Thermodynamics aspect of tannin sorption on polymeric adsorbents

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Abstract

Hypercrosslinked polydivinylbenzene and gel type poly(styrene-co-divinylbenzene) post-crosslinked with isocyanuric acid and macroporous crosslinked poly (N-vinyl acetamide) adsorbent were prepared for adsorbing tannin from aqueous. The sorption isotherms were measured and the isosteric enthalpy was quantitatively correlated with the fractional loading for the tannin sorption onto the three polymeric adsorbents. Surface energetic heterogeneity was observed for the three adsorbents and described with the functions of isosteric enthalpy. The causative factors of the surface heterogeneity of the adsorbents and the mechanism of tannin sorption onto the adsorbents from aqueous were discussed. It was suggested that multiply hydrogen bonding, $\pi-\pi$ interaction and hydrophobic interaction were involved in tannin adsorption onto the polymeric adsorbents.
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1. Introduction

Tannin is a plant secondary metabolite and is found in approximately 80% of woody and 15% of herbaceous dicotyledenous species [1]. It is a polyphenolic compound distinguished with other polyphenolic compounds by its ability to precipitate proteins. Astringency and adverse postingestive influences of tannin on the epithelium of the oral cavity and the foregut cause short-term effects on food intake. If significant amount of tannin reach the duodenum, they may markedly reduce the intestinal activity of pancreatic enzymes (trypsin and amylase) and amino acid absorption from the intestine [2]. Removal tannin from food and medicine products made from plant is of great importance to improve the quality of them.

Polymeric adsorbents is of higher stability, higher selectivity and easier to be regenerated as comparing with porous inorganic materials. They are of adjustable functionality, surface area and porosity. Consequently they have

been broadly applied for the extraction of natural products, waste water treatment for pollution control, rare precious metal recovery, medicine manufacture and in biologic medical field such as hemoperfusion. Various macroporous crosslinked polymeric adsorbents have been used to selectively removal specific organic compounds from contaminated water [3–10]. A new type of permanent porous polymeric adsorbent [11], the so-called hypercrosslinked polymers, has high specific surface area and high micropore content. It is thought as one of the prominent candidates for the alternative of active carbon. The high adsorption performance of hypercrosslinked polymeric adsorbents has been ascribed to their high specific surface areas and high micropore contents in literatures. In our previous work, series of macroporous polymeric adsorbents have been developed for the adsorption of phenols from aqueous solution based on hydrogen bonding [12–15]. Polymeric adsorbents bearing isocyanuric acid as functional group were showed to be capable of eliminating phenols from aqueous solutions [12,14]. And macroporous crosslinked poly(N-vinyl acetamide) was used as adsorbent to adsorb tannin, which showed capability for eliminating tannin from aqueous solutions [15].

Adsorption thermodynamics investigation is of great importance for the developing of adsorbents and sorption

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processes. Sorption isotherm equation, sorption heat are the basic aspects of the design of adsorption process. Thermodynamics investigation could reveals the sorption mechanism as well. Hence it is beneficial to the optimization of designing adsorbent. A lot of work has been focused on the determination of sorption isotherms and their fitted model [16–18]. Generally, sorption isosteric enthalpy varies with the varying of adsorption loading when organic compound is adsorbed onto polymeric adsorbents [12–15]. Which means energy heterogeneity existing on adsorbents. To the best of our knowledge, the surface heterogeneity of polymeric adsorbent has been seldom quantitatively described in literatures at present [19,20]. To develop more effective polymeric adsorbents and to optimize the adsorption process for eliminating tannin from aqueous solutions, the present work is to clarify the basic thermodynamics aspect and the mechanism of tannin sorption onto polymeric adsorbents. Therefore, this work was focused on dealing with the isotherms and isosteric enthalpy of tannin adsorption on hypercrosslinked polydivinylbenzene-isocyanuric acid, gel type crosslinked poly(styrene-*co*-divinylbenzene)-isocyanuric acid and macroporous poly(*N*-vinyl acetamide) adsorbent and clarifying the relationship of isosteric enthalpy with the fractional loading and the sorption mechanism of tannin.

