



Selective adsorption of tannin from flavonoids by organically modified attapulgite clay

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ABSTRACT

In this study, selective adsorption of tannin on organically modified attapulgite clay was investigated. Tannin was selectively removed from model tannin/flavonoids mixtures in the solution. In adsorption isotherm experiments of tannin, obtained data fitted well to the Freundlich model. The surface sites of the octadecyl trimethyl ammonium chloride (OTMAC)-attapulgite were heterogeneous. The effect of pH on tannin adsorption was also investigated and the results showed that the adsorbed amount of tannin was highest at pH 6.0. The enthalpy values of adsorption of tannin on OTMAC-attapulgite at pH 4.0, 6.0 and 8.0 were -49.80 , -74.31 and -38.62 kJ/mol, respectively. At 2–5.3 and 7.4–10, the driving forces for the adsorption may be the hydrophobic force and hydrogen bonding. And at pH 5.3–7.4 the electrostatic force may be the most important one. These facts implied that the selective adsorption of tannin on OTMAC-attapulgite was driven by the collaboration of hydrogen bonding, electrostatic force and hydrophobic interactions of tannin molecular with adsorbent. The low adsorption of isoflavones of soybean and the puerarin was ascribed to less phenolic hydroxyls of them than those of tannin, which made the low electrostatic interactions and hydrogen bonding interactions between the tannin and OTMAC-attapulgite adsorbent.

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1. Introduction

A large group of phenolic compounds in plant associated with plant defenses are biologically active non-nutrients. Tannins are usually contained in most physiologically active compounds extracted from plant. Vegetable tannins are secondary plant metabolites subdivided into condensed and hydrolyzable compounds. The hydrolyzable tannins are gallic and/or gallic acid which easily hydrolyze in acidic media. Condensed tannins are polymeric flavanoids. Tannins are a double-edged sword in biology and health. Intake of a small quantity of the right kind of tannins may be beneficial to human health. However, ingestion of large quantities of tannins may result in adverse health effects. Tannins may injure the intestinal mucosa [1], alter intestinal secretions [2], form insoluble complexes with dietary protein [1,3], inhibit digestive enzymes [4], and increase the excretion of endogenous proteins [5]. Tannin components have also been implicated in the high levels of cheek and esophageal cancers in certain regions of the world [6], and to produce other physiological effects such as immune response, hepatotoxicity and lipid metabolism [7]. Hydrolyzable

tannins are easy to be hydrolyzed into gallic acid, which leads to the loss of metal elements in human body because of the metal chelation [2], which are more toxic than condensed tannins.

Flavonoids, the largest group of phenolic compounds, have long been recognized to possess anti-inflammatory, anti-lergenic, antiviral and anti-proliferative activities, including flavonols, flavones, catechins, proanthocyanidins, anthocyanidins and isoflavonoids [8]. It is known that 70% of medical plants contain tannins [9]. Generally, tannins in Chinese traditional medicine are considered useless or harmful components, especially the hydrolyzable tannins, and should be removed. Adsorbing by polymer resins [7], collagen fiber [10], zirconium pillared clay [11] and insoluble polyvinylpyrrolidone (PVPP) [12] has been reported to remove tannins. Electrochemical removal of tannins from aqueous solution was also reported [13].

Organic–inorganic hybrid adsorbent could be applied to selective adsorption [14]. Recent research proved organically modified montmorillonite could be used to remove tannin [15] and also has selective properties [16]. However, selective adsorption of organically modified attapulgite was not studied. Attapulgite is a special class of clay mineral under the 2:1 layer composition with commonly a lath or fibrous morphology. Attapulgites are hydrated magnesium silicates. In such materials octahedral layers of magnesium with partial substitution with aluminium and/or iron is

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sandwiched between $(\text{SiO})_4$ tetrahedral layer and $\text{Al}(\text{OH})_3$ octahedral unit. The tetrahedral sheet is continuous across ribbons at the apical oxygen alternately pointing up and down in adjacent ribbons. The octahedral sheet is discontinuous with a variable charge imbalance [17]. There are large reserves of attapulgite in South China (Jiang Su, Zhe Jiang and An Hui province) and the USA (Florida).

