Greatly Improved Adsorption of *N*-Methylated Modified Macroporous Cross-Linked Polyacrylamide Toward Tannin from Aqueous Solution

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ABSTRACT: Macroporous cross-linked poly(*N*-methylacrylamide) (PMAM) was prepared and the adsorption behaviors of PMAM toward tannin from aqueous solution was studied in comparison with polyacrylamide (PAM). The swollen property indicated that PMAM had a higher hydrophobicity than PAM while the adsorption showed that PMAM had a greatly improved adsorption toward tannin. The adsorption data could be fitted well by Freundlich model and the values of the thermodynamic parameters of PMAM toward tannin were more negative than PAM. The multiple hydrogen bonding and hydrophobic interaction between PAM/PMAM and tannin were shown to be responsible for the adsorption, whereas a stronger hydrogen bonding and a higher hydrophobicity of PMAM had a contribution to the greatly improved adsorption of PMAM toward tannin. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2033–2038, 2011

Key words: poly(*N*-methylacrylamide); polyacrylamide; adsorption; adsorption thermodynamic parameter; hydrogen bonding

INTRODUCTION

Tannin is a polyphenolic compound with a high-molecular weight (M_w: 500–30,000) and it is existent in the root, stem, and fruit of dicotyledonous plant.[1] Tannin can be divided into condensed tannin (CT) and hydrolytic tannin (HT). CT is a polymer composed of (−)-epicatechin (EC) and (−)-epigallocatechin (EGC) whereas gallotannin and ellagitannin are two forms of HT.[2] Tannin has a strong astringency to skin and it is capable of precipitating protein and alkaloid. Some foods such as beer and syrup containing tannin are very saline and wastewater containing tannin is dangerous to algae, phytoplankton, and fish. To improve the quality of such foods, medical products and drinking water, efficient removal of tannin is important.[3–5]

Adsorption has been proved to be an efficient method for removal of tannin from aqueous solution. In contrast with some typical adsorbents such as activated carbon and clay, synthetic polymeric adsorbents are more applicable in field application due to its high selectivity, diverse chemical structure, and feasible desorption property.[6–8] To increase the adsorption capacity of the synthetic polymeric adsorbents toward a specific organic compound, chemical modification by introducing some specific functional groups onto the surface is often adopted,[9] and these introduced specific functional groups will modify the chemical composition of the surface and the adsorption behaviors of the synthesized adsorbents toward a specific organic compound are hence improved.[10,11]

Hydrogen bonding is a specifically intramolecular or intermolecular interaction and it is also a useful adsorption mechanism. The low energy of hydrogen bonding (8–50 kJ/mol) ensures its reversibility, whereas the directionality and short range of this bond confer its selectivity. As a result, synthesis of polymeric adsorbents with hydrogen bonding donator/acceptor is feasible for adsorption of organic compounds with hydrogen bonding acceptor/donator. Polymeric adsorbent with amide groups can act as hydrogen bonding acceptor and donator,[12] tannin has several phenolic hydroxyl groups, which can be used as hydrogen bonding donator and acceptor. Thus, forming hydrogen bonding between the polymeric adsorbent and tannin stands a good chance. Isocyanuric acid modified hyper-cross-linked polydivinylbenzene is reported to be an excellent polymeric adsorbent for removal of tannin from aqueous solution.[13] However, the virulent chloromethylether used in the preparation procedure limits its field

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Additional Supporting Information may be found in the online version of this article.

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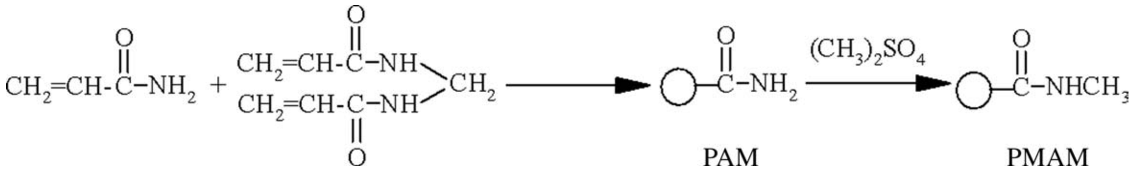


Scheme 1 The synthesis procedure of PAM and PMAM.

application. Therefore, synthesis of novel polymeric adsorbent for the purpose of efficient adsorption of tannin is important.