2. Experimental

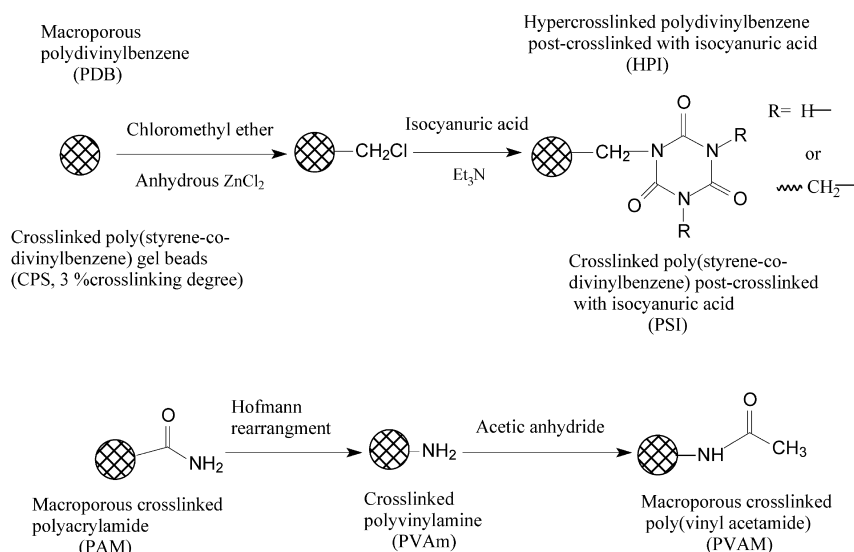### 2.1. Preparation of polymeric adsorbents

The protocol of the preparation of hypercrosslinked polydivinylbenzene post-crosslinked with isocyanuric acid (HPI), gel type poly (styrene-*co*-divinylbenzene) post-crosslinked with isocyanuric acid (PSI) and crosslinked poly (*N*-vinyl acetamide) (PVAM) were illustrated as Scheme 1.

Macroporous polydivinylbenzene (PDB) was prepared with conventional suspension polymerization technique using 45–50% inhibitor-free divinylbenzene as the starting material, 200# gasoline as porogen. The resultant polymer beads were then chloromethylated with chloromethyl ether (its density is greater than 1.08 g/ml) by the method described in Ref. [21]. 10 g chloromethylated PDB was swollen with 60 ml DMF in 250 ml three-neck round bottom flask for a night. 5.0 g isocyanuric acid and 6.0 g triethylamine were added into the reaction vessel and refluxed while stirring for 24 h. The resultant polymer beads were subsequently washed with hot deionized water and extracted in a Wheaton Soxhlet extraction apparatus with alcohol for more than 10 h. Then dried at 50 °C under reduced pressure and thus HPI adsorbent was gotten ready for subsequent use.

Gel type crosslinked poly(styrene-*co*-divinylbenzene) with 3% crosslinking degree was used as the starting material to prepare PSI. Same chloromethylation and post-crosslinking procedure as mentioned above were performed on this starting material.

Macroporous poly(acrylamide-*co*-N,N′-methylenebisacryamide) (PAM) of 20% crosslinking degree was synthesized using free-radical inverse phase suspension polymerization technique. Hofmann rearrangement was performed on the resultant PAM resin. 40 g wet PAM resin were suspended in 100 ml sodium hypochlorite at −15 °C. 30 ml 10 mol × l⁻¹ NaOH were added into the mixture and sustaining the temperature below −10 °C for 10 h with stirring. The resultant crosslinked polyvinylamine (PVAm) beads were collected with a filter and washed with deionized water thoroughly till no Cl⁻ could be detected in supernatant by 0.1 mol × l⁻¹ AgNO₃. The PVAm beads were then reacted with acetic anhydride following to the

Scheme 1. The preparation protocol of HPI, PSI and PVAM adsorbent.

procedure described in Ref. [22]. Then crosslinked poly-(vinyl acetamide) adsorbent was obtained.

2.2. Characterization of polymeric adsorbents

The specific surface area of the polymeric adsorbent was measured with Micromeritics ASAP 2010 surface area measurement instrument following the BET method. Elemental microanalysis was performed on PE-2400 CHN Elemental Analytical Instrument. Water regain, weak acid and weak base exchange capacity of adsorbent were measured following the procedure described in Ref. [23].

2.3. Measurement of sorption isotherms of tannin

0.2000 g adsorbent and 50 ml tannin aqueous solution of known concentration were added into a cone-shaped flask equipped with stopper and shaken in a thermostatic oscillator at fixed temperature for more than 24 h till equilibrium adsorption was reached. Then the concentration of tannin in the supernatant was determined according to the method described by Ref. [24]. The amount of adsorbed tannin per gram of adsorbent was then calculated from the starting and equilibrium concentration of tannin.

