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# Tertiary amino groups modified macroporous crosslinked poly(styrene-*co*-divinylbenzene) and its oxidized adsorbent: Synthesis, characterization, and adsorption behavior

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ABSTRACT

Macroporous crosslinked poly(*p*-vinylphenyltrimethylamine) (PVPTA) and its oxidized adsorbent (OPVPTA) were synthesized and their adsorption behaviors for phenol were comparatively studied in hexane as well as in aqueous solution. The results indicated that the adsorption was enhanced after PVPTA being oxidized, and the adsorption capacity of phenol onto OPVPTA was higher than that onto the commercial Amberlite XAD-4 resin in aqueous solution. The adsorption isotherms in hexane were fitted to Langmuir and Freundlich models, and it was found that the Freundlich model was suitable for characterizing the adsorption, whereas the correlation of the equilibrium adsorption in aqueous solution was linear. The adsorption was very sensitive to the solution pH and the optimum condition was at about the neutral solution. The adsorption thermodynamic parameters were calculated and it revealed that the adsorption was an exothermic, spontaneous, and more ordered process. Investigation of the adsorption mechanism suggested that hydrogen bonding was the primary driving force for the adsorption.

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## 1. Introduction

Phenol and its derivatives are highly toxic and very difficult to degrade biologically and hence have attracted many attentions in the fields of chemistry and environment [1]. Many countries in the world have established rigid regulations on the acceptable phenol emission level. Thereby efficient removal of phenol from wastewater has become an important environmental issue. Many methods have been applied for treatment of wastewater containing phenol, and adsorption based on synthetic polymeric adsorbents is shown to be prominent because of its physiochemical stability, high selectivity, and diverse structure [2–6]. To obtain high selectivity for a specific compound, chemical modification of the ordinary adsorbent is often adopted by modifying the adsorbent with some functional groups [7–9], and these introduced functional groups will modify the chemical composition of the adsorbent surface and hence improve the adsorption [10,11].

Investigations of adsorption thermodynamics are of great importance for developing the polymeric adsorbents and illustrating the adsorption process. Adsorption isotherm, adsorption enthalpy, adsorption free energy, and adsorption entropy are the basic aspects [12–16]. There are a lot of papers focused on the synthesis, adsorption behaviors, and adsorption thermodynamics of the synthetic polymeric adsorbents functionalized with primary, secondary, and tertiary amino groups [17–19], while the polymeric adsorbent modified with the oxidized tertiary amino groups is not available in the literature.

For the adsorption of organic compounds onto the adsorbent, hydrophobic interaction, hydrogen bonding, and π–π staking are considered to be the main driving forces [12]. In aqueous solution, hydrogen bonding between the adsorbent and the adsorbate will be restrained due to hydrophobic interaction. If hydrogen bonding can be understood in non-aqueous solution like hexane, it should be possible to better exploit this special interaction. Meanwhile, hydrogen bonding in non-polar environment will be more straightforward and effective. Some compounds, especially some of the active components like dissociation alkaloids and flavones in Chinese traditional and herbal drugs, are poorly soluble or insoluble in water; extraction of these compounds in aqueous solution will be challenging, while adsorption in non-aqueous solution will be feasible.

In this paper, we have prepared two new polymeric adsorbents, macroporous crosslinked poly(styrene-*co*-divinylbenzene) (PS) modified with tertiary amino groups and its oxidized adsorbent. Their adsorption behaviors, adsorption thermodynamics, and the adsorption mechanism for phenol in hexane as well as in

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aqueous solution have been clarified, and the polymeric adsorbent modified with oxidized tertiary amino groups is expected to be applied to treat the wastewater containing phenolic compounds and extract the active components in Chinese traditional and herbal drugs.

## 2. Materials and methods

### 2.1. Materials

Macroporous crosslinked chloromethylated PS beads were provided from Langfang Chemical Co., Ltd. (Hebei province, China), its crosslinking degree was 6%, and chlorine content was 4.78 mmol/g. The Amberlite XAD-4 resin was purchased from Rohm & Haas Company (Philadelphia, USA). Phenol used in this study was analytical grade and distilled before using. Additionally, 1,2-dichloroethane, dimethylamine aqueous solution (the content of dimethylamine was 33%), disodium ethyldiamine tetraacetate, polyethylene glycol (PEG-400, average molecular weight: 380–420), and 5% sodium hypochlorite aqueous solution were also used and all these chemicals were chemical grades.

