Study on adsorption properties of persimmon tannin-based gels for acidic and basic compounds

Dissertation Abstract

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Abstract

This study reported the preparation of persimmon tannin (PT) gel and its application for adsorption of acidic and basic compounds. PTs are water-soluble compounds, which restricts their practical application as adsorbents in aqueous systems. Hence, insolubilization of PT is required in order to overcome this issue.

Water-insoluble gel has been prepared from PT solution by the autoxidation process using oxygen gas and natural light. Adsorption behaviors of the PT gel were tested for caffeine. The present results suggest that the PT gel can be used as an effective adsorbent to remove caffeine in solution.

Gelation also was performed by modification of PT. In this method, two types of PT gels that is formaldehyde-modified (F) PT gel and amine-modified (A) PT gel were prepared, and their adsorption of methylene blue (MB, a basic dye), and Remazol Brilliant Orange 3R (RBO, an acidic dye), in aqueous solution was studied. The result indicated that the FPT gel is shown to be an effective material for adsorbing basic dyes, while the APT gel effectively adsorbs acidic dyes from aqueous solution.

The last, PT was immobilized on cellulose beads and employed to adsorb caffeine in aqueous solution. The test showed that PT immobilized on cellulose beads can be used as an effective adsorbent for removing caffeine from solutions.

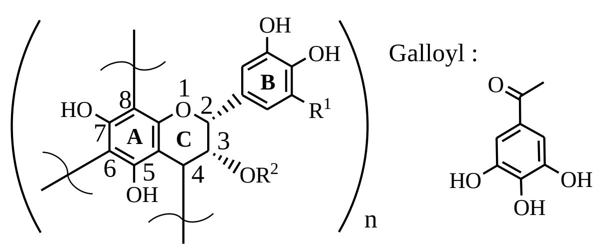
1. Introduction

Persimmons are a number of species of trees in the genus *Diospyros*. There are about 400 species widely found in tropical and subtropical regions. Most are distributed in the Asia, Africa, and Central and South America. Several of the species are edible. Persimmon is a functional material that has been used in various applications such making tanning paper, tanning fishing net, and for removing protein during the brewing process of the Japanese rice wine “sake” [1][2].

Persimmon has various benefits for health such as antioxidant activity, anti-inflammatory activity, hypolipidemic activity, enzyme inhibiting, detoxification effects on snake venom and dispelling the effects of alcohol, etc. These properties are associated with Persimmon proanthocyanidin [3].

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 [1].

Matsuo and Ito [1] first reported on the composition and structure of persimmon condensed tannin (PT). 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 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*. [4], the stereochemistry of the flavan-3-ol unit of the PT is mainly 2,3-cis, which corresponds to epi-type catechins. Proposed structure of PT is shown in Fig. 1.



R^1 = H or OH, R^2 = H or galloyl

Fig. 1 Proposed chemical structure of PT

Tannins are polyphenolic compounds, widely distributed in many plant species, where they serve as defense mechanisms against predators. They form complexes and precipitates with macromolecules such as proteins, lipid, polysaccharides, and heavy metals [5][6][7]. This properties associated with acidic character of the hydroxyl groups and nucleophilic moiety of the phenolic ring of tannin. It makes PT as promising adsorbent.

PTs are water-soluble compounds, which restricts their practical application as adsorbents in aqueous systems. Hence, insolubilization of PT such as crosslinking gelation or immobilization to water-insoluble matrices are required in order to overcome this issue. Various methods have been reported for tannin gelation. Most of them involve formaldehyde or other aldehydes in basic or acidic media [8][9][10]. Other researchers have reported acidic gelation ([11] and autoxidation processes [12].

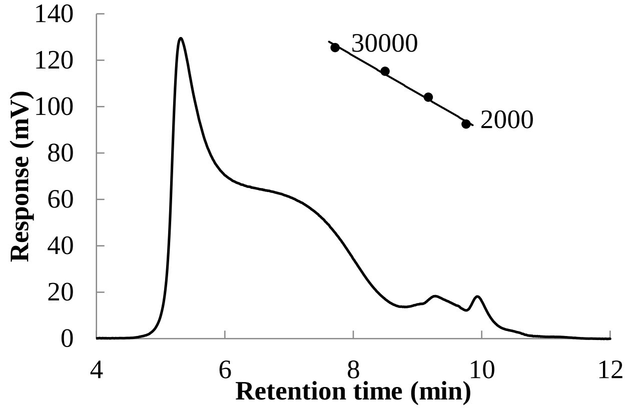


Fig. 2 GPC chromatogram of the soluble PT dissolved in DMF (inset: calibration curves of polystyrene standards)

