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Adsorptive Separation of Tannic Acid from Aqueous Solution by Polymeric Resins

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Abstract: An aminated hypercrosslinked polymeric resin AH-1, a macroporous polymeric resin NG-8 and its aminated derivative NG-9 were used for the adsorption of tannic acid from aqueous solution. The batch system was applied to study the adsorption equilibrium on the three polymeric adsorbents. Equilibrium adsorption data were obtained and fitted very well to Langmuir model. The results showed that the pore size distribution and the tertiary amino group on the polymer played a significant role in tannic acid adsorption performance, and polymer NG-9 showed the highest adsorption capacity due to the suitable pore size distribution and the presence of the tertiary amino group. In addition, a thermodynamic study was carried out to interpret the adsorption mechanism. The kinetic study testified that the tertiary amino group on the polymer matrix could decrease the adsorption rate and the large average pore size of the resin was in favor of the adsorption rate increase.

Keywords: Macroporous polymer, tannic acid, adsorption, thermodynamics, kinetics

INTRODUCTION

Tannins, a kind of plant secondary metabolites, are found in nearly 80% of woody and 15% of herbaceous dicotyledonous species (1). Tannins are polyphenolic compounds with molecular weight between 500 and 3000. A great deal of research has shown that tannins are harmful to animals and humans.

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Tannins can produce toxic and anti-nutritional effects on monogastric and ruminant animals: reduced feed intake, lower nutrient digestibility, and protein availability (2). If the injection made from plants contains tannins, the patient's injection site will be red and swolen (3). Tannins can lead to hepatic necrosis, gastroenteritis, and congestion of the intestinal wall. Besides, tannins can affect the utilization of vitamins and minerals, and inhibition of digestive enzymes for animals and humans (4). Furthermore, tannins are believed to contribute to the color and astringent sensation in fruit juices and beverages made from plants (5). Consequently, the removal or destruction of tannins from food, medicine products, and beverages made from plants has become a matter of significant concern. During the past decades, resin adsorption technology as a separation method has been widely adopted (6, 7). In comparison with such classical adsorbents as silica gels, aluminas, and activated carbons, polymeric adsorbents are more attractive alternatives for their high chemical stability, easy regeneration, and excellent selectivity (6). In recent years, scientists have made more efforts on pore structure control and chemical modification of polymeric adsorbents to improve their adsorption properties (8, 9). In the present work, tannic acid was chosen as the target adsorbate since it widely exists in the plant world, and further, it is often used as a model compound of tannins (10). An aminated hypercrosslinked polymeric resin AH-1, a macroporous polymeric resin NG-8 and its aminated derivative NG-9 were used for the adsorptive removal of tannic acid from aqueous solution. The focus of this work is to examine the effects of the surface chemistry group and pore structure of the polymeric adsorbents on adsorptive properties towards tannic acid.

EXPERIMENTAL

Chemicals

Tannic acid, also known as Chinese gallotannic, was purchased from Shanghai Chemical Reagent Plant (Shanghai City, P.R. China) and dissolved by deionized water in adsorption tests without pH adjustment. The structural formula of tannic acid was shown in Fig. 1. The chemicals used to synthesize AH-1, NG-8, and NG-9 were all supplied by Langfang Electrical Resin Co. Ltd. (Hebei Province, P. R. China).

Adsorbent Synthesis

The aminated hypercrosslinked polymeric resin AH-1was prepared by the method described in literature (9). The macroporous polymeric resin NG-8 was prepared with conventional polymerization technique following the steps: in a 2000 mL round-bottomed flask, 150 g of divinylbenzene, 80 g of

