Effects of Multiple Weak Interactions on the Binding of Phenolic Compounds by Polymeric Adsorbents

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ABSTRACT: To investigate the effects of multiple weak interactions on the binding of phenolic compounds by polymeric adsorbents, macroporous polystyrene (PS) resin and PS-based adsorbents with different hydrogen-bond acceptor atoms (PS—CH_2($-OCH_2CH_2$)$_n$—OCH_3, n = 0, 1, 2, and 3, denoted as PS-EG_0, PS-EG_1, PS-EG_2, and PS-EG_3) were prepared. The phenol adsorption strength order on these adsorbents was PS/PS-EG_0 < PS-EG_1 < PS-EG_2 < PS-EG_3, indicating that the adsorption on PS and PS-EG_0 was driven by hydrophobic and π–π interactions, and the adsorption on PS-EG_1, PS-EG_2, and PS-EG_3 was driven by a hydrogen bond in addition to hydrophobic and π–π interactions. PS-EG_2 may adsorb a second phenol molecule on each binding site and PS-EG_3 may adsorb second and third ones. The adsorption strength of resorcinol increased in the order of PS, PS-EG_1, and PS-EG_2, indicating that the adsorption was driven by 0, 1, and 2 hydrogen bonds in addition to hydrophobic and π–π interactions. Similarly, the adsorption of phloroglucinol on PS, PS-EG_1, PS-EG_2, and PS-EG_3 was driven by 0, 1, 2, and 3 hydrogen bonds in addition to hydrophobic and π–π interactions because the adsorption strength increased in this order. J Appl Polym Sci 102: 4652–4658, 2006

Key words: adsorption; macroporous polymer; separation technique; polymeric adsorbent; phenols

INTRODUCTION

Polymeric adsorbents have been widely used in laboratory and industry scale in many areas, such as removal of toxicants from waste water or waste gas, separation or purification of biochemicals, pharmaceuticals, and natural products, because of their high adsorption capacity, ease of regeneration, and recycling use.[1–5] However, the low adsorption selectivity limits application ranges of the polymeric sorbents. Traditional polymeric adsorbents are usually based on macroporous styrene–divinylbenzene copolymers (e.g., Amberlite XAD-2 and XAD-4, Rohm and Haas Co.) and poly(meth)acrylates (e.g., Amberlite XAD-7, Rohm and Haas Co.). The former adsorbs organic compounds from aqueous solutions through hydrophobic interactions due to van der Waal's forces between the highly hydrophobic surface of the adsorbents and hydrophobic sites of the solutes[6–9]; the latter adsorbs solutes containing hydrogen bond donors from nonpolar organic solvents through hydrogen bonding.[10–12] The low adsorption selectivity of these resins is because the adsorption is usually driven by a single type of weak interactions. In our work, we are focusing on the design of highly selective polymeric adsorbents by mimicking the multiple weak interactions, such as hydrophobic interaction, π–π interaction, hydrogen bonding, and electrostatic interaction, and their synergistic effect of biospecific affinity and molecular recognition.[13,14] In this article, we investigate the adsorption of phenolic compounds driven by hydrophobic and π–π interactions and one or more hydrogen bonds.

Adsorption of phenolic compounds from aqueous solutions has been paid great attention because they are quite common pollutants in wastewaters.[1,8–11,15] Phenolic compounds derived from various industrial activities, human wastes, and also from biological degradation. Polyphenols are also important natural products commonly found in higher plants.[16–19] There is a growing interest in extraction, isolation, and purification of natural polyphenol compounds such as tea polyphenols, proanthocyanidins, leucoanthocyanidins, tannins, flavone glycosides, furofureckol, etc., from plants. Some of them are known to have numerous biological activities and found to be potential candidates for use as drugs, for example, in diseases such as AIDS, heart ailments, ulcer formation, bacterial infection, mutagenesis, and neural disorders.[18–21] In recent years, polymeric adsorbents have been used to isolate and purify natural polyphenol compounds.[22–27] In this article, design of polymeric adsorbents with high adsorption selectivity for phenolic compounds from aqueous solution by applying multiple weak interactions and their synergistic effect were studied.

