore assumed that the amine groups along with the hydroxyl groups of modified tannin gel would function as better adsorbent for precious metals especially Pd(II). Parajuli *et al.* [15] incorporated primary amine and ethylenediamine ligands onto cross-linked lignophenol and showed that the nitrogen-containing soft base compounds have high selectivities to precious metals which are typically soft acids. From these point of view, amine-modified tannin gel (ATG) has been investigated for the precious metal Pd(II) recovery from aqueous solutions and compared with the previous findings using untreated tannin gel (TG).

Materials and Methods

Preparation of tannin gel

Condensed-tannin (28 g) extracted from wattle tree (or commercially mimosa tannin, scientifically *Acacia mearnsii*) was dissolved in 50 mL 0.25 M sodium hydroxide solution at room temperature with constant stirring for 24 h . To the mixture, formalin (37% formaldehyde, 6 mL) was added as a cross-linking agent in basic condition and temperature was gradually raised to 353 K for 12 h in order to facilitate the condensation reaction resulted in polymerization to obtain suitable tannin gel. The tannin gel prepared was sieved to give proper size particles 125-250 µm. Distilled water and 0.05 M nitric acid were used subsequently to remove unreacted reagents or debris.

Preparation of amine-modified tannin gel

The tannin gel particles (containing 70% water) were employed to modify chemically using aqueous ammonia solution with mass concentration of 50 g L^{-1}. All modification experiments were carried out in well-sealed glass bottles placed in a thermostatic shaker with shaking speed 100 min^{-1}. A wide range of preparation parameters were tested to identify factors having the most significant effects on the chemical and physical characteristics of modified tannin gel particles. Variables such as the concentration of ammonia solution, treatment time, temperature and particle size of tannin gel were investigated. Finally the amine-modified tannin gel (ATG) adsorbent was extensively washed with distilled water until it was made sure that the gel particles contain no free ammonia.

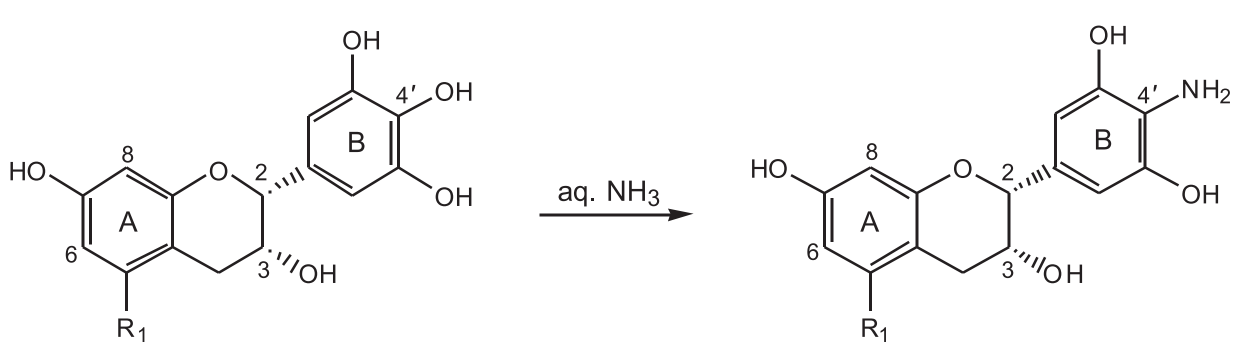


Figure 1. Reaction of Epigallocatechin with ammonia.

Kinetic Studies

Adsorption kinetic studies were conducted batch-wise with ATG (200 mg) in prepared $PdCl_2$ (100 mg L^{-1}, 500 mL) solutions containing in a three necked round-bottomed flask stirred at constant temperature water bath. The Pd(II) concentration of the sampled solutions at different time interval were measured by inductively coupled plasma spectrometer (ICPS-8100, Shimadzu Corp.). The metal ion adsorption capacity of the gel adsorbent was calculated using mass balance calculation.

$$q = \frac{(C_0 - C_e)V}{m}$$

where, *q* is adsorption capacity (mg g^{-1}), C_0 and C_e the initial and final concentrations of metal ion (mg L^{-1}), respectively, V is volume of experimental solution (L) and *m* the mass of the dry tannin gel particles used (g).