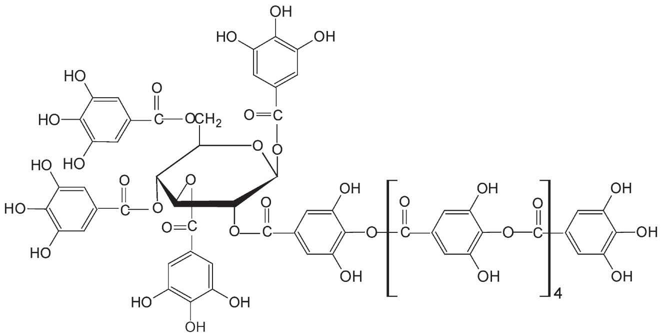

Figure 1. Structure of tannic acid.

liquid paraffin, and 1.5 g of dibenzoyl peroxide were mixed at 303 K. Then 900 g of 1 wt% gelatin aqueous solution was added to the flask. Suitable stirring rate was adjusted, and the polymerization process was performed at 358 K for 12 h. At the end of the reaction, the mixture was cooled to room temperature, and the filtered polymer beads were rinsed three times with hot water. Finally, the polymer beads were extracted with acetone for 10 h in a Soxhlet apparatus, and then dried under vacuum at 333 K.

The amine modified resin NG-9 was synthesized using the following steps: (1) Chloromethylation of NG-8 resin: In a 500 mL round-bottomed flask, 60 g of NG-8 resin was swollen in 360 mL monochloromethylether. Under mechanical stirring, 60 g aluminium chloride was added slowly. The mixture was stirred continuously at 313 K for 12 h. The polymer beads were filtered and then extracted with acetone for 10 h in a Soxhlet apparatus and then dried under vacuum at 333 K. (2) Amination: In a 500 mL round-bottomed flask, 50 g of the chloromethylated NG-8 resin beads were swollen in 250 mL benzene, under mechanical stirring at 298 K for 4 h, and then filtered to remove benzene. After that, 250 g of dimethylamine (40 wt%) was gradually added into the flask in 40 min. The amination reaction continued for 10 h at 318 K. Finally, the residual dimethylamine was filtered and the modified adsorbent was obtained.

Polymer Characterization

The specific surface areas and the pore size distribution of the resins were measured with a Micrometics ASAP-2010 surface area instrument (Micromeritics Instrument Corp., Norcross, GA, USA) with nitrogen as the adsorbate with the BET method. The tertiary amino group content of the aminated polymer was measured according to the literature (6). Infrared spectra of the resins were obtained from a Nicolet 170 SX IR spectrometer (Nicolet Instrument Corp., Madison, WI, USA) employing a pellet of powdered potassium bromide and resin.

Adsorption Isotherms

Prior to use, all the polymeric adsorbents tested were extracted by ethanol in a Soxhlet apparatus for 8 h and then dried under vacuum at 333 K for 10 h. While the adsorbent NG-8 was first "wetted" with 0.5 mL of methanol and then rinsed three times with deionized water before used.

Static adsorption of tannic acid on the adsorbents at three different temperatures (283, 298, and 313 K) was conducted as follows: 0.100 g of dry resin was introduced into a flask and 100 mL of aqueous solution of tannic acid was added into each flask. The initial concentrations (C_0) of the solutions ranged from 100 to 1000 mg/L. The flasks were completely sealed under nitrogen and placed in a constant temperature shaker (Taicang Guangming Experimental Instrument Co. Ltd., Jiangsu Province, P. R. China) at a preset temperature and shaken at 200 rpm for 96 h to ensure the adsorption process reaching equilibrium. The equilibrium concentration (C_e) of tannic acid was determined using a Helious Betra UV/vis spectrometer (Unicam, Cambridge, UK). The corresponding equilibrium adsorption capacities Q_e (mmol/g) were calculated via the following equation:

$$Q_e = V(C_0 - C_e)/WM \tag{1}$$

where V is the volume of solution (L), W is the mass of dry resin (g) and M is the molecular weight of tannic acid (1701 g/mol).