### 2.2. Synthesis of the two polymeric adsorbents

30 g of chloromethylated PS was swollen with 150 ml of 1,2-dichloroethane overnight. Superfluous 1,2-dichloroethane was poured out and 60 ml of dimethylamine aqueous solution was added. The mixture was kept at 313 K for about 10 h until the residual chlorine content of the polymeric beads was lower than 0.2 mmol/g. The resultant polymeric beads were washed with water and ethanol, and extracted with anhydrous ethanol for 8 h, and dried at 323 K in vacuum, thus poly(*p*-vinylphenyltrimethylamine) (PVPTA) was obtained.

For preparation of OPVPTA, 14 g of PVPTA, 0.5 g of disodium ethyldiamine tetraacetate, and 10 ml of PEG-400 were added into a three-neck round-bottomed flask in turn 80 ml of sodium hypochlorite aqueous solution was then added into the reaction vessel drop by drop. The solution pH was adjusted to be higher than 8, and the reaction was retained at 333 K for more than 10 h, and OPVPTA was attained.

### 2.3. The adsorption isotherms

Equilibrium adsorption of phenol onto the two adsorbents was performed at 298, 303, 308, and 313 K, respectively. 0.100 g of PVPTA or OPVPTA and 25 ml of initial phenol solution with known concentration were added into a cone-shaped flask. The initial phenol solution was set about 50, 100, 150, 200, 250, and 300 mg/l for the hexane solution and 200, 400, 600, 800, 1000, and 1200 mg/l for the aqueous solution, respectively. 0.1 mol/l of hydrochloric acid or 0.1 mol/l of sodium hydroxide was used to adjust the pH. The flasks were shaken at a pre-settled temperature for about 24 h until the batch equilibrium was reached, and the equilibrium concentration of phenol, $C_e$ (mg/l), was determined with UV analysis performed on a PerkinElmer lambda 17 UV spectrophotometer. The equilibrium adsorption capacity of phenol, $q_e$ (mg/g), was calculated as:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where $C_0$ was the initial concentration of phenol (mg/l), $V$ was the volume of the phenol solution (l), and $W$ was the weight of the adsorbent (g).

## 3. Results and discussion

### 3.1. Characters of the two adsorbents

The residual chlorine content of PVPTA was 0.18 mmol/g. The weak and strong basic capacity of PVPTA was measured to be 4.40 and 0.20 mmol/g, respectively. For OPVPTA, its weak basic capacity treated by benzyl bromide was 4.25 mmol/g, and the corresponding one untreated was 4.38 mmol/g. The specific surface area of chloromethylated PS, PVPTA, and OPVPTA was scaled to be 28, 32, and 51 m$^2$/g, respectively.

The intense bands at 1263.2 and 669.2 cm$^{-1}$, which can be assigned to the C—Cl stretching for the IR spectrum of chloromethylated PS, almost disappear after reaction of chloromethylated PS with dimethylamine. One new moderate peak with frequency at 1055.5 cm$^{-1}$ related to the C—N stretching appears for PVPTA. For OPVPTA, two new strong vibrations present with frequencies at 980.7 and 922.7 cm$^{-1}$, which involve the N—O stretching of the oxidized tertiary amino groups. As a result, PVPTA and OPVPTA are achieved successfully.

### 3.2. Adsorption isotherms in hexane

Fig. 1 depicts the equilibrium adsorption of phenol onto PVPTA and OPVPTA in hexane by using Freundlich model. It is seen that the adsorption capacity decreases with the increasing of the temperature [20]. Comparing the adsorption capacity of phenol onto OPVPTA with that onto PVPTA at the same temperature and concentration, it reveals that the adsorption capacity of phenol onto OPVPTA is much larger than that onto PVPTA, suggesting the adsorption affinity of OPVPTA for phenol is much higher. Langmuir and Freundlich models are applied to fit the adsorption isotherms.