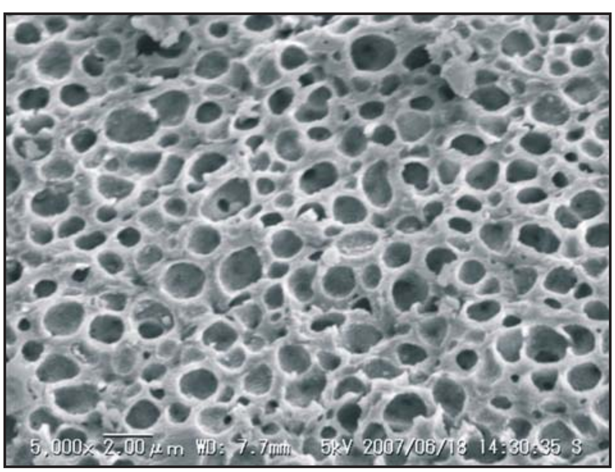
Results and Discussion

Surface analysis

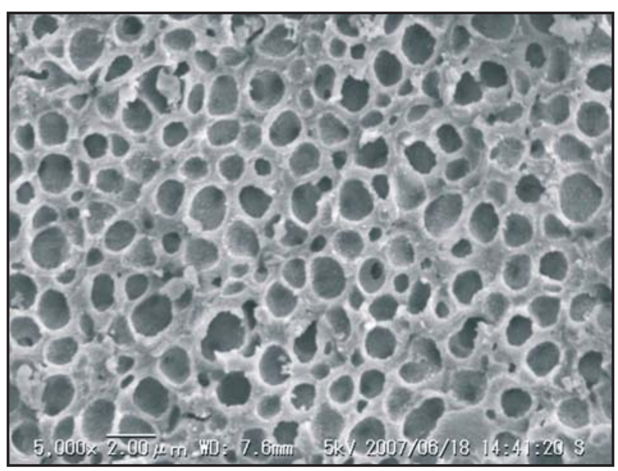
The prepared tannin gel (TG) and amine-modified tannin gel (ATG) were subjected to scanning electron microscopy (SEM), Keyence VE-9800, for surface analysis. Figure 2 shows the structure of TG and ATG. It was clearly observed from the SEM experiment that the gels have porous structure with uniform gel network. This advantageous property gives the gel ability to withstand in highly acidic conditions and vigorous mechanical environment. The interstitial spaces present in the gels, that incorporate solvent in the primary stage, also assure effective mass-transfer performance. Fig. 2 also reveals that the network structure of TG remains intact in ATG after treatment with ammonia solutions.

Elemental analysis

The introduction of nitrogen atom into tannin gel particles was confirmed by elemental analyses of tannin gel (TG) and amine-modified tannin gel (ATG) prepared in different conditions as shown in Table 1. Out of the different parameters considered for the treatment of tannin gel with ammonia, temperature showed marked influence on nitrogen content in the gel structure. The results of elemental analyses made it clear that amine group is present in modified tannin gel and the maximum percent of nitrogen (3.28%) is somewhat low. This is due to the fact that the



2.00 µm
tannin gel (TG)



2.00 µm
amine-modified tannin gel (ATG)

Figure 2. SEM photographs obtained at 5000x magnification, 25 kV voltages and 2 µm scales.

Table 1
Elemental analysis of amine modified tannin gel and untreated tannin gel.

	Preparation conditions				Elemental analysis %			
Sample No.	Treatment time (h)	NH_3 Concentration (%)	Temperature (K)	Particle size (μm)	C	H	O	N
1	**0.5**	10	298	125~250	54.31	4.87	37.72	1.89
2	**1**	10	298	125~250	53.52	4.93	38.03	2.19
3	**3**	10	298	125~250	53.81	4.58	37.28	2.37
4	**7**	10	298	125~250	53.65	4.82	37.3	2.64
5	**24**	10	298	125~250	53.78	4.96	37.44	2.74
6	1	**1**	298	125~250	53.23	4.84	37.58	2.42
7	1	**5**	298	125~250	55.21	4.73	36.41	2.86
8	1	**10**	298	125~250	52.96	4.72	37.44	2.65
9	1	**25**	298	125~250	54.04	4.61	37.15	2.68
10	1	10	**313**	125~250	56.25	5.01	36.23	3.07
11	1	10	**333**	125~250	54.67	5.07	37.3	**3.28**
12	1	10	298	**250~355**	54.03	5.03	37.11	2.43
13	1	10	298	**355~710**	53.63	4.95	37.39	2.24
14	Untreated tannin gel				58.48	5.33	35.99	0.44