Adsorption Kinetics

Kinetic adsorption of tannic acid onto AH-1, NG-8 and NG-9 was carried out in a way similar to the static adsorption tests, except for that 0.500 g of dry resin was introduced into a flask and 500 mL of aqueous solution of tannic acid was added into each flask and the initial concentration of tannic acid was settled at 1000 mg/L in all cases at 298 K. The instantaneous tannic acid uptakes on the resin were calculated by measuring the concentration of tannic acid in solution at different contact times.

RESULTS AND DISCUSSION

Characteristics of Polymeric Adsorbents

Some characteristics of the three adsorbents were tabulated in Table 1. All the three resins had large specific surface area and pore volume. Besides, as shown in Table 1 and Fig. 2, the obvious difference was that the hypercrosslinked resin AH-1 had much richer micropore area than the other adsorbents, while both NG-8 and NG-9 had richer mesopore region and larger average

Table 1. Characteristics of the polymeric resins

Property	AH-1	NG-8	NG-9
Structure	Amine-modified hypercrosslinked polystyrene	Polydivinylbenzene	Amine-modified polydivinylbenzene
Polarity	Moderate polar	Nonpolar	Moderate polar
BET surface area (m^2/g)	822.7	874.2	562.4
Pore volume (cm^3/g)	0.679	1.019	1.052
Micropore area ($d \leq 2$ nm, m^2/g)	491.3	56.9	64.2
Micropore volume ($d \leq 2$ nm, cm^3/g)	0.224	0.009	0.015
Tertiary amino group (mmol/g)	1.50	0	1.44
Average pore diameter (nm)	2.40	6.99	8.82
Average particle size (mm)	0.5	0.5	0.5
Color	Brown	White	Yellow

pore diameter than AH-1. As to NG-8 and NG-9, after amination, the specific surface area and pore volume decreased, while the average pore diameter increased. In addition, compared to NG-8, AH-1 and NG-9 possessed partial polarity for the presence of the tertiary amino group on their network. The presence of the tertiary amino group on both the aminated resins was further supported by the absorbance bands at 2773.1,

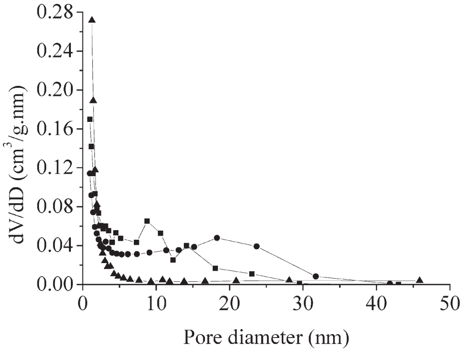

Figure 2. Plots of pore size distribution vs. pore diameter for ▲ AH-1, ■ NG-8, and ● NG-9.

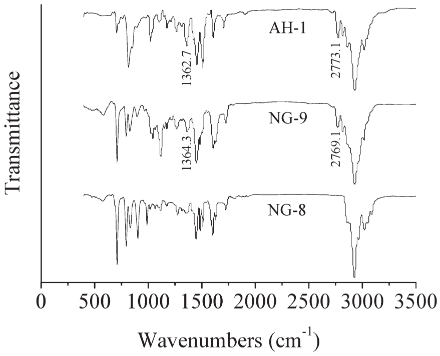

Figure 3. IR spectra of AH-1, NG-8 and NG-9.

1362.1 cm^{-1} for AH-1 and at 2769.1, 1364.3 cm^{-1} for NG-9 in IR spectra from Fig. 3.

