Sorption of phenolic compounds on porous strongly basic anion exchangers based on styrene matrix

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Received 2 March 1994; accepted 1 May 1995

The sorption of phenolic compounds from aqueous solution has been studied by using porous strongly basic anion exchangers based on styrene matrix. The sorption performance is governed by sorbate, sorbent and solution characteristics. The uptake is fast and reversible. However, the pH of aqueous solution of these compounds and the presence of electrolyte effects their sorption performance. The sorption of phenolic compounds by these porous strongly basic anion exchangers has been found to be reversible under dynamic conditions.

The detrimental effect of phenolic compounds in water and the methods adopted for its removal have been briefly surveyed. The removal of phenolic compounds by porous polymeric adsorbents based on styrene matrix has also been studied. Porous strongly basic anion exchangers based on cross-linked products of styrene and divinyl benzene show better uptake of phenolic compounds as compared to non-functional porous polymeric adsorbents based on styrene matrix. The sorption of phenol by macroporous AV-17-2P anion exchanger is also reported. Kumagai and Kaufman have compared the performance of anion exchangers based on styrene and acrylic matrix for the sorption of phenol. Moreover, the adsorption of phenol on strongly basic anion exchangers in OH⁻ and Cl⁻ forms has also been compared. There is also report on the adsorption and desorption of phenol on activated carbon and strongly basic anion exchanger in a fixed bed column. In the present investigation the effect of porous strongly basic anion exchanger based on styrene divinyl benzene copolymer matrix on the uptake of phenol, 3-aminophenol and 4-nitrophenol has been extensively studied with a view to assess their application potential for abatement of water pollution.

**Experimental Procedure**

The chloride form of strongly basic porous anion exchangers based on polymeric divinyl benzene matrix have been studied for the uptake of phenol, 3-aminophenol and 4-nitrophenol from aqueous solutions under static conditions, following the methods adopted earlier. The effect of the variation of the different parameters, one at a time, on the uptake of phenolic compounds on a selected porous anion exchanger has been studied. These parameters are (i) the concentration of phenolic compound in the aqueous solution, (ii) the pH of the aqueous solution, (iii) the nature and the quantity of an electrolyte present in the aqueous solution and (iv) the duration of the equilibration of the aqueous solution of phenolic compound with porous anion exchanger.

The effect of the variation of the different experimental parameters, one at a time, on the breakthrough capacity of porous strongly basic anion exchangers for the concerned phenolic compound has been studied under dynamic conditions. These are (i) the loading flow rate, (ii) the concentration of the phenolic compounds in the influent aqueous solution, (iii) the concentration of salt and electrolyte in the influent solution of the phenolic compound and (iv) the pH of the influent aqueous solution of phenolic compound. In each case one and the same resin bed was repeatedly used after elution of the phenolic compound throughout the course of this investigation.

Due to porous nature of the matrix, the rate of sorption of phenolic compound is fast in general (Fig. 1). The rate of uptake of phenol is fast as compared to that of 4-nitrophenol and 3-aminophenol on BPR(A)-20-0.7-CA. This is due to the fact that the aromatic matrix of the resin prefers a weakly polar compound like phenol than 4-nitrophenol.

Uptake of phenolic compounds by strongly basic anion-exchange resins under dynamic cond-
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Fig. 1—Kinetics of sorption of phenolic compounds by porous strongly basic anion-exchange resin (BPR1-A20-0.7-CA). Quantity of the anion exchange for equilibrium = 0.5 g, Volume of the equilibrated solution = 100 mL, Initial content of phenolic compound in solution = 25 mg/L and Temperature of equilibrium = 30°C.

Fig. 2—Effect of the variation of the loading flow rate on the breakthrough capacity of the porous strongly basic anion-exchange resin (BPR1-A20-0.7-CA). Bed Height = 10 cm, Bed volume = 15 mL, Concentration of phenolic compound in the influent = 25 mg/L.

Fig. 3—Elution of 4-nitrophenol from porous strongly basic anion-exchange resin (BPR1-A20-0.7-CA). Bed height = 10 cm, Bed volume = 15 mL, Content of 4-nitrophenol in the influent = 25 mg/L. Loading flow rate = 10 bed vols/h, Elution flow rate = 3 bed vols/h and Fraction volume = 10 mL.

During the sorption of phenolic compounds, under dynamic conditions it is observed that higher the loading flow rate lower is the uptake. This is but natural, as the contact time with the anion exchanger is reduced due to increased service flow rates resulting into less uptake.