Wattle tannins constitute about 70% pyrogallol type B rings [10]. Only those flavanols having pyrogallol type B rings (vicinal trihydroxyphenyl groups) can be modified and the rest of the flavanols having catechol type B-rings do not react with ammonia [14]. The moles of nitrogen per moles of tannin monomer (flavanol unit whose tentative molecular weight is 300) calculated form elemental analyses data indicated that about 70% of the total flavanol rings present in tannin gel can be successfully modified by ammonia. The elemental analyses also helped to determine the optimum condition for the modification reaction. The reaction was carried out for 1 hour at 333 K with 125~250 μm tannin gel particles and 10% aqueous ammonia as the optimum conditions.

Kinetic comparison of ATG and TG

In order to compare the amine-modified tannin gel (ATG) to tannin gel (TG) for Pd(II) recovery from acid solutions (pH close to pH 2), adsorption experiments were carried out keeping all conditions same. Figure 3 shows the time profiles of palladium(II) adsorption by the two

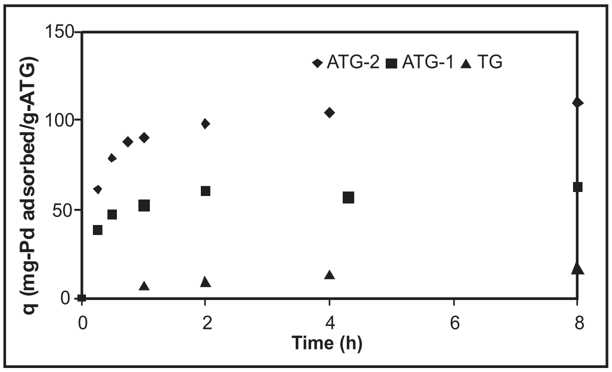


Figure 3. Time profile of Pd adsorption by TG, ATG-1(2.19% N), and ATG-2 (3.28% N).

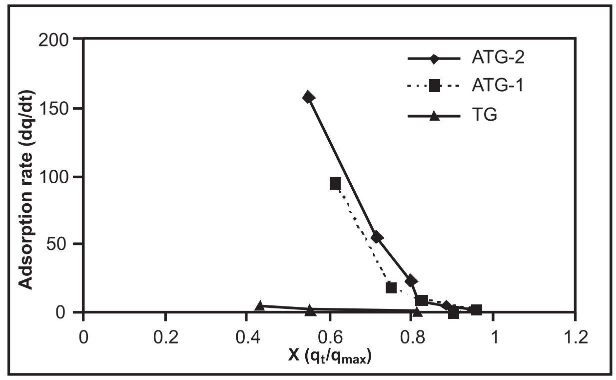


Figure 4. Comparisons between kinetic data of tannin gel (TG) and amine-modified tannin gel (ATG).

types of ATG having different percent of nitrogen (measured by elemental analysis, ATG-1 and ATG-2) in the gel structure and the kinetic data obtained in the previous work using unmodified TG [7].

It is evident that the adsorption of Pd(II) by both of the ATG were very rapid while the TG showed very low adsorption rate under the same conditions. Adsorption equilibriums were reached within two hours for both of the ATG. To give a quantitative explanation the relative adsorption rates of different adsorbents, slopes (dq/dt), which corresponds to the rate, were calculated by using differential method with the help of Least Square Method (LSM) as shown in Figure 4. Both the ATG containing 3.28 percent nitrogen (ATG-2) and 2.19 percent nitrogen (ATG-1) in the gel exhibited intense increase in the rate of adsorption compared to TG under the same conditions. According to this study, the adsorption capacity of TG was found 16 mg g^{-1}, while the capacities of ATG-1 and ATG-2 were 62 mg $g^{-1}$and 110 mg g^{-1}respectively after 8 h adsorption studies. It is worthwhile pointing out that ATG-2 exhibits better performance in adsorption capacity than that of ATG-1. It can be inferred from these data that nitrogen atom introduced into tannin gel contributes to sharp rise in the rate of adsorption and the capacity somewhat depends on the quantity of nitrogen introduced into the gel network. Although the chemical reaction between Pd(II) and TG has already been proposed by Kim *et al.* [11], the interaction pattern with ATG is under study.