Equilibrium Adsorption

Figures 4a–c show the equilibrium adsorption isotherms of tannic acid on the three adsorbents at the temperature of 283, 298, and 313 K, respectively. The adsorption capacities appeared to remarkably increase with increasing equilibrium concentration. It is obvious that the adsorption capacities on the resins decrease by the increase of temperature, which shows a physical exothermal process. The equilibrium adsorption data obtained were correlated with the two well-known adsorption isotherm equations of Freundlich and Langmuir models, respectively (11):

$$\log Q_e = \log K_F + 1/n \log C_e \tag{2}$$

$$C_e/Q_e = C_e/Q_m + 1/(K_L Q_m) \tag{3}$$

where Q_e is the equilibrium adsorption capacity of the adsorbent (mmol/g); C_e is the equilibrium concentration of adsorbate (mmol/L); K_F, n, Q_m and K_L are the characteristic constants. With obtained data of Q_e and C_e, all the isotherm parameters can be determined by plotting log Q_e versus log C_e as well as C_e/Q_e against C_e based on Eqs. (2) and (3), respectively. The correlative relevant parameters and correlation coefficient (R^2) of the Freundlich and the Langmuir isotherm equations are listed in Table 2.

As can be seen from Table 2, the Langmuir equations are more reliable than the Freundlich equations because all the correlation factors (R^2) of the former were larger than those of the latter. The values of Q_m, the maximum monolayer coverage of the adsorbent in the Langmuir theory, indicate that

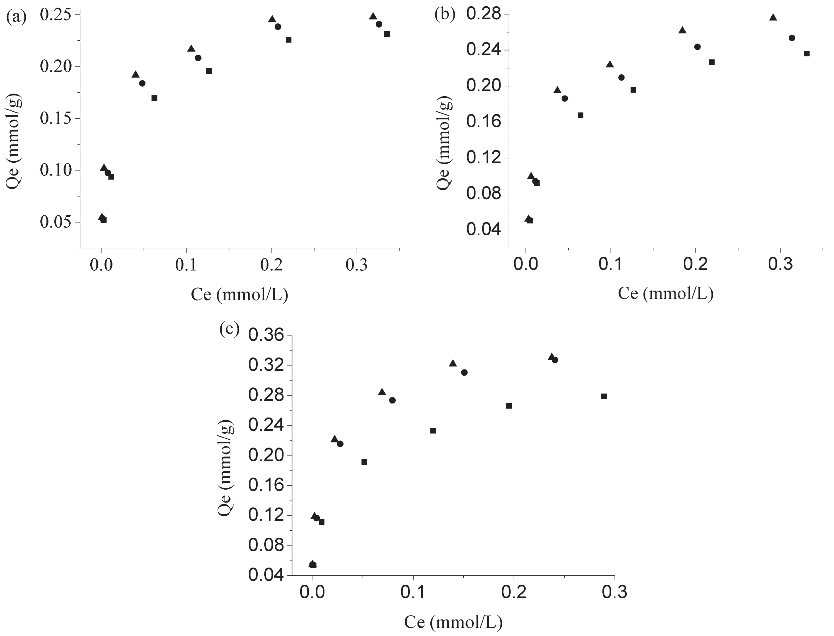

Figure 4. Adsorption isotherms of tannic acid onto (a) AH-1, (b) NG-8 and (c) NG-9 at ▲ 283 K, ● 298 K, and ■ 313 K.

the adsorption capacities towards tannic acid increase in the following order: NG-9 > NG-8 > AH-1. At the same residual concentration (C_e) of 0.01 and 0.2 mmol/L, the adsorption capacities (Q_e) on the three resins were calculated with the correlative Langmuir equations and listed in Table 3.

As shown in Table 3, when $C_e = 0.2$ mmol/L, the increase in the adsorption capacities of tannic acid on NG-9 varied within 19.7–31.8% and 20.7–36.5% at the different temperature comparing with NG-8 and AH-1, respectively. While, when $C_e = 0.01$ mmol/L, the adsorption capacities on NG-9 were higher by 54.1–93.8% and 31.9–52.8% at the tested temperature range than those on NG-8 and AH-1 respectively, suggesting an advantage of NG-9 in the collection of tannic acid from its very dilute solution.

