JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

ARTICLE

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Adsorption Behavior of the Catechins and Caffeine onto Polyvinylpolypyrrolidone

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ABSTRACT: Adsorbent is one of the most important factors for separation efficiency in fixed-bed purification techniques. The adsorption behavior of catechins and caffeine onto polyvinylpolypyrrolidone (PVPP) was investigated by static adsorption tests. The results showed that catechins rather than caffeine were preferred to adsorb onto PVPP since the adsorption selectivity coefficient of total catechins vs caffeine was around 22.5, and that adsorption of catechins could be described by the pseudo-second-order model. Adsorption amount of caffeine onto PVPP in green tea extracts solution was much higher than that in purified caffeine solution although the initial concentration of caffeine was similar in the two solutions, indicating the caffeine might be attached with catechins which were adsorbed by PVPP instead of being adsorbed by PVPP directly. The results also showed that the adsorption capacity of catechins and caffeine decreased with an increase in temperature, and that Freundlich and Langmuir models were both suitable for describing the isothermal adsorption of catechins, but not suitable for caffeine. The predicted maximum monolayer adsorption capacity of total catechins by PVPP was 671.77 mg g^{-1} at 20 °C, which was significantly higher than that by other reported adsorbents. The thermodynamics analyses indicated that the adsorption of catechins onto PVPP was a spontaneous and exothermic physisorption process, revealing lower temperature was favorable for the adsorption of catechins. Elution tests showed that the desorption rates of catechins and caffeine were higher than 91% and 99% after two elution stages; in detail, almost all of the caffeine could be washed down at the water eluting stage, while catechins could be recovered at the dimethyl sulfoxide/ethanol solution eluting stage. Thus, the PVPP could be used as an excellent alternative adsorbent candidate for separating catechins from crude tea extracts, although some investigations, such as exploring the new eluants with low boiling point and high desorption efficiency, should be conducted furthermore.

KEYWORDS: PVPP, catechins, decaffeination, adsorption kinetics, isothermal adsorption, thermodynamics, desorption

INTRODUCTION

Catechins, main components in green tea extracts, have been proved to possess plenty of perfect health benefits, such as effectively scavenging active radicals, antioxidation, antimutagen, anticancer, anti-inflammation, antibiosis, protecting neuron, UV shielding effects and antiobesity as well as reducing risk of cardiovascular diseases.[1,2] Therefore, it seems that catechins can be regarded as desirable natural products for development of functional foods and botanical pharmaceuticals. However, catechins extracted from tea are always contaminated with an amount of other components, such as caffeine, by common extraction technology. Although administration of caffeine can prevent cognitive deficits and neurodegeneration in some models of neurodegenerative disorders, such as Alzheimer's and Parkinson's disease, and it usually has been used as a therapy for diuretic and respiratory stimulant of neonatal apnea, excessive intake of caffeine may unavoidably cause various adverse effects, including sleep deprivation, increasing the risk of cardiovascular disease, reducing fertility rates and increasing miscarriages.[3] Obviously, catechins should be purified and decaffeinated prior to application in pharmaceuticals and functional foods.

Many approaches have been attempted to remove the caffeine from tea extracts or crude catechins. Decaffeination of crude catechins can be sufficiently achieved by extraction with organic solvent such as chloroform or methylene chloride; however, it is now considered highly unsafe due to their potential carcinogenic effects of the residual organic solvents.[4] Supercritical carbon dioxide extraction can efficiently obtain decaffeinated tea products without any harmful residue;[5] unfortunately, this method requires expensive equipment and unavoidably results in a large amount of catechin loss after decaffeination processing.[6] Treating the fresh leaves with hot water is a safe and low cost decaffeination alternative;[7] nevertheless, it is only suitable for producing low-caffeine or decaffeinated green tea. Achieving decaffeinated products via microbial degradation[8] and genetically modified caffeine-free tea plants[9] is far away from industrial application in spite of their cheerful and hopeful prospect. Up to now, fixed-bed chromatography separation is an available and practical technique for purification of catechins. Ye et al. established a method for preparation of partially decaffeinated instant tea by using active carbon as an adsorbent to remove caffeine.[10] Sawdust lignocellulose seemed to be a good adsorbent for purifying the catechins from tea extracts after pretreatment of sawdust with acid/alkali solutions[11] because it adsorbed preferentially catechins rather than caffeine and showed a perfect adsorption selectivity.[12] Furthermore, adsorption capacity of lignocellulose could be significantly increased by 36−40% after

Received: January 7, 2011
Accepted: March 14, 2011
Revised: March 8, 2011
Published: March 14, 2011

being grafted with *N*-vinylpyrrolidone.[13] Recently, another report showed that the synthetic poly(acrylamide-*co*-ethylene glycol dimethacrylate) could also be used as an alternative adsorbent candidate for producing the decaffeined catechins.[14] Since the adsorbent is one of the most important key factors for improving separation efficiency, scientists never stop exploring the novel desirable adsorbents with high adsorption capacity and perfect selectivity.

Insoluble polyvinylpolypyrrolidone (PVPP), a highly cross-linked version of polyvinylpyrrolidone, is an inexpensive and excellent precipitant of polyphenols.[15,16] It is industrially used in beverage production (e.g., beer, wine and juice) for removal of polyphenols, in order to prevent the formation of haze initiated by interaction between polyphenols and proteins.[16] This polyphenol precipitant is biochemically inert[17] and easily regenerative.[18] These findings gave a helpful clue that PVPP could be applied as effective adsorbent in chromatograph separation for decaffeination of tea catechins.

In this study, the adsorption behavior of catechins and caffeine onto PVPP was investigated by static adsorption and desorption tests. The effects of contact time, ambient temperature, and adsorbate concentration on the adsorption characteristics were studied. The kinetic, isothermal and thermodynamic parameters of the adsorption process were determined, and desorption efficiency of the adsorbates by different eluants was also tested.