3. Results and discussions

3.1. Structural aspect of the three polymeric adsorbents

The nitrogen content of the adsorbents is 3.93 mmol $\times$ g^{-1} for HPI and 2.65 mmol $\times$ g^{-1} for PSI, based on elemental microanalysis. Consequently, the contents of isocyanuric acid, the post crosslinker, are 16.9, 11.3% for PSI and HPI, respectively. The weak acid exchange capacity is 0.78, 1.22 mmol $\times$ g^{-1} for HPI and PSI, respectively. These results show that each isocyanuric acid molecule had reacted with more than one chloromethyl group of chloromethylated PDB or CPS. Based on the isocyanuric acid contents and the weak acid exchange capacity, we can roughly estimate that a molar isocyanuric acid molecule reacted with 2.4 molar chloromethyl groups of chloromethylated CPS or 1.62 molar chloromethyl groups of chloromethylated PDB on average. Therefore, it is confirmed that in addition to divinyl benzene, isocyanuric acid crosslinking bridges exist in HPI and PSI adsorbent. For PDB contained divinylbenzene only, HPI, the product of post-crosslinking reaction of PDB with isocyanuric acid, must be a hypercrosslinked polymer. As for PSI, the initial crosslinking degree was only 3%, and contained only 16.9% isocyanuric acid in it, should be a usual crosslinked polymer.

The specific surface areas of dried HPI, PSI and PVAM are 793, ~ 0 and 18.3 m$^2 \times$ g^{-1} respectively. The results indicate that HPI and PVAM are porous materials. The opaque appearance of HPI and PVAM ascertained this

conclusion. The high specific surface area value of HPI ascertained that HPI is a highly crosslinked polymer. And the existing of a great number of micropores in HPI should be the causative factor of its high specific surface area value. PSI was the product of the post-crosslinking reaction of isocyanuric acid with CPS, which was a gel of polystyrene with 3% crosslinking degree. The transparent appearance of PSI showed it was a gel type polymer bead and has no porous structure at dry state. Thus the nearly zero specific surface area value of dried PSI is not a surprising result.

The weak base exchange capacity is 3.86 mmol $\times$ g^{-1} for PVAm and 0.45 mmol $\times$ g^{-1} for PVAM. The 3.41 mmol $\times$ g^{-1} deference of weak base exchange capacity between PVAm and PVAM is taken as the amount of the immobilized acetyl group on PVAM. The water regain of HPI, PSI and PVAM are 0.56, 0.61 and 4.81 ml $\times$ g^{-1} respectively. Which shows PVAM is of high hydrophilicity.

3.2. Isotherms of tannin sorption

The isotherms of tannin adsorption on HPI, PSI and PVAM at different temperature were showed in Fig. 1. All of the isotherms show to be type I isotherms [25]. The high to low sequence of tannin adsorption capacity of the three adsorbents is HPI > PSI > PVAM at the same equilibrium concentration of tannin at 298 K. HPI is of the greatest adsorption capacity for tannin among the three polymeric adsorbents because of it has much greater specific surface area than the other two adsorbents.

When fitting the experimental isotherms to Langmuir equation, significant deviation could be seen as showed in Fig. 1. Whereas the experimental isotherms are consistent with the fitting curves based on Freundlich equation. The parameters of the fitted curves were summarized in Table 1. Based on the consideration of that Langmuire 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 three polymeric adsorbents might be of surface energy heterogeneity. Although the surface energy heterogeneity patterns and the causative factors of the surface energy heterogeneity need to be further explored.

3.3. Isosteric enthalpy of tannin sorption

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

$$\ln C_e = \frac{\Delta H}{RT} + \ln K \tag{1}$$

Where C_e is the equilibrium concentration of adsorbate in supernatant, T is the adsorption temperature, ΔH is the adsorption enthalpy, R and K are constants. The isosteric enthalpy can conveniently obtained based on the isostere, the plot of $\ln C_e$ which related to the same equilibrium adsorption quantity vs. $1/T$. When plot $\ln C_e$ vs. $1/T$, we get
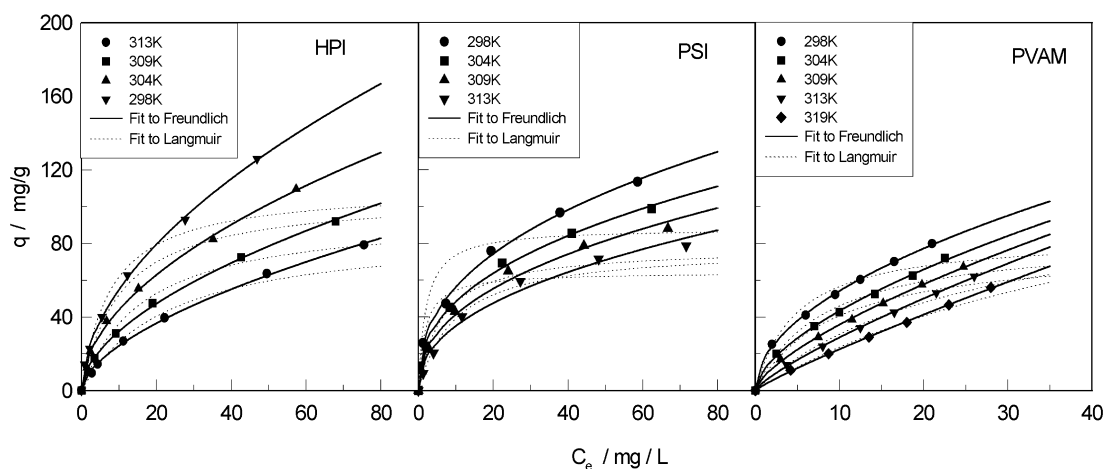
Fig. 1. Isotherms and fitted curves of tannin adsorption on HPI, PSI and PVAM adsorbent at different temperature.

