CHAPTER 4
Studies on Adsorption of Dilute Acetic Acid & Alcohols onto Polymeric Membrane

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4.1. **Introduction**

Organic solvents are liberated with industrial effluents and cause environmental problems. Low concentrated alcohols and acids are liberated with the process effluent in petrochemical industries, and there are several methods available to remove them from the process stream. Examples of such processes include distillation, extraction, neutralization, overliming, vacuum evaporation, stream stripping, and charcoal adsorption [1, 2]. However, separation of the organic solvents from the effluents encounters difficulties because of their presence in lower concentration. Polymeric membranes in the nanofiltration (NF) range can be used for separation of such solvents in low concentrations. The high internal surface areas of membranes can adsorb and desorb a wide variety of compounds depending on the environmental uses. Nowadays, demands for polymeric adsorbents are increasing for some selective separations because of their functionality, surface area, and porosity, etc. The separation techniques based on adsorption, whether it is membrane adsorption or others, are the most promising separation methods due to their non-denaturing capability, high selectivity, energy efficiency, and cost effectiveness for bulk separation and purification of molecules in industries. Membrane based adsorptions are attractive due to their recycling characteristics, low toxicity, green process, high separations from very dilute aqueous solutions, and selectivity. Studies on adsorption of certain important molecules have been reported in the literature considering polymeric resins and membranes as the adsorbent [3–5]. There are a few studies that have been made on nanofiltration separation from dilute aqueous alcohol in a downstream processing study [6]. In adsorption process, the molecules are
accumulated in the external and internal surfaces of the adsorbent from the bulk solution due to various interactions such as hydrophobic, electrostatic attraction and hydrogen bonding.

In the present study, we have reported the recovery of low concentrated alcohols and acetic acid from dilute aqueous solution in the range of 1% to 3% using an adsorption process on membrane. NF membranes were prepared in our laboratory from β-cyclodextrin (β-CD) composite with polysulfone and characterized [7]. We have selected the cyclodextrin as the membrane material for its unique characteristics of uniform macromolecular structure, molecular self-assembling, and so on [7].

Additionally molecular modeling and simulation along with experimental investigation are performed and is expected to provide a thorough understanding between the microscopic and macroscopic properties of solute molecules in porous adsorbent materials. To know the role of interactions between adsorbent (membrane components) and adsorbate (alcohols) in adsorption process, we have performed density functional theory (DFT) and second-order Moller-Plesset (MP2) calculations. These methods are widely used to quantify interactions, and their success in this aspect is documented well in the literature [8, 9]. Because of inclusion of electron correlation, MP2 method gives better interaction energies and is useful in understanding molecular interactions. Earlier computational works comprise application of AM1 and PM3 [10]. However, these two methods are not useful in determining interaction energies. Our prepared membranes contain cyclodextrin molecule which is large enough to perform DFT or MP2 level of calculations. Therefore, we have considered only one glucopyranose unit of the
cyclodextrin molecule and one repeating unit of the polysulfone molecule and calculated interaction energies between adsorbate and adsorbent.

4.2. Experimental Section

4.2.1. Materials

Polysulphone (average molecular weight, $M_n$, 22,000), purchased from Aldrich Chemical Co., St. Louis, MO, USA in pellet form, Polyethylene glycol 1500 supplied by G.S. Chemical testing Lab & Allied industries, New Delhi, India were used as received. β-Cyclodextrin hydrate (purity 99%) and lithium nitrate (99% extra pure) were obtained from Acros Organics, Morris Plains, NJ, USA; N-methylpyrrolidone (purity > 99.5%) was procured from Rankem, Gurgaon, India and used as received. Deionized water obtained from a Milli-Q system was used throughout the whole experiment.

4.2.2. Preparation of Membrane and Characterization

Membranes were prepared and characterized by the methods reported in previous chapters [7, 11].

4.2.3. Adsorption Kinetics

The adsorption study depended on time and was made by addition of 0.0185 g of adsorbent to 250 mL of the aqueous solution containing 0.524 mol L$^{-1}$ of acetic acid, 0.741 mol L$^{-1}$ methanol, 0.514 mol L$^{-1}$ ethanol, 0.328 mol L$^{-1}$ of butanol in different conical flasks. Adsorption experiments were carried out using a shaker (Kuhner AG IRC-1-U) at 200 rpm and 298 K. Each experiment continued for 2 hr of time, and after each experiment, the adsorbents were removed by spatula and alcohol concentration was measured from the calibration curve drawn from the values of refractive index and
concentration of alcohols. Refractive index of the samples was measured by a digital refractometer (Model Rz-02941-35, Cole Parmer). For acetic acid, the concentrations were measured by titration method. For calculating the equilibrium adsorption capacity of the adsorbent the mass balance equation was applied.