MATERIALS AND METHODS

Materials and Reagents. PVPP, purchased from Sigma (St. Louis, MO, USA), was soaked with sodium hydroxide (1 mol L^{-1}) and hydrochloric acid (1 mol L^{-1}) in turn for 24 h, and thoroughly washed to pH 7 with ultrapure water (EASYpure II UV ultrapure water system, Barnstead International, Dubuque, IA, USA), and then collected by vacuum filtration with double-ring filter paper (Hangzhou Xinhua Paper Industry Co., Ltd., Hangzhou, China). After pretreatment, particle size and moisture content of the wet PVPP were around 0.3−1.2 mm and 68.8%. High performance liquid chromatography (HPLC) grade acetonitrile and methanol were purchased from Tedia Company Inc. (OH, USA). HPLC reference compounds including (−)-epigallocatechin gallate (EGCG), (−)-epigallocatechin (EGC), (−)-epicatechin gallate (ECG), (−)-epicatechin (EC), (+)-gallocatechin gallate (GCG), (+)-gallocatechin (GC), (+)-catechin gallate (CG) and (+)-catechin (C) were supplied by National Institute of Japan (Kagoshima, Japan), and pure caffeine was a Sigma product (St. Louis, MO, USA). Green tea extract (GTE) was prepared in the laboratory, and the concentrations of GC, EGC, C, EC, EGCG, GCG, ECG, CG and caffeine were 24.14, 146.24, 7.34, 61.04, 320.89, 15.26, 85.89, 1.69, and 71.27 mg g^{-1}. The GTE solutions were prepared by dissolving an amount of GTE in ultrapure water and centrifuging at 4000*g* and 4 °C for 10 min (Beckman J2 HS; Beckman Instruments Inc., Fullerton, CA, USA) to remove the sediment. All other chemicals used were analytical reagents except where stated otherwise. Ultrapure water was used throughout this study.

Adsorption Kinetics Test. Four hundred milliliters of prepared GTE solution (1%, w/v) was transferred into a 1000 mL conical flask. After being sealed with parafilm (Pechiney Plastic Packaging Inc., Chicago, IL, USA), the flask was incubated in a shaking water bath (Model HZS-H, Harbin Donglian Electronic & Technology Development Co. Ltd., Heirongjiang, China) at 25 °C and 150 r min^{-1} for around 30 min to reach a constant temperature. The pretreated PVPP (19.200 g wet weight, equivalent to 6.000 g dry weight) was then added into the flask. Samplings (1.0 mL) were done in specific time intervals (from 0 to 1760 min) after PVPP addition. The samples were centrifuged at 12000*g* and 4 °C for 10 min, and catechins and caffeine concentration in the supernatants were analyzed by HPLC. Amount of adsorbed catechins and caffeine onto PVPP was calculated according to eq 1. In order to understand the mechanism of the adsorption process and evaluate performance of the adsorbents for adsorbates, we tried to fit the experimental data to the pseudo-first-order (eq 2) and pseudo-second-order (eq 3) kinetic models, respectively.

$$Q_t = V_0(C_0 - C_t)/M \quad (1)$$

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (2)$$

$$t/Q_t = 1/(k_2 Q_e^{\,2}) + t/Q_e \quad (3)$$

where Q_t and Q_e (mg g^{-1}) are the amounts of the adsorbates adsorbed on adsorbents at contact time t (min) and equilibrium, respectively; V_0 (mL) is the volume of green tea extract solution; C_0 and C_t (mg mL^{-1}) are the initial concentration of adsorbates before adsorption and the adsorbate concentration at contact time t; M (g) is the dry weight of the PVPP used; k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constants of the pseudo-first-order and pseudo-second-order models, respectively.

Isothermal Adsorption Test. Equilibrium adsorption experiments were serially conducted at different temperatures. GTE solutions with serial initial concentrations (C_0) of 1.6%, 1.8%, 2.0%, 2.5% and 3.0% were prepared. The prepared solution (30 mL) with each concentration was transferred into a 50 mL conical flask in which 1.600 g wet weight PVPP (dry weight 0.500 g) was added. Subsequently, all flasks were sealed with parafilm and shaken (150 r min^{-1}) in a water bath at 20 °C for 24 h. One milliliter of solution was sampled from each flask and centrifuged at 12000*g* and 4 °C for 10 min. The supernatants were used for HPLC analysis. Sample sets for another two isothermal adsorption tests at 40 and 60 °C were also prepared accordingly. After HPLC analysis, equilibrium adsorption capacity (Q_e) was calculated according to previous equation (eq 1). In order to describe the adsorption mechanism, we attempted to fit Langmuir (eq 4) and Freundlich (eq 5) isothermal models to the obtained data.

$$1/Q_e = 1/(Q_m k_L C_e) + 1/Q_m \quad (4)$$

$$\ln Q_e = (1/n)\ln C_e + \ln k_F \quad (5)$$

where Q_e and Q_m (mg g^{-1}) are equilibrium adsorption capacity and maximum monolayer adsorption capacity, k_L (mL mg^{-1}) is the affinity constant, C_e (mg mL^{-1}) is the residual concentration of adsorbates in solution at equilibrium; $1/n$ is a Freundlich constant related to the heterogeneity factor, and k_F ($mg^{(n-1)/n}$ g^{-1} $mL^{1/n}$) is the Freundlich constant related to the capacity.

Thermodynamics Analysis. The thermodynamic parameters Gibbs free energy ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$), evaluating the feasibility and endothermic nature of the adsorption process, were obtained according to eq 6 and eq 7.[19]

$$\Delta G° = -RT \ln K_D \quad (6)$$

$$\ln K_D = \Delta S°/T - \Delta H°/RT \quad (7)$$

where $\Delta G°$ (kJ mol^{-1}), $\Delta H°$ (kJ mol^{-1}) and $\Delta S°$ (J $mol^{-1}K^{-1}$) are the Gibbs free energy, enthalpy change and entropy change of adsorption process; R is the universal gas constant (8.314 J mol^{-1} K^{-1}); T is absolute temperature (K); and K_D (mL g^{-1}) is the distribution coefficient (Q_e/C_e) at equilibrium.

Desorption Test. Static elution with two stages was used to study the desorption efficiency of catechins and caffeine from PVPP. Adsorption was conducted as described previously, by mixing the pretreated PVPP (dry weight 1.000 g) with 30 mL of prepared GTE solution (2.5%, w/v) and incubated at 20 °C and 150 r min^{-1} for 24 h in the shaking water bath. The PVPP was collected after adsorption on a Buchner funnel by vacuum filtration, and incubated with water (120 mL) at 20 °C and