It is commonly known that the surface area, pore structure, polarity, as well as the surface chemistry group of an adsorbent put much influence on its adsorption capacity (12, 13). The specific surface area of NG-9 was lowest among the three resins, but its adsorption capacity was highest, thus the significant difference in the adsorption capacity was not only related to the specific surface area. It is reasonable that the largest amount loaded on NG-9 is attributed to the presence of tertiary amino group on its network and the suitable pore size distribution. According to the Lewis acid-base theory, the benzene ring of aromatic-based resin and the tertiary amino

Table 2. Regression parameters of Freundlich and Langmuir isotherm equations

		Freundlich equation			Langmuir equation		
Adsorbent	T(K)	n	K_F	R^2	Q_m (mmol/g)	K_L (L/mmol)	R^2
AH-1	283	4.021	0.3714	0.9619	0.2527	117.76	0.9980
AH-1	298	3.519	0.3748	0.9750	0.2490	77.52	0.9978
AH-1	313	3.146	0.3657	0.9800	0.2430	49.57	0.9967
NG-8	283	2.914	0.4821	0.9266	0.2874	58.38	0.9971
NG-8	298	2.769	0.4464	0.9460	0.2681	46.97	0.9981
NG-8	313	2.764	0.3974	0.9664	0.2522	37.69	0.9973
NG-9	283	3.378	0.5403	0.9799	0.3378	141.64	0.9977
NG-9	298	3.598	0.5214	0.9922	0.3356	98.01	0.9958
NG-9	313	3.305	0.3900	0.9922	0.2895	58.06	0.9937

group on it can be viewed as Lewis bases, while tannic acid as a polyphenolic compound can be viewed as a Lewis acid (8). Therefore, the Lewis acid-base interaction may occur between the tannic acid molecule and the benzene ring as well as the tertiary amino group on the resin, which leads to the formation of a hydrogen-bonding complex. Tertiary amino nitrogen has a large dipole moment, thus the tertiary amino group of NG-9 acts as the stronger Lewis base than benzene ring of NG-8. So the interaction between the tannic acid and NG-9 is expected to be stronger than that between the tannic acid and NG-8. This is probably the primary reason for the increased adsorption capacity of NG-9 over that of NG-8.

The tertiary amino group content of NG-9 was similar to AH-1, so the much larger adsorption capacity of NG-9 was not only aroused by tertiary amino group. Some researches showed that the optimum ratio of the adsorbent pore diameter to the adsorbate molecule diameter was in the range of 2–6 (6). The molecule diameter size of tannic acid was 1.6 nm (14), and towards such large adsorbate molecule, the pore diameter of NG-9 was

Table 3. Equilibrium adsorption capacity for tannic acid onto polymeric resins

	$C_e = 0.01$ mmol/L			$C_e = 0.2$ mmol/L		
Adsorbent	283 K	298 K	313 K	283 K	298 K	313 K
AH-1	0.1367	0.1087	0.0806	0.2424	0.2339	0.2208
NG-8	0.1059	0.0857	0.0690	0.2647	0.2423	0.2227
NG-9	0.1980	0.1661	0.1063	0.3263	0.3193	0.2666

obviously more suitable than that of AH-1, because part of the micropore area of AH-1 was too small to be used in the tannic acid adsorption process.

Thermodynamics for Tannic Acid Adsorption

The change of adsorption enthalpy herein were calculated by Van't Hoff equation (15):

$$\ln K_{\mathrm{L}} = \ln K_0 + (-\Delta H/RT) \tag{4}$$

where K_{L} is the constant of the well fitting Langmuir equation, ΔH is the enthalpy change during the adsorption process, R is the gas constant, T is the absolute temperature, and K_0 is a constant. ΔH was then calculated from the slope of the line plotted by ln K_{L} versus $1/T$, and some of the plotted lines were shown in Fig. 5.

The change of adsorption free energy (ΔG) can be calculated with the Gibbs equation (16):

$$\Delta G = -RT\ln K \tag{5}$$

where K is the equilibrium adsorption coefficient, now it is the characteristic constant K_{L} in Langmuir equation.

