Persimmon Tannin Gel: Formation by Autoxidation and Caffeine Adsorption Properties

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Persimmon Tannin Gel: Formation by Autoxidation and Caffeine Adsorption Properties

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Water-insoluble gel was prepared from persimmon tannin (PT) solution by the autoxidation process. The gelation reaction proceeded by applying oxygen gas and natural light to the aqueous PT solution, without using harmful reagents or catalysts. Adsorption behavior of the PT gel was assessed using caffeine. Batch adsorption studies were conducted to evaluate the influence of experimental parameters such as contact time, initial concentration of adsorbates, adsorbent dose and temperature. The equilibrium data were analyzed using Freundlich and Langmuir isotherm models. Thermodynamic parameters such as Gibbs free energy, enthalpy, and entropy changes were also calculated, showing that caffeine adsorption on the PT gel is an exothermic process and feasible at lower temperatures. The present results suggest that the PT gel can be used as an effective adsorbent for removing caffeine from solutions.

Keywords: adsorption, autoxidation, caffeine, gel, isotherm, persimmon tannin

Introduction

Tannins are a group of polyphenol compounds that are distributed widely in many plant species, where they serve as defense mechanisms against predators. Persimmon fruits (*Diospyros kaki* L.) are rich in soluble and non-soluble condensed tannins (proanthocyanidins). Low molecular weight soluble tannins are believed to be responsible for the astringency of the persimmon fruit (Matsuo and Ito, 1978). Tannins are also known to form complexes and precipitates with macromolecules, such as proteins and polysaccharides, alkaloids, and heavy metals (Haslam, 1989).

Chemical characterization of persimmon tannin (PT) has long been hampered because of its heterogeneous character and high molecular weight. Matsuo and Ito (1978) first reported on the composition and structure of persimmon condensed tannin. Their proposed structure consists of coupled flavan-3-ols, catechin, catechin-3-*O*-gallate, gallocatechin, and gallocatechin-3-*O*-gallate residues as the repeating units, with a molar ratio of 1:1:2:2, respectively. They also showed

Fig. 1. Proposed PT chemical structure.

R^1 = H or OH
R^2 = H or galloyl
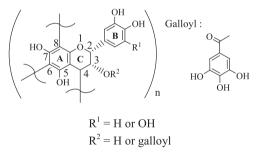
that the PTs are large molecular weight (ca. 13.8 kDa) polymers belonging to the proanthocyanidin B group, with carbon-carbon interflavan linkages between C-4 of one unit and C-8 (or C-6) of another. According to Xu *et al.* (2012), the stereochemistry of the flavan-3-ol unit of the PT is mainly 2,3-cis, which corresponds to epi-type catechins as shown in Fig. 1.

Kaki-shibu, a fermented product made from the juice of immature astringent persimmons, is an important source of condensed tannins traditionally used in tanning paper (fiber hardening) and fishing nets (corrosion prevention), and for removing protein during the brewing of rice wine "*sake*" and soy sauce in Japan (Sugiura and Subhadrabandhu, 1996).

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Various experimental methods have been described for tannin gelation. Most of these involve the use of formaldehyde or other aldehydes in a basic or acidic medium (Nakano *et al.*, 2001; Kim and Nakano, 2005; Tondi *et al.*, 2009), while other researchers have reported on acid gelation (Vázquez *et al.*, 2002, 1994). Recently, we developed a simple and environmentally friendly method for preparing water-insoluble persimmon tannin gels based on commercial *kaki-shibu* without the use of harmful reagents or catalysts (Kunimoto, 2011). Oxygen gas and natural light are applied to the persimmon tannin solution during the gelation process. In the adsorption experiment for green tea components, the gel was found to be selective for caffeine. Green tea contains caffeine and low molecular weight polyphenols, principally catechins. Caffeine is responsible for the stimulating effect of tea, while the health benefits are mainly due to catechins. In recent years, there has been increasing interest in developing an environmentally friendly method for removing caffeine from food products.