Organic modification is a useful process to change the properties and characterizations of the attapulgite, by which the hydrophobic arms are grafted on the attapulgite. The modification by ammonium citrate tribasic [18], hyperbranched aliphatic polyester [19], γ -methacryloxypropyl trimethoxysilane [20] and cetyltrimethylammonium bromide [21] has been reported. It is known that native attapulgite is ineffective adsorbents towards water soluble organic molecules [22,23]. It was found the octodecyl trimethyl ammonium chloride modified attapulgite (OTMAC-attapulgite) exhibited strong adsorptive capabilities for organic molecules with phenolic hydroxyls in our previous works [24,25]. Based on the fact that tannin has many phenolic hydroxyls, the OTMAC modified attapulgite is a potential useful adsorbent for selective adsorption of tannin.

The present work is the removal of the tannin from flavonoids by selective adsorption on the OTMAC-attapulgite. Isoflavone of soybean, and puerarin were the flavonoids selected to investigate the adsorption selectivity of the OTMAC-attapulgite.

2. Materials and methods

2.1. Materials

The attapulgite used in this work was supplied by Oilbetter Co. (China). OTMAC was obtained from the Feixiang Chemicals Co. (China). Soybean isoflavones and puerarin were obtained from Jinan Xinna Medicine Science and Technology Co. Ltd. (China), the former composed of daidzin and genistin, and the latter showing a single component, both from high performance liquid chromatography (HPLC). Other chemicals and solvents were obtained from Chinese Chemicals Company and were of analytical grade.

2.2. Adsorbent

The OTMAC-attapulgite was prepared and characterized according to our previous report [25]. Fourier transform infrared spectroscopy, BET surface area, and X-ray diffraction, respectively demonstrated that octodecyl trimethyl ammonium had been grafted, the resulting OTMAC-attapulgite had a surface area of $63.96 \text{ m}^2/\text{g}$, a large reduction from that of native attapulgite ($167.24 \text{ m}^2/\text{g}$), and the structure of attapulgite was maintained after modification.

2.3. Selective adsorption

Original solutions of puerarin/tannin mixtures in water and soybean isoflavones/tannin mixtures in mixed solvents of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (50:50, v/v), as model systems for adsorption tests, were prepared in different ratios. Adsorption experiments were conducted by addition of 50 ml of adsorbates solution and 0.20 g of adsorbent in airtight volumetric flasks. The flasks were shaken at 30°C for 3 h. Preliminary investigations showed that a 3-h adsorption period was sufficient for reaching equilibrium. After equilibration, each mixture was centrifuged (4000 rpm, 10 min) and the supernatant (equilibrium solution) were collected. The composition of each original solution and its corresponding equilibrium solution were determined by HPLC (Waters 2996, Waters Corporation, Milford, MA) installed with a Sunfire C18 ($5 \mu\text{m}$, $250 \text{ mm} \times 4.6 \text{ mm}$).

2.4. Effect of pH on adsorption of tannin

Adsorbent (0.10 g) was suspended in 50 ml tannin solution with a concentration of 1.0 mg/ml. The initial pH values of the tannin solutions were adjusted to different values in the range of 2.0–10.0 with 0.10 M NaOH or 0.10 M HCl. Adsorption was conducted by constant shaking for 3 h at 30°C . Supernatant was collected after centrifugation (4000 rpm, 10 min) and the uptake of the tannin was monitored spectrophotometrically by measuring the absorbance at λ_{max} of 275 nm.

2.5. Adsorption isotherms

Adsorbent (0.10 g) was suspended in 50 ml tannin solution at natural pH and of known concentration. Adsorption experiments were conducted by constant shaking for 3 h at 30, 45 and 60°C , respectively. Supernatant was collected after centrifugation (4000 rpm, 10 min) and the uptake of the tannin was determined as per Section 2.4.

3. Results and discussion

3.1. Selective adsorption

The adsorption of OTMAC-attapulgite towards tannins from flavonoids was judged by comparing the HPLC pattern of the original solution and that of the equilibrium solution (for examples, see Figs. 1 and 2). The essential disappearance in the equilibrium solution of the peaks at 2.7 min (Fig. 1) and 7.1 min (Fig. 2) pertaining to tannins in the original solution indicates highly favored absorption towards tannins.