Acrylamide (AM) is an important monomer to produce polyacrylamide (PAM). PAM is widely used in medicine, water treatment, and paper-making process. The amino group of PAM is a highly active site and PAM can be modified by hydrolyzation reaction, Mannich reaction, and Hofmann degradation. However, to the best of our knowledge, no report is focused on the *N*-methylated reaction of PAM and the adsorption behavior of the *N*-methylated modified resin toward tannin.[14,15]

In this article, PAM was firstly synthesized from AM by inverse phase suspension polymerization, and *N*-methylated reaction of PAM was then performed and poly(*N*-methylacrylamide) (PMAM) resin was prepared. Subsequently, the adsorption of PAM and PMAM toward tannin from aqueous solution was comparatively investigated, the thermodynamic parameters were calculated and the possible interaction between PAM/PMAM and tannin were elucidated.

EXPERIMENTAL

Materials

Dimethylsulfoxide (DMSO), tetrabutyl ammonium hydroxide, and dimethyl sulfate used in this study were chemical reagents, whereas AM was an analytical reagent, they were all used without further purification. Tannin and tea polyphenol [(−)-EGC gallate $\geq$ 50%] applied as the adsorbates were analytical reagents.

Preparation of PAM and PMAM

As shown in Scheme 1, PAM with cross-linking degree of 20% was synthesized by inverse phase suspension polymerization according to the method in Ref. 17. As for the preparation of PMAM from PAM, the PAM beads were firstly swollen by DMSO overnight at room temperature, and 15 g of potassium hydroxide and 3 mL of tetrabutyl ammonium hydroxide were added into the mixture. Subsequently, 15 mL of dimethyl sulfate was added into the mixture drop by drop and the reaction was kept at 368 K for 15 h. The resulting solid particles were filtered from the mixture, washed with deionized water, and extracted with anhydrous ethanol for 8 h, and to produce the *N*-methylated PAM, PMAM.

Characterization of PAM and PMAM

The specific surface area and porosity of the resin were determined via N_2 adsorption-desorption curves with the temperature at 77 K using a Micromeritics Tristar 3000 surface area and porosity analyzer. The Fourier transform infrared (FT-IR) spectrum of the resin was collected on a Nicolet 510P FT-IR instrument via KBr disk method. The swelling capacity of the resin was measured as follows. The resin in the dry state and in the swollen state in water for 24 h was taken photos with the same magnifications, the diameter of the resin was measured, and the swelling capacity of the resin (R_v) was calculated as:

$$R_v = (D_t/D_0)^3 \tag{1}$$

where D_0 and D_t is the diameter of the resin in the dry state and in the swollen state in water for 24 h.

Adsorption experiment

Adsorption isotherms of PAM/PMAM toward tannin were measured at 293, 298, 303, 308, and 313 K, respectively. First, accurately weighted HJ-P01 resin and 25 mL of tannin aqueous solution with known concentration, C_0 (mg/L), were added into a cone-shaped flask equipped with a stopper, then the flasks were shaken at a speed of 150 rpm in a thermostatic oscillator at a presettled temperature until the equilibrium was reached, and the equilibrium concentration of tannin, C_e (mg/L), was thereafter determined according to the method in Ref. 16. The adsorption capacity of the resin toward tannin, q_e (mg/g), was finally calculated as:

$$q_e = (C_0 - C_e)V/W \tag{2}$$

where V is the volume of the tannin aqueous solution (L) and W is the weight of the resin (g).

RESULTS AND DISCUSSION

Structures of PAM and PMAM

The specific surface area of PAM and PMAM are measured to be 14.87 and 15.24 m^2/g, revealing that