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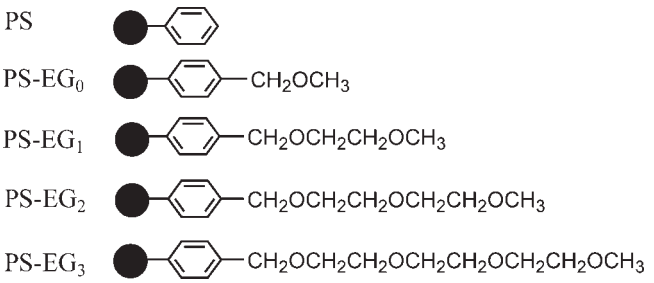

Figure 1 Structures of polymeric adsorbents.

EXPERIMENTAL

Materials

Macroporous styrene-10 wt %-divinylbenzene copolymer was synthesized by radical suspension copolymerization in the presence of toluene and liquid olefin (1 : 3, w/w) as the porogenic agent (100% weight ratio to the monomers). Methoxy ethanol (analytical grade) was purchased from Tianjin Yingda (Tianjin, China). Diethylene glycol monomethyl ether (99%) was purchased from ACROS Organics (Belgium). Triethylene glycol monomethyl ether (95%) was purchased from Sigma–Aldrich. 1,4-Dioxane (analytical grade) was purchased from Tianjin Chemical Plant (Tianjin, China). Phenol, catechol, resorcinol, hydroquinone, pyrogallol, and phloroglucinol were of analytical grade and were recrystallized before use.

Synthesis of polymeric adsorbents

Chloromethylation of macroporous polystyrene (PS) resin was carried out by treating PS with $ClCH_2OCH_3$/$ZnCl_2$ using 1,2-dichloroethane as solvent. The chloromethylated PS resin (3.93 mmol Cl/g) was allowed to swell in 1,4-dioxane in a three-neck round-bottom flask, and 10 mol equivalent of methanol was added to the flask. The mixture was stirred while bubbling nitrogen gas over for 30 min. Ten mole equivalent of NaH was added slowly to the flask and the mixture was refluxed until no residual chloride of the resin (about 20 h) was detected. After thoroughly washing the resulting resin with 1,4-dioxane, water, ethanol, and ether, the resin was denoted as PS-EG_0. Similarly, PS-EG_1, PS-EG_2, and PS-EG_3 were prepared by using methoxy ethanol, diethylene glycol monomethyl ether, and triethylene glycol monomethyl ether, respectively, to replace methanol in the aforementioned procedure. The functional group contents of PS-EG_0, PS-EG_1, PS-EG_2, and PS-EG_3 are 4.00, 3.74, 3.63, and 3.49 mmol/g, respectively, based on the chloride content of the chloromethyl PS resin.

Adsorption

Resin sample ($\sim$ 0.04 g) was soaked with 0.2 mL of ethanol for half an hour in an Erlenmeyer flask. Then 20 mL of phenol in 0.1 *N* HCl aqueous solution was added into the above flask and then the flask was shaken in a thermostatic oscillator at a fixed temperature for 12 h. The concentration of the phenol in the supernatant was measured by UV spectrophotometry. The adsorption capacity was calculated using the following formula:

$$q_e = (C_0 - C_e)V/W$$

where q_e is the equilibrium adsorption capacity (mmol/g); C_0 and C_e are the initial and equilibrium liquid-phase solute concentrations (m*M*), respectively; V is the liquid phase volume (L); and W is the amount of adsorbent (g).

