Adsorption of phenol, bisphenol A and nonylphenol ethoxylates onto hypercrosslinked and aminated adsorbents

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The presence of phenolic compounds in aquatic environments poses potential human health and ecological risks. In this study, we evaluated porous resins as adsorbents for removal of three compounds, phenol, bisphenol A and nonylphenol ethoxylates from aqueous solutions. The adsorption isotherms were well fitted by the Langmuir equation, and the strength of the adsorption was affected by the properties of polymeric adsorbent (surface area, pore size, functional group and matrix) and phenolics (distribution coefficient \( K_{OW} \), adsorption coefficient \( K_d \), water solubility \( S_w \) and dissociation constant \( pK_a \)). Four possible interactions, i.e., hydrophobic effect, \( \pi-\pi \) bonds, hydrogen bonding and electrostatic interaction, were discussed to explore the underlying mechanism in the adsorption affinity of phenol and BPA. Hydroxyl on the aromatic rings strengthened the interactions between phenol and aminated polymeric adsorbent and thus the adsorption affinity. Adsorption of NPEO\(_{10}\) to polymeric adsorbents was dominated by pore size and molecular morphology, even on the aminated polymeric adsorbents (MN-100, MN-150). The results from thermodynamic analysis show that the adsorption of BPA and NPEO\(_{10}\) by polymeric adsorbents was thermodynamically favorable and generally endothermic whereas the adsorption process of phenol was exothermic. These results help us better understand the adsorption behavior and mechanism of phenolic compound onto carbon-based adsorbent.

1. Introduction

In recent years, environmental concerns about the fate, transport, reactivity, and bioavailability of phenolic compounds have drawn much attention of many researchers. Among these chemicals, bisphenol A (BPA) and nonylphenol ethoxylates (NPEOs) are particularly important because of their wide use in industry as materials for component of polymers and nonionic surfactants. Also, the two chemicals have the potential to disrupt endocrines [1,2]. BPA comes under this category because of its weak oestrogen-like effect [1]; NPEOs are related to endocrine disrupting chemicals as their biodegradation intermediates; nonylphenol mono- and di-ethoxylates and nonylphenol, are more toxic and persistent than their parent substances in the environment [2,3]. Moreover, as a surfactant, NPEOs can remarkably enhance the solubility of hydrophobic organic contaminants, and thus worsen water quality and increase the difficulty and cost of water treatment. Exposure to BPA and NPEOs can affect the reproductive behavior of higher life forms, such as fish, wildlife, humans, and even endanger the balance of ecosystems [4]. So, removal of these compounds from waste water is important for environmental protection.

Many works have been done on adsorption of the two chemicals from their aqueous solutions by natural and engineered adsorbents, such as bentonite [5], sand [6], river sediment [7,8], mineral materials [8], and carbonaceous adsorbents [10]. The adsorption of BPA was reported to be a process of physical interaction and weakly electrostatic interaction between the adsorbates and the hosts [8,9]; several studies confirmed the presence of hydrophobic effect and hydrogen bonding for the BPA adsorption process [11,12]. The studies of NPEOs adsorption indicated that both the hydrophobic and hydrophilic moieties of surfactant molecules play an important role in the adsorption process, regardless of whether the surface is hydrophobic or hydrophilic [5–7]. Interactions between the surfactant and the adsorbent surfaces are also essential. Interactions between the oxygen atom of the oxyethylene group and the surface of the adsorbent lead to strong adsorption of ethoxylated non-ionic surfactants [13]. These pioneering studies greatly improved the understanding of alkylphenols interactions with the adsorbents. Such interactions are supportive of their adsorption affinity.

Although many aspects of the interactions on phenolic compounds adsorption in aqueous systems have been studied, the roles
of the surface area, surface chemistry, and matrix of adsorbents as well as the molecular size (steric hindrance) of adsorbate are yet to be fully understood [14–16]. Most research in this field has ignored the influence of octane-water distribution coefficient ($K_{ow}$), adsorption coefficient ($K_a$) and water solubility of adsorbate on the adsorption process. Currently, advances in polymer science have provided opportunities to select well-structured polymeric adsorbent with high surface area, pore size, and suitable surface chemistry, such as hypercrosslinked polymeric adsorbents MN-200 and aminated polymeric adsorbents (MN-100, MN-150) [17–19]. Moreover, one of the main advantages of these polymeric adsorbents is that it can be regenerated more easily than other materials by using organic solvents such as ethanol, methanol, or acetone [20].

