Adsorptive removal of phenolic compounds by using hypercrosslinked polystyrenic beads with bimodal pore size distribution

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Abstract

Hypercrosslinked polystyrenic beads with bimodal pore size distribution were prepared through Friedel–Crafts modification by using macroreticular poly(vinylbenzylchloride-divinylbenzene) copolymer beads as base polymers. Their adsorption behaviors were investigated with the aqueous solution of phenolic compounds such as phenol, 4-chlorophenol, and 2,4-dichlorophenol. The biporous hypercrosslinked beads showed not only faster adsorption kinetics than commercial polystyrenic adsorbents, but also larger adsorption capacities. The adsorption isotherms for the bi-solute system were represented in a three-dimensional coordinate, and their adsorption behaviors could be explained from the data for the adsorption of a single phenolic component.

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1. Introduction

Phenolic hydrocarbons are widely used in pharmaceutical, petrochemical, and other chemical manufacturing processes, and waste waters containing such phenolic compounds must be treated before being discharged. Activated carbons have been applied as adsorbents for the removal of phenolic pollutants from wastewater in view of their high surface area and pore volume [1,2]. Commercial activated carbons, however, have some disadvantages such as high costs for regeneration and production of fines due to their brittle nature [3]. Over the last two decades, polymeric adsorbents have also been used as alternatives of activated carbons to remove or recover various organic compounds from the
polluted water [4,5]. Since most of polymeric adsorbents have a lower adsorption capacity for many organic compounds than activated carbons mainly due to their lower surface area [6], it is desirable to obtain higher surface area for better use in the removal of organic compounds. A novel method for the synthesis of polystyrene networks was consisted of post-crosslinking the linear polystyrene chains by means of Friedel–Crafts reaction in highly swollen state producing methylene bridges between neighboring phenyl groups [7,8]. This hypercrosslinked polymer beads made a third type of polymeric adsorbents in addition to the traditional gelular or macroporous copolymer, and expanded the scope for the potential applications of adsorption methods, for example, sorption of organic vapors [9] or organic compounds from water [10,11], toxic trace metal removal [12,13], ion exchange resin [14,15], and pre-concentration of hydrophilic aromatic compounds by reversed-phase HPLC [16].

In this work, hypercrosslinked polystyrene beads having bimodal pore size distribution were prepared through Friedel-Craft modification of macroreticular type base polymer beads. They are expected to make more useful adsorbents of volatile organic compounds, because the existence of both micropores and macropores can offer effective adsorption and kinetics. The role of macropores has been well investigated in some of very systematic works on the interaction of diffusion and reaction in the macroreticular resin beads [17–19]. These hypercrosslinked polystyrene adsorbents were applied for the adsorptive removal of phenolic compounds such as phenol, 4-chlorophenol (MCP, monochlorophenol), and 2,4-dichlorophenol (DCP, dichlorophenol) in aqueous solution. The adsorption behaviors of the hypercrosslinked polymer beads were compared with those of commercial polymeric adsorbents such as Amberlite XAD-2, Amberlite XAD-4, and Ambersorb XE340. The adsorption kinetics were measured and the adsorption isotherms for a single phenolic compound were correlated by the Freundlich model [20]. The multicomponent equilibrium isotherms were constructed to better understand the interaction of adsorbates in the solutions.

2. Experimental

2.1. Preparation of polystyrene adsorbents with bimodal pore size distribution

Base polystyrene beads were prepared by conventional suspension copolymerization of styrene monomer and divinylbenzene (DVB) as reported in many literatures [21,22]. Vinylbenzyl chloride was used as a styrenic functional monomer and the degree of crosslinking in the base polymer was 20%. The base polymer beads [20%-PVBC] were swollen in 1,2-dichloroethane for about 2 h and the slurry was cooled to −4 °C in ice bath and then ferric chloride was added as catalysts into the slurry solution. After the catalysts were dispersed throughout the base polymer beads, the temperature was raised to 80 °C. After 24 h, reaction mixture was quenched by the addition of methanol. Catalyst and solvent were washed with methanol, a mixture of acetone and 0.5 M HCl, and finally deionized water. The resulting polymer beads were dried under vacuum at 80 °C to make hypercrosslinked polymeric adsorbents having bimodal pore size distribution, denoted as 20%-PVBC (F.C.).