RESULTS AND DISCUSSION

Phenolic compounds contain benzene rings, which may be adsorbed by hydrophobic and π–π interactions, and hydroxyl groups, which may be adsorbed by forming hydrogen bonds. Thus, we designed a series of polymeric adsorbents with polystyrene matrix, which may interact with the phenolic benzene rings through hydrophobic and π–π interactions, and different number of ether groups, which may form hydrogen bonds with the phenolic hydroxyl groups. According to thermodynamic principles and experimental results, when two or more weak interactions occur simultaneously in an adsorption process, they act synergistically and the total adsorption energy is greater than the sum of the energies when they act individually.[13,14] The structure of these polymeric adsorbents was shown in Figure 1. The ether groups were introduced into the polystyrene matrix by treating chloromethyl polystyrene resin with alcohols. The introduction of the ether groups was confirmed by the resin chloride residual content reaching near 0 and two strong IR absorptions at 1100 and 2923 cm^{-1}, which are the characteristic absorption bands of ether groups, appeared, as shown in Figure 2.

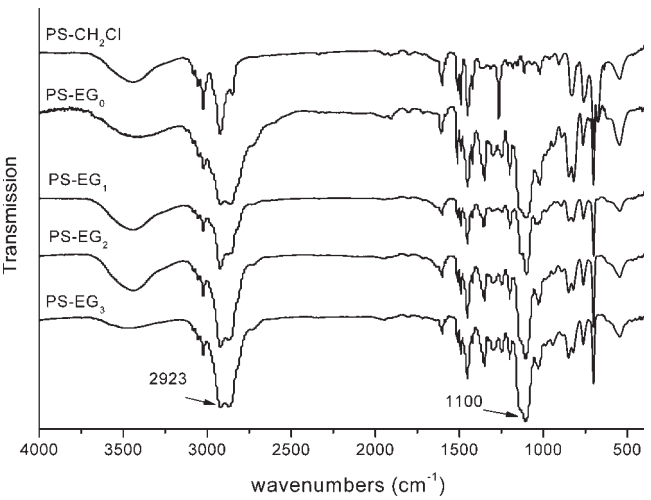

Figure 2 IR spectra of polymeric adsorbents.

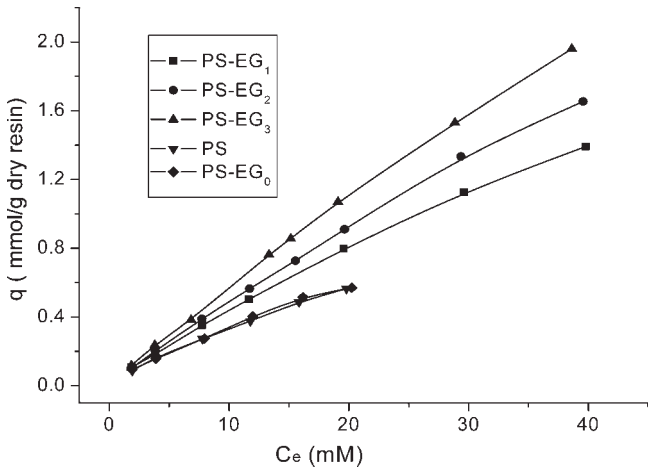

Figure 3 Isotherms for the adsorption of phenol on polymeric adsorbents.