The amount of adsorbate adsorbed onto membranes was determined by following:

\[ q_t = \frac{(C_i - C_t)V}{w} \]  

(4.1)

where, \( C_i \) is the initial concentration of adsorbate (mmol L\(^{-1}\)), \( C_t \) is the concentration of alcohol at time \( t \) (mmol L\(^{-1}\)), \( q_t \) is the adsorption density at a definite time \( t \), \( V \) is the total volume of the reaction mixture (L), and \( w \) is the mass of adsorbent (g).

In order to study the kinetics of adsorption of alcohols onto the membrane, different kinetic models such as pseudo-first-order [12], pseudo-second order [13] and intraparticle diffusion [14] models were used.

4.2.3.1. Pseudo-first-order Model

The pseudo-first-order model expresses the adsorption rate of an adsorbate from a liquid phase, is called the Lagergren rate equation [12], and is represented as

\[ \frac{dq}{dt} = k_1 (q_e - q_t) \]  

(4.2)

where, \( q_e \) (mg g\(^{-1}\)) is adsorption capacity at equilibrium, \( q_t \) (mg g\(^{-1}\)) is adsorption capacity at \( t \) and \( k_1 \) (min\(^{-1}\)) is the rate constant. Integrating equation 4.2 at \( q = 0, t = 0, \) and \( q = q_e, t = t \), equation (4.2) becomes

\[ \log (q_e - q_t) = \log q_e - (k_1 t/2.303) \]  

(4.3)
The value of the adsorption rate constant \((k_1)\) is determined from the plot of \(\log (q_e-q_t)\) vs \(t\).

### 4.2.3.2. Pseudo-second-order Model

This model was developed by Ho and McKay [13] and the rate of adsorption is given as

\[
\frac{dq}{dt} = k_2 (q_e - q_t)^2
\]  

(4.4)

where, \(k_2\) (g.mg\(^{-1}\).min\(^{-1}\)) is the rate constant for the pseudo-second-order adsorption reaction and other symbols are same as given in equation 4.2. At boundary condition the second order rate equation becomes

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]  

(4.5)

The value of \(q_e\) and \(k_2\) can be evaluated from the linear plot of equation 4.5.

### 4.2.3.3. Intraparticle diffusion model

This model is called Weber’s diffusion model [14], and according to which, the adsorbate particle is transported to the adsorbent surface through several steps such as external surface diffusion, pore diffusion, surface diffusion, and adsorption on the pore surface or it may be a combination of one or more steps. For a rapidly stirred batch process, the diffusive mass transfer is related to the apparent diffusion coefficient. If the adsorption rate is dependent on the rate of diffusion then the process is diffusion-controlled. Weber’s diffusion model is expressed by

\[
q_t = k_{intra} t^{1/2} + C
\]  

(4.6)
where, \( q_t \) (mg g\(^{-1}\)) is the concentration of adsorbate in the solid phase at time \( t \) (min), \( k_{\text{intra}} \) (mg g\(^{-1}\) min\(^{-1/2}\)) is the rate constant of intraparticle diffusion, and \( C \) is a constant. Plot of \( q_t \) vs \( t^{1/2} \) gives a straight line from where \( C \) and \( k_{\text{intra}} \) can be calculated. With an increasing value of \( C \), the boundary effect increases.

### 4.2.4. Equilibrium Study

For adsorption isotherms, experiments were carried out by taking a fixed amount of adsorbent (0.0185 g) in 250 mL of aqueous acetic acid solution at natural pH with a concentration range of (0.174 to 0.611) mol L\(^{-1}\). Similarly, for aqueous alcohols, experiments were carried out at natural pH with a concentration range of (0.247 to 0.865) mol L\(^{-1}\) for methanol, (0.171 to 0.6) mol L\(^{-1}\) for ethanol, and (0.109 to 0.382) mol L\(^{-1}\) for butanol in a thermostated shaker maintained at (30 ± 0.5)°C. The equilibrium time for adsorption isotherms was considered as 60 min which was confirmed from the kinetics study. The pH of the solution was in the range of pH (4 to 8) by using buffer reagents of appropriate dosages. After reaching the equilibrium, the aqueous phase was analysed by a refractometer. Here we used three different models, viz., Langmuir, Freundlich, and Temkin models to study the equilibrium adsorption data.

#### 4.2.4.1. Langmuir Isotherm

Langmuir adsorption isotherm gives a quantitative representation of a monolayer formation of adsorbate on the outer surface of the adsorbent till saturation [15]. Also uniform energies of adsorption onto the adsorbent surface can be obtained by this model. The model equation is represented as

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e}
\]  

(4.7)
The adsorption parameters were determined by following linear equation

\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e}
\]  

(4.8)

where, \(C_e\) is the equilibrium concentration of the adsorbate (mmol L\(^{-1}\)), \(q_e\) is the amount of adsorbate adsorbed per gram of the adsorbent at equilibrium (mmol g\(^{-1}\)), \(q_m\) is the maximum monolayer coverage capacity (mmol g\(^{-1}\)), \(K_L\) is Langmuir isotherm constant (L mg\(^{-1}\)).