In this study, PT gel was prepared by three methods such as autoxidation using oxygen, modification using formaldehyde and amine, and immobilization of PT on cellulose. Firstly, we prepared PT gel by autoxidation. PT was gelated by applying oxygen gas and natural light to the aqueous PT solution without using any harmful reagents and catalysts. Adsorption behaviors of the PT gel were tested for caffeine. Secondly, gelation was performed by modification of PT. In this method, two types of PT gels were prepared by modification of PT using formaldehyde and amine compound. Their adsorption to dyes in aqueous solution was studied. Lastly, PT was immobilized on cellulose beads and employed to adsorb caffeine in aqueous solution.

2. Characterization of PT

Chemical characterization of PT has long been hampered because of its heterogeneous character and high molecular weight. Composition of proanthocyanidins contained in the fruit of the persimmon varies depending on the variety and seeds [13], ripening [14] persimmon juice squeezed fruit astringent, physical properties of these proanthocyanidins through steps such as fermentation and filtration.

Gel Permeation Chromatography (GPC) allows us to assess the size distribution of the PT. The chromatogram shows a pronounced peak at approximately 5.31 minutes (Fig. 2). This peak corresponds to the ultrahigh molecular weights (MWs) that exceed the GPC column size exclusion limit of approximately 600,000. Thus, the sample contains very high molecular weight gel components.

Ultra-violet (UV) absorption spectra of green tea catechins exhibited quite different pH. On adjusting the solution pH to 10, gallated catechins such as epicatechin-3-*O*-gallate (ECg) and epigallocatechin-3-*O*-galate (EGCg) show intense absorption at 322 nm, whereas non-gallated catechins such as epicatechin (EC) and epigallocatechin (EGC) show much weak absorption, as shown in Fig. 3. We assigned this spectral change to deprotonation of phenolic hydroxyl group of the galloyl group. The 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 the another unit. It is possible to estimate the content of the 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 can estimate the content of gallated catechins containing in the PT solution to be 38%.

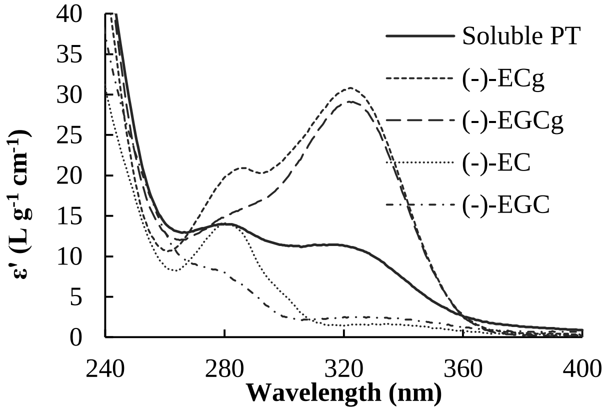


Fig. 3 UV absorption spectra of the soluble PT and green tea catechins

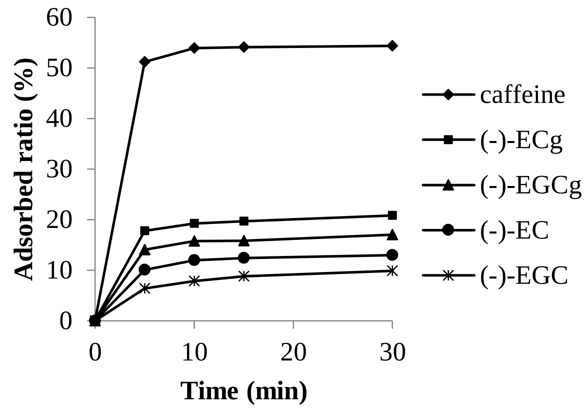
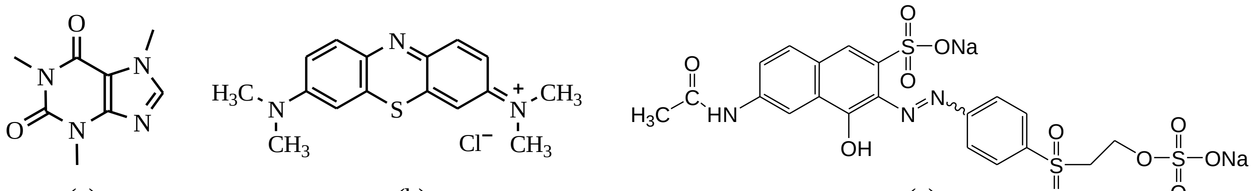