The adsorption isotherms of phenol on these resins at 298 K were shown in Figure 3. Except for the hydrophobic backbone and aromatic rings, PS resin has no other groups. Thus, the adsorption of phenol on PS resin must have been driven by hydrophobic and π–π interactions. π–π Interaction is a strong interaction between π systems[28] and it occurs in many systems, such as host–guest interaction in supramolecular chemistry[29] and the intercalation of drugs into DNA.[30] Figure 3 shows that the adsorption isotherm of phenol on PS-EG_0 is almost the same to that on PS resin. PS-EG_0 contains aromatic polystyrene matrix and a hydrogen-bond acceptor atom, ether oxygen, in each functional group. It has been reported that a single hydrogen bond alone contributes little to adsorption in aqueous solutions because water molecules are strong hydrogen-bond formers.[13] Thus, it seems that hydrogen bonding contributes little to the phenol adsorption on PS-EG_0. It has been reported that donor-H-acceptor angles have an energetic preference for linearity or near-linearity.[31] If the hydrophobic and π–π interactions and the hydrogen bond occurred simultaneously in the adsorption of phenol on PS-EG_0, the angle of O—H···O should be quite small, and thus the hydrogen bond had little energy contribution to the binding. In other words, when a phenol molecule was adsorbed onto PS-EG_0 through hydrophobic and π–π interactions, the energy gain caused by further formation of a hydrogen bond could not offset the energy increase caused by the bond-angle strain and the entropy loss due to rotation restriction of some bonds upon the hydrogen bond formation. It can be seen from Figure 3 that the phenol adsorption strengths on PS-EG_1, PS-EG_2, and PS-EG_3 were significantly greater than those on PS and PS-EG_0, indicating that the hydrogen bond formed between the hydroxyl group of phenol and ether oxygen atom of the adsorbents, in addition to hydrophobic and π–π interactions.

Figure 3 showed that the phenol adsorption strengths on PS-EG_1, PS-EG_2, and PS-EG_3 were significantly greater than those on PS and PS-EG_0. Thus hydrogen bonding may contribute to the adsorption on PS-EG_1, PS-EG_2, and PS-EG_3 in addition to the hydrophobic and π–π interactions. Figure 4(a) showed

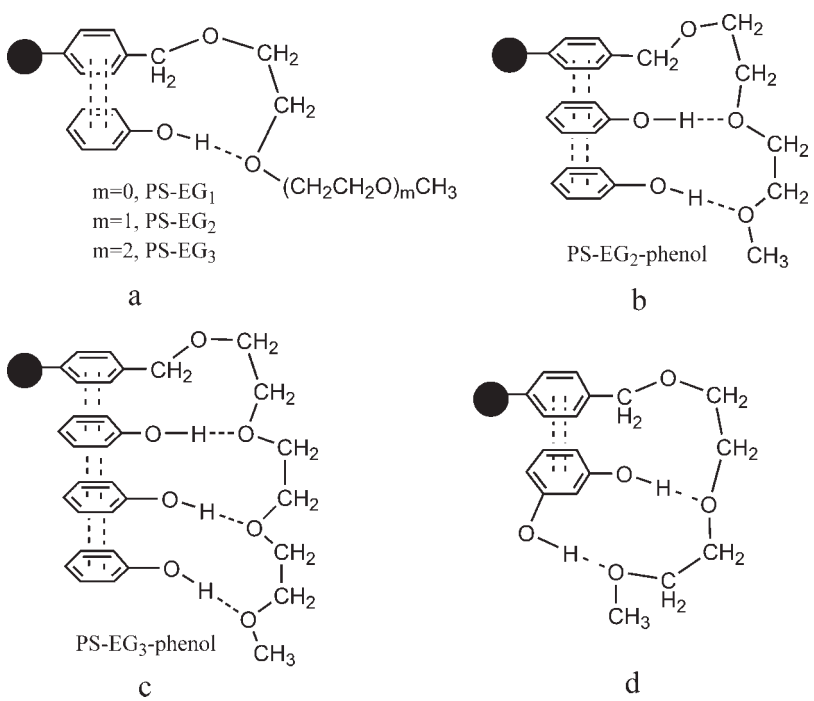

Figure 4 Schematic illustration of (a) mono-layer adsorption of phenol on PS-EG_1, PS-EG_2, or PS-EG_3; (b) double-layer adsorption of phenol on PS-EG_2; (c) triple-layer adsorption of phenol on PS-EG_3; and (d) adsorption of resorcinol on PS-EG_2.