As already discussed, the uptake of phenolic compounds on the strongly basic anion exchanger is partly by chemisorption and partly by ion-exchange, therefore, their elution by solvents from the resin bed is going to be incomplete. However, the presence of methanol along with 1N HCl is selected as the eluting agent for the elution of 4-nitrophenol as shown in Fig. 3. With this eluting agent, the desorption of phenol and 3-aminophenol is very good as shown in Fig. 4. Elution of 4-nitrophenol requires comparatively larger quantity of eluting agent due to poor solubility.

On a strongly basic anion exchanger the uptake increases as the pH increases.

Results and Discussion

The partial elution of 4-nitrophenol (69.5% of the total sorption) from the resin matrix by methanol (Fig. 3) proves that the sorption of phenolic compound by the strongly basic anion exchanger is partly by chemisorption and partly by ion-exchange. The uptake of phenolic compound on porous strongly basic anion exchanger is presented in Table 1. The uptake may not be correlated with a particular characteristic of the exchanger and may be affected by various controlling parameters like ion-exchange capacity, surface area and the acidic or basic nature of the absorbate.
The strongly basic anion exchangers BPR\(_A\)-15-0.7-CA and BPR\(_A\)-20-0.7-CA, the surface area and average pore diameter are more or less similar but phenol uptake on later is more (5.29 mg/g) as compared to (4.90 mg/g) for the former (Table 1). This is due to difference in their anion-exchange capacities, 2.80 meq/g and 3.12 meq/g, respectively. On any anion exchanger, the uptake of 4-nitrophenol is generally more, followed by phenol and then 3-aminophenol, since 4-nitrophenol is preferentially taken up by the Cl\(^-\) form of the anion exchanger. In the case of a salt form of a strongly basic anion exchanger, the uptake of phenolic compounds is influenced by the structure which is the back-bone of the resin\(^8\).

The sorption of phenolic compounds occurs by the strongly basic anion exchangers in both by the regular exchange and also due to Van der Waal's forces. This has been proved by the incomplete, removal of phenolic compound from the resin.

### Table 1—Uptake of phenolic compounds on porous strongly basic anion exchangers based on styrene-divinyl benzene co-polymer matrix (BPR\(_A\)-series)

<table>
<thead>
<tr>
<th>Anion exchanger (BPR(_A)-CA series)</th>
<th>Ion-exchange capacity meq/g</th>
<th>Surface* area, m(^2)/g</th>
<th>Average pore diameter, (\mu)m</th>
<th>Uptake of phenolic compound, mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>-15-0.6-CA</td>
<td>2.83</td>
<td>1.13</td>
<td>20.54</td>
<td>0.1578</td>
</tr>
<tr>
<td>-20-0.6-CA</td>
<td>3.02</td>
<td>0.80</td>
<td>27.66</td>
<td>0.2213</td>
</tr>
<tr>
<td>-25-0.6-CA</td>
<td>3.00</td>
<td>0.69</td>
<td>40.24</td>
<td>0.1276</td>
</tr>
<tr>
<td>-15-0.7-CA</td>
<td>2.85</td>
<td>1.10</td>
<td>66.19</td>
<td>0.0376</td>
</tr>
<tr>
<td>-20-0.7-CA</td>
<td>3.12</td>
<td>0.95</td>
<td>62.34</td>
<td>0.0278</td>
</tr>
<tr>
<td>-25-0.7-CA</td>
<td>2.50</td>
<td>0.68</td>
<td>31.80</td>
<td>0.1510</td>
</tr>
</tbody>
</table>

*Surface area values based on mercury porosimeter.

| Quantity of the anion exchanger for equilibrium | 0.5 g (air dry) |
| Volume of the equilibrated solution            | 100 mL |
| Initial concentration of phenolic compound     | 25 mg/L |
| Duration of equilibrium                        | 16 h |
| Temperature of equilibration                   | 30°C |

### Table 2—Effect of the nature and the quantity of an electrolyte in the aqueous solution of phenolic compound on its uptake by porous anion exchanger based styrene-divinyl benzene co-polymer matrix (BPR\(_A\)-20-0.7-CA)