The main objective of this study is to investigate the mechanism and predominant factors controlling the adsorption of the pheno
clics to porous polymeric adsorbent. Phenol, one of the top priority contaminants was employed for comparison. Due to the fact that nonylphenol ethoxylates (NPEOs) are produced and used as mix-
tures, we selected the abbreviation NPEO10 as a representative of commercial nonylphenol ethoxylates, which are complex mixtures of a series of homologues, with 10 ethoxy units being present in the highest concentration. Hypercrosslinked polymeric adsorbent MN-200 and NDA-150, aminated polystyrene polymeric adsorbent MN-150 and MN-100 were selected as adsorbent. Impacts of solution chemistry conditions on adsorption were evaluated.

2. Materials and methods

2.1. Materials

Phenol, bisphenol A, and NPEO10 were obtained from Sigma-
Aldrich Chemical Co. and used as received. Commercial available polymeric adsorbents MN-200, MN-100 and MN-150 were supplied by Shanghai Office, Purolite International Co., Ltd. The commercial adsorbent NDA-150 was donated by Jiangsu N&G Environmental Technology Co. Ltd. (Jiangsu, China). Water used in the study was purified by distillation.

2.2. Polymeric adsorbents

The polymeric adsorbents were conditioned in methanol–
hydrochloric acid mixtures and finally in water before the adsorption experiments. Nitrogen adsorption and desorption experiments were carried out at 77 K to determine the surface properties of the polymeric adsorbents. Infrared spectra of the four polymeric adsorbents were obtained with a Nicolet 170 SX IR Spectrometer (Mad-
ison, WI, USA). Their zeta potentials were determined using a Malvern Instruments Zetamaster. (Zetamaster, Malvern Ltd, U.K.). The elemental analysis of the polymeric adsorbents was performed using a Perkin-Elmer 240 C Elemental Analytical Instrument (Wellesley, MA, USA). The BET surface area was calculated from desorption isotherms using the standard Brunauer-Emmett-Teller equation. The mesoporous pore size distribution was determined from desorption isotherms using the Barrett, Joyner and Halenda (BJH) method. All calculations were performed automatically by an Accelerated Surface Area and Porosimeter system (ASAP 2010, Micromeritics, USA).

2.3. Adsorption assay

Equilibrium adsorption experiments were carried out at 288,
303 and 318 K. Polymeric adsorbent (0.0500 g) was introduced into a series of 150 mL conical flasks and 100 mL of the phenolics from their stock aqueous solution was then added to each flask, respectively. The initial phenol and NPEO10 concentrations ($C_0$) of the solutions were 200, 400, 600, 800 and 1000 mg L$^{-1}$; due to the poor water solubility of Biphenol A, its initial concentrations ($C_0$) of the solutions were 20, 40, 60, 80 and 100 mg L$^{-1}$. The flasks were then completely sealed and placed in an incubator shaker (New Brunswick, model G25) at a pre-set temperature at a shaking speed of 130 rpm. Adsorption experiments were run continuously for 72 h to ensure equilibrium. The pH of the samples before and after the sorption experiments was measured, which was within 6.5–7.5 for different systems and kept unchanged. A separate set of experiments was carried out for the adsorption of the phenolics to MN-200 and MN-150 over a pH range of 1.0–12.0 (pH adjusted with NaOH and HCl).

The concentration of the phenolics was determined after equi-
lbrium by UV-VIS spectrophotometry at 274 nm for Phenol, 276 nm for Bisphenol A and 230 nm for NPEO10 (UV3100-PC, Map-
da, China). Quartz glass cells (Hellma) of 10 mm path length were used. Linear calibration curves (absorbance versus concentration) were used to determine the concentration of the phenolics. The adsorption capacity, $q_e$ (mmol g$^{-1}$), was calculated using the following:

$$q_e = V(C_0 - C_e)/M \cdot m \quad (1)$$

where $C_0$ is the initial adsorbate concentration (mg L$^{-1}$), $C_e$ is the residual concentration at equilibrium (mg L$^{-1}$), $V$ is the volume of solution (L), $M$ is the molecular weight of adsorbates, and $m$ is the mass of dry polymeric adsorbent (g).