the interaction scheme of the adsorption of phenol on PS-EG_1 ($m = 0$). For the adsorption of phenol on PS-EG_2 and PS-EG_3, because there is only one hydrogen-bond donor in a phenol molecule, only one hydrogen bond can be formed in the adsorption of a phenol molecule. The interaction mode of the adsorption was proposed to be similar to that on PS-EG_1, as shown in Figure 4(a). This is because if the third or forth oxygen atom from the resin's benzene ring formed the hydrogen bond with phenol, three or six more single bonds would be restrained from their free rotation and thus this is very unfavorable entropically. Thus the adsorption of phenol on PS-EG_2 and PS-EG_3 should not be stronger than that on PS-EG_1. However, the adsorption capacities increased with the number of ether oxygen atoms increasing (in the order of PS-EG_1, PS-EG_2, and PS-EG_3), as shown in Figure 3. Table I showed the parameters of fitting the adsorption isotherms shown in Figure 3 with Langmuir adsorption isotherm equation. It can be seen from Table I that the fitted maximum adsorption capacity of phenol on PS-EG_1 was 3.97 mmol/g, in consistent with the amount of functional group capacity of the adsorbent (3.74 mmol/g), indicating that the adsorption is monolayer adsorption or each functional group of the adsorbent bound maximally one phenol molecule. However, the fitted maximum adsorption capacities (8.09 and 11.57 mmol/g, respectively) of PS-EG_2 and PS-EG_3 were much greater than the corresponding adsorbent functional group capacities (3.63 and 3.49 mmol/g, respectively). We proposed that the adsorption of phenol on PS-EG_2 and PS-EG_3 may be double-layer and triple-layer forms, respectively, as shown in Figures 4(b) and 4(c). The double-layer adsorption isotherm equation was deduced below.

Adsorption equilibrium equations and equilibrium constants for the first layer and the second layer are given as follows:

$$\text{The first layer:}\quad \mathrm{R} + \mathrm{A} \overset{K_1}{\rightleftharpoons} \mathrm{RA} \quad K_1 = \frac{q_1}{q_0 C_e} \tag{1}$$

$$\text{The second layer:}\quad \mathrm{RA} + \mathrm{A} \overset{K_2}{\rightleftharpoons} \mathrm{RA_2} \quad K_2 = \frac{q_2}{q_1 C_e} \tag{2}$$

where R is the binding site of the adsorbent; A is the solute; K_1 and K_2 are the equilibrium constants for the first layer and the second layer, respectively; C_e is equilibrium liquid-phase solute concentrations; q_0, q_1, and q_2 are, respectively, the amounts of the sites unoccupied, occupied with monolayer adsorption, and occupied with double-layer adsorption.

Then,

$$q_f = q_0 + q_1 + q_2 \tag{3}$$

$$q_e = q_1 + 2q_2 \tag{4}$$

where q_f and q_e are the functional group capacity of the adsorbent and equilibrium adsorption capacity, respectively.

From eqs. (1)–(4) double-layer adsorption isotherm equation can be obtained as

$$q_e = \frac{q_f K_1 C_e + 2q_f K_1 K_2 C_e^2}{1 + K_1 C_e + K_1 K_2 C_e^2} \tag{5}$$

When the adsorption is monolayer, K_2 equals 0, and then eq. (5) can be written as Langmuir isotherm equation:

$$q_e = \frac{q_f K C_e}{1 + K C_e} \tag{6}$$

where q_f, the functional group capacity of the adsorbent, equals the maximum adsorption capacity, q_m.