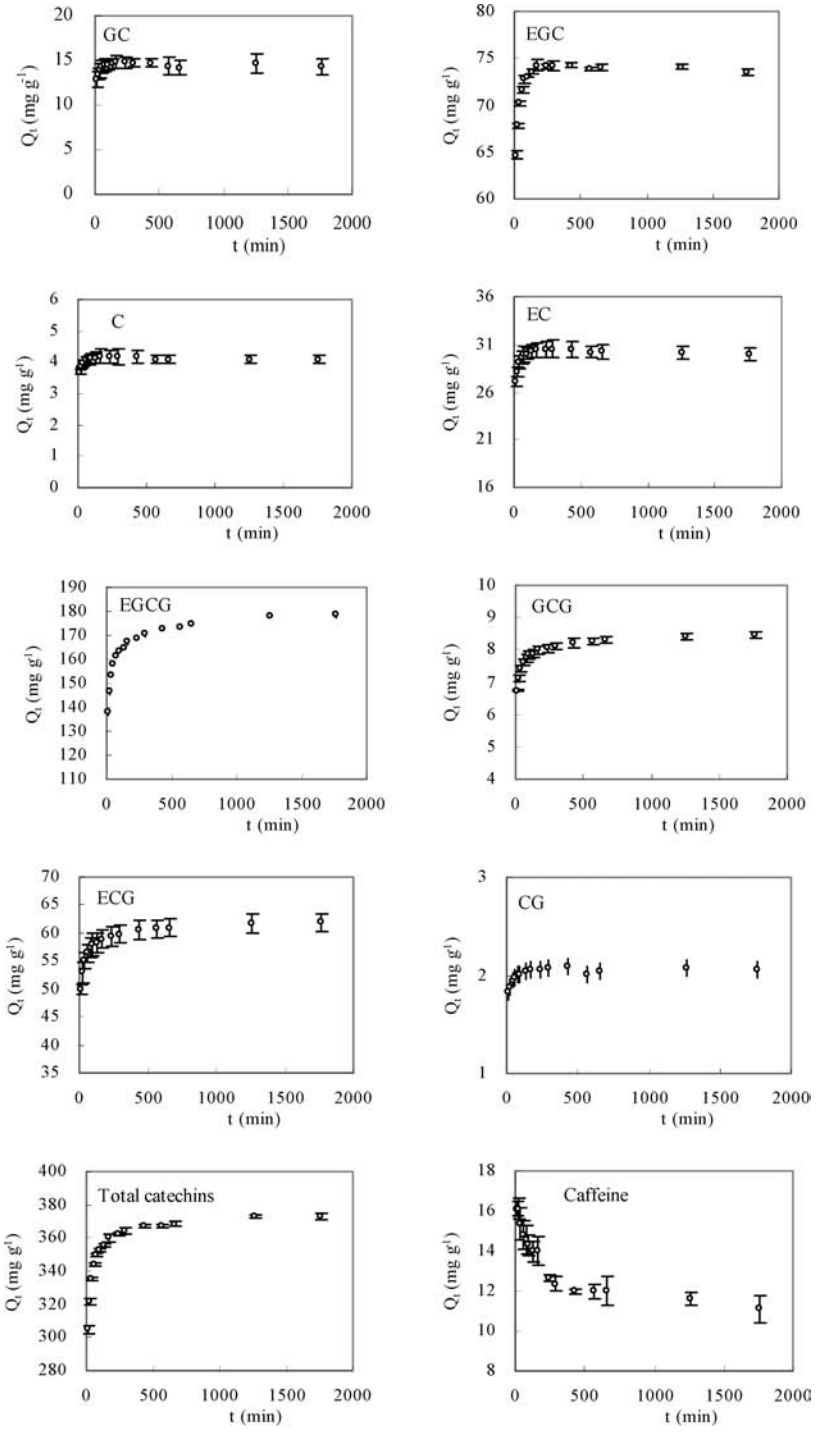

Figure 1. Change in adsorption amount of components onto PVPP along with contact time. The bar shows the standard deviation of triplicate tests.

150 r min^{-1} for 60 min at the first elution stage. Then the PVPP was collected again by vacuum filtration, and further incubated with 60 mL of dimethyl sulfoxide (DMSO)/ethanol (8/2, v/v) for 60 min at the second elution stage. After filtration, the volume of the two separated eluates was carefully measured. The catechins and caffeine in adsorption solutions (before or after) and separated eluates (first and second elution stages) were monitored by the HPLC. The desorption rate of each adsorbate was expressed as percentage of desorption amount in adsorption amount.

Caffeine and Catechins Analysis. HPLC (model LC20A, Shimadzu Co., Kyoto, Japan) was used to estimate catechins and caffeine in tested solutions. The HPLC analysis conditions were as follows: injection volume, 10 μL; column, TC-C_{18} 5 μm, 4.6 × 250 mm (Agilent Technologies Inc., Santa Clara, CA, USA); oven temperature, 28 °C; mobile phase A, acetonitrile/acetic acid/water (6/1/193); mobile phase B, acetonitrile/acetic acid/water (60/1/139); gradient elution, 30% mobile phase B to 85% mobile phase B by linear gradient increasing during the early 35 min and holding at 85% mobile phase B for further 5 min; flow rate, 1 mL min^{-1}; detecting wavelength, 280 nm. Caffeine and catechins were identified by comparing with authentic standard. Detailed operation was carried out as described in previous paper.[20]

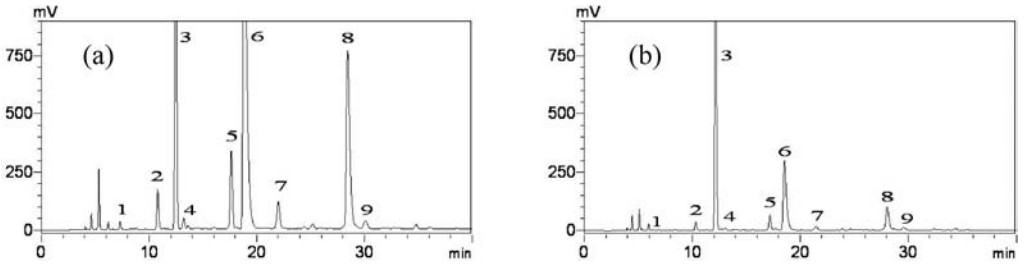

Figure 2. HPLC result of GTE solution (1.0%) before or after adsorption by PVPP: (a) initial green tea extracts solution (1.0%), (b) adsorption for 94 min. Peaks: 1, GC; 2, GC; 3, caffeine; 4, C; 5, EC; 6, EGCG; 7, GCG; 8, ECG; and 9, CG.

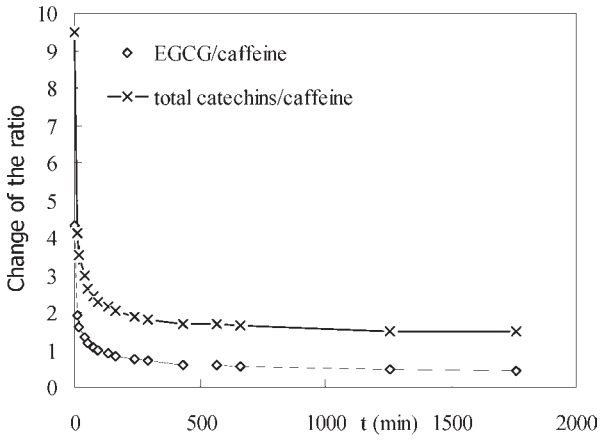

Figure 3. The ratio change of EGCG/caffeine and total catechins/caffeine in solution along with the contact time. The bar shows the standard deviation of triplicate tests.