In this paper, we report on the preparation and characterization of a PT gel. This PT gel was employed to adsorb caffeine from solutions. The adsorption properties of the PT gel for caffeine were also studied using an equilibrium isotherm study.

Materials and Methods

Materials and reagents   Caffeine was purchased from Nacalai Tesque (Kyoto, Japan). Green tea catechin standards, (+)-catechin (C), (−)-epicatechin (EC), (−)-epicatechin-3-*O*-gallate (ECg), (−)-epigallocatechin (EGC), (−)-epigallocatechin-3-*O*-gallate (EGCg), were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Soluble PT (*kaki-shibu*) was a generous gift from Kakitafu Co. Ltd. (Osaka, Japan). The chemical structure of caffeine and some catechins are shown in Fig. 2. Other chemicals were commercial products of analytical grade. Ultra-pure water (Arium 611UV system, Sartorius, Germany) was used throughout the study.

Preparation of PT gel and adsorbates   The PT gel was prepared by autoxidation process, where the gelation reaction was carried out at room temperature on exposure to natural light and O_2 gas. The soluble PT (500 mL) was place in a 1,000 mL Erlenmeyer flask equipped with a three-way stopcock that was attached a rubber balloon. The flask was kept under the positive pressure of oxygen, by using an oxygen-filled balloon. The start of gelation was observed as an increase in the viscosity of the solution. After the gelation was complete (in 3 weeks), the gelled residue was crushed and washed with water several times until the supernatant was clear. The obtained gel was kept in a brown bottle under a wet condition, and was termed PT gel. The same batch of
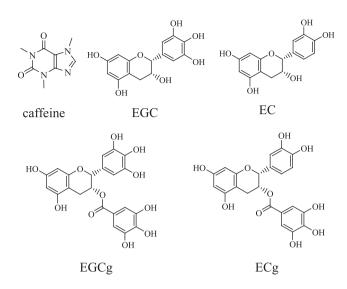

Fig. 2. Chemical structure of green tea components.

PT gel was used in all adsorption experiments.

A stock solution of caffeine (1,000 mg/L) was prepared by dissolving the required amount of caffeine in ultrapure water. The stock solution was diluted with ultra-pure water to obtain the desired concentrations, ranging from 25 to 100 mg/L.

Characterization of PT and PT gel   The molecular weight of the freeze dried sample, obtained from the soluble PT, was determined using a gel permeation chromatography (GPC) instrument (GL-7400 Series, GL Sciences Inc., Japan) with a UV detector. The column used was an Inertsil WP300 Diol ($\phi 4.6 \times 250$ mm, 5 μm; GL Sciences Inc.), protected with a precolumn of the same material. The isocratic method used a mobile phase consisting of *N*, *N*-dimethylformamide (DMF) containing 0.3% (v/v) glacial acetic acid, 1.7% (v/v) water and 0.05 M lithium chloride. The flow-rate was maintained at 0.3 mL/min, and the column temperature was 35°C. The elution was monitored at 280 nm. Calibration curves were constructed using polystyrene standards with molecular weights ranging from 2,000 to 30,000.

The UV-vis absorption spectra were recorded on a Shimadzu UV-2500 spectrophotometer (Shimadzu Corp., Kyoto, Japan) with 2 nm resolution, using quartz cuvettes with 10 mm pathlength. The freeze dried PT sample was used for this measurement.

For infra-red (IR) analysis, the PT gel was dried by vacuum drying. The IR spectrum of the dried gel was recorded on a Horiba FT-720 Fourier transform infrared (FT-IR) spectrometer (Horiba, Kyoto, Japan). FT-IR measurements were carried out by the KBr method at 20 scans per spectrum with 4 cm^{-1} resolution.