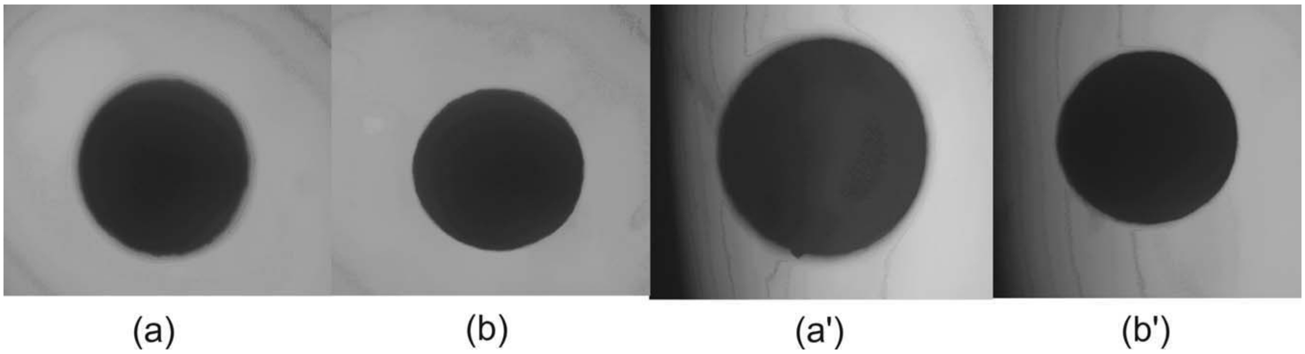


Figure 1 The detected pictures of PAM and PMAM ((a) and (b) are the pictures of PAM and PMAM at the initial state (dry resin), and (a′) and (b′) are the pictures of PAM and PMAM after being swollen in water for 24 h).

the *N*-methylated reaction of PAM induces few changes for the specific surface area of the resin. The pore volume of PAM and PMAM are given to be 0.094 and 0.096 cm^3/g, and the average pore diameter is 25.31 and 24.94 nm, indicating that the pore structure of the two resins is also similar. The water capacity of PAM and PMAM are 5.00 and 2.50 mL/g, implying that PMAM has a higher hydrophobicity than PAM after loading methyl groups on the surface.

As shown in Figure 1, the frequencies of the vibrational bands related to $CO{-}NH_2$ and $CO{-}NHCH_3$ of PAM and PMAM are quite different. The frequency of carbonyl groups of PAM related to $CO{-}NH_2$ is detected to be 1690 cm^{-1}. With regard to PMAM, in addition to the vibration at 1690 cm^{-1}, a strong vibration with frequency at 1530 cm^{-1} also appears and this strong vibration may be assigned to the coupling of C—N stretching and N—H bending of $NHCH_3$ groups. This result indicates that *N*-methylated reaction of PAM is an equimolecular reaction between PAM and dimethyl sulfate and PMAM is obtained successfully.

The swollen property of PAM and PMAM in water

Figure 1 displays the photographs of PAM and PMAM at the initial state (dry resin) and at the state after being swollen in water for 24 h, they are all taken with the same magnifications. It is seen that the size of PAM and PMAM at the initial state is close. After being swollen in water for 24 h, the size of PAM and PMAM is larger than the corresponding one at the initial state. In particular, the size of PMAM at the state after being swollen in water for 24 h is obviously smaller than that of PAM, which means that PMAM is more hydrophobic than PAM and this result agrees with the fact that the water capacity of PMAM is less than that of PAM.

Adsorption isotherms

Figure 2 displays the adsorption isotherms of PAM and PMAM toward tannin from aqueous solution. The adsorption capacity of PAM and PMAM toward tannin increases with increasing the equilibrium concentration of tannin, whereas it decreases with increasing the temperature, indicating that the adsorption is an exothermic process.[17] In addition, the adsorption of PMAM toward tannin is greatly improved in comparison with PAM, which may be from introduction of the methyl groups. The adsorption of PMAM toward tannin is very effective and the adsorption capacity is measured to be 207.4 mg/g at 100 mg/L of equilibrium concentration. Langmuir and Freundlich models are employed to describe the adsorption process.

Langmuir model is given as[18]:

$$C_e/q_e = C_e/q_m + 1/(q_m K_L) \qquad (3)$$

here q_m is the maximum adsorption capacity (mg/g) and K_L is a constant (L/mg).

Freundlich model can be expressed as[19]:

$$\log q_e = \log K_F + (1/n)\log C_e \qquad (4)$$

where K_F is a characteristic parameter $[(mg/g)(L/mg)^{1/n}]$ and it is an indicator of adsorption capacity, and n refers to as the adsorption intensity (dimensionless) and it is an indicator of the favorableness of the adsorption.

The regression equations, parameters K_L, K_F, n, and the correlation coefficients are summarized in Supporting Information Tables s1 and s2, respectively. It is seen that the Freundlich model is more suitable for the adsorption than Langmuir model since the correlation coefficients are higher than 0.99, which means that the adsorption is a multi-layer process and the two resins possess surface energetic heterogeneity.[18,20] K_F of PMAM is much greater than the corresponding one of PAM, consistent with the fact that the adsorption of tannin onto PMAM is greatly improved in comparison with PAM, *n* of PAM and PMAM are all larger than 1 and *n* of PMAM is greater than the corresponding n of PAM, implying that the adsorption of tannin onto PMAM is more favorable.