2.2. Adsorption of phenolic compounds

Adsorption experiments were conducted at 25 °C by adding desired quantities of the polymeric adsorbents into a 125 ml polypropylene bottle filled with aqueous phenolic solution up to 100 ml which was loaded in a thermostatted shaker at 140 rpm. The adsorption kinetic experiment for a single phenolic compound was carried out by measuring its concentration in the samples collected from 0.5 to 24 h. The liquid samples taken after about 24 h were analyzed by high performance liquid chromatography (HPLC, Young-Lin 930), equipped with Rheodyne injection valve and UV detector. Concentration of phenolic compounds was measured using a μ-Bondapack C18 column and mobile phase of a mixture of water and acetonitrile (4:6) with flow rate of 0.8 ml/min. Similar experiments were performed for the dilute bi-solute system to
obtain the adsorption isotherm for the multicomponent system and to examine the interaction between two different solutes. Not only hypercrosslinked polymer beads but also commercial polymer beads such as, Amberlite XAD-2, Amberlite XAD-4 and Amber sorb XE340, which were purchased from Rohm and Haas (Philadelphia, USA), were used as polymeric adsorbents for phenolic compounds.

3. Results and discussion

3.1. Properties of hypercrosslinked polymer beads [20%-PVBC (F.C.)]

The base polymer beads were prepared by the conventional suspension polymerization using toluene and isooamy alcohol as porogenic agent. The particle size distribution of prepared base polymer beads was broad, ranging from 200 to 1400 μm. The particle size used in modification reaction was between 600 and 1000 μm through fractionation using sieves having mesh No. from 18 to 30. The swelling ratios of macroporous base polymer beads with acetone were about 1.4. After Friedel–Crafts modification, the pore size distributions were measured by Ar adsorption for micropores and by N₂ adsorption for meso- and macropores, respectively, and illustrated in Fig. 1. It was found that macroporous hypercrosslinked polymer beads have both the macropores produced by the porogenic agent and the micropores formed via Friedel–Crafts reaction. The physical properties of polymeric adsorbents used in this work are shown in Table 1.

![Fig. 1. Pore size distribution of base polymer beads and Friedel–Crafts modified polymer beads.](image)

Table 1
The physical properties of various porous polymeric adsorbents

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore diameter (Å)</th>
<th>Swelling ratio^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambersorb XE340</td>
<td>460</td>
<td>0.38</td>
<td>133</td>
<td>1.1</td>
</tr>
<tr>
<td>Amberlite XAD-2</td>
<td>350</td>
<td>0.76</td>
<td>109</td>
<td>1.3</td>
</tr>
<tr>
<td>Amberlite XAD-4</td>
<td>880</td>
<td>1.14</td>
<td>51</td>
<td>1.4</td>
</tr>
<tr>
<td>20%-PVBC (F.C.)</td>
<td>1030</td>
<td>0.95</td>
<td>90</td>
<td>1.1</td>
</tr>
</tbody>
</table>

^a Swelling solvent: acetone.
3.2. Adsorption kinetics

Kinetics of adsorption are directly related to the efficiency of adsorption [23]. Adsorption kinetics with hypercrosslinked polymeric adsorbent were compared with those with commercial polymeric adsorbents. Fig. 2 indicates that the hypercrosslinked polymeric adsorbent showed faster adsorption kinetics and larger adsorption capacities than commercial polymeric adsorbents. Maximum uptake of 20%-PVBC (F.C.) was two times larger than that of other commercial polymeric adsorbents, mainly due to their larger surface area.

The adsorption of phenolic compounds from an aqueous solution was assumed to follow reversible first order kinetics [24]. The heterogeneous equilibrium between the phenolic solution and the polymeric adsorbents may be expressed as

\[ A \frac{k_1}{k_2} B, \]  

where \( A \) and \( B \) are the phenolic compound in liquid phase and on the adsorbent surface, respectively. \( k_1 \) is the forward reaction rate constant and \( k_2 \) the backward reaction rate constant. If \( a \) is the initial concentration of phenolic compound in liquid phase and \( x \) the amount transferred from liquid phase to solid phase at time \( t \), the rate can be expressed as

\[ \frac{dx}{dt} = k_1(a - x) - k_2x. \]  

If \( X_e \) represents the concentration of phenolic compounds adsorbed at equilibrium (\( dx/dt = 0 \)), we have

\[ k_1(a - X_e) - k_2X_e = 0 \]  

and

\[ k_C = \frac{k_1}{k_2} = \frac{X_e}{a - X_e}, \]  

where \( k_C \) is the adsorption equilibrium constant. Then Eq. (2) becomes

\[ \frac{dx}{dt} = (k_1 + k_2)(X_e - x). \]  

The form of this equation indicates that the adsorption may be considered as first order in the departure from equilibrium, where the overall rate is

![Fig. 2. Adsorption kinetics of phenolic compounds over various polymeric adsorbents at 25 °C.](image-url)
constant ($k$) is the sum of the rate constants for the forward and backward reactions. Therefore, integration of the equation leads to

$$k_1 + k_2 = \frac{1}{t} \ln \left( \frac{X_e}{X_e - x} \right).$$

(6)