3. Results and discussion

3.1. Polymeric adsorbent characterization

Four polymeric adsorbents with different physicochemical properties were selected as adsorbents. Their properties are pre-
sented in Table 1. The BET surface area of MN-200 is the largest; while, the corresponding ones of NDA-150, MN-150 and MN-100 are between 815 and 850 m$^2$ g$^{-1}$. The latter three have similar BET surface areas and micropore structures and they show a similar average pore diameter.

Fourier transform infrared (FTIR) spectroscopy was used to identify functional groups on the polymeric adsorbent surfaces (Fig. S1). FTIR spectra indicate the presence of tertiary amino groups on MN-100 and MN-150 (absorbance bands at 2772 and 2816 cm$^{-1}$) [21]. Tertiary amino groups are not detected in the IR spectra of MN-200 and NDA-150 polymeric adsorbents. The zeta potential of the polymeric adsorbents at different pH values is a function of the surface charge. Zero crossover points are observed at pH 4.5, 5.0, 6.8 and 7.2 for NDA-150, MN-200, MN-100 and MN-150 respectively (Fig. S2). The surface charge of the polymeric adsorbent at the pH of the adsorption experiments (pH 7 ± 0.5) would be negative for the MN-200 and NDA-150. The tertia
y amine functionality of the MN-100 and MN-150 rendered their surface positive, neutral or negative dependent on small shifts in pH.

3.2. Role of polymeric adsorbent properties in adsorption

The amounts of the phenolic compounds adsorbed on a unit millimole basis per gram of the polymeric adsorbents ($q_e$) against the equilibrium concentration ($C_e$) have been plotted in Fig. 1.

For phenol and BPA adsorption by hypercrosslinked polymeric adsorbents MN-200 and NDA-150, the adsorption capacities are consistent with their specific surface area and micropore area (Table 1, MN-200 > NDA-150), indicating that the interactions between the phenolic compounds and the surface of hypercrosslinked polymeric
adsorbents, especial micropore surface, may be key factors to their adsorption affinity. Although the characteristic parameters of amminated polymeric adsorbents MN-100 are all greater than those of MN-150 in Table 1, the adsorption capacities of phenol and BPA on MN-100 are less than MN-150 in Fig. 1 panel C and D, indicating that the functional groups on the aminated polymeric adsorbents surface may play a prominent role. The elemental analysis certified that the two polymeric adsorbents contain significant mass of nitrogen, 1.8% (mass) of MN-150 and 1.1% (mass) of MN-100, which are almost identical to the values from literature [21]. In particular, the amounts of BPA adsorbed by hypercrosslinked polymeric adsorbents MN-200 are obviously higher than those by aminated polymeric adsorbents MN-150 while the amounts of phenol adsorbed have no distinct disparity on the two polymeric adsorbents. These

<table>
<thead>
<tr>
<th>Property</th>
<th>MN-200</th>
<th>NDA-150</th>
<th>MN-150</th>
<th>MN-100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>Hypercrosslinked polystyrene</td>
<td>Aminated polystyrene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BET surface area (m²/g)</td>
<td>1155.8</td>
<td>836.1</td>
<td>815.3</td>
<td>850.4</td>
</tr>
<tr>
<td>Micropore area (m²/g)</td>
<td>697.17</td>
<td>390.5</td>
<td>382.4</td>
<td>410.9</td>
</tr>
<tr>
<td>Pore volume (cm³/g)</td>
<td>0.951</td>
<td>0.772</td>
<td>0.487</td>
<td>0.517</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>5.19</td>
<td>6.80</td>
<td>5.45</td>
<td>5.57</td>
</tr>
<tr>
<td>Particle size (mm)</td>
<td>0.4–0.6</td>
<td>0.4–0.6</td>
<td>0.4–0.6</td>
<td>0.4–0.6</td>
</tr>
</tbody>
</table>