RESULTS AND DISCUSSION

Adsorption Kinetics of Catechins and Caffeine onto PVPP. Kinetics curve can describe the adsorption behavior of catechins and caffeine onto PVPP at different contact times. It will provide some helpful clues for developing industrial-scale operation techniques during the adsorption batch process. Figure 1 showed that the adsorption amount (Q_t) of eight catechin monomers and total catechins onto PVPP increased sharply during the first 10 min after addition of PVPP into the GTE solution, and almost reached their equilibrium points within 300 min. Surprisingly, the Q_t value of caffeine seemed to reach its maximum point within 20 min, and decreased gradually during the following contact time. Relatively, after adsorption for 94 min, only less than 20% of the initial catechins remained in the solution, while more than 65% of the initial caffeine did (Figure 2). The equilibrium adsorption amount (Q_e) of total catechins (372.78 mg g^{-1}) was almost 32 times as high as that of caffeine (11.09 mg g^{-1}) on adsorbent PVPP. The ratios of EGCG/caffeine and total catechins/caffeine in solution decreased dramatically from 4.31 and 9.44 to 0.43 and 1.49 along with the contact time (Figure 3). After calculation according to the equation $K_{A/B} = k_D^A/k_D^B$ ($K_{A/B}$ is the adsorption selectivity coefficient of component A vs B; k_D^A and k_D^B are distribution coefficients of components A and B at equilibrium, respectively), the adsorption selectivity coefficient of total catechins vs caffeine was around 22.5 by PVPP, much higher than that by other adsorbents.[12,14] These results implied that the PVPP was favored to adsorb catechins rather than caffeine.

The different kinetic models, pseudo-first-order and pseudo-second-order models, are usually used to explain the adsorption mechanism of adsorbates onto adsorbents.[12,14] It is assumed that the rate of occupation of the adsorption sites is proportional to the number of unoccupied sites in the pseudo-first-order model,[21] while it is proportional to the square of the number of unoccupied sites in the pseudo-second-order model.[22] After model fitting, the rate constant and determination coefficient (r^2) along with the relative error of Q_e between experiment and calculation from the two models are summarized in Table 1. The equilibrium adsorption capacities ($Q_{e,cal}$) of catechins predicted from the pseudo-second-order model were much closer to the experimental values ($Q_{e,exp}$) (relative error < 0.52%) than those from the pseudo-first-order model (relative error > 79.0%), and r^2 values of the pseudo-second-order model ($r^2 > 0.999$) were also higher than those of the pseudo-first-order model (0.9673−0.9957). Consequently, the adsorption process of catechins onto PVPP followed the pseudo-second-order model (Figure 4), suggesting that adsorption reaction of catechins onto PVPP surface was a rate-controlling step,[22,23] i.e., the adsorption rate depended on the particle surface of PVPP and on the concentration of catechins in solution.

The rate constant (k_2) of the pseudo-second-order model, an index of adsorption efficiency, expresses adsorbent amount (g) for adsorption of 1 mg of adsorbate in 1 min. Smaller k_2 means higher efficiency of adsorption. Fitting showed that the k_2 of total catechins was around 0.0005 g mg^{-1} min^{-1}, and the k_2 value of different catechin monomers decreased substantially with increase in molecular weight and number of hydroxyl groups of the monomer (EGCG > ECG > EGC > EC). It implied that catechins could be efficiently adsorbed by PVPP, and that a larger molecule with many more hydroxyl groups in the monomer could be bound more easily and strongly on the adsorbent besides the initial adsorbate concentration. Therefore, hydrogen bonds between the proton donor from the catechins and the carbonyl group from PVPP together with π-bond overlap (delocalized electrons) and hydrophobic associations between the aromatic ring of the catechins and pyrrolidone ring of the PVPP might play important roles in the adsorption process (Figure 5). Similar manners had been thoroughly illustrated in studies on the interaction between polyphenols and haze-active proteins,[24,25] because the structure of PVPP had been considered similar to the haze-active proteins in some cases.[16] The k_2 values were different between epi-catechins and their epimers, suggesting that adsorption might also be influenced by the structure and initial concentration of monomer.

The initial adsorption rate (h_2) of the pseudo-second-order model was also calculated according to the equation $h_2 = k_2 Q_e^2$, expressing adsorption amount of adsorbate by 1 g of PVPP in 1 min. The h_2 value of total catechins, being 63.38 mg g^{-1} min^{-1}, was much higher than that of caffeine. Low rate constant (k_2) and high initial adsorption rate (h_2) might result in high adsorption

Table 1. Molecular Characteristics and Kinetic Parameters in GTE/PVPP Adsorption System[a]

	GC	EGC	C	EC	EGCG	GCG	ECG	CG	total catechins	caffeine
molecular weight	306.3	306.3	290.3	290.3	458.4	458.4	442.4	442.4	/	194.2
no. of hydroxyl groups	6	6	5	5	8	8	7	7	/	0
init concn (mg mL^{-1})	0.25	1.40	0.07	0.56	2.89	0.14	0.98	0.04	6.33	0.67
$Q_{e.exp}$ (mg g^{-1})	14.77	74.27	4.19	30.50	178.42	8.48	61.88	2.08	372.78	11.09
Pseudo-First-Order Model										
$Q_{e.cal}$ (mg g^{-1})	2.48	11.83	0.58	4.11	42.84	1.83	12.52	0.31	73.61	0.91
h_1 (mg g^{-1} min^{-1})	0.0689	0.3193	0.0145	0.1083	0.5372	0.0230	0.1774	0.0060	1.1610	−0.0049
k_1 (min^{-1})	0.0277	0.0270	0.0249	0.0263	0.0125	0.0126	0.0142	0.0198	0.0158	−0.0054
r^2	0.9864	0.9957	0.9827	0.9939	0.9716	0.9707	0.9673	0.9959	0.9979	0.8661
rel error (%)	98.35	99.30	90.48	98.64	99.86	97.85	99.68	79.39	99.94	93.72
Pseudo-Second-Order Model										
$Q_{e.cal}$ (mg g^{-1})	14.80	74.65	4.20	30.62	178.87	8.49	62.00	2.09	373.59	11.17
k_2 (g mg^{-1} min^{-1})	0.0396	0.0069	0.1275	0.0198	0.0006	0.0131	0.0022	0.1599	0.0005	−0.0040
h_2 (mg g^{-1} min^{-1})	8.6811	38.6085	2.2508	18.5924	17.7261	0.9455	8.3022	0.7004	63.3784	−0.5047
r^2	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9997	0.9999	0.9990
rel error (%)	0.24	0.52	0.40	0.42	0.25	0.18	0.20	0.43	0.22	0.70

[a] The adsorption rate constant (k_1) and equilibrium adsorption amount (Q_e) were determined experimentally by plotting of $\ln(Q_e - Q_t)$ versus t according to eq 2. The parameters k_2 and Q_e were determined by plotting of t/Q_t versus t according to eq 3. Initial concentration of GTE: 1%. Adsorption temperature: 25 °C. Time duration: 0−1760 min. Key: exp, experimental data; cal, calculated from the model; $h_1 = k_1 Q_{e.cal}$; $h_2 = k_2 Q_{e.cal}^2$. Relative error = $100(|Q_{e.cal} - Q_{e.exp}|)/Q_{e.exp}$.