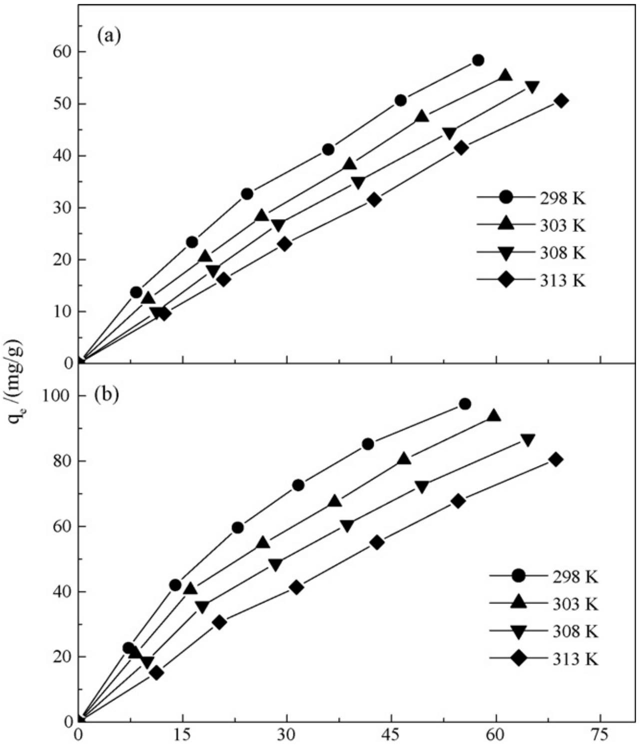

**Fig. 1.** Adsorption isotherms of phenol onto PVPTA (a) and OPVPTA (b) in hexane with the temperature at 298, 303, 308, and 313 K.

Langmuir model [4,8]:

$$C_e/q_e = C_e/q_m + 1/(q_m K_L) \tag{2}$$

Freundlich model [10,12]:

$$\log q_e = \log K_F + \left(1/n\right) \log C_e \tag{3}$$

where $C_e$ is the equilibrium concentration of phenol (mg/l), $q_e$ is the equilibrium adsorption capacity of phenol (mg/g), $q_m$ is the maximum adsorption capacity (mg/g), and $K_L$, $K_F$, and $n$ are the characteristic constants.

We fit the data of the adsorption isotherms in Fig. 1 to Langmuir and Freundlich models, and the regression equations, parameters $K_L$, $K_F$, and $n$, as well as the correlation coefficients $R$ are listed in Tables 1 and 2, respectively. It can be seen that all of the experimental adsorption isotherms coincide with the fitted results based on the Freundlich model since all of the correlation coefficients are higher than 0.99. As known to us all, Langmuir model is on the supposition that the surface of the adsorbent is homogeneous, whereas Freundlich model is applied to the adsorption on a heterogeneous surface [21]. So we deduce that the adsorbent surface may be energy heterogeneous. In addition, $K_F$ is considered to be an indicator of the adsorption capacity [12]. The $K_F$ values of OPVPTA are higher than the corresponding ones of PVPTA in Table 2, consistent with the fact that the adsorption capacity of phenol onto OPVPTA is larger than that onto PVPTA.

Following the derivative van't Hoff equilibrium equation [18,19]:

$$\ln C_e = \frac{\Delta H}{RT} + \ln K \tag{4}$$

where $T$ is the absolute temperature (K), $R$ is the ideal gas constant, $\Delta H$ is the adsorption enthalpy (kJ/mol), and $K$ is a constant. From Eq. (4), adsorption enthalpy can be figured out from the adsorption isosters, plot of $\ln C_e$ vs. $1/T$.

Adsorption Gibbs free energy $\Delta G$ can be calculated as [12,17]:

$$\Delta G = -nRT \tag{5}$$

where $\Delta G$ is the adsorption Gibbs free energy (kJ/mol) and $n$ is the constant in the Freundlich model.

Adsorption entropy $\Delta S$ can be obtained as:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{6}$$

The adsorption enthalpy, adsorption free energy, and adsorption entropy of phenol onto PVPTA and OPVPTA are presented in Table 3. It is shown that the adsorption enthalpy is negative, showing an exothermic process [20]. The adsorption enthalpy decreases with the increasing of the phenol uptakes on the adsorbent, which is caused by the surface energy heterogeneity of the adsorbent [12]. As far as the adsorption free energy is concerned, it is also negative, indicating a spontaneous process. The negative adsorption entropy suggests that a more ordered arrangement is shaped on the adsorbent surface.

Comparing the adsorption enthalpy, adsorption free energy, and adsorption entropy of phenol onto OPVPTA with those onto PVPTA, it illustrates that the adsorption enthalpies onto OPVPTA are more negative than those onto PVPTA, displaying the interaction of OPVPTA with phenol is stronger than that of PVPTA with phenol. The adsorption free energies and entropies onto OPVPTA are also more negative than those onto PVPTA, which implies the adsorption onto OPVPTA is more spontaneous and ordered.