a linear line and the isosteric enthalpy could be calculated from the slope of the line. The isosteres corresponding to the equilibrium adsorption quantities ranged from 15 to 75 mg/g at 5 mg/g interval for tannin adsorption on the tested three adsorbents were shown in Fig. 2. The linear regression correlative coefficients of the isosteres and the corresponding isosteric enthalpy were summarized in Table 2. The results suggested a well consistency of the experimental data with van't Hoff equilibrium equation. As above mentioned, surface heterogeneity was observed for all three adsorbents as the isosteric enthalpy varied with the changing in sorption loading of tannin on the surface of the three adsorbents.

3.4. Heterogeneity of adsorbents

In order to clarify the pattern of surface heterogeneity of the polymeric adsorbents, we adopted Do's model to fit the isosteric enthalpy [20]. Do's model is based on the isosteric enthalpy and it takes the enthalpy as a function of the fractional loading of adsorbate as given below

$$\Delta H(\theta) = \Delta H_0(\theta) - \delta H f(\theta) \tag{2}$$

Where $\Delta H(\theta)$ is the isosteric enthalpy corresponding to the adsorbate loading fraction of θ, ΔH_0 is the isosteric enthalpy at zero loading and δH represents the variation of the isoteric enthalpy with the loading fraction from zero to one ($\theta = 1$ means monolayer coverage). The ratio of δH to ΔH_0 reflects the extent of the energetic heterogeneity of the surface. The larger the ratio, the greater the extent of surface energy heterogeneity. $f(\theta)$ is a distribution function of surface energy taking θ as the variable factor and is used to represent the heterogeneity pattern. The following equation

Table 1
Fitting parameters for Langmuir and Freundlich isotherm

T (K)	Langmuir isotherm $1/q_e = 1/q_m b C_e + 1/q_m$			Freundlish isotherm $q_e = B C_e^{1/n}$		
	q_m	b	R	B	$1/n$	R
HPI						
313	87.26	0.043	0.9983	6.24	0.591	0.9972
309	95.96	0.061	0.9977	8.97	0.553	0.9952
304	106.15	0.096	0.9953	13.20	0.528	0.9979
298	81.90	0.247	0.9758	15.96	0.534	0.9992
PSI						
313	77.63	0.101	0.9977	12.74	0.438	0.9989
309	77.57	0.161	0.9958	15.62	0.421	0.9920
304	64.22	0.553	0.9719	19.15	0.401	0.9994
298	88.27	0.493	0.9835	22.19	0.403	0.9977
PVAM						
317	84.10	0.205	0.9847	2.94	0.881	0.9985
313	83.47	0.122	0.9894	4.62	0.794	0.9996
309	78.80	0.106	0.9850	7.33	0.688	0.9984
304	109.65	0.0387	0.9954	10.75	0.604	0.9988
298	146.62	0.0191	0.9986	16.60	0.513	0.9989

q_e, equilibrium adsorption quantity; C_e, equilibrium concentration of adsorbate in solutions; q_m, adsorption quantity for monolayer coverage; b, adsorption equilibrium constant; B and $1/n$, arbitrary constant; R, correlative coefficient of linear regression.