The slope and intercept of \(1/q_e\) vs \(1/C_e\) plot gives the values of \(q_m\) and \(K_L\) respectively [16]. The equilibrium parameter \(R_L\) is a dimensionless constant represented as the separation factor or equilibrium parameter and is given as

\[
R_L = \frac{1}{1 + K_L C_o}
\]  

(4.9)

where, \(C_o\) is initial concentration

Here, \(R_L\) indicates the nature of adsorption. When \(R_L > 1\), nature of adsorption is unfavorable; if \(R_L = 1\), it is linear; if \(0 < R_L < 1\), the nature of adsorption is favorable; and when \(R_L = 0\), the nature of adsorption is irreversible.

4.2.4.2. Freundlich Isotherm

Freundlich adsorption isotherm usually used to describe the adsorption characteristics onto the heterogeneous surface [17]. The model equation is

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

(4.10)

where, \(K_f\) is Freundlich isotherm constant (mmol g\(^{-1}\)), \(n\) is adsorption intensity, \(C_e\) is equilibrium concentration of adsorbate (mmol L\(^{-1}\)) and \(q_e\) is the amount of adsorbate
adsorbed per gram of the adsorbent at equilibrium (mmol g$^{-1}$). From equation 4.10 we have,

$$\log q_e = \log K_f + (1/n) \log C_e$$

(4.11)

Here, $K_f$ is an approximate indicator of adsorption capacity and $1/n$ is a function of strength of adsorption [18].

The Freundlich model is suitable for highly heterogeneous surfaces and gives good representation of data for a restricted range of concentration only. When it is fitted for high and moderate concentrations, it gives poor fit for adsorption data at low concentrations.

### 4.2.4.3. Temkin Isotherm

The Temkin isotherm model [19] has been used for chemisorptions of the adsorbate onto the adsorbent assuming that the heat of adsorption for all the molecules in the layer decreases linearly with the coverage due to the interactions between adsorbate and adsorbent [19]. The equation is represented as

$$q_e = \frac{RT}{b} \ln (K_T C_e)$$

(4.12)

and in linear form

$$q_e = B \ln K_T + B \ln C_e$$

(4.13)

where, $B = RT/b$, $b$ (mol kJ$^{-1}$) is the Temkin isotherm constant, $K_T$ (L mg$^{-1}$) is the equilibrium binding constant, $q_e$ (mg g$^{-1}$) is the solute concentrations in solid phase and $C_e$ (mg L$^{-1}$) is the solute concentrations in liquid phase, $T$ is temperature in (K) and $R$ ((8.314 $\times$ 10$^{-3}$) kJ mol$^{-1}$ K$^{-1}$) is the gas constant. The isotherm parameters, $b$ and $K_T$, can be calculated from the linear plot of $q_e$ versus $\ln C_e$ in equation 4.13 whose slope and intercept give the value of $b$ and $K_T$, respectively.
4.2.5. Determination of Enthalpies

Enthalpies of the adsorption process can be determined by using van’t Hoff method. The equation is

\[
\Delta G^\circ = -RT \ln K = -RT \ln \left(\frac{\Psi q}{C_e}\right)
\]  

where, \(\Delta G^\circ\), \(R\), \(T\), and \(K\) are the standard free energy change of adsorption, the universal gas constant, temperature and the equilibrium constant, respectively. When adsorption is limited to the linear region of the isotherm, i.e., at low concentration of solute, the equilibrium constant is related to the adsorption affinity \((q/C_e)\). \(\Psi\) is the term for activity coefficient of the solute in the two phases and activity of the unbound sites. When solute concentration is low, \(\Psi\) remain constant.

The second thermodynamic relationship used in the van’t Hoff method is

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]  

where, \(\Delta H^\circ\) is the standard enthalpy change and \(\Delta S^\circ\) is the standard entropy change of adsorption. Combining the two equations 4.14 and 4.15, the following equation is obtained

\[
\ln \left(\frac{q}{C_e}\right) = -\frac{\Delta H^\circ}{RT} + \left[\frac{\Delta S^\circ}{R} - \ln \Psi\right]
\]  

Thus, a plot of \(\ln (q/C_e)\) vs \(1/T\) should give a straight line with a slope of \(-\Delta H^\circ/R\), from which \(-\Delta H^\circ\) can be calculated under the assumption that \(\Delta H^\circ\), \(\Delta S^\circ\) and \(\Psi\) are constant over the temperature range of study.