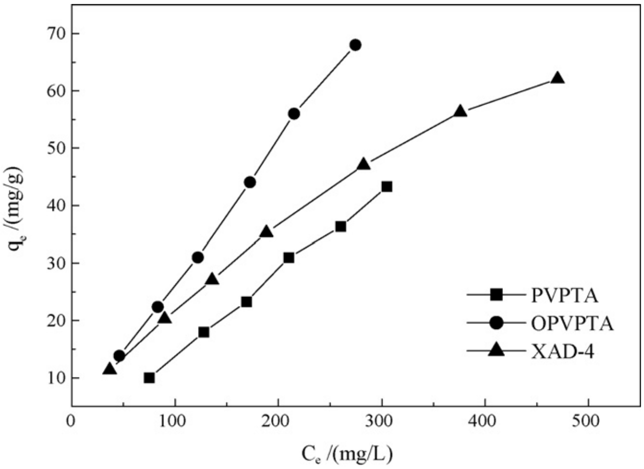

**Fig. 2.** Comparison of adsorption of phenol onto PVPTA, OPVPTA, and XAD-4 in aqueous solution with the temperature at 298 K.

### 3.3. Comparison of adsorption of phenol onto PVPTA, OPVPTA, and XAD-4 in aqueous solution

It is known that the Amberlite XAD-4 resin is usually applied to treat wastewater containing phenol, and in this study we have compared the adsorption of phenol onto our synthesized two resins, PVPTA and OPVPTA with the commercial XAD-4 resin. As can be seen from Fig. 2 that the adsorption capacity of phenol onto PVPTA is smaller than that onto XAD-4 resin at the same equilibrium concentration, whereas the corresponding one onto OPVPTA is larger than that onto XAD-4 resin, indicating that the adsorption is much enhanced after PVPTA being oxidized, and OPVPTA is possibly feasible for treatment of wastewater containing phenol.

### 3.4. pH effect for the adsorption in aqueous solution

Fig. 3 displays the correlation of the adsorption capacity of phenol onto PVPTA and OPVPTA with the solution pH at 298 K, and it is shown that the effect of the solution pH on the adsorption capacity is the same. The adsorption is sensitive to the solution pH and the maximum adsorption capacity is observed at the neutral pH (about 6.0). We do not adjust the solution pH in the subsequent section.

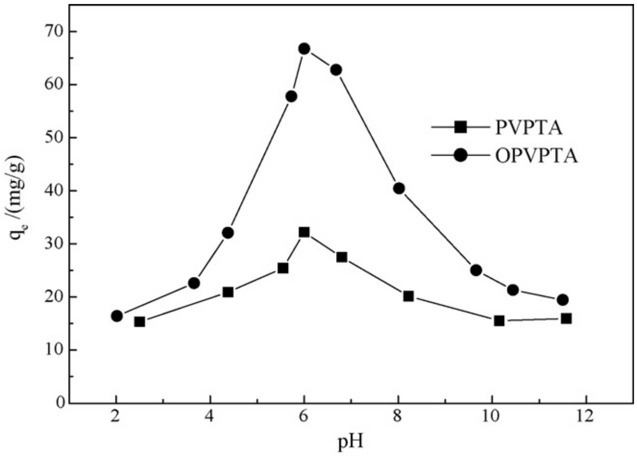

**Fig. 3.** Effect of solution pH on the phenol adsorption onto PVPTA and OPVPTA in aqueous solution.

**Table 1**
Regression equations of $(C_e/q_e) - C_e$ for the adsorption of phenol onto the two adsorbents in hexane using Langmuir model