The above equation can be written in the form of

$$\ln \left( 1 - \frac{x}{X_e} \right) = -(k_1 + k_2)t = -kt.$$  

(7)

The overall rate constant $k$ for a given concentration of phenolic compounds was calculated by the slope of straight line in plotting $\ln(1 - x/X_e)$ versus $t$. The forward and backward rate constants were calculated by using Eqs. (4) and (7), and listed in Table 2. Hypercrosslinked polymer [20%-PVBC (F.C.)] showed higher overall rate constant than other commercial polymeric adsorbents except Amberlite XAD-2. The overall rate constants of Amberlite XAD-2 were larger than those of other polymeric adsorbents, which is due to their larger backward rate constants. Even if the time required for reaching to adsorption equilibrium is the shortest with XAD-2, their adsorption capacity is the lowest due to their low surface area. As expected, macropores formed during the preparation of base polymer beads should have improved the adsorption kinetics with

<table>
<thead>
<tr>
<th>Adsorbents Adsorbate</th>
<th>Overall rate constant $k = k_1 + k_2$ (h$^{-1}$)</th>
<th>Forward rate constant $k_1$ (h$^{-1}$)</th>
<th>Backward rate constant $k_2$ (h$^{-1}$)</th>
<th>$k_c(k_1/k_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%-PVBC (F.C.)</td>
<td>Phenol</td>
<td>3.64</td>
<td>1.51</td>
<td>2.13</td>
</tr>
<tr>
<td>Ambersorb XE340</td>
<td></td>
<td>1.43</td>
<td>0.35</td>
<td>1.08</td>
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<tr>
<td>Amberlite XAD-4</td>
<td></td>
<td>3.12</td>
<td>0.68</td>
<td>2.44</td>
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<tr>
<td>Amberlite XAD-2</td>
<td></td>
<td>6.65</td>
<td>0.88</td>
<td>5.77</td>
</tr>
<tr>
<td>20%-PVBC (F.C.)</td>
<td>4-Chlorophenol (MCP)</td>
<td>1.04</td>
<td>0.68</td>
<td>0.36</td>
</tr>
<tr>
<td>Ambersorb XE340</td>
<td></td>
<td>0.50</td>
<td>0.19</td>
<td>0.31</td>
</tr>
<tr>
<td>Amberlite XAD-4</td>
<td></td>
<td>0.89</td>
<td>0.32</td>
<td>0.57</td>
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<tr>
<td>Amberlite XAD-2</td>
<td></td>
<td>2.28</td>
<td>0.37</td>
<td>1.91</td>
</tr>
<tr>
<td>20%-PVBC (F.C.)</td>
<td>2,4-Dichlorophenol (DCP)</td>
<td>1.12</td>
<td>0.93</td>
<td>0.19</td>
</tr>
<tr>
<td>Ambersorb XE340</td>
<td></td>
<td>0.74</td>
<td>0.47</td>
<td>0.27</td>
</tr>
<tr>
<td>Amberlite XAD-4</td>
<td></td>
<td>0.73</td>
<td>0.52</td>
<td>0.21</td>
</tr>
<tr>
<td>Amberlite XAD-2</td>
<td></td>
<td>1.17</td>
<td>0.54</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Table 2
Rate constants for the removal of phenolic compounds by various polymeric adsorbents at 25 °C

<table>
<thead>
<tr>
<th>Adsorbents Adsorbate</th>
<th>$k_0$ (mmol/g)(mmol/l)$^{1/n}$</th>
<th>$n$</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%-PVBC (F.C.)</td>
<td>Phenol</td>
<td>1.04</td>
<td>0.39</td>
</tr>
<tr>
<td>Amberlite XAD-4</td>
<td></td>
<td>0.21</td>
<td>1.02</td>
</tr>
<tr>
<td>Ambersorb XE340</td>
<td></td>
<td>0.09</td>
<td>1.75</td>
</tr>
<tr>
<td>Amberlite XAD-2</td>
<td></td>
<td>0.01</td>
<td>2.94</td>
</tr>
<tr>
<td>20%-PVBC (F.C.)</td>
<td>4-Chlorophenol (MCP)</td>
<td>1.31</td>
<td>0.45</td>
</tr>
<tr>
<td>Amberlite XAD-4</td>
<td></td>
<td>0.56</td>
<td>0.63</td>
</tr>
<tr>
<td>Ambersorb XE340</td>
<td></td>
<td>0.35</td>
<td>0.81</td>
</tr>
<tr>
<td>Amberlite XAD-2</td>
<td></td>
<td>0.24</td>
<td>0.75</td>
</tr>
<tr>
<td>20%-PVBC (F.C.)</td>
<td>2,4-Dichlorophenol (DCP)</td>
<td>10.06</td>
<td>0.86</td>
</tr>
<tr>
<td>Amberlite XAD-4</td>
<td></td>
<td>1.80</td>
<td>0.56</td>
</tr>
<tr>
<td>Ambersorb XE340</td>
<td></td>
<td>0.85</td>
<td>0.63</td>
</tr>
<tr>
<td>Amberlite XAD-2</td>
<td></td>
<td>0.83</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Table 3
Coefficients of Freundlich isotherm for all adsorbents at 25 °C
hypercrosslinked polymer beads. The largest equilibrium constants of hypercrosslinked polymeric adsorbents were in good correlation with their largest adsorption capacities.