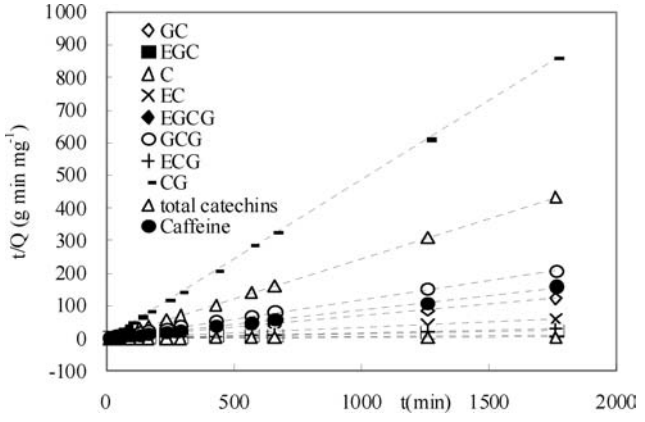

Figure 4. Fitting of the pseudo-second-order model.

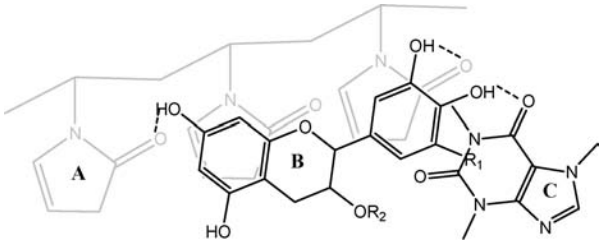

Figure 5. Interaction between adsorbates and adsorbent: (A) the PVPP backbone; (B) catechin monomer (R_1 = H or OH, R_2 = H or galloyl group); (C) caffeine; the dashed line means the hydrogen bond.

selectivity for catechins by PVPP. Although k_2 and h_2 values of caffeine were negative in prediction of pseudo-second-order model, the model might still be suitable for describing the adsorption process of caffeine onto PVPP because the predicted Q_e was very close to the experimental one. In addition, the study

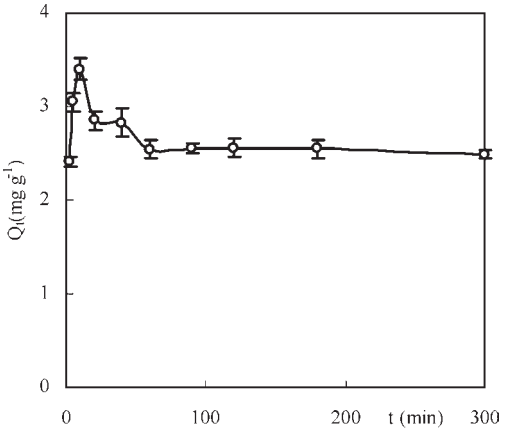

Figure 6. Adsorption of caffeine by adsorbent in caffeine/PVPP system. Initial concentration of caffeine (0.72 mg mL^{-1}) is similar to that in 1% GTE solution, and the predicted pseudo-second-order equation is $t/Q_t = 0.4021t - 0.9113$ ($r^2 = 0.9997$, relative error between experimental and predicted Q_e being 0.12%) where $Q_e = 2.49$ mg g^{-1}, $k_2 = -0.1774$, and $h_2 = -1.0973$.

also suggested that the pseudo-second-order model might be applied for description of a much more complex adsorption system along with much longer contact time compared to the pseudo-first-order model.[22]

Due to the unexpected adsorption behavior of caffeine onto PVPP along with contact time in the complex GTE/PVPP system, another confirmation test was conducted using pure caffeine as only adsorbate in simple model system. The result showed that the adsorption behavior of caffeine onto adsorbent in the caffeine/PVPP model system was similar to that in the GTE/PVPP complex system and followed the pseudo-second-order model ($r^2 = 0.9997$ and predicted relative error = 0.12%), while the Q_e value of caffeine (2.49 mg g^{-1}) was quite lower than