4.2.6. Computational Details

The gas phase geometrical minima of the species are optimized without any constraints using exchange-correlation functional with gradient corrected correlation provided by Lee, Yang and Parr (B3LYP) [20] with 6-31++G(d,p) basis set. The
interaction energy between alcohols and cyclodextrin, polysulfone were calculated using supermolecular approach given follows

\[ \Delta E_{AB} = E_{AB} - E_A - E_B \]  \hspace{1cm} (4.17)

Additionally, to check the consistency in results, we repeated the calculations at BH and H/6-31++ G(d,p) and MP2/6-31++G(d,p) level of theory. Interaction between the components mainly involves hydrogen bonding between OH group of the alcohol (or acetic acid) and O sites in membrane components. Efficiency of this functional to handle hydrogen bonded systems is well documented [20-22]. MP2/6-311++G(d,p) calculations also gives better interaction energies due to inclusion of electron correlation. In all cases, Basis Set Superposition Error (BSSE) was taken care using counterpoise correction method. All calculations were performed in Gaussian 09 [23].

4.3. Results and discussion

4.3.1. Kinetic Study

The kinetics of adsorption of the aqueous solution at a fixed initial concentration of acetic acid (0.524 mol L\(^{-1}\)) and alcohols (0.741 mol L\(^{-1}\) methanol, 0.514 mol L\(^{-1}\) ethanol, and 0.328 mol L\(^{-1}\) butanol) at at natural pH on the three membranes were performed to get an idea of the adsorption process and presented in the Figures 4.1-4.4.
Figure 4.1: Adsorption density as a function of time of acetic acid on α, β, γ-CD.

Figure 4.2: Adsorption density as a function of time of alcohols on α-CD Membrane.
Figure 4.3: Adsorption density as a function of time of alcohols on β-CD Membrane.

Figure 4.4: Adsorption density as a function of time of alcohols on γ-CD Membrane.

The values of the pseudo-first-order adsorption rate constant $k_f$ are determined using equation 4.3 by plotting $\log (q_e - q_t)$ against $t$ for adsorption onto the membrane at 293K. Similarly, the kinetic parameters of pseudo-second-order model are
determined using equation 4.5 by plotting $t/q_t$ vs $t$. Weber-Morris kinetic parameters are obtained by plotting $q_t$ vs $t^{1/2}$ (equation 4.6).

Figures 4.5-4.13 represent kinetic isotherm models for acetic acid. The values of $q_{e,exp}$ and $q_{e,cal}$ for the pseudo-first-order and pseudo-second-order model are tabulated in Table 4.1.

![Figure 4.5: Pseudo-first-order for acetic acid in α-CD.](image)

![Figure 4.6: Pseudo-second-order for acetic acid in α-CD.](image)
Figure 4.7: Intraparticle for acetic acid in α-CD.

Figure 4.8: Pseudo-first-order for acetic acid in β-CD.
Figure 4.9: Pseudo-second-order for acetic acid in β-CD.

Figure 4.10: Intraparticle for acetic acid in β-CD.
Figure 4.11: Pseudo-first-order for acetic acid for $\gamma$-CD.

Figure 4.12: Pseudo-second-order for acetic acid in $\gamma$-CD
Figure 4.13: Intraparticle for acetic acid in γ-CD.

Table 4.1: Kinetic model constants for Acetic acid Adsorption on membrane.

<table>
<thead>
<tr>
<th>Acetic acid</th>
<th>( q_{e,\text{exp}} ) (mmol g(^{-1}))</th>
<th>Pseudo-first-order kinetic model</th>
<th>Pseudo-second-order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_1 ) (min(^{-1}))</td>
<td>( q_{e,\text{cal}} ) (mmol g(^{-1}))</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>α-CD</td>
<td>1.12</td>
<td>0.036</td>
<td>1.026</td>
</tr>
<tr>
<td>β-CD</td>
<td>1.17</td>
<td>0.036</td>
<td>1.037</td>
</tr>
<tr>
<td>γ-CD</td>
<td>1.14</td>
<td>0.036</td>
<td>1.032</td>
</tr>
</tbody>
</table>

Figures 4.14-4.22 represent kinetic isotherm models for acetic acid. The values of \( q_{e,\text{exp}} \) and \( q_{e,\text{cal}} \) for the pseudo-first-order and pseudo-second-order model are tabulated in Table 4.2-4.4.
Figure 4.14: Pseudo-first-order plot for alcohols on α-CD Membrane.

Figure 4.15: Pseudo-second-order plot for alcohols on α-CD Membrane.
Figure 4.16: Intraparticle diffusion model plot on α-CD.

Figure 4.17: Pseudo first order plot for alcohols on β-CD Membrane.
Figure 4.18: Pseudo-second-order plot of alcohols on β-CD Membrane.

Figure 4.19: Intraparicle diffusion model plot on β-CD.
Figure 4.20: Pseudo-first-order plot for alcohols on γ-CD Membrane.

Figure 4.21: Pseudo-second-order plot for alcohols on γ-CD Membrane.
Figure 4.22: Intraparticle for alcohol on γ-CD.