Fig. 1. Adsorption isotherms of phenol, biphenol A (BPA) and NPEO₁₀ by polymeric adsorbents, MN-200 in panel A; NDA-150 in panel B; MN-150 in panel C; MN-100 in panel D at different temperature, i.e., 288 K ( ■ ); 303 K ( ○ ) and 318 K ( △ ). The adsorbed concentrations of BPA and NPEO₁₀ by the polymeric adsorbents are labeled on the left y axis, and the corresponding equilibrium concentrations are labeled on the bottom x axis; the adsorbed concentrations of phenol are labeled on the right y axis, and the corresponding equilibrium concentrations are labeled on the top x axis. Lines are data fittings with the Langmuir model.
results indicate that the contribution of polymeric adsorbent surface area and functional groups was different from the adsorption of BPA and phenol. All of the isotherms for NPEO_{10} by the four polymeric adsorbents show a plateau in the adsorbed amount. The shape of the isotherms is similar for hypercrosslinked or aminated polymeric adsorbents, indicating that the interactions between NPEO_{10} and hypercrosslinked or the aminated polymeric adsorbents might be the same. The amounts of NPEO_{10} adsorbed at the plateaus increase with increasing temperature. The influence of temperature on NPEO_{10} adsorption of the hypercrosslinked polymeric adsorbents (MN-200 and NDA-150) was weaker than for the aminated polymeric adsorbents (MN-100 and MN-150). The amount of NPEO_{10} adsorbed at the plateaus on the four polymeric adsorbents at 318 K shows a slight difference, that is, MN-200 > NDA-150 and MN-100 > MN-150, which indicates the specific surface area and average pore size played an important role in NPEO_{10} adsorption.

Two isotherm models (Langmuir model and Freundlich model) were applied to the experimental data in order to obtain further information at different equilibrium concentrations. The equations that describe the models are as follows:

\[
\frac{C_e}{q_a} = \frac{1}{K_M} + \frac{1}{M K_L}
\]

(2)

\[
\log q_a = \log K_f + n \log C_e
\]

(3)

where \(K_f\) is a direct measure of the intensity of the adsorption process (m^2 mol\(^{-1}\)); \(M\) is a constant related to the surface area occupied by a monolayer of adsorbate, reflecting the adsorption capacity (mmol g\(^{-1}\)); \(K_L\) is a system constant related to the bonding energy; and the slope \(n\) is a measure of the adsorption intensity or surface heterogeneity. The results of the data fit with the Langmuir and Freundlich models and the related correlation coefficients \(R^2\) are shown in Table 2.

The experimental data fit better with the Langmuir model \((R^2 > 0.991)\) than with the Freundlich model \((R^2\) ranges from 0.569 to 0.994). Li and Eli have also reported that surfactant adsorption isotherms are not well described by the Freundlich model [22]. The fitting results of the models show that the phenolic molecules were united as a “monolayer” on the surface of the polymeric adsorbents. A basic assumption of the Langmuir model is that the adsorbed molecules exhibit monolayer adsorption. Only the results from Langmuir model fitting are discussed herein.

### 3.3. Role of adsorbate properties in adsorption

Adsorption of phenolic compounds can be defined as the process of adsorbate molecules accumulating from a bulk solution on the exterior and interior surfaces of polymeric adsorbent. Hydrophobic effect, \(\pi-\pi\) bonds, hydrogen bonding, and electrostatic interactions are the most representative interactions present in the adsorption by porous polymeric adsorbents in aqueous phase, and the exact strength of the forces depends on the details of the species involved, typically for the adsorbates with certain functional groups [23]. So, considering only polymeric adsorbent may not be applicable when these interactions and contribution to the overall adsorption are a function of the properties of both the phenolic compounds and the polymeric adsorbents. The selected physicochemical properties of phenolic compounds are listed in Table 3. These parameters are important tools to interpret the contributions of interactions in the adsorption process.

Nonpolar molecules, or groups, tend to be associated in water; in other words, they tend to cluster together in associations by hydrophobic attractions and concentrate on the surface of the polymeric adsorbent [24]. Hydrophobic effect is emphasized in several studies that discussed humic acid [25], naphthylamine [26], and proteins [27] adsorption on polymeric adsorbents. If hydrophobic effect is the dominant mechanism for the interactions between the phenolics and polymeric adsorbents, the adsorption can be predicted using the hydrophobic parameters of phenolics, such as \(K_{OW}\) listed in Table 3, which is defined as the ratio of the equilibrium concentrations of the two-phase system consisting of water and n-octanol. Although the \(K_{OW}\) values of the phenolic compounds are positively correlated with \(K_{f}\) (the intensity of adsorption process) listed in Table 2, the adsorption amounts \(M\) are not corresponding to the values of \(K_{f}\).