| $T$ (K) | Regression equations | $K_L$ | | $q_m$ | | $R$ |
|---|---|---|---|---|---|---|
| | | Values | Errors | Values | Errors | |
| PVPTA | | | | | | |
| 298 | $C_e/q_e = 0.0076C_e + 0.5639$ | 0.0135 | 0.0192 | 131.5789 | 5.3758E−4 | 0.9901 |
| 303 | $C_e/q_e = 0.0055C_e + 0.7779$ | 0.0071 | 0.0175 | 181.8182 | 4.5622E−4 | 0.9868 |
| 308 | $C_e/q_e = 0.0025C_e + 1.0456$ | 0.0024 | 0.0321 | 400.0000 | 7.8574E−4 | 0.8507 |
| 313 | $C_e/q_e = 0.0016C_e + 1.2548$ | 0.0013 | 0.0159 | 625.0000 | 3.6952E−4 | 0.9090 |
| OPVPTA | | | | | | |
| 298 | $C_e/q_e = 0.0054C_e + 0.2667$ | 0.0202 | 0.0074 | 185.1852 | 2.2502E−4 | 0.9965 |
| 303 | $C_e/q_e = 0.0051C_e + 0.3431$ | 0.0149 | 0.0151 | 196.0784 | 4.1070E−4 | 0.9872 |
| 308 | $C_e/q_e = 0.0045C_e + 0.4570$ | 0.0098 | 0.0203 | 222.2222 | 5.1402E−4 | 0.9743 |
| 313 | $C_e/q_e = 0.0025C_e + 0.6701$ | 0.0037 | 0.0334 | 400.0000 | 7.7992E−4 | 0.8508 |

**Table 2**
Regression equations of $\log q_e - \log C_e$ for the adsorption of phenol onto and OPVPTA in hexane by using Freundlich model

| $T$ (K) | Regression equations | $K_F$ | | $n$ | | $R$ |
|---|---|---|---|---|---|---|
| | | Values | Errors | Values | Errors | |
| PVPTA | | | | | | |
| 298 | $\log q_e = 0.4576 + 0.7482 \log C_e$ | 2.8681 | 0.0252 | 1.3365 | 0.0174 | 0.9989 |
| 303 | $\log q_e = 0.2639 + 0.8306 \log C_e$ | 1.8361 | 0.0135 | 1.2039 | 0.0091 | 0.9997 |
| 308 | $\log q_e = 0.0316 + 0.9414 \log C_e$ | 1.0755 | 0.0432 | 1.0622 | 0.0285 | 0.9981 |
| 313 | $\log q_e = -0.0600 + 0.9609 \log C_e$ | 0.8710 | 0.0168 | 1.0407 | 0.0110 | 0.9997 |
| OPVPTA | | | | | | |
| 298 | $\log q_e = 0.7792 + 0.7124 \log C_e$ | 6.0146 | 0.0618 | 1.4037 | 0.0440 | 0.9924 |
| 303 | $\log q_e = 0.6722 + 0.7403 \log C_e$ | 4.7011 | 0.0566 | 1.3508 | 0.0389 | 0.9945 |
| 308 | $\log q_e = 0.5118 + 0.7992 \log C_e$ | 3.2494 | 0.0655 | 1.2513 | 0.0439 | 0.9940 |
| 313 | $\log q_e = 0.2577 + 0.9066 \log C_e$ | 1.8101 | 0.0654 | 1.1030 | 0.0426 | 0.9956 |

### 3.5. *Adsorption of phenol in aqueous solution*

Fig. 4 displays the adsorption isotherms of phenol onto PVPTA and OPVPTA in aqueous solution. The relationship between the equilibrium adsorption capacity and the equilibrium concentration is linear, and all of the adsorption isotherms are straight lines and pass through the origin.

In the van't Hoff method, the temperature dependence of the equilibrium constant can be related to the adsorption enthalpy. The first used equation in the van't Hoff method is shown as [22]:

$$\Delta G^\circ = -RT\ \ln K = -RT \ln \left[ k \left( \frac{q_e}{C_e} \right) \right] \tag{7}$$

where $\Delta G^\circ$ is the standard Gibbs free energy, $R$ is the universal gas constant, $T$ is the absolute temperature, and $K$ is the adsorption equilibrium constant. The phenol concentrations in our experiments are confined to be low, and the adsorption isotherms are linear. So we believe that the equilibrium constant can be directly related to the adsorption affinity $(q_e/C_e)$. The proportionality factor $k$ contains the activity coefficients of phenol in the two phases and that of the unbound adsorption sites, it is also possible that $k$ will be constant in our experiment.