Table 4.2: Kinetic model constants for Alcohol Adsorption on α-CD membrane.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$q_{e,exp}$ (mmol g⁻¹)</th>
<th>$k_1$ (min⁻¹)</th>
<th>$q_{e,cal}$ (mmol g⁻¹)</th>
<th>$R^2$</th>
<th>$k_2$ (g mmol⁻¹ min⁻¹)</th>
<th>$q_{e,cal}$ (mmol g⁻¹)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>1.997</td>
<td>0.043</td>
<td>1.23</td>
<td>0.984</td>
<td>0.082</td>
<td>2.12</td>
<td>0.997</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.021</td>
<td>0.039</td>
<td>1.04</td>
<td>0.982</td>
<td>0.131</td>
<td>1.11</td>
<td>0.997</td>
</tr>
<tr>
<td>BuOH</td>
<td>0.897</td>
<td>0.039</td>
<td>1.33</td>
<td>0.987</td>
<td>0.128</td>
<td>0.973</td>
<td>0.994</td>
</tr>
</tbody>
</table>
Table 4.3: Kinetic model constants for Alcohol Adsorption on β-CD membrane.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$q_{e,exp}$ (mmol g$^{-1}$)</th>
<th>Pseudo-first-order kinetic model</th>
<th>Pseudo-second-order kinetic Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$q_{e,cal}$ (mmol g$^{-1}$)</td>
</tr>
<tr>
<td>MeOH</td>
<td>2.08</td>
<td>0.046</td>
<td>1.25</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.108</td>
<td>0.034</td>
<td>1.05</td>
</tr>
<tr>
<td>BuOH</td>
<td>0.932</td>
<td>0.039</td>
<td>0.736</td>
</tr>
</tbody>
</table>

Table 4.4: Kinetic model constants for Alcohol Adsorption on γ-CD membrane.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$q_{e,exp}$ (mmol g$^{-1}$)</th>
<th>Pseudo-first-order kinetic model</th>
<th>Pseudo-second-order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$q_{e,cal}$ (mmol g$^{-1}$)</td>
</tr>
<tr>
<td>MeOH</td>
<td>2.10</td>
<td>0.046</td>
<td>1.24</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.12</td>
<td>0.039</td>
<td>1.02</td>
</tr>
<tr>
<td>BuOH</td>
<td>0.95</td>
<td>0.039</td>
<td>1.35</td>
</tr>
</tbody>
</table>

In all cases, it is observed that $q_{e,exp}$ and $q_{e,cal}$ values from the pseudo-second-order kinetic model are very close to each other. The calculated correlation coefficients are also closer to unity for pseudo-second-order kinetics than that for the pseudo first-order kinetic model. Therefore, the sorption can be approximated more appropriately by the pseudo-second-order kinetic model than the pseudo-first-order kinetic model for the adsorption of aqueous solution of acetic acid and alcohols onto the membrane. Though intraparticle diffusion curves give good agreement to the linear fitting,
they do not pass through the origin in all the three alcohol systems. This suggests that intraparticle diffusion is not the rate-controlling step for the adsorption process.

4.3.2. Adsorption Study

Adsorption isotherms measured for acetic acid applying the Langmuir isotherm model are shown in Figures 4.23-4.25. For alcohols, adsorption isotherms are represented in Figures 4.26-4.34. Among alcohols, it is observed that methanol has higher $q_e$ values than ethanol. Again, compared to butanol, ethanol has higher $q_e$ values at all aqueous residual concentrations. The observed effect of the adsorbate on CD membrane as adsorbent is noteworthy. In general, cyclodextrin provides high adsorption behavior for alcohols owing to their hydroxyl groups which interact through hydrogen bonding. Polysulfone may also provide hydrogen bonding with alcohol molecules via its S atom. This type of mechanism was also observed for adsorption of alcohols from aqueous solutions on membrane [24]. To optimize the adsorption system, it is essential to establish the most appropriate relationship for the equilibrium curves, and hence we interpreted the adsorption equilibria from Langmuir, Freundlich, and Temkin models. The values of the calculated adsorption parameters and corresponding correlation coefficients ($R^2$) are given in Tables 4.5-4.8. In all cases, it is seen that $R_L$ values are greater than 0 but less than 1, indicating that Langmuir isotherm is favorable in this work. The Freundlich isotherm model (equation 4.11) was examined by plotting $\ln q_e$ vs $\ln C_e$. The values of $1/n$ for observed alcohols are found to be less than unity, indicating that the adsorption process is favorable. The Temkin isotherm constants for alcohol adsorption onto the CD membrane obtained from the plots has also been given determined. It is observed that the values of the
correlation coefficients ($R^2$) are in the range of 0.974–0.991, signifying a satisfactory representation of the Temkin model. Comparing the correlation coefficients ($R^2$) of the models, it is observed that Langmuir isotherm gives the most satisfactory representation for the experimental data, and it is observed that the calculated values of $q_m$ are close to experimental values for Langmuir isotherm. The maximum monolayer coverage capacity ($q_m$) shows that the adsorption trend follows the order methanol > ethanol > butanol.