Fig. 4 Adsorption of caffeine and catechins on the PT gel: initial concentration of caffeine and catechins of 100 ppm, gel dose of 1 g/20 mL, contact time of 30 minutes, temperature of 30 °C

3. Autoxidation of PT and green tea components adsorption properties

Recently, we have developed a simple and eco-friendly method for preparing water-insoluble persimmon tannin gels based on commercial *kaki-shibu* without using any harmful reagents and catalysts [15]. Oxygen gas and the natural light are applied to the persimmon tannin solution in the gelation process. We have tested adsorption of the PT gel for green tea components. As shown in Fig. 4, caffeine was adsorbed about 56%, whereas four kinds of catechins were adsorbed only 10-20%. This result indicates that adsorption of caffeine on the PT gel is much stronger than that of catechins. Caffeine (Fig. 5(a)) is a typical purine base carrying four basic



(a) (b) (c)

Fig. 5 Chemical structure of caffeine (a), MB (b), and RBO (c)

nitrogens in the heterocyclic ring. These electron-rich nitrogens may play an important role in the interaction with the PT gel. For catechins, the gallate-type catechins such as EGCg and ECg showed stronger adsorption than the non-gallate type catechins, EC and EGC [16]. The maximum adsorption capacity of a monolayer was found to be 65.8 mg/g for the PT gel.

4. Formaldehyde- and amine- modified PT and dyes adsorption properties

The autoxidation PT gel showed a selective adsorption for basic compounds, but it required considerable time for its preparation. Herein, we extended our work by reporting the preparation of a PT gel formed with formaldehyde in acidic conditions (FPT) and amine-modified PT (APT) gel. The adsorption properties of the gel for basic dyes such as methylene blue (MB), a basic/cationic dye, and remazol brilliant orange 3R (RBO), an acidic/anionic dye, are studied. As shown in Table 1, the observed adsorbed ratio of MB is higher for the FPT gel than the APT gel. This is due to the positive charges of MB (Fig. 5(b)) that can interact with the electronegative phenolic OH moieties of FPT gel, while RBO (Fig. 5(c)) has repulsion with those moieties. To enhance adsorption properties of the PT gel to RBO, PT gel was modified by the aminomethylation reaction [17]. The adsorbed ratio of RBO is higher in APT gel than in FPT gel. Electrostatic attraction works between the APT gel and RBO, while MB experiences repulsion with APT gel. Thus, the aminomethylation of the PT gel enhanced its adsorption to acidic dyes. These results showed that the FPT gel is an effective adsorbent for basic/cationic dyes, whereas the APT gel is an effective adsorbent for acidic/anionic dyes.

Tabel 1. Adsorbed ratio of MB and RBO in FPT and APT gel

Gel	Adsorbed ratio (%)	
	MB	RBO
FPT*	58.4	2.3
APT**	3.3	96.6

(Initial adsorbate concentration: 100 mg/L; contact time: 60 min; temperature: 30 ^{0}C; gel dose: *0.1 g, **0.05g; volume of adsorbate solution: 20 mL; pH: natural)

5. Immobilization of PT on cellulose beads and caffeine adsorption properties

In application, continuous process is preferable. It is required a spherical shape of adsorbent with constant diameter. In this study, cellulose beads was chosen as insoluble matrices. PT solution is mixed with beads cellulose and the obtained PT-immobilized on cellulose (PTIC) gel was harvested every week until week 6 (42 days). The gels were employed to adsorb caffeine in aqueous solution. Fig. 6 showed the highest adsorbed ratio at week 6 of PTIC gel, and the minimum value at day 1, the rest exhibited values in between. The adsorbed ratio of week 2, week 4, and week 6 PTIC gel did not differ significantly. Immobilization of PT on cellulose beads started to saturate in week 2, so that an increase of immobilization time will not increase the number of PT that were immobilized on cellulose beads.

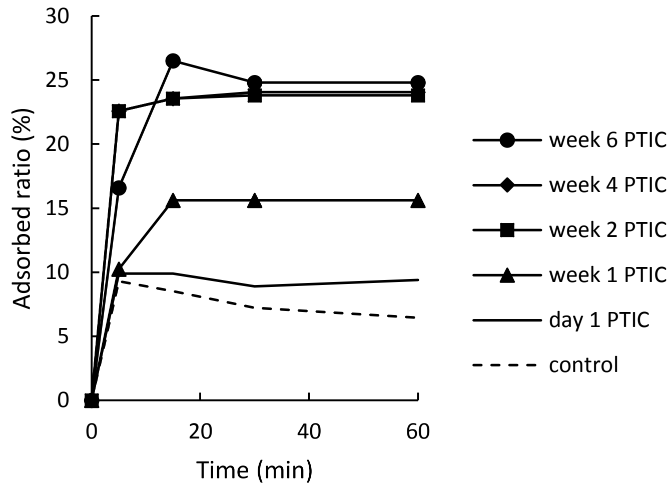


Fig. 6 Adsorption of caffeine and catechins on the PT gel: initial concentration of caffeine and catechins of 100 ppm, gel dose of 1 g/20 mL, contact time of 30 minutes, temperature of 30 °C