Adsorption isotherms of phenol on PS-EG_2 and PS-EG_3 were fitted by the double-layer adsorption isotherm, eq. (5). Fitted parameters were listed in Table I. As can be seen in Table I, the first layer adsorption equilibrium constant K_1 is $14.3M^{-1}$ for PS-EG_2, in agreement to the adsorption equilibrium constant of phenol on PS-EG_1, $13.2M^{-1}$. The fitted functional group capacity ($q_f = 3.63$ mmol/g) agrees to the deter-

TABLE I
Parameters for the Adsorption Isotherms of Phenol Shown in Figure 3 and Resorcinol Shown in Figure 5 Fitted with Langmuir Equation and Eq. (5)

	Langmuir			Eq. (5)			
Adsorbent	K (M^{-1})	q_m (mmol/g)	R	K_1 (M^{-1})	K_2 (M^{-1})	q_f (mmol/g)	R
Phenol							
PS-EG_1	13.21	3.97	0.9984				
PS-EG_2	6.55	8.09	0.9988	14.31	4.45	3.63	0.9993
PS-EG_3	5.29	11.57	0.9997	10.63	2.68	5.75	0.9998
Resorcinol							
PS-EG_1	11.18	3.74	0.9912				
PS-EG_2	13.25	3.63	0.9946				
PS-EG_3	11.48	4.43	0.9983	14.24	2.20	3.49	0.9983

mined value (3.63 mmol/g) for PS-EG_2. These results show that the putative double-layer adsorption of phenol on PS-EG_2 is true. The fitted functional group capacity for PS-EG_3 was 5.75 mmol/g, which is greater than the determined resin's functional group capacity, 3.49 mmol/g. Thus the adsorption of phenol on PS-EG_3 may be in three-layers manner.

The adsorption isotherms of resorcinol on PS, PS-EG_1, PS-EG_2, and PS-EG_3 at 298 K were shown in Figure 5. As in the case of the adsorption of phenol on PS, the adsorption of resorcinol on PS should be driven only by the hydrophobic and π–π interactions. The adsorption capability of resorcinol on PS was lower than that of phenol on PS (comparing Figs. 3 and 5). This is because resorcinol is less hydrophobic than phenol, or one more hydroxyl group and its hydrated water molecules of resorcinol, compared with phenol, caused its unfavorable binding entropy loss to be greater. The driving forces of the adsorption of resorcinol onto PS-EG_1 should be similar to that of phenol onto the resin, i.e., the hydrophobic and π–π interactions and one hydrogen bond. Thus the adsorption capacity of resorcinol on PS-EG_1 is higher than that on PS. Figure 5 also shows that the adsorption strength of resorcinol on PS-EG_2 was greater than that on PS-EG_1. Thus, the interactions between PS-EG_2 and the adsorbed resorcinol may contain two hydrogen bonds in addition to the hydrophobic and π–π interactions, as shown in Figure 4(d). Adsorption strength of resorcinol on PS-EG_3 was greater than on PS-EG_2. This may be due to the adsorption of the second resorcinol molecule on each functional group of PS-EG_3.

Adsorption isotherms of resorcinol on PS-EG_1, PS-EG_2, and PS-EG_3 shown in Figure 5 were fitted by Langmuir equation (monolayer model) and eq. (5) (double-layer model). The fitted parameters were summarized in Table I. As seen from Table I, if resorcinol adsorption on PS-EG_3 was monolayer, the maximum capacity was 4.43 mmol/g, exceeding the functional group capacity (3.49 mmol/g). When the adsorption isotherm was fitted with double layers model, the first layer adsorption constant is 14.24 M^{-1}, which is similar to the adsorption constant of resorcinol on PS-EG_2. These results indicate that PS-EG_3 adsorbed resorcinol through double-layers manner. The second layer adsorption strength, however, was much weaker than that of the first layer, because only one hydrogen bond can be formed for the second resorcinol molecule adsorbed.