![Figure 4.23: Adsorption isotherm of acetic acid on α-CD membrane.](image)

Figure 4.23: Adsorption isotherm of acetic acid on α-CD membrane.
Figure 4.24: Adsorption isotherm of acetic acid on β-CD membrane.

Figure 4.25: Adsorption isotherm of acetic acid on γ-CD membrane.
Figure 4.26: Adsorption isotherm of methanol on α-CD membrane.

Figure 4.27: Adsorption isotherm of methanol on β-CD membrane.
Figure 4.28: Adsorption isotherm of methanol on γ-CD membrane.

Figure 4.29: Adsorption isotherm of ethanol on α-CD membrane.
Figure 4.30: Adsorption isotherm of ethanol on β-CD membrane.

Figure 4.31: Adsorption isotherm of ethanol on γ-CD membrane.
Figure 4.32: Adsorption isotherm of butanol on α-CD membrane.

Figure 4.33: Adsorption isotherm of butanol on β-CD membrane.
Figure 4.34: Adsorption isotherm of butanol on γ-CD membrane.

Table 4.5: Isotherm constants for adsorption of acetic acid in CD membrane.

<table>
<thead>
<tr>
<th>Acetic acid</th>
<th>$q_{m, exp}$ (mmol g$^{-1}$)</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Tempkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$ (mmol g$^{-1}$)</td>
<td>$K_L$ (g mmol$^{-1}$)</td>
<td>$R^2$</td>
<td>$R_L$</td>
</tr>
<tr>
<td>α-CD</td>
<td>1.17</td>
<td>1.43</td>
<td>8.22</td>
<td>0.996</td>
</tr>
<tr>
<td>β-CD</td>
<td>1.22</td>
<td>1.46</td>
<td>9.51</td>
<td>0.994</td>
</tr>
<tr>
<td>γ-CDI</td>
<td>1.20</td>
<td>1.44</td>
<td>8.90</td>
<td>0.995</td>
</tr>
</tbody>
</table>

Table 4.6: Isotherm constants for adsorption of alcohols in α-CD membrane.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$q_{m, exp}$ (mmol g$^{-1}$)</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Tempkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$ (mmol 1 g$^{-1}$)</td>
<td>$K_L$ (g mmol$^{-1}$)</td>
<td>$R^2$</td>
<td>$R_L$</td>
</tr>
<tr>
<td>MeOH</td>
<td>2.027</td>
<td>2.32</td>
<td>10.00</td>
<td>0.996</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.040</td>
<td>1.38</td>
<td>6.62</td>
<td>0.992</td>
</tr>
<tr>
<td>BuOH</td>
<td>0.897</td>
<td>1.25</td>
<td>8.24</td>
<td>0.988</td>
</tr>
</tbody>
</table>
Table 4.7: Isotherm constants for adsorption of alcohols in β-CD membrane.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$q_m, exp$ (mmol g$^{-1}$)</th>
<th>$q_m$ (mmol g$^{-1}$)</th>
<th>$K_L$ (g mmol$^{-1}$)</th>
<th>$R^2$</th>
<th>$R_L$</th>
<th>$1/n$</th>
<th>$K_f$ (mmol g$^{-1}$)</th>
<th>$R^2$</th>
<th>$B$</th>
<th>$K_T$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>2.108</td>
<td>2.36</td>
<td>12.46</td>
<td>0.997</td>
<td>0.084</td>
<td>0.215</td>
<td>2.33</td>
<td>0.965</td>
<td>0.387</td>
<td>366.12</td>
<td>0.978</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.121</td>
<td>1.39</td>
<td>9.10</td>
<td>0.995</td>
<td>0.167</td>
<td>0.312</td>
<td>1.44</td>
<td>0.960</td>
<td>0.286</td>
<td>105.64</td>
<td>0.974</td>
</tr>
<tr>
<td>BuOH</td>
<td>0.959</td>
<td>1.19</td>
<td>13.55</td>
<td>0.999</td>
<td>0.160</td>
<td>0.345</td>
<td>1.49</td>
<td>0.975</td>
<td>0.260</td>
<td>136.03</td>
<td>0.991</td>
</tr>
</tbody>
</table>

Table 4.8: Isotherm constants for adsorption of alcohols in γ-CD membrane.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$q_m, exp$ (mmol g$^{-1}$)</th>
<th>$q_m$ (mmol g$^{-1}$)</th>
<th>$K_L$ (g mmol$^{-1}$)</th>
<th>$R^2$</th>
<th>$R_L$</th>
<th>$1/n$</th>
<th>$K_f$ (mmol g$^{-1}$)</th>
<th>$R^2$</th>
<th>$B$</th>
<th>$K_T$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>2.054</td>
<td>2.34</td>
<td>10.39</td>
<td>0.996</td>
<td>0.101</td>
<td>0.240</td>
<td>2.30</td>
<td>0.962</td>
<td>0.415</td>
<td>218.77</td>
<td>0.978</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.081</td>
<td>1.39</td>
<td>7.46</td>
<td>0.993</td>
<td>0.182</td>
<td>0.345</td>
<td>1.42</td>
<td>0.954</td>
<td>0.299</td>
<td>79.43</td>
<td>0.970</td>
</tr>
<tr>
<td>BuOH</td>
<td>0.912</td>
<td>1.23</td>
<td>9.54</td>
<td>0.990</td>
<td>0.215</td>
<td>0.413</td>
<td>1.53</td>
<td>0.965</td>
<td>0.316</td>
<td>66.37</td>
<td>0.992</td>
</tr>
</tbody>
</table>