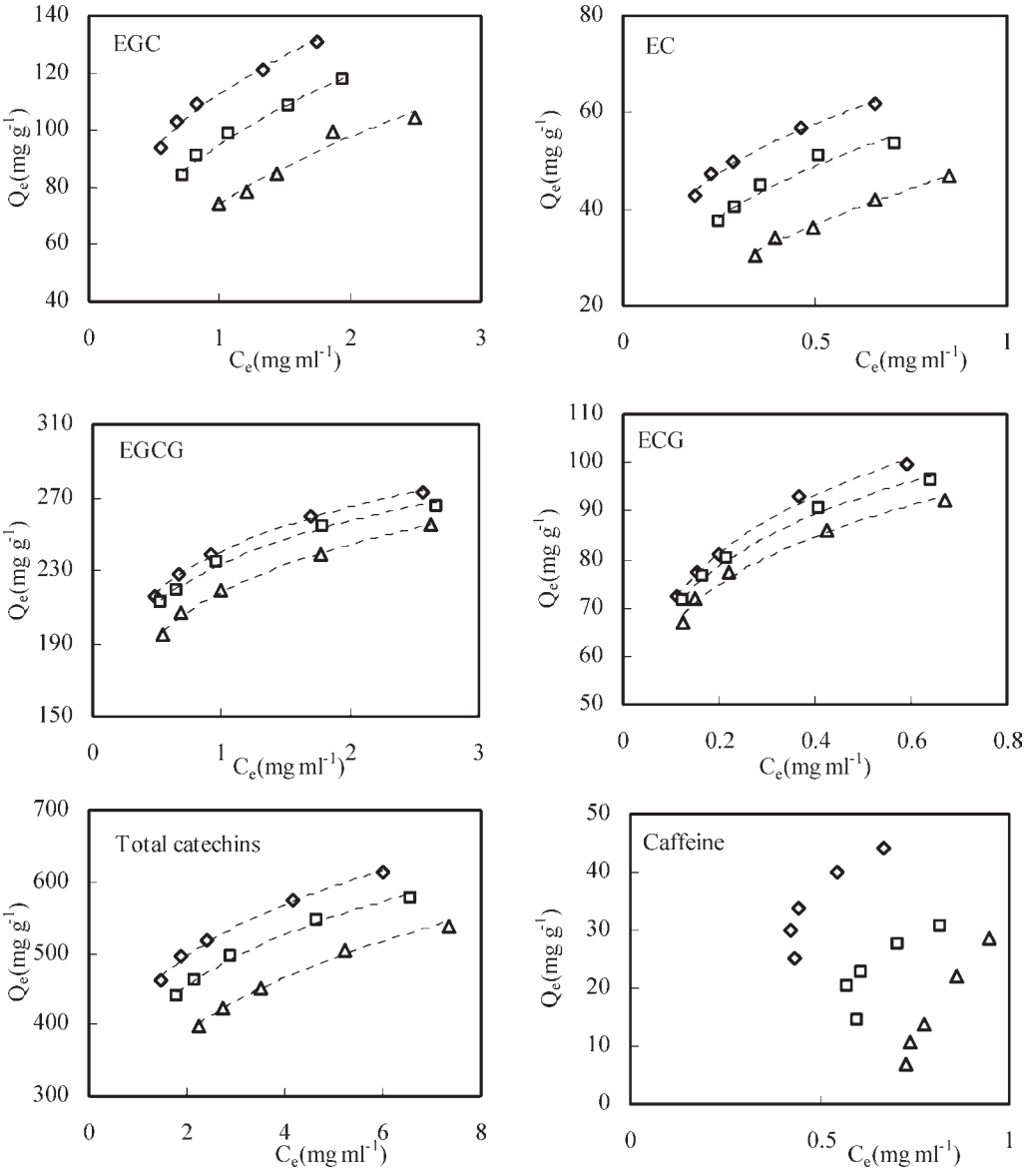

Figure 7. Effect of equilibrium concentration of adsorbates and temperature on adsorption amounts: ◇ 20 °C, □ 40 °C, △ 60 °C.

that in the complex system even though the initial caffeine concentration of the two systems was similar (Figure 6). It implied that adsorption of caffeine in the GTE/PVPP system was significantly affected by the catechins. Catechins might enhance the adsorption amount of caffeine onto PVPP by the interactions between catechins and caffeine because these interactions were always found in tea infusion.[26,27] Therefore, in some case, caffeine might be attached with catechins instead of being adsorbed by PVPP directly (Figure 5). On the other hand, enhanced adsorption of caffeine in GTE/PVPP system could be explained as another possibility that the interaction between catechins and PVPP might activate the occupation sites for caffeine on the PVPP surface. In fact, this possibility should be ignored since caffeine on the adsorbents could be easily washed down by a simple rinsing solution, such as distilled water as shown in the desorption result of this study.

Isothermal Adsorption. The adsorption isotherms, one of the most important parameters to identify the mechanism of the adsorption process, describe the relationship between equilibrium adsorption capacity (Q_e) of adsorbent and equilibrium concentration of the adsorbates in the liquid phase (C_e) at a given temperature. As shown in Figure 7, the Q_e value of catechin monomers and total catechins increased along with an increase in C_e. The result confirmed the prediction of the pseudo-second-order model in the previous kinetic tests. It indicated that the adsorbate concentration in solution played an important role as a driving force to overcome mass transfer resistance for adsorbate transportation between the liquid membrane and the adsorbent surface.[28] If the concentration of catechins in solution was higher, the unoccupied adsorption sites on the PVPP surface were surrounded by many more catechin molecules, the adsorption process would be carried out more sufficiently. Figure 7 also showed that higher Q_e values were observed at lower temperature, revealing that relatively low temperature was favorable to the adsorption of catechins onto PVPP. High temperature could accelerate the movement of adsorbates in solution and make them quickly reach the adsorbent surface; on the other hand, it might also make the adsorbates escape easily from adsorbent.[14]

Decreased Q_e might also be explained the change of desorption rate for catechins being much faster along with an increase in temperature than that of adsorption rate. Although the Q_e value of caffeine also decreased along with increasing temperature in a similar manner as catechins, surprisingly, it changed with the C_e in an unexpected way (Figure 7). This observation also indicated that caffeine might not be adsorbed directly onto the PVPP surface. K_A^B calculation showed that the selectivity coefficient of total catechins vs caffeine decreased dramatically with an increase in initial concentration of GTE solution, while it increased with an increase in the temperature (Figure 8). It implied that low initial GTE concentration and high temperature might theoretically benefit to improving the separation efficiency of caffeine and catechins. However, concerning the effect of temperature and C_e on the Q_e change of catechins and easy elution of caffeine, techniques with application of relative lower processing temperature (such as 20 °C) and higher initial concentration of GTE solution (such as 3% or higher) might be much more suitable for industrial decaffeination of crude catechins.

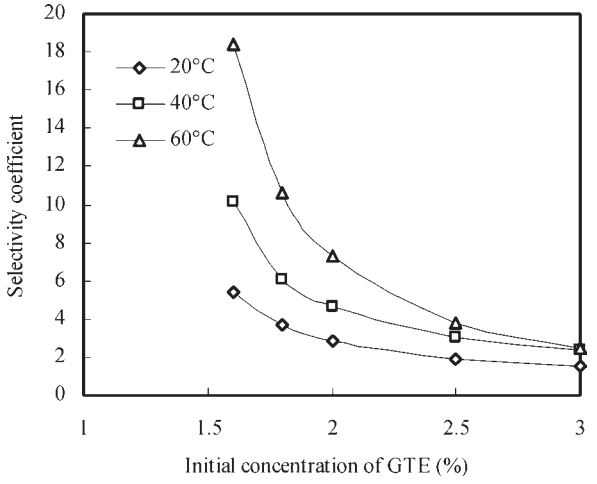

Figure 8. Effect of GTE initial concentration and temperature on the selectivity coefficient of total catechins vs caffeine.