The second applied equation in the van't Hoff method is given as:

$$\Delta G^\circ = \Delta H^\circ - T\ \Delta S^\circ \tag{8}$$

where $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$ are the standard Gibbs free energy, enthalpy, and entropy, respectively. Combining Eqs. (7) and (8), and we can get:

$$\ln \left[ \frac{q_e}{C_e} \right] = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} - \ln k \tag{9}$$

If $\Delta H^\circ$, $\Delta S^\circ$, and $k$ remain constant over the temperature range in this study, Eq. (9) suggests that plot of $\ln(q_e/C_e)$ vs. $1/T$ should yield a straight line with a slope of $-\Delta H^\circ/R$. The adsorption enthalpy of

**Table 3**
Adsorption thermodynamic parameters of phenol onto PVPTA and OPVPTA in hexane

| $q$ (mg/g) | $-\Delta H$ (kJ/mol) | $-\Delta G$ (kJ/mol) | | | | $-\Delta S$ /(J/(mol K)) | | | |
|---|---|---|---|---|---|---|---|---|---|
| PVPTA | | 298 K | 303 K | 308 K | 313 K | 298 K | 303 K | 308 K | 313 K |
| 10 | 37.1470 | 3.3113 | 3.0328 | 2.7200 | 2.7082 | 113.5426 | 112.5881 | 111.7760 | 110.0281 |
| 20 | 32.5161 | 3.3113 | 3.0328 | 2.7200 | 2.7082 | 98.0027 | 97.3046 | 96.7406 | 95.2329 |
| 30 | 26.9374 | 3.3113 | 3.0328 | 2.7200 | 2.7082 | 79.2822 | 78.8931 | 78.6279 | 77.4096 |
| 40 | 23.6118 | 3.3113 | 3.0328 | 2.7200 | 2.7082 | 68.1225 | 67.9175 | 67.8305 | 66.7847 |
| 50 | 20.1282 | 3.3113 | 3.0328 | 2.7200 | 2.7082 | 56.4326 | 56.4205 | 56.5201 | 55.6550 |
| OPVPTA | | | | | | | | | |
| 10 | 45.6854 | 3.4778 | 3.4029 | 3.2042 | 2.8703 | 141.6362 | 139.5462 | 137.9260 | 136.7895 |
| 20 | 42.0772 | 3.4778 | 3.4029 | 3.2042 | 2.8703 | 129.5282 | 127.6380 | 126.2110 | 125.2617 |
| 30 | 38.9428 | 3.4778 | 3.4029 | 3.2042 | 2.8703 | 119.0101 | 117.2934 | 116.0344 | 115.2476 |
| 40 | 35.8333 | 3.4778 | 3.4029 | 3.2042 | 2.8703 | 108.5755 | 107.0310 | 105.9386 | 105.3131 |
| 50 | 35.1599 | 3.4778 | 3.4029 | 3.2042 | 2.8703 | 106.3158 | 104.8086 | 103.7523 | 103.1517 |

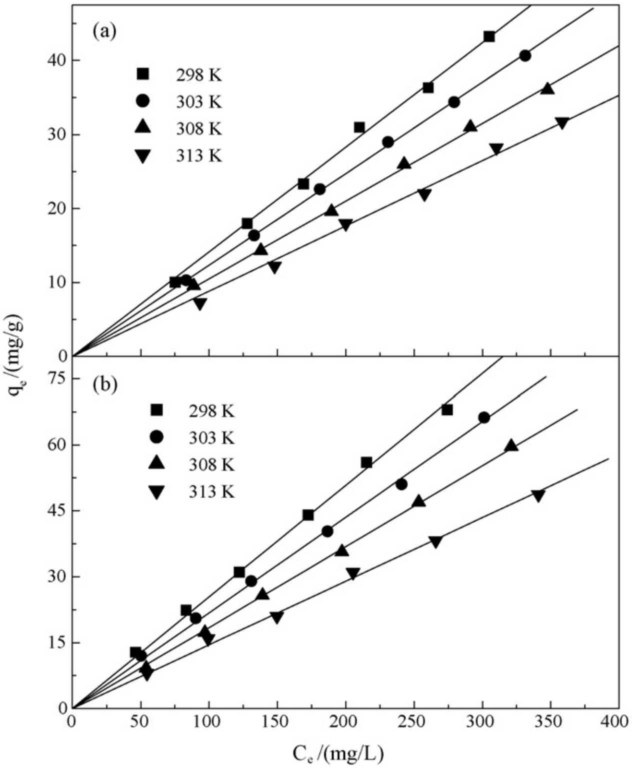

**Fig. 4.** Adsorption equilibrium data of phenol onto PVPTA (a) and OPVPTA (b) in aqueous solution with the temperature at 298, 303, 308, and 313 K.

phenol onto PVPTA and OPVPTA in aqueous solution can then be figured out to be −23.92 and −27.05 kJ/mol, respectively.