Table 2
Isosteric enthalpy of tannin adsorption on HPI, PSI and PVAM adsorbent

| q_e (mg/g)	HPI		PSI		PVAM	
	$-\Delta H$ (kJ/mol)	R	$-\Delta H$ (kJ/mol)	R	$-\Delta H$ (kJ/mol)	R
15.0	83.6	0.9871	69.4	0.9889	73.9	0.9943
20.0	81.0	0.9893	66.3	0.9928	64.9	0.9945
25.0	78.9	0.9910	63.9	0.9941	58.3	0.9950
30.0	77.2	0.9924	61.9	0.9946	52.9	0.9951
35.0	75.8	0.9935	60.2	0.9950	48.3	0.9953
40.0	74.6	0.9944	58.8	0.9962	44.4	0.9953
45.0	73.5	0.9952	57.5	0.9968	40.9	0.9956
50.0	72.6	0.9958	56.4	0.9977	37.8	0.9956
55.0	71.7	0.9964	55.3	0.9976	35.0	0.9960
60.0	70.9	0.9968	54.4	0.9985	32.4	0.9960
65.0	70.1	0.9972	53.5	0.9986	30.0	0.9961
70.0	69.5	0.9976	52.7	0.9997	27.8	0.9962
75.0	68.8	0.9978	52.0	0.9999	25.8	0.9963
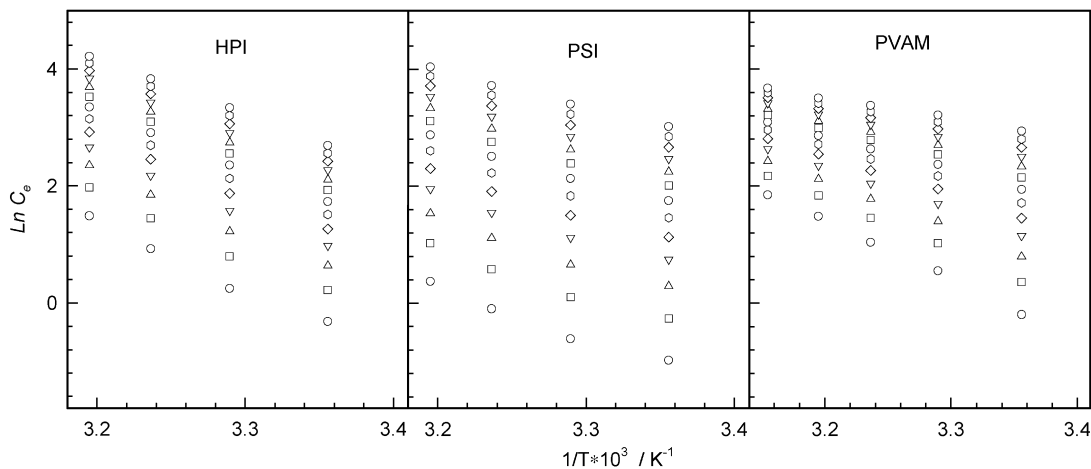
Fig. 2. Plot ln C_e vs. $1/T$ for tannin adsorption on HPI, PSI and PVAM adsorbent (The equilibrium adsorption quantity ranged from 15 mg $\times$ g^{-1} up to 75 mg $\times$ g^{-1} at the intervals of 5 mg $\times$ g^{-1}).

is taken as the functional form of $f(\theta)$ in Do's model

$$f(\theta) = \frac{\beta\theta}{[1 + (\beta - 1)\theta]} \qquad (3)$$

Where β is called as pattern parameter as it characterizes the pattern of surface heterogeneity. If we define the surface heterogeneity parameter α as

$$\alpha = \frac{\delta H}{\Delta H^0} \qquad (4)$$

Then Eq. (2) can be rewritten as below

$$\Delta H = \Delta H_0 \left\{ 1 - \alpha \times \frac{\beta\theta}{[1 + (\beta - 1) \times \theta]} \right\} \qquad (5)$$

Based on the Eq. (5), the heterogeneity pattern corresponding to different β values was described in Fig. 3. As can be seen from Fig. 3, isosteric enthalpy linearly decreased with the increasing in fractional loading as $\beta = 1$. The larger the β value, the rapider decreasing in isosteric enthalpy at the initial adsorption stage and slower decreasing in isosteric enthalpy near monolayer coverage loading. It suggests that the fraction of the high-energy adsorption site on the
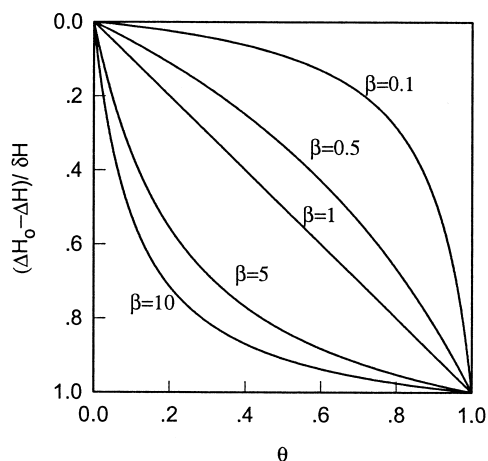

Fig. 3. Plot of reduced isosteric enthalpy vs. fractional loading.

adsorbent surface is smaller when the β value of the adsorbent is greater.