This selective adsorption of tannin from flavonoids might be ascribed to the collaboration of hydrogen bonding between tannin molecule and hydroxyl functional group of attapulgite per se, and hydrophobic interaction of tannin molecule with $-\text{N}^+(\text{C}_{18}\text{H}_{37})(\text{CH}_3)_3$, the hydrophobic arm grafted by modification. Tannin molecules, although contain phenolic hydroxyls, the aromatic rings were still hydrophobic. It was indicated that tannins first approach the surface of the adsorbents by hydrophobic bonding, and then combine with adsorbents by multi-hydrogen bonding formed between phenolic hydroxyls of tannin and the hydrogen bonding sites on the adsorbent [15,26]. The principal adsorption active group distributed on the surface of attapulgite is hydroxyl, with which hydrogen bonding can be formed, and a hydrophobic group is grafted on the attapulgite by modification of OTMAC, hence it is tentatively deduced that the initial step of tannin adsorption to OTMAC-attapulgite might also be driven by hydrophobic forces, and then tannin molecules combine with OTMAC-attapulgite by multi-hydrogen bonding. Soybean isoflavones and puerarin are also hydrophobic, so that they are also able to approach the surface of the adsorbent; but due to the less abundance of phenolic hydroxyls in them, the multi-hydrogen bonding with the attapulgite of these two molecules are somewhat weaker than that of tannin.

3.2. Effect of pH on adsorption of tannin

Tannin as an acid can be ionized in aqueous solution. To investigate the relevance of electrostatic force to the adsorption of tannin on OTMAC-attapulgite, adsorption tests were conducted on tannin solutions at different pHs ranging from 2.0 to 10.0.

The adsorbed amount of tannin increased with increasing of pHs from 2.0 to 6.0, reached a maximum at pH 6.0, and then decreased sharply with further increasing of pHs up to 10 (Fig. 3). Since the solubility of tannin showed little changes at the pHs tested (results also plotted in Fig. 3), the possibilities of pH fluctuation induced