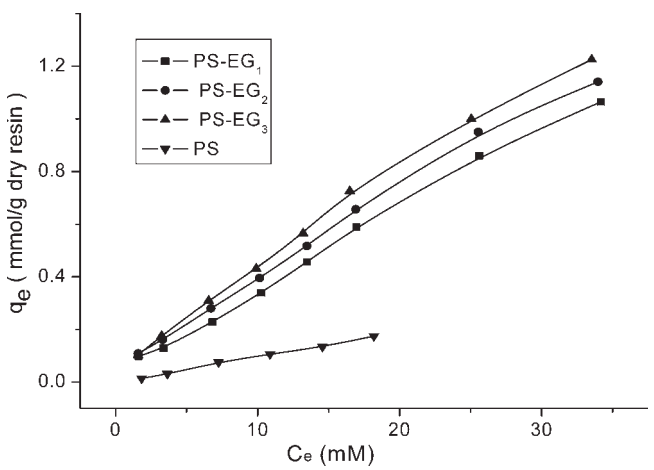

Figure 5 Isotherms for the adsorption of resorcinol on different adsorbents.

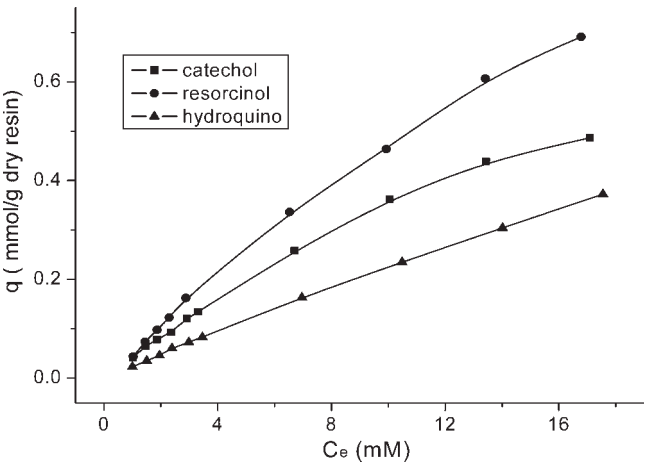

Figure 6 Isotherms for the adsorption of catechol, resorcinol, and hydroquinone on PS-EG_2.

Figure 6 showed the adsorption isotherms of three isomers of benzenediols, catechol, resorcinol, and hydroquinone on PS-EG_2. The order of the adsorption strengths on PS-EG_2 was resorcinol, catechol, and hydroquinone. The lower adsorption strength of catechol than that of resorcinol may be due to existence of an intramolecular hydrogen bond, in catechol. The higher adsorption strength of catechol, when compared with that of hydroquinone, indicates that two hydrogen bonds in addition to the hydrophobic and π–π interactions are formed in the adsorption of catechol. Thus the intramolecular hydrogen bond may be relative weak, maybe due to that O—H···O in the intramolecular hydrogen bond is far from linearity from steric view. Kjaergaard et al. showed experimentally and theoretically that the intramolecular hydrogen bond in catechol in the vapor phase or in the CS_2 solution is relatively weak.[32] The intramolecular hydrogen bond in aqueous solution should be even weaker because of the hydrogen-bonded hydration of the hydroxyl groups, while in the adsorption of catechol, the adsorption hydrogen bonds may be adjusted close to the linearity by proper rotation of other bonds. The rings containing the two hydrogen bonds for the adsorption complexes of catechol and resorcinol were formed by 10 and 11 atoms [as shown in Fig. 4(d) for resorcinol], respectively. In another study

(will be published elsewhere), we found that the adsorption of catechol was stronger than that of resorcinol on a polymeric adsorbent driven by hydrophobic interaction and two hydrogen bonds, which formed the 12- and 13-atom rings, respectively. Thus, 11- or 12-atom ring may be relative stable in these cases. The low adsorption strength of hydroquinone on PS-EG_2 may be due to the distant position of the two hydroxyl groups. As mentioned earlier, donor-H-acceptor angles have an energetic preference for linearity or near-linearity.[31] The distance of two ether bonds oxygen atoms on functional groups on PS-EG_2 may be not long enough to form two hydrogen bonds with hydroquinone.