All of the above considerations did not deal with the interaction between adsorbed adsorbate molecules. In fact, when the loading is not too low, the interaction between adsorbed adsorbate molecules usually affects on adsorption enthalpy at somewhat extent. Therefore, the effect of this interaction should be included when the isosteric enthalpy is discussed. If we presume that the contribution of the energy of this interaction to the isosteric enthalpy is a linear function of loading, and define μ as the interaction energy of the adsorbed adsorbate molecules, then Eq. (5) should be rewritten as following

$$\Delta H = \Delta H_0 \left\{ 1 - \alpha \times \frac{\beta\theta}{[1 + (\beta - 1) \times \theta]} \right\} + \mu\theta \qquad (6)$$

Four parameters are contained in Eq. (6). They are isosteric enthalpy at zero loading ΔH_0, surface heterogeneity factor α, surface heterogeneous pattern characteristic parameter β and interaction energy of adsorbed adsorbate μ. ΔH can be directly figured out from the isostere and θ can be calculated from the measured adsorbed quantity of adsorbate and the maximum adsorption capacity gotten from the extrapolation of the well fitted isotherm if monolayer adsorption is assumed to be occurred.

Based on the above discussions, we can figure out the surface heterogeneity of the tested polymeric adsorbents by fitting the measured isosteric enthalpy to Eq. (6) with nonlinear method. Table 3 and Fig. 4 showed the fitting results for tannin adsorption on HPI, PSI and PVAM adsorbent. The standard errors and dependence values listed in Table 3 indicate that the fitting results are acceptable. Parameter μ refers to the interaction energy of the adsorbed adsorbate and should be free from the adsorbents. The approximately equal μ value for the tested adsorption systems suggested that the fitting results are reasonable. The coherence of the experimental results of isosteric enthalpy with the fitted curves ascertained the reliability of the fitting.

Table 3
Nonlinear fitting results of isosteric enthalpy

Parameter	HPI			PSI			PVAM		
	Value	Std Err[a]	D[a]	Value	Std Err	D	Value	Std Err	D
$-\Delta H_0$ (kJ/mol)	100.6	9.637×10^{-1}	0.9998	88.6	7.43×10^{-1}	0.9998	135.5	3.13×10^{0}	0.9997
α	0.28	2.805×10^{-3}	0.9986	0.37	1.87×10^{-3}	0.9975	0.72	3.85×10^{-3}	0.9974
β	9.24	7.892×10^{-1}	0.9995	7.90	4.80×10^{-1}	0.9996	10.95	8.05×10^{-1}	0.9996
μ	-8.35	6.617×10^{-1}	0.9989	-8.63	5.83×10^{-1}	0.9992	-8.65	6.52×10^{-1}	0.9887

[a] Std Err, Standard error; D, Dependence.

Which means Eq. (6) can efficiently describe the surface heterogeneity of the tested three adsorbents.

As above mentioned, larger β refers to a rapider decreasing in isosteric enthalpy at the initial adsorption stage and a slower decreasing near monolayer coverage. We also mentioned that a larger β implies a smaller fraction of high-energy adsorption site. The conclusion that gel type adsorbent PSI is of the greatest fraction of high-energy adsorption site among the three tested adsorbents could be drawn from Table 3, for the corresponding β of PSI is the smallest.

We have been mentioned above that larger α refers to a greater extent of surface energy heterogeneity of the concerned adsorbent. Thus we can conclude that the surface heterogeneity extent sequence of the tested adsorbents would be PVAM > PSI > HPI, because the corresponding α values listed in Table 3 following the same order. This is a surprising result if we ascribe the surface energy heterogeneity of the adsorbent to the physical surface roughness as commonly accepted for inorganic porous adsorbents. Because hypercrosslinked polymeric adsorbent HPI is of permanent porous structure and high specific surface area while gel type polymeric adsorbent PSI has no pore structure at dry state, the surface of HPI should be much rougher than the surface of PSI. The surface of HPI should be rougher than PVAM too, for the specific surface area of HPI is much higher than PVAM. Therefore the physical roughness of polymeric adsorbent surface could not reflect

Fig. 4. Isosteric enthalpy dependence on fractional loading of tannin adsorption and the fitted curves.

the surface energy heterogeneity. The causative factors of surface energy heterogeneity should to be further clarified.