Adsorption experiment   The batch method was used to study the adsorption behavior of the PT gel. Adsorption

experiments were conducted to study the effect of contact time, caffeine concentration, gel dose, and temperature. Experiments were carried out in 20mL screw cap tubes by varying the PT gel dose from 0.1 to 2 g per 20 mL caffeine solution and the initial caffeine concentration from 25 to 100 mg/L. The mixture was agitated at 250 rpm at temperatures ranging from 30 to 60°C. Contact time varied from 0 to 30 min. Then, the mixture was centrifuged, filtered and the absorbance of the filtrate was determined by HPLC under the following conditions: column temperature, 40°C; sample volume, 10 μL; mobile phase, methanol/water including 0.2% phosphoric acid 20:80 (v/v); flow rate, 0.8 mL/min; measurement wavelength, 280 nm. The HPLC system consisted of a Shimadzu LC-10ATvp pump, SPD-M10Avp UV detector and CTO-10Avp column oven, and a CAPCELLPAK C18 column (4.6 × 100 mm, 3 μm; Shiseido Co., Ltd., Tokyo, Japan).

All experiments were performed in duplicate. Adsorbed ratio (%) and the amount of caffeine adsorbed on the PT gel, q_e (mg/g), was calculated using the following equations:

$$\text{Adsorbed ratio} = ((C_0 - C_t)/C_0) \times 100 \qquad (1)$$

$$q_e = (C_0 - C_e)V/M \qquad (2)$$

where C_0, C_t, and C_e are the initial, at time t, and equilibrium caffeine concentrations in solution (mg/L), respectively, V is the volume of solution (L), and M is the mass of adsorbent (g). The equilibrium data were analyzed using the Langmuir and Freundlich isotherms, and characteristic parameters for each isotherm were determined.

Results and Discussion

Characterization of PT and PT gel   GPC was used to assess PT size distribution. The chromatogram shows a pronounced peak at approximately 5.31 min (Fig. 3). This peak corresponds to ultra high MWs that exceed the GPC column size exclusion limit of approximately 600,000. Thus, the sample contains very high molecular weight gel components.

Previously, we reported on the UV absorption spectra of green tea catechins and showed that gallated and non-gallated catechins exhibited quite different pH dependence (Okumura *et al.*, 2007). As shown in Fig. 4, on adjusting the solution pH to 10, gallated catechins, such as ECg and EGCg, show intense absorption at 322 nm, whereas non-gallated catechins, such as EC and EGC, show much weaker absorption. We assigned this spectral change to deprotonation of the phenolic hydroxyl group of the galloyl group. PT consists of gallated and non-gallated catechins linked with carbon-carbon linkages between the C-4 carbon of one unit and the C-8 (or C-6) of another unit. It is possible to estimate
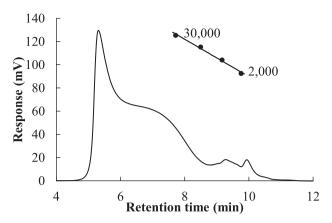

Fig. 3. GPC chromatogram of soluble PT dissolved in DMF (inset: calibration curves of polystyrene standards with molecular weights ranging from 2,000 to 30,000).
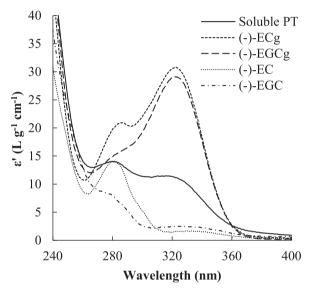

Fig. 4. UV absorption spectra of the soluble PT and green tea catechins.

the content of gallated catechin units in the PT based on their characteristic absorptions at 322 nm. By assuming the absorption coefficient ε' of gallated catechins to be an average of those of ECg and EGCg, we estimated the content of gallated catechins in the PT solution to be 38%.

Fig. 5 shows the IR spectra of the PT gel and the two catechin standards, EGCg and C. The PT gel and EGCg show similar spectral patterns to each other. Thus, the C = O stretching of the gallate group is observed in the 1690 cm^{-1} region. In the 1400 − 1600 cm^{-1} region, the aromatic C = C stretching modes are dominantly observed. The mixed C-O stretching and OH bending vibrations are observed in the 1150 − 1350 cm^{-1} region.