### 3.6. Adsorption mechanism

For the adsorption in hexane we considered, it is not possible to form ionic bonds, covalent bonds, and coordinate bonds between the two adsorbents and phenol in hexane, hydrophobic interaction is also not existent. The adsorption enthalpies of phenol onto the two adsorbents are calculated to be −37.1470 to −20.1282 kJ/mol and −45.6854 to −35.1599 kJ/mol, respectively (Table 3), which are in the range of hydrogen bonding [23]. The nitrogen atom of the tertiary amino groups of PVPTA and oxygen atom of OPVPTA can form hydrogen bonding with the hydrogen atom of the hydroxyl group of phenol, so we deduce that hydrogen bonding is principally responsible for the adsorption in hexane.

We have also measured the adsorption isotherm of anisole (not possess hydrogen bonding donator) onto the two adsorbents in hexane at 298 K, and there is no adsorption of anisole onto two the two adsorbent. Accordingly, it is confirmed that hydrogen bonding is the main driving force. For the larger adsorption capacity and more negative adsorption enthalpy of phenol onto OPVPTA than those onto PVPTA, maybe the stronger hydrogen bonding ability of the oxygen atom of OPVPTA from the nitrogen atom of PVPTA works [24].

In addition, we have performed theoretical calculations to predict the interaction energy of PVPTA with phenol and that of OPVPTA with phenol [25]. Becke three parameter Lee–Yang–Parr method with 6-311G basis set was performed, and trimethylamine and oxidized trimethylamine were employed as the molecular analogues for PVPTA and OPVPTA, respectively. The results indicate that there appears a strong hydrogen bonding between the nitrogen atom of trimethylamine and the hydrogen atom of the hydroxyl group of phenol with its bond length (N···H—O) of 1.712 Å and bond angle (∠NHO) of 163.9°, and the hydrogen bonding energy of trimethylamine with phenol is predicted to be −55.13 kJ/mol. For OPVPTA, the oxygen atom of oxidized trimethylamine forms a much stronger hydrogen bonding with hydrogen atom of hydroxyl group with its bond length (O···H—O) of 1.582 Å and bond angle (∠OHO) of 167.3°, and the hydrogen bonding energy is calculated to be −88.24 kJ/mol, more negative than that of PVPTA with phenol. Therefore, the calculations validate the hydrogen bonding mechanism.

As regards the adsorption in aqueous solution, it is generally presumed that the weak basic adsorbent like PVPTA adsorbs phenol in aqueous solution through two kinds of interactions [4,17], one is ion-exchange interaction between the negatively charged phenolic ion and the protonated amino group, the other is hydrogen bonding between the tertiary amino group of PVPTA and the hydrogen atom of the hydroxyl group of phenol. For the tested system, phenol cannot be ionized fully in aqueous solution because of its high p$K_a$, and the ion-exchange interaction can be ignored, hydrogen bonding is principally responsible for the adsorption [19]. The effect of the solution pH on the adsorption of phenol onto OPVPTA is the same as that of PVPTA (Fig. 3), implies the same adsorption mechanism of phenol onto OPVPTA. In addition, OPVPTA is more hydrophilic than PVPTA because of introduction of the oxygen atom on the tertiary amino groups, while the adsorption phenol onto OPVPTA is enhanced greatly in aqueous solution, illuminating that hydrogen bonding is also the main driving force for the adsorption in aqueous solution.

## 4. Conclusions

PVPTA was synthesized from chloromethylated PS and its tertiary amino group was oxidized successfully by sodium hypochlorite. The adsorption capacities of phenol onto OPVPTA increased heavily both in hexane and in aqueous solution. Langmuir model, which was based on a homogeneous surface model, was not suitable to picture the adsorption, while Freundlich model fitted the tested two adsorption systems well.

Adsorption enthalpy, adsorption Gibbs free energy, and adsorption entropy were calculated from the adsorption isotherms, and it was shown that the adsorption of phenol onto the two adsorbents in hexane was an exothermic, spontaneous, more ordered arrangement process. In addition, adsorption enthalpy, adsorption Gibbs free energy, and adsorption entropy of phenol onto OPVPTA were more negative than those onto PVPTA. The adsorption enthalpies of phenol onto PVPTA and OPVPTA in aqueous solution were computed to be −23.92 and −27.05 kJ/mol, respectively. PVPTA and OPVPTA adsorbed phenol mainly through hydrogen bonding in hexane and in aqueous solution.

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