The Langmuir isothermal model is usually used to describe the monolayer adsorption with constant heat onto the adsorbent surface with a finite number of homogeneous sites.[29] The Freundlich model can be applied for explaining the multilayer adsorption on a heterogeneous adsorbent surface with different energy sites.[21] Fitting showed that the isothermal adsorption behavior of catechins onto PVPP could be described by these two models because their r^2 values of model equations were higher than 0.93 (Table 2), revealing that the adsorption behavior of catechins onto PVPP was influenced directly and significantly by the concentration of adsorbates in solution and the unoccupied sites on the adsorbent surface.[30] This result was in good line with the previous kinetic tests. The interaction between different

Table 2. Isothermal Parameters for the Adsorption of Catechins and Caffeine onto PVPP

	catechins									
	GC	EGC	C	EC	EGCG	GCG	ECG	CG	total	caffeine
20 °C										
Freundlich										
$1/n$	0.2031	0.2757	0.2188	0.2788	0.1385	0.1130	0.1972	0.3224	0.1951	0.7920
k_F ($mg^{(n-1)/n}$ g^{-1} $mL^{1/n}$)	32.42	112.75	13.51	70.01	240.45	16.10	111.54	8.54	433.65	62.19
r^2	0.9673	0.9790	0.9909	0.9865	0.9979	0.9775	0.9941	0.9888	0.9946	0.7726
Langmuir										
k_L (mL mg^{-1})	32.67	2.69	100.10	7.55	6.27	181.51	17.65	98.21	1.48	−0.11
Q_m (mg g^{-1})	26.95	157.51	8.48	73.58	284.74	13.00	106.84	3.70	671.77	−611.62
r^2	0.9532	0.9895	0.9830	0.9943	0.9780	0.9723	0.9706	0.9965	0.9921	0.7214
40 °C										
Freundlich										
$1/n$	0.2534	0.3253	0.2261	0.3529	0.1397	0.1109	0.1827	0.3178	0.2100	1.5744
k_F ($mg^{(n-1)/n}$ g^{-1} $mL^{1/n}$)	30.35	95.08	12.00	62.44	233.42	15.68	105.52	6.96	393.11	43.60
r^2	0.9666	0.9484	0.9970	0.9706	0.9927	0.9852	0.9947	0.9862	0.9848	0.6238
Langmuir										
k_L (mL mg^{-1})	16.47	1.78	60.31	4.24	5.66	174.27	17.13	86.01	1.14	−0.58
Q_m (mg g^{-1})	26.71	150.43	8.23	73.05	280.47	12.78	103.64	3.19	651.26	−36.04
r^2	0.9395	0.9800	0.9974	0.9891	0.9920	0.9811	0.9886	0.9697	0.9980	0.5138
60 °C										
Freundlich										
$1/n$	0.3370	0.3944	0.2697	0.4581	0.1639	0.1162	0.1818	0.3862	0.2560	4.8234
k_F ($mg^{(n-1)/n}$ g^{-1} $mL^{1/n}$)	26.53	74.31	12.27	50.52	217.93	15.37	100.10	8.51	326.70	41.18
r^2	0.9960	0.9608	0.9769	0.9934	0.9991	0.9820	0.9823	0.9856	0.9968	0.9188
Langmuir										
k_L (mL mg^{-1})	8.26	0.99	41.67	2.20	4.69	168.48	16.81	45.45	0.75	−0.97
Q_m (mg g^{-1})	25.05	147.45	8.16	71.09	270.29	12.39	99.10	3.84	633.17	−3.64
r^2	0.9981	0.9662	0.9633	0.9815	0.9735	0.9547	0.9920	0.9907	0.9908	0.7947

Table 3. Thermodynamic Parameters for Adsorption of Catechins and Caffeine onto PVPP

			$\Delta G°$ (kJ mol^{-1})		
	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	20 °C	40 °C	60 °C
GC	−18.77	−20.88	−12.65	−12.24	−11.82
EGC	−14.42	−9.36	−11.68	−11.49	−11.31
C	−15.55	−9.68	−12.71	−12.52	−12.32
EC	−15.66	−11.10	−12.41	−12.18	−11.96
EGCG	−2.98	35.08	−13.26	−13.96	−14.66
GCG	−2.03	38.87	−13.42	−14.19	−14.97
ECG	−3.27	37.55	−14.28	−15.03	−15.78
CG	−11.02	2.07	−11.63	−11.67	−11.71
total catechins	−9.22	12.29	−12.82	−13.07	−13.31
caffeine	−27.03	−57.06	−10.31	−9.17	−8.03

catechins on the PVPP surface might be ignored because low initial concentration of catechins was applied in this study, therefore, the two isothermal models were both suitable for describing the adsorption of catechins onto PVPP. According to the Langmuir model, the maximum monolayer adsorption amounts (Q_m) of total catechins were predicted to be higher than 630 mg g^{-1} at 20−60 °C (Table 2), which was around 4 times as high as other reported adsorbents, such as lignocellulose,[11,12] graft-modified lignocellulose[13] and synthesized adsorbents.[14,31] Table 2 also showed that the predicted Q_m decreased with an increase in temperature, displaying a similar tendency with the Q_e observation (Figure 7). The predicted K_F, a Freundlich constant related to the adsorption capacity, exhibited a similar pattern along with the temperature change as Q_m from the Langmuir model. All heterogeneous factors ($1/n$) of catechins were lower than 0.5 as predicted by the Freundlich model, revealing that the adsorption of catechins onto PVPP was a favorable process.[32] A similar conclusion could be drawn by calculation of dimensionless separation factor (R_L, indicating the isotherm adsorption process to be either unfavorable when $R_L > 1$, linear when $R_L = 1$, favorable when $0 < R_L < 1$ or irreversible when $R_L = 0$), which was defined as $R_L = 1/(1 + K_L C_0)$ (where K_L was the affinity constant of the Langmuir model, and C_0 was the initial concentration of adsorbates) by Hall et al.[33] because all the R_L was lower than 0.35 in this study. Isothermal adsorption behavior of caffeine along with the temperature change was similar to that of catechins, however, it could be described neither by the Langmuir nor by the Freundlich model because of their poor predicted parameters (Table 2). This phenomenon also supported the previous assumption in kinetics test. Interaction between catechins and caffeine might really affect the behavior of caffeine at the interface of liquid and solid. Testing should be conducted furthermore to illustrate the effect of catechins on the adsorption behavior of caffeine on the PVPP surface.