Adsorption properties

a) Adsorption of green tea components   In a preliminary experiment, we tested PT adsorption of green tea components. As shown in Fig. 6, caffeine was adsorbed at about

56%, whereas four kinds of catechins were adsorbed only at 10 − 20%. This result indicates that adsorption of caffeine on the PT gel is much stronger than that of catechins. Caffeine is a typical purine base carrying four basic nitrogens in the heterocyclic ring (Fig. 2). These electron-rich nitrogens may play an important role in the interaction with the PT gel. For catechins, the gallate-type catechins (EGCg and ECg) showed stronger adsorption than the non-gallate type catechins, EC and EGC (Minoda *et al.*, 2010).

b) Effect of contact time and initial concentration on adsorbed ratio of caffeine   Contact time is an important parameter because it determines the rate of adsorbate removal. As shown in Fig. 7, a fast rate of adsorption is found in the first 5 min, while equilibrium was attained in about 15 min. Adsorption is higher in the beginning due to the large surface area of adsorbents available for adsorption of the adsorbates; as these sites become occupied, adsorption became less efficient (Elass *et al.*, 2011).

Figure 8 shows that an increase in initial caffeine concentration decreases the adsorbed ratio slightly. This is due to the increase in the number of caffeine molecules competing for available binding sites on the PT gel. Thus, the available active sites of the PT gel become saturated at higher concentrations of caffeine (Aksu *et al.*, 2010; Kumar *et al.*, 2011).

c) Effect of adsorbent dose   Figure 9 shows that the percentage of caffeine removal varies with varying adsorbent mass and increases with increasing adsorbent dose. The percentage of caffeine removal increases from 15% to 72% with an increase, from 0.1 g to 2 g, in adsorbent dose. This is due to the increase in the number of active adsorption sites available for adsorption.

d) Effect of temperature on adsorbed ratio of caffeine and thermodynamic parameters   Experiments were performed at temperatures ranging from 30 to 60°C. The adsorbed ratio decreased with increasing temperature, from 30 to 60°C, at 25 − 100 mg/L caffeine concentration (Fig. 10). This observation indicates that the adsorption is an exothermic process.

Thermodynamic parameters, such as change in Gibbs free energy (ΔG^o) (kJ/mol), enthalpy (ΔH^o) (kJ/mol) and entropy (ΔS^o) (J/K.mol) were determined using the following equation

$$\ln K = -\Delta G^o/RT = \Delta S^o/(R) - \Delta H^o/(RT) \qquad (3)$$

where K is the equilibrium constant, T is the temperature in Kelvin, R is the gas constant. The values of ΔH^o and ΔS^o were obtained from the slope and intercept, respectively, of Eq. 2. Thermodynamic parameters of adsorption are shown in Table 1.

The ΔG^o for physisorption ranges from −20 kJ/mol to 0 kJ/mol and for chemisorption from −80 kJ/mol to −400 kJ/
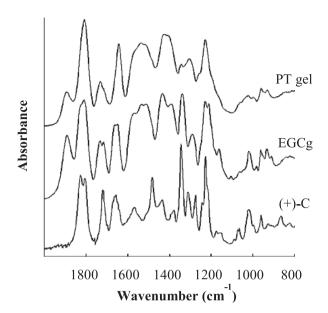

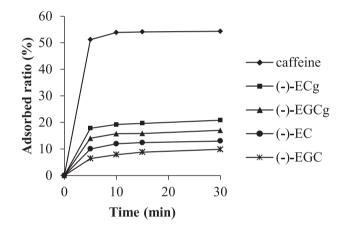**Fig. 5.** IR spectra of the PT gel and catechin standards.