Conclusion

Amine groups have been introduced into condensed-tannin gel with the treatment of aqueous ammonia. Although the highest percentage of amine-introduction was achieved at high temperature, the quantity is rather small relative to the hydroxyl groups contained in the tannin gel. The surface of the newly prepared gel was highly porous which is suitable for migration of metal ions in order to reach the active sites for adsorption. The physical structure of tannin gel network was unchanged after ammonia treatment that implies the suitability of the new gel to use in metal recovery from acidic solutions. The introduction of amine groups into tannin gel has significantly enhanced the rate as well as capacity of palladium recovery. This low-cost, easily prepared, biodegradable adsorbent ATG can potentially be used for the recovery of Pd(II) and possibly some other precious metals from aqueous solutions.

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References

1. **Nakano, Y., Takeshita, K. and Tsutsumi, T.** 2001. Adsorption mechanism of hexavalent chromium by redox within condensed tannin gel. *Water Res*. 35: 496-500.
2. **Liao, X., Li, L. and Shi, Bi.** 2004. Adsorption recovery of Thorium(IV) by Myrica rubra tannin and larch tannin immobilized onto collagen fibers. *J. Radioanal. Nucl. Chem.* 260:619-625.
3. **Ma, H., Liao, S., Liu, X. and Shi, Bi.** 2006. Recovery of Platinum(IV) and Palladium(II) by bayberry tannin immobilized collagen fiber membrane from water solution. *J. Membr. Sci*. 278:373-380.
4. **Nakajima, A. and Sakaguchi, S.** 2000. Uptake and removal of iron by immobilized persimmon tannin. *J. Chem. Technol. Biotechnol.* 75:977-982.
5. **Zhan, X., Miyazaki, A. and Nakano, Y.** 2001. Mechanisms of lead removal from aqueous solutions using a novel tannin gel adsorbent synthesized from natural condensed tannin. *J. Chem. Eng. Japan* 34: 1204-1210.
6. **Ogata, T. and Nakano, Y.** 2005. Mechanisms of gold recovery from aqueous solutions using a novel tannin gel adsorbent synthesized from natural condensed tannin. *Water Res*. 39:4281-4286.
7. **Kim, Y.H. and Nakano Y.** 2005. Adsorption mechanism of palladium by redox within condensed-tannin gel. *Water Res*. 39:1324-1330.
8. **Nakano, Y., Tananka, M., Nakamura, Y. and Konno, M.** 2000. Removal and recovery system of hexavalent chromium from waste water by tannin gel particles. *J. Chem. Eng. Japan* 33:747-752.
9. **Özacar, M., Soykan, C. and Şengil, Ì.A.** 2006. Studies on synthesis, characterization, and metal adsorption of mimosa and valonia tannin resins. *J. Appl. polym. Sci.* 102:786-797.
10. **Drewes, S.E. and Roux, D.G.** 1963. Condensed tannins, interrelationships of flavonoid components in wattle-bark extract. *J. Biochem.* 87:167-171.
11. **Kim, Y.H., Ogata, T. and Nakano, Y.** 2007. Kinetic analysis of Palladium(II) adsorption process on condensed-tannin gel based on redox reaction models, *Water Res.* 41:3043-3050.
12. **Ogata, T., Kim, Y. H. and Nakano, Y.** 2007. Selective recovery process for gold utilizing a functional gel derived fro natural condensed tannin. *J. Chem. Eng. Japan* 40:270-274.
13. **Pearson, R.G.** 1963. Hard and soft acids and bases. *J. Am. Chem. Soc*. 85:3532-9.
14. **Kida, K., Suzuki, M., Takagaki, A. and Nanjo, F.** 2002. Deodorizing effects of tea catechins on amines and ammonia. *Biosci. Biotechnol. Biochem.* 66:373-377.
15. **Parajuli, D., Kawakita, H., Inoue, K. and Funaoka, M.** 2006. Recovery of Gold(III), Palladium(II), and Platinum(IV) by aminated lignin derivatives. *Ind. Eng. Chem. Res*. 45:6405-6412.