<table>
<thead>
<tr>
<th>Phenolic compound</th>
<th>Uptake of phenolic compound, mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in water</td>
</tr>
<tr>
<td>Phenol</td>
<td>5.29</td>
</tr>
<tr>
<td>4-Nitrophenol</td>
<td>7.45</td>
</tr>
<tr>
<td>3-Aminophenol</td>
<td>4.90</td>
</tr>
</tbody>
</table>

| Quantity of the anion exchanger for equilibrium | 0.5 g (air dry) |
| Initial concentration of phenolic compound in solution | 25 mg/L |
| Volume of the equilibrated solution            | 100 mL |
| Duration of equilibrium                        | 16 h |
| Temperature of equilibration                   | 30°C |
matrix alone as shown in Fig. 3. When an electrolyte like sodium chloride or sodium sulphate is present in the solution, Cl\(^-\) or SO\(_4\)\(^-\) ions compete with phenolate ion and this results in reduction in the uptake of phenolic compound by ion-exchange phenomenon, but the uptake due to Van der Waal's forces remains unaffected as has been observed in the case of non-functional adsorbents\(^5\). This may be a possible reason for reduction in uptake of phenolic compounds in the presence of an electrolyte on a strongly basic anion exchanger in Cl\(^-\) form (Table 2).

In the case of a strongly basic anion exchanger in Cl\(^-\) form, higher the pH, higher is the uptake of phenolic compound in general (Table 3). At lower pH, phenolic compounds are undissociated and hence very little uptake is possible by ion-exchange. Chemisorption is not encouraged as electrons are not available for hydrogen bonding and the exchanger is in salt form and, therefore, uptake is mostly poor. Higher the pH, higher is the concentration of phenolate ion and consequently the anion exchanger shows higher uptake. However, at certain pH value, the maximum uptake is observed for each phenolic compound. With fur-

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**Table 3—Effect of the variation of pH of the equilibrating solution of phenolic compounds on its uptake by porous strong base anion-exchange resin (BPR,\(A_2\)-20-0.7-CA)**

<table>
<thead>
<tr>
<th>Original pH</th>
<th>Uptake of phenolic compounds, mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phenol</td>
</tr>
<tr>
<td>1.73</td>
<td>2.94</td>
</tr>
<tr>
<td>2.50</td>
<td>3.24</td>
</tr>
<tr>
<td>3.00</td>
<td>4.12</td>
</tr>
<tr>
<td>6.45</td>
<td>5.29</td>
</tr>
<tr>
<td>10.18</td>
<td>5.49</td>
</tr>
<tr>
<td>11.55</td>
<td>8.08</td>
</tr>
<tr>
<td>12.40</td>
<td>7.84</td>
</tr>
</tbody>
</table>

Quantity of the anion exchanger: 0.5 g
Volume of the equilibrating solution: 100 mL
Phenol content of the solution: 25 mg/L
Duration of equilibration: 24 h
Temperature of equilibration: 30°C

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**Table 4—Effect of the variation of the concentration of phenolic compound and the presence of an electrolyte in the influent solution on its loading on porous strong base anion exchanger based on styrene-divinyl benzene co-polymer matrix (BPR,\(A_2\)-20-0.7-CA)**

<table>
<thead>
<tr>
<th>Concentration of phenolic compound in the influent, mg/L</th>
<th>Quantity loaded up to breakthrough point, mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 (aqueous solution)</td>
<td>Phenol</td>
</tr>
<tr>
<td>210.00</td>
<td>115.72</td>
</tr>
<tr>
<td>100 (aqueous solution)</td>
<td>283.50</td>
</tr>
<tr>
<td>25 (1% NaCl solution)</td>
<td>18.75</td>
</tr>
</tbody>
</table>

Quantity loaded up to breakthrough point, mg:

- Phenol: 115.72
- 4-nitrophenol: 207.50
- 3-aminophenol: 44.38

Quantity eluted out, mg:

- Phenol: 115.70
- 4-nitrophenol: 270.05
- 3-aminophenol: 44.28
ther increase in pH the uptake is reduced due to increased competition by OH⁻ ions for the exchange site (Table 3).

In the range of solution concentration studied here, higher the concentration of the phenolic compound higher is its sorption. The data obtained fit with Freundlich adsorption isotherms (Fig. 5).

With increase in the concentration of phenolic compounds in the influent the sorption on the strongly basic anion exchanger bed increases and with the presence of an electrolyte in the influent it decreases (Table 4). Since in each case one and the same resin bed has been used for the sorption or desorption studies, the reversible uptake of phenolic compounds is established. Similarly positive concentration ratios (i.e., the ratio of the quantity of solution of the phenolic compound treated up to the breakthrough point to the quantity of eluant required for desorption of phenolic compound from the resin bed) are achieved in each case.

References