The change of adsorption entropy (ΔS) can be calculated via the Gibbs–Helmholtz relationship (16):

$$\Delta S = (\Delta H - \Delta G)/T \tag{6}$$

Values of the enthalpy changes (ΔH, kJ/mol), free energy changes (ΔG, kJ/mol), and entropy changes (ΔS, J/mol K) calculated from the data obtained in the present study were thoroughly presented in Table 4.

From Table 4, the exothermic adsorption processes are testified by the negative values of the enthalpy changes, while their magnitudes (<40 kJ/

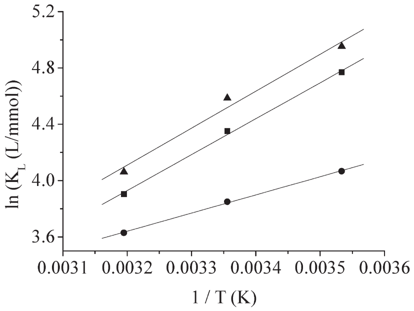

Figure 5. Determination of adsorption enthalpy change of tannic acid on ■ AH-1, ● NG-8 and ▲ NG-9.

Table 4. Calculated thermodynamic parameters for adsorption of tannic acid in the temperature range of 283–313 K

			ΔG (kJ/mol)		
Adsorbent	ΔH (kJ/mol)	ΔS (J/mol K)	283 K	298 K	313 K
AH-1	−21.21	−35.20	−11.22	−10.78	−10.16
NG-8	−10.73	−4.08	−9.57	−9.54	−9.44
NG-9	−21.81	−35.62	−11.65	−11.36	−10.57

mol) manifested a physical sorption process. The much larger absolute values of adsorption isosteric enthalpy changes of NG-9 and AH-1 mean the interaction between tannic acid and both the aminated resins are stronger than that between it and NG-8 due to the Lewis acid-base interaction. The adsorption free energy changes are always negative proving that the adsorption of tannic acid on adsorbent surface is spontaneous process. In addition, the absolute values of adsorption free energy changes of NG-9 and AH-1 are larger than those of NG-8, suggesting that the adsorption of tannic acid is easier onto the aminated resins. The entropy changes during the adsorption of tannic acid onto all the employed adsorbents are negative, indicating that the activity of tannic acid molecules decreases on the adsorbents than that in the aqueous solution. In comparison with NG-8, the absolute values of the adsorption entropy changes of NG-9 and AH-1 are large obviously, which indicates that the tannic acid molecules are more tight and ordered on the aminated resins. The above results indicate that the tertiary amino group on the resin matrix plays a significant role on adsorption of tannic acid.

Kinetics for Tannic Acid Adsorption

Kinetic sorption of tannic acid onto the three resins was carried out to explore their practicability in removal of tannic acid from aqueous solution. The influence of the contact time on the uptake of tannic acid onto the three resins was shown in Fig. 6.

The adsorption rate constants for removal of tannic acid by the resins were determined using the pseudo-first and pseudo-second order rate equations (17, 18):

$$\ln(1 - Q_t/Q_e) = -k_1 t \tag{7}$$

$$1/(Q_e - Q_t) = k_2 t + 1/Q_e \tag{8}$$

where Q_t is the adsorption uptake (mmol/g) of tannic acid at time t and Q_e is the equilibrium uptake (mmol/g), k_1 and k_2 are the velocity constants of the

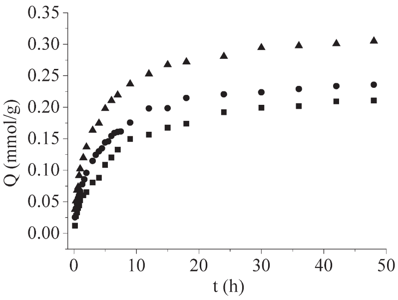

Figure 6. Effect of contact time on the uptake of tannic acid onto ■ AH-1, ● NG-8, and ▲ NG-9.

pseudo-first and pseudo-second order kinetic equations, respectively. The kinetic data obtained over a period of 48 h were plotted relating $\ln(1 - Q_t/Q_e)$ with the contact time t as well as $1/(Q_e - Q_t)$ against t based on Eqs. (7) and (8) respectively, and then k_1 and k_2 were therefore obtained from the slope of the linear relationship. The values of the rate constants and the relevant parameters were listed in Table 5.