In order to clearly explain the relationship between the adsorption affinity and the hydrophobic effect, we calculated single-concentration point adsorption coefficients \(K_r\) of the phenolic compounds at two equilibrium concentrations (0.1 and 0.3 mmol/L) on the polymeric adsorbent surface (Fig. 2) to quantitatively compare the adsorption affinities.

\(K_r\) is the distribution coefficient at a given equilibrium concentration (mmol/L) calculated from the fitted Langmuir equations. The \(K_r\) values of BPA are 5.0–8.0 times higher than those of phenol at 0.1 mmol/L and 0.3 mmol/L, which may be ascribed to its higher value of \(K_{OW}\) and the lower value of \(S_w\). The \(K_r\) values of NPEO_{10} fall in between them, which may be due to its highest water solubility. The relationship between \(K_r\) \(S_w\) and \(K_{OW}\) indicates that hydrophobic effect is an important mechanism for the adsorption of the phenolics onto the polymeric adsorbent, especially for BPA adsorption process.

The \(\pi-\pi\) electron donor-acceptor interaction has been considered as one of the predominant driving forces for the adsorption of chemicals with benzene rings on the polymeric adsorbent.

### Table 2

<table>
<thead>
<tr>
<th>Resin</th>
<th>(T) (K)</th>
<th>(K_r) mmol (^{-1})</th>
<th>(M) (mmol g(^{-1}) resin)</th>
<th>(R^2)</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(R^2)</td>
</tr>
<tr>
<td>MN-200</td>
<td>288</td>
<td>0.47</td>
<td>17.9</td>
<td>0.87</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>0.45</td>
<td>28.3</td>
<td>0.76</td>
<td>0.990</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>0.42</td>
<td>44.4</td>
<td>0.84</td>
<td>0.997</td>
</tr>
<tr>
<td>NDA-150</td>
<td>288</td>
<td>0.38</td>
<td>9.3</td>
<td>0.66</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>0.37</td>
<td>11.6</td>
<td>0.72</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>0.36</td>
<td>13.5</td>
<td>0.80</td>
<td>0.998</td>
</tr>
<tr>
<td>MN-150</td>
<td>288</td>
<td>0.63</td>
<td>8.6</td>
<td>0.46</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>0.59</td>
<td>20.1</td>
<td>0.63</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>0.54</td>
<td>33.7</td>
<td>0.72</td>
<td>0.999</td>
</tr>
<tr>
<td>MN-100</td>
<td>288</td>
<td>0.51</td>
<td>4.9</td>
<td>0.35</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>0.47</td>
<td>9.8</td>
<td>0.52</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>0.42</td>
<td>16.0</td>
<td>0.80</td>
<td>0.997</td>
</tr>
</tbody>
</table>

*P is the abbreviation of phenol; B is the abbreviation of BPA; N is the abbreviation of NPEO_{10}.兴奋
The contribution of $\pi-\pi$ bonds between the phenolics and the polymeric adsorbent with benzene rings is beyond dispute. Each carbon atom in a polymeric adsorbent has a $p$-electron orbit perpendicular to polymeric adsorbent surface. Therefore, the strength of $p-p$ interaction is expected to scale up with the number of aromatic rings. The two benzene rings of biphenol A molecule have stronger attractions with the rings on the surface of the polymeric adsorbent. The predominance of hydrophobic effect and $p-p$ interaction might lead to the higher adsorption affinity of BPA than that of phenol and NPEO10, and the higher values of adsorption coefficients ($K_d$) as depicted in Fig. 2.