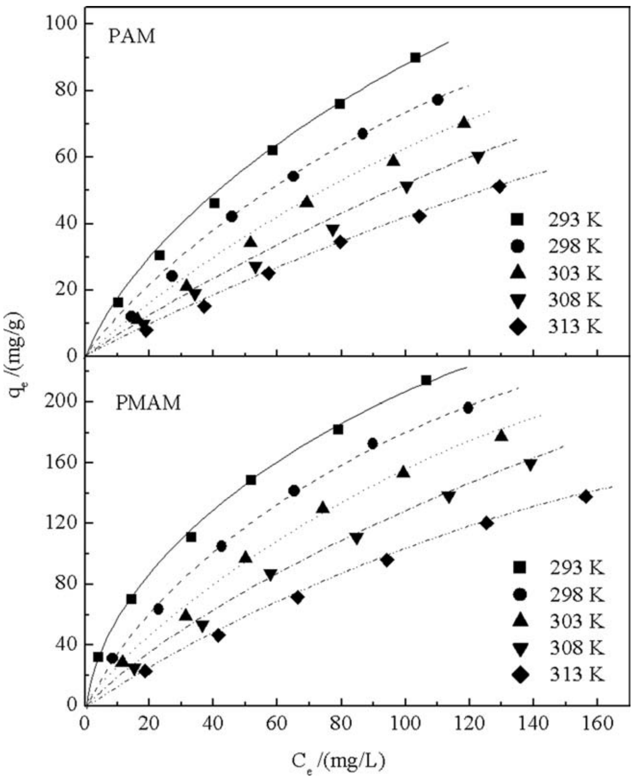


Figure 2 Adsorption isotherms of PAM and PMAM towards tannin from aqueous solution.

Adsorption thermodynamics

Following the van't Hoff equilibrium equation[10,21]:

$$\ln C_e = \frac{\Delta H}{RT} + \ln K \tag{5}$$

where ΔH is the adsorption enthalpy (kJ/mo1), R is the ideal gas constant and K is a constant. The adsorption enthalpy can be figured out from the isosteric lines (plotting of ln C_e v.s. $1/T$ in Supporting Information Fig. S2). The isosteric lines can be fitted straight lines and the adsorption enthalpies can be calculated from the slopes of the straight lines.

As the adsorption isotherms can be fitted by Freundlich model, Gibbs free energy can be calculated as[10,18]:

$$\Delta G = -n\mathrm{RT} \tag{6}$$

where ΔG is the Gibbs free energy (kJ/mol) and n is the constant in Freundlich model.

Adsorption entropy ΔS can be calculated using Gibbs-Helmholtz equation:

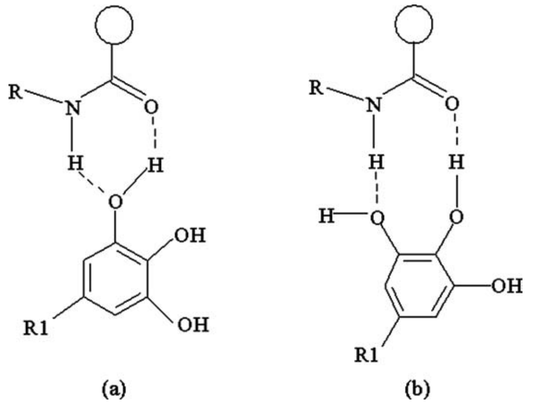
$$\Delta S = (\Delta H - \Delta G)/T \tag{7}$$

The ΔH, ΔG, and ΔS of PAM and PMAM toward tannin are summarized in Table I. The ΔH are all negative, showing an exothermic process.[17] The ΔH decreases with increasing the adsorption capacity resulted from the surface energetic heterogeneity of the resin.[13] As for the ΔG, it is seen that they are also negative, indicating that the adsorption process is a spontaneous process. The negative ΔS imply that more ordered arrangement of tannin is shaped on the resin surface after the adsorption.