Figure 6 shows that for the three resins, the amount of tannic acid adsorbed increases gradually with contact time during the sorption process and the adsorption is very slow to equilibrium maybe for the weak diffusion ability of the large size of tannic acid molecule. From Table 5, it can be found that the rate law for a pseudo-second order is more fixed with very high correlation coefficients ($R^2 > 0.995$). The value of rate constant (k_2) of the tested resins in the following order: NG-8 > NG-9 > AH-1. As shown in Table 1, the average pore diameter of NG-9 is larger than that of NG-8, but the adsorption rate of the former is smaller than that of the latter. It must be mentioned that the average pore diameter is measured using dry polymer beads, in aqueous solution, the matrix of macroporous resin is stable (19), but the tertiary amino group on the resin will extend for its hydrophilic character, which leads to the hindrance of the effective pore path for the diffusion of adsorbate molecule. Besides, due to the presence of tertiary amino group on NG-9, stronger adsorption of tannic acid onto its surface will lead to

Table 5. Kinetic parameters for adsorption of tannic acid onto polymeric resins

	$\ln(1 - Q_t/Q_e) = -k_1 t$		$1/(Q_e - Q_t) = k_2 t + 1/Q_e$	
Adsorbent	k_1 (h^{-1})	R^2	k_2 (g/mmol h)	R^2
AH-1	0.0442	0.9291	0.6196	0.9952
NG-8	0.0538	0.9072	1.0235	0.9953
NG-9	0.0540	0.905	0.8303	0.9966

a slower diffusion of adsorbate into the bulk of the beads and hence to a delayed uptake of tannic acid from the solution. In addition, due to its hydrophilicity, tertiary amino group on NG-9 may be combined with water molecule to form "water clusters" by hydrogen-bonding interaction (20, 21), which can effectively reduce the accessibility of the pores and lead to a slower diffusion rate for tannic acid. AH-1 has a similar content of tertiary amino group to NG-9, but its average pore diameter is smallest among the three resins, so AH-1 shows the lowest value of the adsorption rate constant towards tannic acid.

CONCLUSIONS

The batch adsorption equilibrium of tannic acid on the three polymeric adsorbents was studied. The results showed that the pore structure and the tertiary amino group of the polymers influenced the adsorption capacity. The resin NG-9 exhibited the highest adsorption capacity due to the suitable pore size distribution and the presence of tertiary amino group on the resin matrix.

Negative values of the isosteric enthalpy changes indicated that the adsorption towards tannic acid of the tested resins was exothermic. The adsorption free energy changes were always negative, demonstrating that the adsorption was a spontaneous process. The entropy changes were negative, indicating that the weaker activity of tannic acid molecules on the adsorbent than that in the aqueous solution. The absolute values of the three thermodynamic parameters of NG-9 and AH-1 were all larger than those of NG-8, suggesting that the tertiary amino group on the resin matrix played an important role on adsorption of tannic acid.

Kinetic sorption study of tannic acid on the tested resins indicated a pseudo-second order kinetic mechanism for the adsorption system. For such a large adsorbate as tannic acid, a larger pore diameter of the polymer could be in favor of the increase of the adsorption rate. Otherwise, the presence of the tertiary amino group on the polymeric backbone led to a lower adsorption rate in aqueous solution maybe for the hindrance of the extending tertiary amino group and water clusters built up.

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