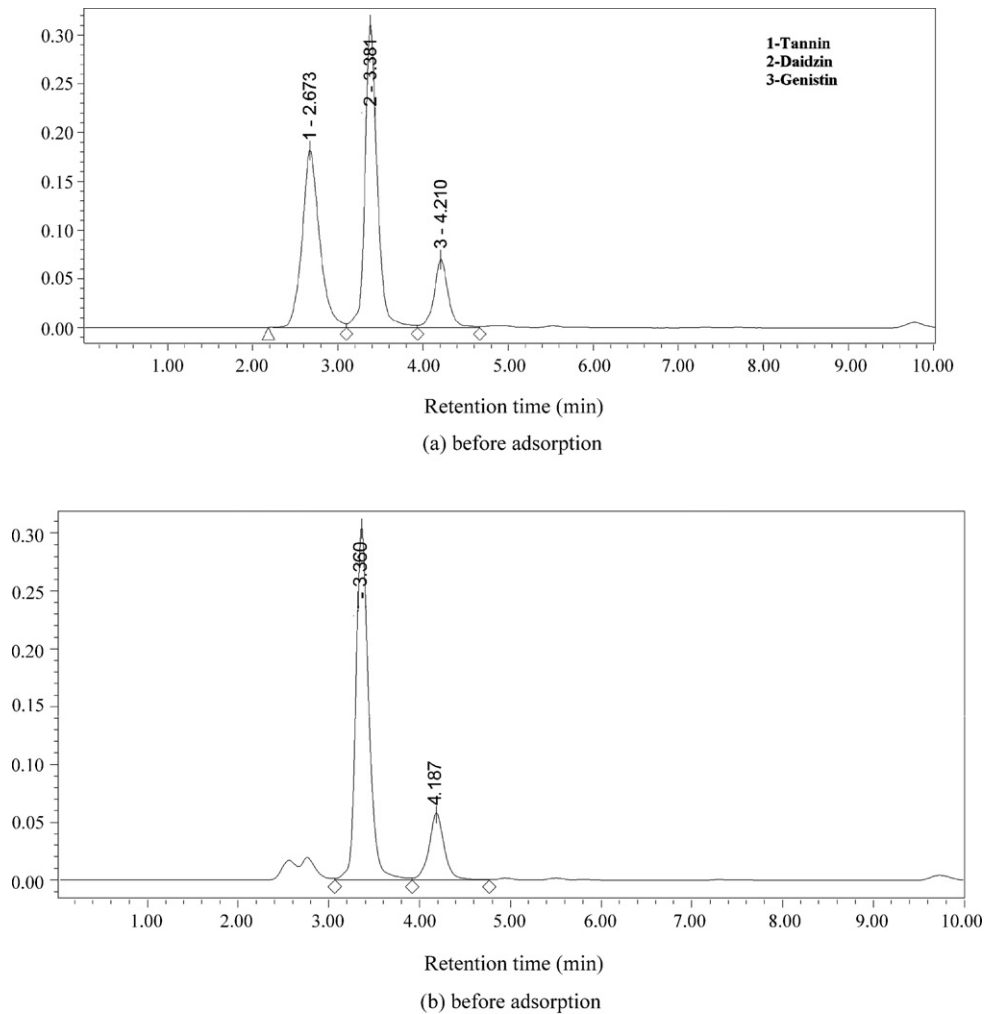


Fig. 1. HPLC chromatogram of the mixed solution of isoflavones of soybean and tannic acid (a) before and (b) after adsorption by organo-attapulgit (initial content of isoflavones of soybeans and tannic acid in the solution was 500 mg/l, respectively; mobile phase: 0.4% H_3PO_4 : CH_3OH = 45:55 (v:v); column: sunfire C18, 4.6 mm \times 250 mm, 5 μm ; flow rate: 0.6 ml/min; detector: PDA, 270 nm; injection volume: 2 μl).

tannin precipitation is excludable. The ionization of tannin as a weak organic acid is strongly dependent on environmental pHs. The pK_a value of the tannin used in this work was determined at 7.4. The pK_a value of the OTMAC-attapulgit was determined at 5.3. Hence at higher pHs in the range of 2–5.3, both of the OTMAC-attapulgit and tannin carries less positive charges related with lower expelling electrostatic force, which is in agreement of the positive correlation of tannin adsorption with pH increases. And similar agreements exist between changes in molecular charges and adsorption amount as influenced by pH at 7.4–10. The driving forces for counteracting the expelling electrostatic force should be attributable to hydrophobic force and hydrogen bonding. Positive charges carried by tannin decreased and negative charges on the OTMAC-attapulgit increased with increasing of pH from 5.3 to 7.4, which caused the change of the electrostatic force between them at pH 5.3–7.4. And the electrostatic force may be the most important force for the maximum adsorption of tannin on OTMAC-attapulgit at pH 6.0.

3.3. Adsorption isotherms

The isotherms of tannin adsorption on adsorbent at different temperature were showed in Fig. 4. The experimental isotherm

data fitted to Freundlich equation (Eq. (2)) better than to Langmuir equation (Eq. (1)), while the experiment data was fitted to the two models. The parameters of the fitted curves were summarized in Table 1.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \quad (1)$$

$$\ln q_e = \ln K_F + \ln \frac{C_e}{n} \quad (2)$$

where q_e is the amount of tannin adsorbed, C_e the equilibrium concentration of tannin, and Q_0 and b are the Langmuir constants related to maximum monolayer capacity and energy of adsorption, respectively, K_F and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity.