Comparing the adsorption thermodynamic parameters of PMAM with PAM, it is known that the ΔH of PMAM is more negative than PAM, indicating the interaction between PMAM and tannin is greater than that between PAM and tannin. ΔG of PMAM is also more negative than PAM, suggesting the adsorption of tannin onto PMAM is more spontaneous.

TABLE I
Adsorption Thermodynamic Parameters of Tannin onto PAM and PMAM in Aqueous Solution

		$-\Delta G$/(kJ/mol)					$-\Delta S$/(J/mol·K)				
q_e/(mg/g)	$-\Delta H$/(kJ/mol)	293 K	298 K	303 K	308 K	313 K	293 K	298 K	303 K	308 K	313 K
PAM											
20	49.49	3.250	2.691	2.704	2.725	2.653	157.8	157.0	154.4	151.8	149.6
25	48.98	3.250	2.691	2.704	2.725	2.653	156.1	155.3	152.7	150.2	148.0
30	47.26	3.250	2.691	2.704	2.725	2.653	150.2	149.6	147.1	144.6	142.5
35	45.17	3.250	2.691	2.704	2.725	2.653	143.1	142.6	140.2	137.8	135.8
40	43.62	3.250	2.691	2.704	2.725	2.653	137.8	137.4	135.0	132.8	130.9
45	42.61	3.250	2.691	2.704	2.725	2.653	134.3	134.0	131.7	129.5	127.7
50	41.70	3.250	2.691	2.704	2.725	2.653	131.2	130.9	128.7	126.5	124.8
PMAM											
20	77.49	4.127	3.474	3.230	3.032	2.928	250.4	248.4	245.1	241.8	238.2
30	69.07	4.127	3.474	3.230	3.032	2.928	221.7	220.1	217.3	214.4	211.3
40	67.08	4.127	3.474	3.230	3.032	2.928	214.9	213.4	210.7	208.0	205.0
50	61.18	4.127	3.474	3.230	3.032	2.928	194.7	193.6	191.2	188.7	186.1
60	60.58	4.127	3.474	3.230	3.032	2.928	192.7	191.6	189.3	186.8	184.2
70	58.19	4.127	3.474	3.230	3.032	2.928	184.5	183.6	181.4	179.1	176.6
80	54.51	4.127	3.474	3.230	3.032	2.928	172.0	171.3	169.2	167.1	164.8
90	52.69	4.127	3.474	3.230	3.032	2.928	165.7	165.2	163.2	161.2	159.0
100	50.42	4.127	3.474	3.230	3.032	2.928	158.0	157.5	155.7	153.9	151.7



Scheme 2 The possible multiple hydrogen bonding model between PAM/PMAM and tannin

The possible interaction between PAM/PMAM and tannin

Polymeric adsorbents adsorb organic compounds from aqueous solution through ionic bond, covalent bond, coordinate bond, van der Waals force, $\pi-\pi$ stacking, hydrogen bonding, and hydrophobic interaction.[22,23] In this tested system, it is impossible to form ionic bond, covalent bond, and coordinate bond between PAM/PMAM and tannin. Van der Waals force should also not be possible due to the much great adsorption enthalpy of PAM/PMAM toward tannin. No benzene ring is existent on the skeleton and the functional groups of PAM/PMAM and hence $\pi-\pi$ stacking shouldn't take function in the adsorption. Therefore, it is suggested that hydrogen bonding and hydrophobic interaction should be the main driving forces for the adsorption.

$CO{-}NH_2$ and $CO{-}NHCH_3$ of PAM/PMAM can act as both of hydrogen bonding donator and acceptor. Tannin has several phenolic hydroxyl groups which can also be acted as hydrogen bonding donator and acceptor. So formation of hydrogen bonding between $CO{-}NH_2$/$CO{-}NHCH_3$ of PAM/PMAM and hydroxyl groups of tannin is absolutely possible. The adsorption enthalpy of PAM and PMAM toward tannin is calculated to be −41 to 50 kJ/mol and −50 to 78 kJ/mol, respectively, which is close to (a little higher than) the upper limit of hydrogen bonding.[12] In addition, as phenol is applied as the adsorbate, and the adsorption of PAM/PMAM toward phenol from aqueous solution is performed, it is found that no phenol molecules are adsorbed on PAM/PMAM. Therefore, it is deduced that multiple hydrogen bonding is mainly involved between PAM/PMAM and tannin. The possible multiple hydrogen bonding model is illustrated in Scheme 2. As shown in Scheme 2(a), the hydrogen atom of the amino group of PAM/PMAM acts as hydrogen bonding donator and forms hydrogen bonding with the oxygen atom of the hydroxyl group of tannin, whereas the oxygen atom of the carbonyl group of PAM/PMAM is used as hydrogen bonding acceptor and forms hydrogen bonding with the hydrogen atom of the hydroxyl group of tannin, and an approximate hexahydric ring is preferred.[24] In Scheme 2(b), the hydrogen atom of the amino group and the oxygen atom of the carbonyl group of PAM/PMAM form hydrogen bonding with two neighboring hydroxyl group of tannin.