Fig. 6. Adsorption of caffeine and catechins on the PT gel: initial concentration of caffeine and catechins of 100 ppm, gel dose of 1 g/20 mL, contact time of 30 min, temperature of 30°C.
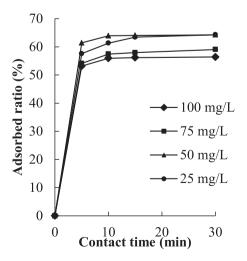

Fig. 7. Effect of contact time on the adsorption of different initial concentrations of caffeine at 30°C and PT gel dose of 1 g/20 mL.

mol (Ye *et al.*, 2011; Allen *et al.*, 2004). The values of ΔG^o shown in Table 1 indicated that the adsorption can be designated as spontaneous physisorption. In addition, the values of ΔG^o reveal that the adsorption is feasible at low temperatures. The ΔG^o for hydrogen bonding and dipole force are 2 − 40 kJ/mol and 2 − 29 kJ/mol, respectively (von Oepen *et al.*, 1991; Doğan *et al.*, 2009; Weng *et al.*, 2009).
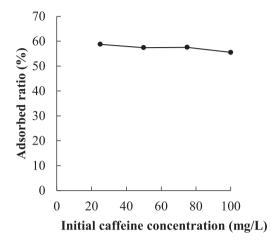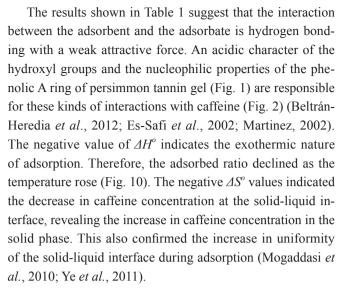
The results shown in Table 1 suggest that the interaction between the adsorbent and the adsorbate is hydrogen bonding with a weak attractive force. An acidic character of the hydroxyl groups and the nucleophilic properties of the phenolic A ring of persimmon tannin gel (Fig. 1) are responsible for these kinds of interactions with caffeine (Fig. 2) (Beltrán-Heredia *et al.*, 2012; Es-Safi *et al.*, 2002; Martinez, 2002). The negative value of ΔH^o indicates the exothermic nature of adsorption. Therefore, the adsorbed ratio declined as the temperature rose (Fig. 10). The negative ΔS^o values indicated the decrease in caffeine concentration at the solid-liquid interface, revealing the increase in caffeine concentration in the solid phase. This also confirmed the increase in uniformity of the solid-liquid interface during adsorption (Mogaddasi *et al.*, 2010; Ye *et al.*, 2011).

e) Adsorption isotherms Plotting q_e vs C_e can be used as a qualitative approach to identify a suitable isotherm model. As shown in Fig. 11, curves were approximately linear. This indicated a constant affinity for a wide range of concentrations of adsorbates along with cooperative adsorption. Langmuir and Freundlich equations are the appropriate model for this adsorption (Hinz, 2001).
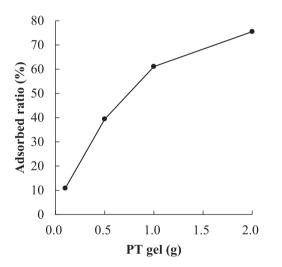

Fig. 8. Effect of initial concentration on caffeine adsorption at 30°C, with a PT gel dose of 1 g/20 mL and contact time of 30 min.

Fig. 9. Effect of PT gel dose on caffeine adsorption at an initial caffeine concentration of 100 mg/L, contact time of 30 min, and temperature of 30°C.
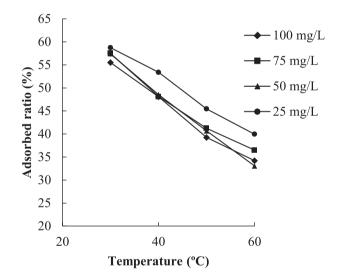

Fig. 10. Effect of temperature on the adsorption of different initial concentration of caffeine, with a PT gel dose of 1 g/20 mL, and contact time of 30 min.

Table 1. Thermodynamic parameters for caffeine adsorption on the PT gel.

C_0 (mg/L)	K				ΔG^o (kJ/mol)				ΔH^o (kJ/mol)	ΔS^o (J/K.mol)
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C		
25	115.2	92.6	67.4	53.8	−12.0	−11.8	−11.3	−11.0	−21.8	−32.4
50	109.0	76.3	55.4	39.9	−11.8	−11.3	−10.8	−10.2	−28.0	−53.3
75	109.5	75.1	56.8	46.5	−11.8	−11.2	−10.8	−10.6	−23.8	−39.9
100	100.9	74.9	52.2	42.0	−11.6	−11.2	−10.6	−10.4	−25.0	−44.3

Fig. 11. Adsorption isotherm of caffeine on the PT gel.