Table 1
Langmuir and Freundlich constants for the sorption of tannin on organo-attapulgit

Temperature (K)	Langmuir			Freundlich		
	b	Q_0	R^2	K_F	n	R^2
303	0.006491	106.383	0.8913	20.0078	3.0276	0.9869
318	0.005392	163.934	0.8756	19.0678	3.4317	0.9826
333	0.011537	208.333	0.8041	31.1961	5.9630	0.9940

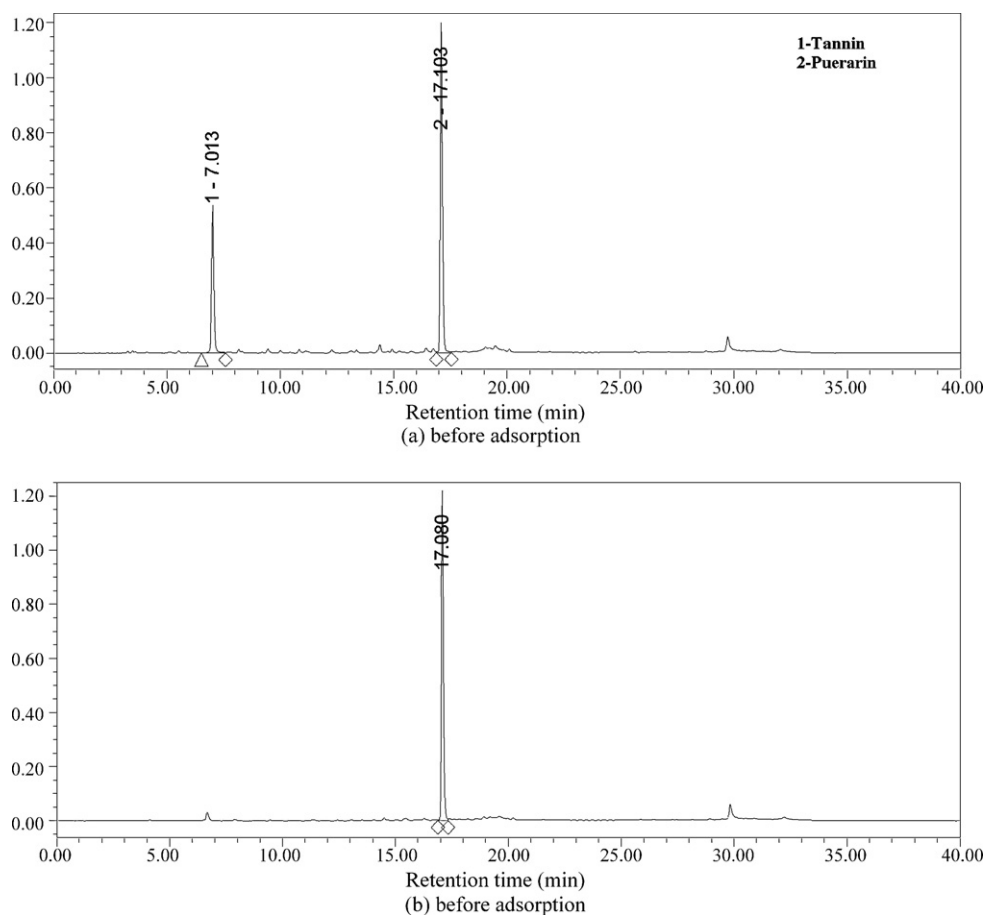


Fig. 2. HPLC chromatogram of the mixed solution of puerarin and tannic acid (a) before and (b) after adsorption by organo-attapulgit (initial content of puerarin and tannic acid in the solution was 500 mg/l, respectively; mobile phase: (A) aqueous solution of 0.4% CH₃COOH, (B) CH₃OH; column: sunfire C18, 4.6 mm × 250 mm, 5 μm; flow rate: 1.0 ml/min; detector: PDA, 275 nm; injection volume: 6 μl; gradient: 0–30 min with 0–100% B, 30–40 min with 100–0% B).

Based on the consideration that Langmuir isotherm is founded on the basis of homogenous surface while Freundlich isotherm promises to be applied to adsorption process occurred on heterogeneous surface, we deduced that the used adsorbent might be of surface energy heterogeneity. Although the surface energy heterogeneity pattern need to be further explored. The magnitude of the exponent $1/n$ gives an indication of the favorability and the capacity of the adsorbent/adsorbate system. It is generally stated that the values of $1/n$ in the range 0.1–1 represent good adsorption. In the present work, the exponent was $0.1 < 1/n < 1$ indicating favorable adsorption. Satisfactory fitting of the Freundlich model to the adsorption isotherms of tannin on hide collagen fibers [27], chitosan-montmorillonite [28], hyper-crosslinked polydivinylbenzene, macroporous crosslinked poly(*N*-vinyl acetamide) and gel type poly(styrene-co-divinylbenzene) post-crosslinked with isocyanuric acid adsorbents [29] has been reported.