3.5. The causative factors of surface energy heterogeneity of polymeric adsorbent and adsorption mechanism of tannin

We have showed that the surface energetic heterogeneity of the tested polymeric adsorbents is independent of their surface roughness. It is well known that rougher inorganic material surface leads to greater surface energy heterogeneity due to the surface remaining valences. As for functionalized polymeric adsorbents in aqueous solution, the so-called 'surface force field' includes van der Waals force, hydrophobic effect, hydrogen bonding, static electrical interaction, and $\pi-\pi$ interaction. Simply correlating the surface energetic heterogeneity with the physical surface roughness should not be enough. The surface energetic heterogeneity closely correlates with the distribution of the functional groups, which depends on the pore size distribution of the polymer matrix and the functionalizing procedure. To clarify the origin of surface energetic heterogeneity of polymeric adsorbents depends on revealing the adsorption mechanism.

Tannin sorption on HPI, PSI and PVAM adsorbent gave unusual high initial isosteric enthalpy (ΔH_0) as shown in Table 3. This fact might be ascribed to the collaboration of hydrogen bonding of tannin molecule with amide functional group of adsorbents, $\pi-\pi$ interaction derived from phenylene groups of HPI and PSI with tannin molecule and hydrophobic interaction of adsorbed adsorbate with polymeric adsorbents. It is well known that amide group can act as both hydrogen bond donor and hydrogen bond acceptor [26]. Meanwhile tannin molecule has multiple hydroxyl groups. Thus the formation of multiple hydrogen bond between tannin and polymeric adsorbent bearing amide as functional group is of great possibility. The formation of multiple hydrogen bond between tannin and the three tested polymeric adsorbents could be illustrated with Scheme 2.

If the formation of multiple hydrogen bond is the real case for tannin sorption on polymeric adsorbent bearing amides as functional groups, then reasonable explanation could be drawn out for the unusual high ΔH_0 and the difference among the surface heterogeneity patterns of the
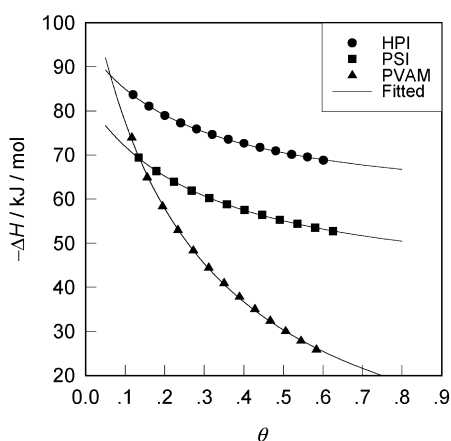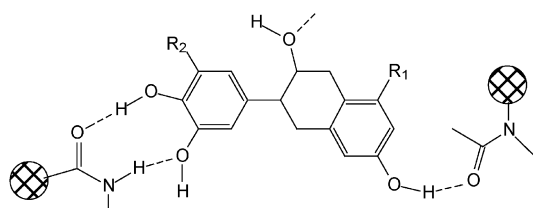
Scheme 2. Sketch map of the multiple hydrogen bond between tannin and adsorbent bearing amide as functional group.

tested adsorbents. The upper limit of hydrogen bond energy is about $50 \, kJ \times mol^{-1}$ according to Ref. [26]. Thus the initial isosteric adsorption enthalpy reaches to more than $100 \, kJ \times mol^{-1}$ is an acceptable result. Both HPI and PSI bear isocyanuric acid as functional group. Greater weak acid exchange capacity and much smaller surface area of gel type PSI adsorbent as comparing with that of hypercrosslinked HPI adsorbent suggests that the density of functional group of PSI is significantly higher than that of HPI adsorbent. Hence smaller β value for PSI adsorbent as comparing with that for HPI would be predictable because more sites available to the formation of multiple hydrogen bond exists on the surface of PSI. With the increasing in the loading of adsorbate, the opportunity to forming multiple hydrogen bond decreased and significant deviations of ΔH to ΔH_0 were observed for tannin sorption on both HPI and PSI.

PVAM is highly hydrophilic crosslinked polymer. Its water regain reaches to $4.81 \, ml \times g^{-1}$. In despite of more functional group exists on the surface of PVAM (the mount acetyl amide group of PVAM reaches to 3.41 mmol per gram of dried adsorbent as showed in Section 3.1), the β value of PVAM is greater than that of HPI according to the fitting results listed in Table 3. We deduce that the hydrophobic interaction of the adsorbed tannin molecules affects on the forming of multiple hydrogen bond. The hydrophobic interaction makes the adsorbed tannin molecules oriented on the surface of PVAM and blocks the formation of the multiple hydrogen bond. Only at the initial adsorption stage, the distance between adsorbed tannin molecules is great enough. Thus the adsorbed tannin molecules are free from hydrophobic interaction derived from the adsorbed molecules and forming multiple hydrogen bonds with the adsorbent is possible only at the initial sorption stage. Therefore greater β and α value were observed for PVAM.