The maximum adsorption capacity was found to be 48.3 mg/g at 30°C. Adsorption of caffeine on the PTIC gel is a favorable physisorption process. This result was slightly lower than adsorption of caffeine on the autoxidation PT gel. It was associated with PTIC bead size that larger than autoxidation PT gel.

6. Conclusion

The PT gel contains very high molecular weight gel components which consists of 38% of gallated catechin unit. In this study, PTs were gelated to overcome soluble issues of PT in aqueous solution. PTs gel were prepared by three methods such as autoxidation using oxygen, modification using formaldehyde and amine, and immobilization of PT on cellulose beads.

PT gel prepared by autoxidation using oxygen gas and natural light to the aqueous PT solution without using any harmful reagents and catalysts. Adsorption behaviors of the PT gel were tested for green tea components. The PT gel effectively adsorb caffeine from aqueous solution. The maximum adsorption capacity was found to be of 65.8 mg/g. Adsorption of caffeine on the PT gel is favorable physisorption. In addition, interaction between the adsorbent and the adsorbate is hydrogen bonding and weak attractive force. These data suggest that the PT gel can be used as an effective adsorbent to remove caffeine from green tea drinks.

In this method, two types of PT gels that is formaldehyde-modified (F) PT gel and amine-modified (A) PT gel were prepared, and their adsorption of methylene blue (MB, a basic dye), and Remazol Brilliant Orange 3R (RBO, an acidic dye), in aqueous solution was studied. The result indicated that the FPT gel is shown to be an effective material for adsorbing basic dyes, while the APT gel effectively adsorbs acidic dyes from aqueous solution.

Lastly, PT was immobilized on cellulose beads and employed to adsorb caffeine in aqueous solution. PT was successfully immobilized on cellulose viscopearls in an aqueous condition having adsorbed caffeine from aqueous solution. Adsorption of caffeine on the PTIC gel is a favorable physisorption process. The adsorbent is expected to be an effective adsorbent for removing caffeine from tea production.

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平成２７年１月３０日

学位論文審査報告書（甲）

１．学位論文題目（外国語の場合は和訳を付けること。）

Study on adsorption properties of persimmon tannin-based gels for acidic and basic compounds

（酸性および塩基性物質に対する柿タンニンゲルの吸着特性に関する研究）

２．論文提出者　(1) 所　　属　　物質科学　　専攻

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３．審査結果の要旨（600～650 字）

提出学位論文に関して各審査委員が個別に審査を行うとともに，平成 26 年 12 月 26 日に第 1 回審査会を実施し，平成 27 年 1 月 30 日に行われた口頭発表会に引き続き，審査委員による第 2 回審査会を開催し，以下のとおり判定した．

柿渋は，フラバン-3-オール誘導体を基本骨格とするプロアントシアニジン（柿タンニン）を含有し，古くから清酒の滓下げ剤などに利用されてきた植物性ポリフェノールである．本論文では，柿タンニンから不溶性のゲルを調製し，分光法によりゲルのキャラクタリゼーションを行うと共に，酸性および塩基性物質に対する吸着特性を吸着等温線や熱力学解析に基づき検討している．その結果，柿タンニンの自動酸化により調製したゲルは，緑茶成分のうちカフェインを強く吸着する一方，抗酸化成分であるカテキンに対する吸着は弱いことを見出した．また，ゲルのフラバン-3-オールユニットのフェノール環にアミノメチル基を導入することにより，酸性色素に対する強い吸着性を有する柿タンニンゲルを創製し，当該ゲルを用いて環境廃水中からの色素の吸着除去が可能であることを示した．

以上，本研究で得られた柿タンニンゲルの吸着特性に関する知見は，ポリフェノール性ゲルの食品や環境分野への応用の可能性を示すだけでなく，分子間相互作用に関して本質的な理解を与え，学術的にも重要である．従って，本論文は博士（学術）の学位に値するものと判断する．

４．審査結果　(1) 判　　定（いずれかに○印）（合　格）・　不合格

(2) 授与学位　　博　士（　学術　）