Table 2. Isotherm parameters for caffeine adsorption on the PT gel.

Isotherm model	Parameter	Temperature (ºC)			
		30	40	50	60
Freundlich	n	1.09	1.17	1.19	1.19
	K_F (L/g)	0.87	0.84	0.75	0.69
Langmuir	q_m (mg/g)	65.8	56.7	47.3	43.5
	K_L (10^3 L/mg)	9.36	9.21	8.06	6.92

Langmuir and Freundlich isotherms were used to evaluate caffeine adsorption on the PT gel. The linear form of Langmuir's isotherm model is given by the following equation:

$$1/q_e = 1/(q_m K_L C_e) + 1/q_m \qquad (4)$$

where q_m is the Langmuir constant relating to complete coverage (mg/g), K_L is the Langmuir energy constant, indicating adsorptivity of the solute.

The linear form of the Freundlich isotherm is given by the following equation:

$$\log q_e = (1/n) \log C_e + \log K_F \qquad (5)$$

where n is the Freundlich isotherm constant related to adsorption intensity, K_F is the Freundlich isotherm constant related to adsorption capacity (L/g).

The value of n indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of n is equal to unity, the adsorption process is linear; if the value is below to unity, this implies that the adsorption process is chemical; if the value is above unity, adsorption is a favorable physical process (Kumar *et al.*, 2011).

Fitting the data with the Langmuir and Freundlich equations resulted in high correlation coefficients, varying from 0.991 to 0.999. This indicates that the PT gel surface is homogeneous and coverage of caffeine at the outer surface of the PT gel is a monolayer (Ye *et al.*, 2011; Kumar *et al.*, 2011). The isotherm parameters of adsorption are listed in Table 2. Values of n suggest that the adsorption is physisorption.

The maximum adsorption capacity of a monolayer was 65.8 mg/g for the PT gel. This value is lower than the adsorption of activated carbon (275 mg/g; Sotelo *et al.*, 2012) but higher than the adsorption of NIPAAm-based hydrogels (10.2 − 18.7 mg/g; Chern *et al.*, 2004) and the natural clay adsorbent sepiolite (48.7 mg/g; Sotelo *et al.*, 2013). As shown in Fig. 6, the PT gels showed higher adsorption to caffeine compared to catechins, revealing the possibility of removing caffeine and retaining catechins in food products.

Langmuir constant, K_L, can be used to predict the affinity between adsorbate and adsorbent using separation factor or dimensionless equilibrium parameter, R_L,

$$R_L = 1/(1 + K_L C_0) \qquad (6)$$

The R_L value suggested the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). The R_L was found to be 0.517 to 0.853 for caffeine concentrations of 25 − 100 mg/L and temperatures of 30 − 60°C (Kumar *et al.*, 2011). This indicates a favorable adsorption.

Conclusion

In this study, the PT gel was prepared by autoxidation process. The PT gel contained very high molecular weight gel components, consisting of 35 − 45% gallated catechin units. The PT gel effectively adsorbed caffeine from an aqueous solution.

Adsorption of caffeine on the PT gel was influenced by contact time, initial caffeine concentration, adsorbent dose, and temperature. Equilibrium was reached by 15 min. Adsorbed ratio increased with decreasing caffeine concentration and temperature. In other words, the adsorbed ratio increased with increasing adsorbent dose.

The adsorption isotherms follow both the Langmuir and Freundlich models. The maximum adsorption capacity was found to be 65.8 mg/g. Adsorption of caffeine on the PT gel is favorable physisorption.

The $\varDelta G^o$ and $\varDelta H^o$ values indicated the spontaneous and exothermic nature of adsorption. In addition, the interaction between adsorbent and adsorbate is hydrogen bonding with a weak attractive force.

These data suggest that PT gels can be used as an effective adsorbent to remove caffeine from green tea drinks.

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