To confirm the hydrogen bonding between PAM/PMAM and tannin, the adsorption isotherms of PAM/PMAM toward tea polyphenol are compared (Fig. 3). The concentration of tea polyphenol was determined by the method in Ref. 24. It is seen that the adsorption capacity of PAM/PMAM toward tea polyphenol is much smaller than tannin. Tea polyphenol has less phenolic hydroxyl groups than tannin, and the probability of forming hydrogen bonding between PAM/PMAM and tea polyphenol is less than that between PAM/PMAM and tannin. The smaller adsorption capacity toward tea polyphenol than tannin confirms the hydrogen bonding between PAM/PMAM and tannin.

The water capacity of PAM is 5.00 mL/g, displaying that PAM is strongly hydrophilic. It can easily be wetted by water and the surface of PAM is entirely surrounded by water molecules in aqueous solution. Tannin will also interact with water molecules in aqueous solution due to its hydrophilic hydroxyl groups. Before tannin are adsorbed onto the surface of PAM, they must break the bond (may be intermolecular hydrogen bonding) between tannin and water molecules in addition to the bond between PAM and water molecules. Subsequently, tannin will take the place of the water molecules and form hydrogen bonding with PAM. This process can be called "solvent replacement,"[25,26] and it should be an exothermic process.[27,28] Due to the strong hydrophilicity of PAM, the adsorption sites

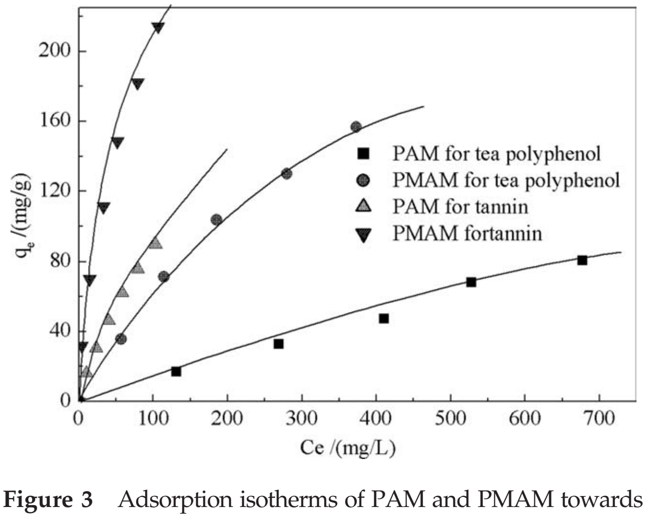


Figure 3 Adsorption isotherms of PAM and PMAM towards tannin and tea polyphenol from aqueous solution at 293 K

of PAM are completely occupied by water molecules. Before tannin are adsorbed onto the surface of PAM, more energy is consumed to break the bond between tannin and water molecules as well as the bond between PAM and water molecules, and hence the adsorption capacity of tannin onto PAM is smaller, and the adsorption enthalpy of tannin onto PAM is less than that onto PMAM. That is, the hydrophobic interaction between PMAM and tannin should also play an important role in the adsorption due to the higher hydrophobicity of PMAM.

CONCLUSIONS

PMAM was synthesized from PAM successfully by *N*-methylated reaction and the synthesized PMAM adsorbed tannin from aqueous solution effectively. Freundlich model characterized the adsorption isotherms better than Langmuir model and the adsorption was shown to be an exothermic, spontaneous, and more ordered arrangement process. The multiple hydrogen bonding and hydrophobic interaction between PAM/PMAM and tannin were responsible for the adsorption while a stronger hydrogen bonding and a higher hydrophobicity of PMAM contributed to the greatly improved adsorption of PMAM toward tannin.

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