3.3. Adsorption isotherms

Adsorption isotherms were measured for all phenolic compounds on various polymeric adsorbents and the results were shown in Fig. 3. The adsorption isotherm of DCP could not be obtained in the same equilibrium concentration range of liquid phase with other adsorbates, due to high adsorption capacity and low solubility in water. The adsorption capacities for phenol decreased in the following order: 20%-PVBC (F.C.) > Ambersorb XE340 ≈ Amberlite XAD-4 > Amberlite XAD-2. The adsorption capacity of polymeric adsorbents would increase as the solubility of adsorbate in water decreased. The adsorption isotherms were simulated by Freundlich model as 

\[ q_e = k_F C_e^{1/n} \]

where \( q_e \) is the adsorption amount per unit mass of the adsorbent, \( C_e \) is the concentration of adsorbate at equilibrium, and \( k_F \) and \( n \) are parameters indicating the capacity and intensity of adsorption, respectively. The corresponding parameters of all adsorbents were summarized in Table 3, where the standard deviation for the correlation was in the range of 0.2–2.5%.

It could be anticipated from the highest adsorption capacity in Fig. 2 that 20%-PVBC (F.C.) has the highest \( k_F \) value. However, \( n \) representing the intensity of adsorption was relatively lower compared with other commercial polymeric adsorbents and this means weak interaction between adsorbate and adsorbent. Therefore, this characteristic of hypercrosslinked polymer beads could help to make polymeric adsorbent regenerated under mild condition.

The adsorption isotherms of dilute bi-solute system over 20%-PVBC (F.C.) polymeric adsorbents were illustrated in Figs. 4–6. These experiments were performed to obtain the adsorption isotherm for the multicomponent system and to examine the adsorption behavior between solutes with different solubility in water. In the system of phenol and MCP of Fig. 4, it can be seen that the equilibrium concentration of each component decreased due to the presence of other component as indicated by the bold line. Competitive
adsorption between phenol and MCP is expected since the adsorption intensities are similar. Similar explanation can be made for the system of MCP and DCP of Fig. 5. In the system of phenol and DCP of Fig. 6, however, the equilibrium concentration of phenol was seriously influenced by the existence of DCP while there were no significant changes in the adsorption amounts of DCP. Since DCP is more hydrophobic than phenol, it is preferentially adsorbed on the polymeric adsorbents via strong hydrophobic interaction with adsorbents.

These adsorption trends of bi-solute systems could be explained with the adsorption intensity parameter \((n)\) and capacity \((k_F)\) for the single

Fig. 4. Adsorption isotherms for the 4-chlorophenol (MCP)/phenol system over 20%-PVBC (F.C.) at 25 °C.

Fig. 5. Adsorption isotherms for the 2,4-dichlorophenol (DCP)/4-chlorophenol (MCP) system over 20%-PVBC (F.C.) at 25 °C.
component adsorption in Table 3. The adsorption capacities of each adsorbate could be related to the difference of adsorption strength. In the phenol and MCP system having similar adsorption strength, the adsorption capacity of each component decreased with the increase of the concentration of other component. However, the adsorption capacities of DCP, due to higher adsorption strength compared with other adsorbates, were affected only slightly by the presence of other component.

4. Conclusion

Hypercrosslinked polystyrenic beads were prepared through Friedel–Crafts modification of macroreticular-type (above 20% DVB) poly(vinylbenzylchloride-divinylbenzene) copolymer beads used as base polymer. Their adsorption behaviors were observed for the aqueous solution of phenolic compounds such as phenol, MCP, and DCP. Hypercrosslinked polymer beads showed higher adsorption capacities by about two times than other commercial polymeric adsorbents and their adsorption kinetics were faster due to presence of macropores. The equilibrium isotherms for the adsorption of phenolic compounds were obtained from batch experiments and could be correlated by Freundlich model. The adsorption isotherms of bisolute system were constructed in a 3-D illustration, and their adsorption equilibria could be explained in terms of the adsorption intensity parameter and the adsorption capacity from the single component adsorption.

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