The adsorption process is affected by external physicochemical parameters such as pH, temperature, competing compounds in solution, the chemical structure of the adsorbent and adsorbate, the polarity of the adsorbent, the specific surface area, and the pore volume distribution, etc. It is also noted that the surface area and pore radius depend linearly on adsorption capacity with pore radius $\leq$ 90 Å [24]. In the studied adsorption process, the chemical nature of the adsorbents plays a more important role than the physical structure. High affinity for all of the adsorbate molecules on cyclodextrin membrane may be due to the hydrophilic nature of hydroxyl groups in alcohols and can be reduced by increasing the number of -CH$_2$- groups which are hydrophobic in nature. The effect of pH on adsorption for acetic is shown in Figure 4.35 and for alcohols are shown in
**Figures 4.36-4.38.** It is seen from the figure that the variation is marginal only. Higher adsorption at acidic pH may be due to the polar-polar interactions between alcohols and cyclodextrin molecule. The adsorption was found to be more at lower pH for hydrogen bonding. At higher pH, the hydrogen interactions decrease and dissociate to form $\text{H}^+$ and their corresponding anions [25]. **Figures 4.39 and 4.40** show the SEM photographs of the CD membrane before and after adsorption. From **Figure 4.39** (before adsorption), it is observed that the membrane has a porous structure throughout and has a rough surface. The higher degree of roughness is attributed to more adsorption capacity.

![Graph showing adsorption as a function of pH](image.png)

**Figure 4.35:** Adsorption of acetic acid as a function pH.
Figure 4.36: Adsorption of methanol as a function of pH.

Figure 4.37: Adsorption of ethanol as a function pH.
At higher pH, the hydrogen interactions decrease and dissociate to form \( \text{H}^+ \) and their corresponding anions [25].

**Figure 4.38:** Adsorption of butanol as a function pH.

**Figure 4.39:** SEM images (a) side view (b) front view of \( \beta \)-CD membrane before treatment
Figure 4.40: SEM images (a) side view (b) front view of β-CD membrane after treatment.

Figure 4.39 and Figure 4.40 show the SEM photographs of the CD membrane before and after adsorption. From Figure 4.39 (before adsorption), it is observed that the membrane has a porous structure throughout and has a rough surface. The higher degree of roughness is attributed to more adsorption capacity [19].

4.3.3. Adsorption Enthalpy

Temperature dependence of adsorption equilibria was determined by measuring the adsorption at three different temperatures, viz., (25, 30 and 35)°C. The adsorption isotherms of acetic acid and alcohols onto the β-CD membrane at three different temperatures have been shown in Figures 4.41-4.44, and it is seen that the adsorption intensity increases with a decrease in temperature, indicating an exothermic adsorption process.
Figure 4.41: Effect of temperature on adsorption of acetic acid.

Figure 4.42: Effect of temperature on adsorption of methanol.
Figure 4.43: Effect of temperature on adsorption of ethanol.

Figure 4.44: Effect of temperature on adsorption of butanol.

The temperature dependent adsorption affinity \( q/C_e \) was evident from the slopes of isotherms which were interpreted from van’t Hoff equation given by equation 4.16. Figures 4.45-4.56 show van’t Hoff plots for acetic acid and alcohols in the three membranes. Values of \( \Delta H^\circ \) for acetic acid are found to be -14.75 kcal mol\(^{-1}\) \( (R^2 = 0.99) \), -
14.71 kcal mol\(^{-1}\) \((R^2 = 0.991)\), -14.05 kcal mol\(^{-1}\) \((R^2 = 0.992)\) in \(\alpha\)-CD, \(\beta\)-CD, \(\gamma\)-CD membranes respectively. In \(\alpha\)-CD membrane, \(\Delta H^o\) values for methanol, ethanol, butanol are found to be -8.51 kcal mol\(^{-1}\) \((R^2 = 0.999)\), -6.53 kcal mol\(^{-1}\) \((R^2 = 0.999)\) and -5.73 kcal mol\(^{-1}\) \((R^2 = 0.999)\). In \(\beta\)-CD membrane, \(\Delta H^o\) values for methanol, ethanol, butanol are found to be -15.13 kcal mol\(^{-1}\) \((R^2 = 0.996)\), -14.02 kcal mol\(^{-1}\) \((R^2 = 0.999)\) and -13.61 kcal mol\(^{-1}\) \((R^2 = 0.999)\). In \(\gamma\)-CD membrane, \(\Delta H^o\) values for methanol, ethanol, butanol are found to be -13.44 kcal mol\(^{-1}\) \((R^2 = 0.999)\), -10.56 kcal mol\(^{-1}\) \((R^2 = 0.997)\) and -6.51 kcal mol\(^{-1}\) \((R^2 = 0.996)\). As we know, the adsorption enthalpy determines the strength of solute-sorbent binding interaction which significantly affects the adsorption affinity. Thus, the adsorbate, which shows the highest affinity gives highest adsorption enthalpy and the adsorbate having lowest affinity gives the lowest adsorption enthalpy.