Thermodynamics for Adsorption of Adsorbates onto PVPP. Thermodynamic parameters such as Gibbs free energy ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) for the adsorption of catechins and caffeine onto PVPP are given in Table 3. It implies that adsorption of catechins and caffeine onto PVPP was a feasible and spontaneous process since all the $\Delta G°$ values for adsorbates were negative, and that adsorption of catechins was much easier than that of caffeine since values of ΔG for catechins were lower than that for caffeine. The adsorption process could be classified into physisorption when $\Delta G°$ ranged from −20 kJ mol^{-1} to 0 kJ mol^{-1} and chemisorption when $\Delta G°$ ranged from −400 kJ mol^{-1} to −80 kJ mol^{-1}.[34] From this view, adsorption of catechins and caffeine onto PVPP might belong to physisorption process. $\Delta H°$ reflects the amount of heat released when the reaction occurs at constant pressure. The negative values of $\Delta H°$ implied that the adsorption of catechins and caffeine onto PVPP was an exothermic process, and the adsorption process became difficult at high temperature which was supported by the decrease in Q_e values of adsorbates along with an increase in temperature. Relevantly, the effect of temperature on adsorption of caffeine was more dramatic than that of catechins as the $\Delta H°$ value for caffeine was much lower. According to thermodynamic laws, the adsorption of total catechins onto PVPP occurred spontaneously even at high temperature since positive $\Delta S°$ (12.29 J mol^{-1} K^{-1}) and negative $\Delta H°$ (−9.22 kJ mol^{-1}) values were observed, while spontaneity for the adsorption of caffeine decreased along with an increase in temperature since negative $\Delta S°$ (−57.06 J mol^{-1} K^{-1}) and $\Delta H°$ (−27.03 kJ mol^{-1}) values were observed. This was in good line with the previous observation on selectivity coefficient of total catechins vs caffeine which increased with increasing temperature (Figure 8). It suggested clearly that hydroxyl groups in adsorbate molecular might play an important role for interaction on the interface of adsorbate and adsorbent. Furthermore, there were some differences in thermodynamics between ester-catechins (such as EGCG, GCG, ECG and CG) and non-ester-catechins (such as EGC, GC, EC and C), i.e., positive $\Delta S°$ and negative $\Delta H°$ values for the former and both negative $\Delta S°$ and $\Delta H°$ for the latter (Table 3). It implied that the adsorption spontaneity of ester-catechins was obviously stronger than that of non-ester-catechins, revealing that adsorption characteristics were also impacted by the number of hydroxyl groups in the adsorbate molecule. This result confirmed the previous finding in the kinetic test (Figure 5), i.e., adsorption of catechins onto PVPP might be mainly driven by hydrogen bonds besides hydrophobic association. Thermodynamically, low temperature was favorable to enhance adsorption amounts for catechins, while high temperature was favorable to improve the adsorption selectivity for catechins, especially for ester-catechins. Therefore, the suitable adsorption temperature should be further optimized before applying in large scale production when PVPP was used as adsorbent for separating ester-catechins from crude tea extracts.

Desorption of Adsorbates from PVPP. When the PVPP was collected after adsorption and incubated with 120 mL of water for 60 min at the first desorption stage, more than 90% of adsorbed or attached caffeine was eluted, while less than 15% of adsorbed catechins was eluted (Table 4). Especially, the desorbed catechins mainly were non-ester-type ones (such as GC, EGC, C and EC). More than 75% of adsorbed catechins was eluted by DMSO/ethanol (8/2, v/v) solution at the second desorption stage, and minor remaining caffeine was also eluted. After the two stages, the total desorption rate of catechins and caffeine was higher than 91% and 99%, respectively. This result supported the previous assumption that caffeine might be attached indirectly onto PVPP because it could be easily eluted or washed down by the water. High desorption efficiency of catechins from PVPP by DMSO/ethanol solution might be attributed to the disturbance effect of DMSO on the hydrogen bond interactions and hydrophobic associations between PVPP and catechins since DMSO was usually used as an interfering reagent to disturb these interactions between polyphenols and

Table 4. Desorption of Adsorbates from PVPP by Two Stage Elution[a]

	catechins										
	GC	EGC	C	EC	EGCG	GCG	ECG	CG	total	caffeine	catechins/caffeine
adsorption amount (mg)	19.89 ± 0.31	106.9 ± 1.2	8.45 ± 0.12	48.28 ± 0.49	230.5 ± 1.3	13.24 ± 0.21	79.57 ± 0.89	2.651 ± 0.022	509.1 ± 8.7	26.16 ± 0.40	19.46 ± 0.19
desorption amount in first elution stage (mg)	7.35 ± 0.16 (36.95)	46.1 ± 1.9 (43.17)	1.692 ± 0.049 (20.00)	17.76 ± 0.33 (36.79)	0.441 ± 0.014 (0.19)	0.1897 ± 0.0025 (1.44)	0.145 ± 0.014 (0.19)	0.0524 ± 0.0035 (1.89)	73.76 ± 2.78 (14.49)	24.21 ± 0.72 (92.55)	3.05 ± 0.14
desorption amount in second elution stage (mg)	12.979 ± 0.072 (65.26)	59.3 ± 1.9 (55.52)	5.39 ± 0.13 (63.79)	29.75 ± 0.70 (61.62)	203.4 ± 2.0 (88.27)	11.80 ± 0.39 (89.12)	65.2 ± 2.9 (81.92)	2.193 ± 0.048 (82.64)	390.0 ± 3.5 (76.61)	1.922 ± 0.081 (7.34)	203.2 ± 4.5
total desorption (mg)	20.33 ± 0.10 (102.23)	105.46 ± 0.68 (98.69)	7.082 ± 0.079 (83.79)	47.51 ± 0.38 (98.39)	203.9 ± 2.0 (88.46)	11.98 ± 0.39 (90.55)	65.3 ± 2.9 (82.09)	2.245 ± 0.046 (84.71)	463.8 ± 6.3 (91.10)	26.13 ± 0.78 (99.90)	/

[a] During adsorption pretreated PVPP (dry weight 1.000 g) was incubated with 30 mL of GTE solution (2.5%, w/v) at 20°C for 24 h. The collected PVPP after filtration was incubated with 120 mL of water and with 60 mL of DMSO/ethanol (8/2, v/v) at 20°C for 60 min in the first and second elution stages in turn. The data are shown as mean ± standard deviation of triplicate tests (desorption rates in parentheses).

haze-active proteins,[25,35] while the characteristic of haze-active proteins was in some cases similar to the PVPP as reported by Siebert and Lynn[16] and Laborde et al.[36] The desorption result also showed that the ratio of catechins to caffeine in DMSO/ethanol eluate (203.2) was much higher than that in water eluate (3.05) and in adsorbate (19.46), and also higher than our previous reports focusing on other adsorbates;[12,14] in another words, catechins were enriched at the second desorption stage, while caffeine was enriched at the first desorption stage. Therefore, this desorption procedure was suitable for decaffeination of crude tea extracts when PVPP was used as an adsorbate. DMSO is difficult to be evaporated under normal atmosphere because of its high boiling point (189 °C); however, it belongs to a nontoxic-level reagent and is sometimes used as a vehicle for topical application of pharmaceuticals.[37] Thus, decaffeinated catechins in DMSO might directly be applied for developing some functional products such as UV-light shelter. Alternatively, other eluants with low boiling point and high desorption efficiency should be further explored in order to expand the application area of catechins.

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Funding Sources

This study was financed by the "Key R&D Project" of Science and Technology Office of Zhejiang Province and "R&D Project" of Education Office of Zhejiang Province.

ACKNOWLEDGMENT

The authors thank Dr. Takeda for kind supply of the HPLC reference catechins.

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