Figure 7 showed the adsorption isotherms of phloroglucinol on PS, PS-EG_1, PS-EG_2, and PS-EG_3. The adsorption strengths increased with the length of side chain, in order of PS, PS-EG_1, PS-EG_2, and PS-EG_3. We proposed that the number of hydrogen bonds between the adsorbents and phloroglucinol is 0, 1, 2, and 3, respectively. The reason is similar to the resorcinol adsorption onto these adsorbents.

Figure 8 showed the adsorption isotherms of pyrogallol and phloroglucinol on PS-EG_3. The adsorption strength of phloroglucinol was higher than that of pyrogallol. The reason is similar to that of the stronger adsorption of resorcinol than catechol on PS-EG_2.

CONCLUSIONS

The adsorption of phenolic compounds on polystyrene-based ether-containing adsorbents may be driven by hydrophobic and π–π interactions and hydrogen bonding. The relative phenol adsorption strengths in five polymeric adsorbents were PS/PS-EG_0 < PS-EG_1 < PS-EG_2 < PS-EG_3. The driving forces were only hydrophobic and π–π interactions for PS and PS-EG_0, a hydrogen bond in addition to the hydrophobic and π–π interactions for PS-EG_1, PS-EG_2, and PS-EG_3. PS-EG_2 can adsorb two phenol molecules and PS-EG_3 can adsorb three phenol molecules maximally on each functional ether chain of the adsorbents. The adsorption of catechol and resorcinol on PS-EG_2 and PS-EG_3 was driven by hydrophobic and π–π interactions and two hydrogen bonds. PS-EG_3 adsorbed phloroglucinol with hydrophobic and π–π interactions and three hydrogen bonds as driving forces. These results may be useful in designing selective polymeric adsorbents for phenolic compounds, especially for the purification of natural polyphenol compounds.

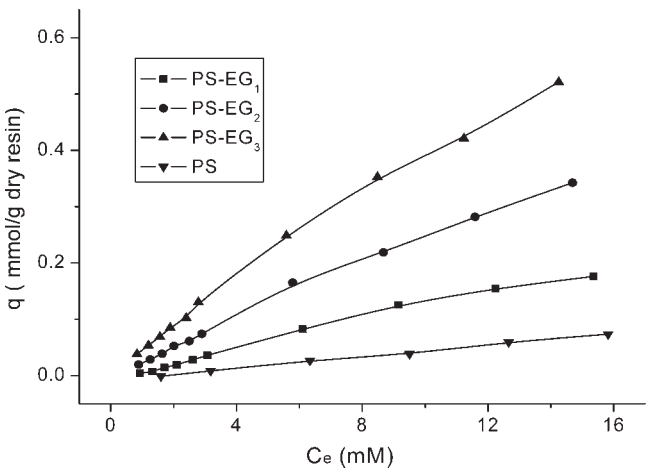

Figure 7 Isotherms for the adsorption of phloroglucinol on different adsorbents.

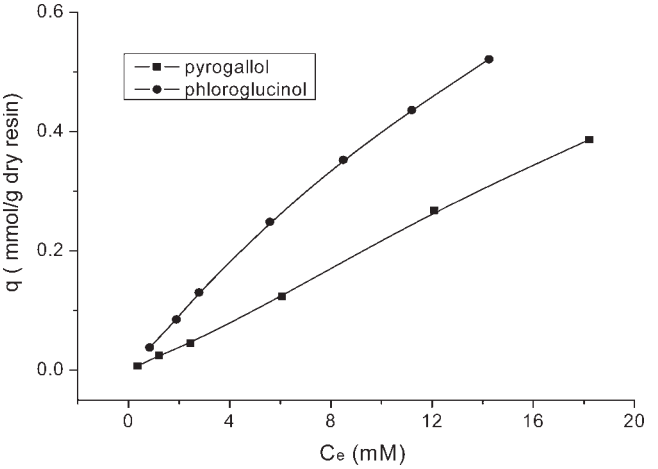

Figure 8 Isotherms for the adsorption of pyrogallol and phlorogulcinol on PS-EG_3.

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