The above discussion has revealed that the formation of multiple hydrogen bond is responsible for the exceptional high initial isosteric enthalpy (ΔH_0) of tannin sorption on the test three polymeric adsorbents and the surface energetic heterogeneity of the adsorbents. It has been stated above also that hydrophobic interaction between adsorbed tannin molecules is the causative factor of rapidly decreasing of isosteric enthelpy of tannin sorption on PVAM. There is another question need to be answered. That is how to explain the significant differences among the isosteric enthalpy for tannin adsorption on the three adsorbents

when moderate sorption loading was reached. The isosteric enthelpy of tannin sorption on HPI was significantly greater than on PSI and the isosteric enthelpy of tannin sorption on PSI was significantly greater than on PVAM (Fig. 4). We have mentioned above that $\pi-\pi$ interaction derived from the phenylene groups should be involved in tannin sorption onto HPI and PSI adsorbent. Unlike HPI and PSI, the framework of PVAM has no phenylene groups. Tannin sorption on PVAM should be free from $\pi-\pi$ interaction derived from the phenylene groups. In addition, the hydrophobic interaction is also responsible to the existing of significant difference of isosteric enthalpy between tannin sorption on highly hydrophilic PVAM and on somewhat hydrophobic PSI adsorbent. Because organic compounds tend to aggregate together in aqueous by hydrophobic interaction [27], the energy barrier of hydrophobic interaction of tannin molecules need to be overcome before it is adsorbed onto the hydrophilic PVAM adsorbent form aqueous solution. As to the tannin sorption occurred on PSI or HPI, which is of somewhat hydrophobicility, the loss of sorption heat for breaking the adsorbate aggregation in solution could be compensated or at least, partly compensated by the adsorbate–adsorbent hydrophobic interaction. Thus the net adsorption heat of tannin adsorption on PVAM is smaller than that on PSI and HPI when moderate sorption loading is get. But $\pi-\pi$ interaction and hydrophobic interaction would be not the causative factor of the difference between the isosteric enthalpy of tannin adsorption on HPI and PSI, for the two adsorbents have approximate equal hydrophobicity, similar framework and bear the same type of functional groups. The significant difference of these two adsorbents laid on the crosslinking degree and the pore structure. HPI is a hypercrosslinked polymer and its specific surface area is much larger than that of PSI. The compact structure formed by rigid crosslinking bridges of HPI forces the polymer chain to form strained conformations and therefore, some energy was stored. When adsorbate molecule is entrapped on the hypercrosslinked polymeric adsorbent, the strained conformations of the polymer chain will be transformed into stretched conformations by adsorbate–adsorbent interaction and the stored energy will be released as adsorption heat. That is to say adsorption potential energy trap exists on hypercrosslinked polymeric adsorbents HPI. Hence, the isosteric enthalpy corresponding to hypercrosslinked polymeric adsorbent would be higher than common crosslinked polymeric adsorbent.

4. Conclusion

The tested three polymeric adsorbents, hypercrosslinked polydivinylbenzene-isocyanuric acid, gel type crosslinked poly(styrene-*co*-divinylbenzene)-isocyanuric acid and macroporous poly(*N*-vinyl acetamide), can efficiently adsorb tannin from aqueous. Langmuir isotherm, which

based on homogeneous surface model does not available to describe the sorption rule of tannin on these three adsorbent. Freundlich equation fits the tested three adsorption systems well. All of the tested adsorbents exhibit surface heterogeneity for the adsorption of tannin from aqueous. The surface heterogeneity of the polymeric adsorbents could be quantitatively described with an isosteric enthalpy function of fractional loading based on Do's model. The formation of multiple hydrogen bond at the initial adsorption stage, hydrophobic interaction of adsorbed tannin molecules is responsible to significant changing in isosteric enthalpy of tannin adsorption on HPI, PSI and PVAM with the varying of adsorption loading. The significant isosteric enthalpy between tannin sorption on PVAM and HPI and/or PSI adsorbent should be ascribed to the hydrophobic and $\pi-\pi$ interaction derived from phenylene groups. Adsorption potential energy trap might exist on hypercrosslinked polymeric adsorbent.

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