3.4. Heterogeneity of adsorbents

The distribution coefficient K_D can be employed to describe the binding ability of adsorbent surface for an element. The values of the adsorption were calculated as [30]

$$K_D = \frac{C_S}{C_W} \quad (3)$$

where C_S is the concentration of tannin in solid particles (mg/g) and C_W is the concentration of tannin in water (mg/l).

The distribution coefficient K_D decreased with the increase in the adsorbent amount from 0.020 to 0.20 g at a fixed adsorbate concentration (0.10 mg/ml), natural pH, and temperature of 30 °C (Fig. 5). This was consistent with the argument that surface sites of the adsorbent were heterogeneous. If the surface was homogeneous, the K_D values at a given pH should not change with adsorbent amount [30]. According to the surface site heterogeneity model,

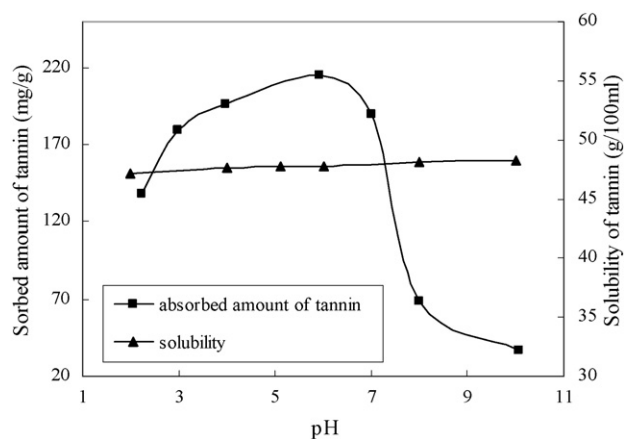


Fig. 3. Effect of pH on the adsorption of tannin on the organo-attapulgit and the solubility of tannin in aqueous solution (adsorption experiments: adsorbent dosage 0.10 g, contact time 3 h, C_0 1.0 mg/ml, temperature 30 °C).

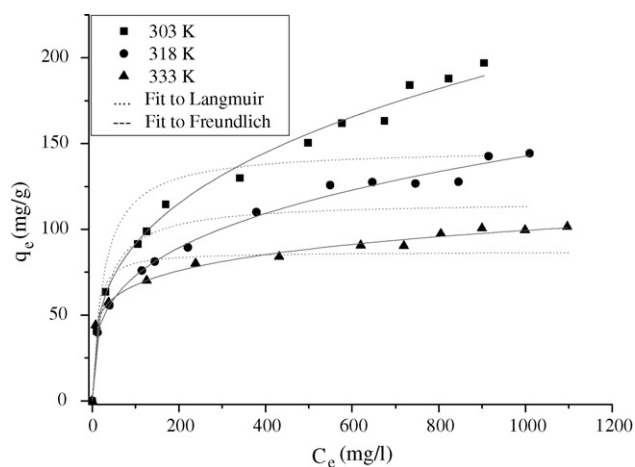


Fig. 4. Adsorption isotherms of tannin on the organo-attapulgit (adsorbent dosage 0.100 g, contact time 3 h).

the surface was composed of sites with a spectrum of binding energies. At low adsorbent dose, all types of sites were entirely exposed for adsorption and the surface got saturated faster, showing a higher q_e values. But at higher particle concentrations the availability of higher energy sites decreased with a larger fraction of lower energy sites becoming occupied, resulting in a lower q_e values (Fig. 5).

3.5. Thermodynamic parameters

Following van't Hoff equilibrium equation, i.e.

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (4)$$

where T is the adsorption temperature, ΔH is enthalpy for the adsorption, ΔS is entropy for the adsorption, R and K are constants. The equilibrium constant, K was obtained from the equation $K = (C_0 - C_e)/C_e$, where C_0 is the initial concentration of adsorbate, C_e is the equilibrium concentration of adsorbate in supernatant.