Hydrogen bonding is one mechanism for the adsorption of organic compounds on carbon-based adsorbents. The –OH substitution on the phenolics and the nitrogen-containing groups on the polymeric adsorbent surface may form hydrogen bonding; the hydrogen bonding may also form between the surface-adsorbed and dissolved phenolics. So, the existence of –OH substitution on the phenolics is advantageous to the adsorption on the aminated polymeric adsorbents. On the other hand, the surface of the hypercrosslinked polymeric adsorbent was negatively charged at the final solution pH ($7 \pm 0.5$) higher than their $pH_{PZC}$ (pH 4.5–5.0) and hydroxyl is an electron-donating functional group. So, –OH substitution on the phenolic molecules and negatively charged surfaces have the same sign of charge and can repel each other. On the other hand, the pH ($7 \pm 0.5$) of solution was lower than the $pK_a$ of the phenolics (Table 2) and close to the $pH_{PZC}$ of the aminated polymeric adsorbents, suggesting that both the adsorbates and adsorbents might not be highly charged in the experiment; the phenolics used in this work should be primarily in neutral form. Therefore, electrostatic interaction between the phenolics and aminated polymeric adsorbents cannot be major factors controlling the adsorption process. As discussed above, the amounts of adsorbed phenol have no distinct disparity on the hypercrosslinked polymeric adsorbent MN-200 and aminated polymeric adsorbent MN-150 while the amounts of adsorbed BPA on MN-200 are obviously higher than those on MN-150, which might be ascribed to the negative contribution of electrostatic repulsion to phenol adsorption by MN-200. At the same time, adsorption of biphenol A by the polymeric adsorbents is dependent mainly on the cooperation of hydrophobic effect and $\pi-\pi$ interaction. A series

### Table 3

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>$M_m$</th>
<th>$S_w$</th>
<th>log $K_{ow}$</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td><img src="image" alt="Phenol Structure" /></td>
<td>94</td>
<td>67</td>
<td>1.46</td>
<td>10</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td><img src="image" alt="Bisphenol A Structure" /></td>
<td>228</td>
<td>0.12–0.3</td>
<td>3.32</td>
<td>8, 9</td>
</tr>
<tr>
<td>Decylethoxylene nonylphenol</td>
<td><img src="image" alt="Decylethoxylene nonylphenol Structure" /></td>
<td>660</td>
<td>Soluble</td>
<td>4.09</td>
<td>–</td>
</tr>
</tbody>
</table>

$M_m$ is the molar mass (g/mol). $S_w$ is the solubility in water at room temperature (g/L). log $K_{ow}$ is the log scale octanol–water partition coefficient. $pK_a$ is the negatively log-transformed acid dissociation constant.

* Data are from Ref. [14].
* Data are from Ref. [15].
* Data are from Ref. [1].
* Data are from Ref. [16].

Fig. 2. Adsorption coefficients ($K_d$) of the phenolic compounds on the four polymeric adsorbents.
of adsorption experiments were carried out at different pH values to test the hypothesis as depicted in Fig. 3.

The reduced amounts of the two phenolics adsorbed with pH over their pK_a could be due to the increased electrostatic repulsion between the dissociated phenolics and negatively charged polymeric adsorbent. The adsorption amounts of NPEO_10 remain practically constant within the tested pH range, indicating that there could be different interactions contributing to its adsorption process. The adsorption amounts of NPEO_10 on the four polymeric adsorbents and their adsorption coefficients (K_d) have no special difference as shown in Figs. 1 and 2. However, the shape of their isotherms is obviously different between hypercrosslinked and aminated polymeric adsorbent, indicating the different contribution originated from the polymeric adsorbent surface and the molecular morphology. The adsorption amounts of NPEO_10 by MN-100 are higher than MN-150 in Fig. 1 at 318 K, which showed the importance of pore volume and size (MN-100 > MN-150).

Molecular size and shape of NPEO_10 should determine the availability of different adsorption sites on the polymeric adsorbent. Different adsorption mechanisms respond to the change of environmental conditions differently; thus, the relative contribution of an individual mechanism to the overall adsorption is of major importance to predicting phenolic adsorption on polymeric adsorbents, which can be further understood by investigating thermodynamic parameters.

3.4. Role of temperature in adsorption

Temperature has an important effect on the adsorption process of the phenolics. As shown in Fig. 1, the adsorption amounts of BPA and NPEO_10 increase with increasing temperature while the adsorption amounts of phenol present opposite trends. Thermodynamic parameters, Gibbs energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) can provide information on the inherent energetic changes involved during the adsorption process. The relationship among the enthalpy change (ΔH°), Gibbs energy change (ΔG°) and entropy change (ΔS°) of the adsorption process is expressed as:

ΔH° = ΔG° + TΔS°  

The Gibbs energy change (ΔG°) indicates the degree of spontaneity of the adsorption process. In this study, Eq. (5) was employed to calculate ΔG° [30] as follows:

ΔG° = -RT ln K_L  

where K_L is a thermodynamic constant determined from the Langmuir equation, T is the absolute temperature in Kelvin, and R is the universal gas constant (8.314 J mol⁻¹ K⁻¹). The calculated ΔG° values are listed in Table S1. The value of ΔG° becomes more negative (absolute value of ΔG° increases) as the temperature increases from 288 K to 318 K, suggesting that adsorption is more spontaneous at high temperatures. The less negative the ΔG°, the weaker the driving force of sorption. For a given polymeric adsorbent (MN-200) at a certain temperature (303 K), ΔG° became more negative when the amount of adsorbed phenolics on a unit mass basis increased as depicted in Fig. 3, meaning the driving force became stronger. This
is in keeping with the calculation $K_t$ of the adsorption intensity in Table 2.

On the other side, the trend of phenol adsorption amounts with temperature is different with the BPA and NPEO$_{10}$, indicating the driving force is not the only factor affecting adsorption amounts. Combining Eqs. (4) and (5) yields Eq. (6).

$$\ln K_t = -\frac{\Delta H^\circ}{R} + \frac{\Delta S^\circ}{R}$$

In $K_t$ was plotted against $1/T$ (Fig. 4), $\Delta S^\circ$ and $\Delta H^\circ$ were calculated from the intercepts and slopes of the resulting curves [31].

By analyzing the curves in Fig. 4, we can get an estimation of $\Delta H^\circ$ from the respective slope listed in Table S1. Basically, the positive values of the total change of enthalpy $\Delta H^\circ$ in cases of Biphenol A and NPEO$_{10}$ indicates that the whole adsorption process is endothermic, which fact is supported by the adsorption capacity increasing with temperature in the studied range as shown in Fig. 1. On the other hand, the negative values of $\Delta H^\circ$ of phenol indicates that the whole adsorption process is exothermic and the adsorption capacity decreases with temperature.

It seems probable that the phenolic molecules (including benzene ring and phenolic group) can interact with the surface of polymers (including benzene ring, and amino groups) to form surface complexation. The acidic active groups of phenolic molecules will interact with the basic groups on the surface of the polymers easily, which is helpful for the adsorption and also is a factor for the change of adsorption capacities when the temperature increases. Furthermore, the surface complexation offers differences in strength, binding kinetics, and directionality, which are controlled by the polymeric adsorbent specific area, pore size and the molecular structure of the phenolics; the net enthalpy change for the adsorption process is based on the difference in enthalpy of different interactions. Hence, the net enthalpy change can be negative or positive, depending on the balance of interactions prevailing during the adsorption process. The negative values of the change in entropy $\Delta S^\circ$ show the decreasing randomness at the polymeric adsorbent–solution interface during the adsorption and the phenolic molecules were more orderly adsorbed on the surface of polymeric adsorbent. Finally, the mechanism of phenolic adsorption was not only determined by various interactions but also by steric structure of polymeric adsorbent.

4. Conclusion

The experimental results and thermodynamic models discussed in this paper support the importance of surface area, functional groups, pore structure, adsorbate property, and solution temperature in the adsorption of phenolics by porous polymeric adsorbents:

1. The adsorption affinity and capacity of the phenolics on the hypercrosslinked polymeric adsorbent is surface area dependent while this on the aminated polymeric adsorbent is obviously affected by functional group.

2. Electron-donating substituent hydroxyl on the aromatic ring of phenolics can influence the interaction positively with aminated polymeric adsorbent and negatively with hypercrosslinked polymeric adsorbent.

3. The adsorption capacity of phenol on polymeric adsorbents is hydrogen bonding and electrostatic interactions dependent, the contribution of coordination interactions changing with the type of polymeric adsorbent. While, the adsorption capacity of BPA on polymeric adsorbents is hydrophobic effect and $-\pi$-$\pi$ bonds dependent. The adsorption process of NPEO$_{10}$ has no obvious correlation with the polymeric adsorbent surface area and functional group.

4. Thermodynamic analysis can help us further identify different contribution of interactions and observe underlying mechanism during the phenolic adsorption process.

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Appendix A. Supplementary data

Supplementary data for this article can be found in the online version, at doi:10.1016/j.reactfunctpolym.2011.07.001.

Reference


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