ΔH was calculated from the slope of van't Hoff equilibrium by plotting of $\ln K$ versus $1/T$. In this study, the values of enthalpy change for tannin adsorption on attapulgit at pH 4.0, 6.0 and 8.0 were -49.80 , -74.31 and -38.62 kJ/mol, respectively. The negative value of the enthalpy change indicated an exothermic adsorption process of tannin onto the adsorbent. Similar trend was observed for adsorption of tannin on polymeric adsorbents [29] and

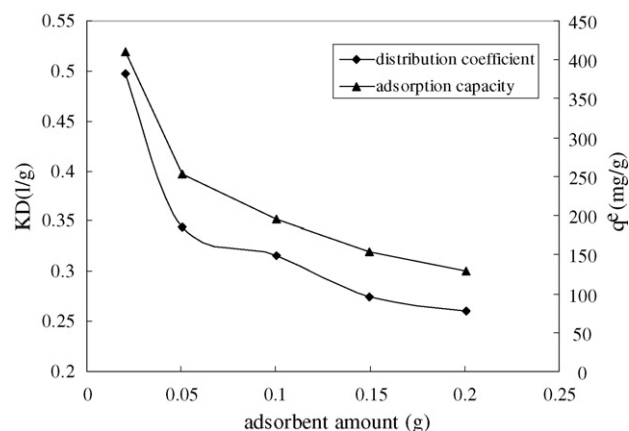


Fig. 5. Effect of adsorbent amount on the distribution coefficient (K_D) and adsorption capacity (q_e) (contact time 3 h, C_0 1.0 mg/ml, temperature 30 °C).

cationic surfactant-modified bentonite [15]. The energy released during the adsorption process compensates for the entropy loss of adsorbed molecules. The stronger the forces, the more the energy released. The energy released by different forces during adsorption is unequal. Larger molecules may have more functional groups available to simultaneously bind with the surface [31]. The cumulative effect of multiple binding to the surface can be very large [32]. Thus according to the energy of the tannin adsorption on OTMAC-attapulgit, the dominant forces contributing to the adsorption may be determined and then the adsorption mechanism can be deduced. Oepen et al. [33] measured the ranges of energy of adsorption from different forces: Van der Waals forces 4–10 kJ/mol, hydrophobic bond forces about 5 kJ/mol, hydrogen bond forces 2–40 kJ/mol, coordination exchange about 40 kJ/mol, dipole bond forces 2–29 kJ/mol, chemical bond forces >60 kJ/mol. In this study, the enthalpy for the adsorption of tannin on OTMAC-attapulgit was -49.80 kJ/mol for pH 4.0 and -38.62 kJ/mol for pH 8.0, this fact might also conclude that the hydrophobic interaction and hydrogen bonding interaction may be the most important adsorption mechanism, and the difference of the two enthalpies may be ascribe to more hydrogen bonding formed at pH 4.0 than at pH 8.0, which was consist with the results of per Section 3.2 that more effective adsorption of tannin at pH 4.0 than at pH 8.0. The enthalpy for the adsorption of tannin on OTMAC-attapulgit was -74.31 kJ/mol for pH 6.0, the highest value of the three, which might be ascribe to the electronic interaction, a chemical interaction.

4. Conclusion

Organically modified attapulgit has been shown to be an effective solid phase selective adsorbent for tannin. The adsorbed amount of tannin on the adsorbent was highest at pH 6.0. The values of enthalpy change for tannin adsorption at pH 4.0, 6.0 and 8.0 were -49.80 , -74.31 and -38.62 kJ/mol, respectively. The selective adsorption of tannin from flavonoids might be ascribed to the collaboration of hydrogen bonding of tannin molecule with hydroxyl functional group of adsorbent, electrostatic interaction and hydrophobic interaction of adsorbed adsorbate with adsorbent. At 2–5.3 and 7.4–10, the driving forces for the adsorption may be the hydrophobic force and hydrogen bonding. And at pH 5.3–7.4 the electrostatic force may be the most important one. The adsorption isotherms fitted the Freundlich better than Langmuir model. The heterogeneous surface of the adsorbent was composed of sites with a spectrum of binding energies.

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