**Figure 4.45:** Adsorption enthalpy of acetic acid in \(\alpha\)-CD.
**Figure 4.46:** Adsorption enthalpy of acetic acid in β-CD.

**Figure 4.47:** Adsorption enthalpy of acetic acid in γ-CD.
Figure 4.48: Adsorption enthalpy of methanol in α-CD.

Figure 4.49: Adsorption enthalpy of ethanol in α-CD.
Figure 4.50: Adsorption enthalpy of butanol in α-CD.

Figure 4.51: Adsorption enthalpy of methanol in β-CD.
Figure 4.52: Adsorption enthalpy of ethanol in β-CD.

Figure 4.53: Adsorption enthalpy of butanol in β-CD.
Figure 4.54: Adsorption enthalpy of methanol in γ-CD.

Figure 4.55: Adsorption enthalpy of ethanol in γ-CD.
4.3.4. Adsorptive Interaction

Calculated BSSE corrected interaction energies [26, 27] between membrane components and solvent molecules (acetic acid, methanol, ethanol and butanol) at three different levels of theory, B3LYP/6-31++G(d,p), MP2/6-31++G(d,p) and BHandH/6-31++G(d,p) are presented in Table 4.9.

Table 4.9: Gas phase interaction energy $\Delta E_{\text{int}}$ (kcal mol$^{-1}$) at three levels of theories. (O-sites are shown in Figure 4.57).

<table>
<thead>
<tr>
<th></th>
<th>B3LYP/631++G(d,p)</th>
<th>MP2/6-31++G (d,p)</th>
<th>BHandH/6-31++G (d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid-CD (O-16)</td>
<td>-10.859</td>
<td>-11.612</td>
<td>-15.165</td>
</tr>
<tr>
<td>Acetic acid -PS (O-54)</td>
<td>-8.948</td>
<td>-9.112</td>
<td>-11.321</td>
</tr>
<tr>
<td>MeOH-CD (O-16)</td>
<td>-33.737</td>
<td>-34.613</td>
<td>-40.296</td>
</tr>
<tr>
<td>EtOH-CD (O-16)</td>
<td>-33.597</td>
<td>-34.556</td>
<td>-40.104</td>
</tr>
<tr>
<td>BuOH-CD (O-16)</td>
<td>-33.552</td>
<td>-34.522</td>
<td>-40.070</td>
</tr>
<tr>
<td>MeOH-PS (O-54)</td>
<td>-6.54</td>
<td>-7.22</td>
<td>-12.64</td>
</tr>
<tr>
<td>EtOH-PS (O-54)</td>
<td>-6.23</td>
<td>-7.25</td>
<td>-12.49</td>
</tr>
<tr>
<td>BuOH-PS (O-54)</td>
<td>-6.16</td>
<td>-7.35</td>
<td>-12.41</td>
</tr>
</tbody>
</table>
To assign the electronegative sites in polysulfone and CD, initially we performed Hirshfeld population [28, 29] analyses and estimated charges at different sites. In glucopyranose unit, atom number O-16 (Figure 4.57) bears more negative charges (-0.185 au) whereas in polysulfone unit, atom number O-54 possesses more negative charge (-0.323 au) compared to other positions. This reflects interaction in which these positions exhibit more affinity towards the –OH groups in alcohols.
Figure 4.57: Optimized structure of the membrane components–alcohol adducts at the B3LYP/6-31++G(d,p) level of theory.

In all the three levels of theories, trend of interaction energy is in the order, methanol > ethanol > butanol, a trend which resembles with the experimental adsorption affinity values. A higher value of interaction energy leads to stronger adsorption [30] and it plays the key role on adsorption. Thus interaction energy is an index of the strength of adsorptive interaction on the adsorbent surface. However membrane material and pore size can be affected in the adsorption of solvents.

Quantitative structure activity relationship (QSAR) analysis of the three alcohols has also been preferred. Different values such as log P, dipole moment, electron affinity, ionization potential, and molar refractivity are evaluated using Scigress software version 2.4 and plotted with adsorptive affinity values (Figure 4.58). From the figure it is seen that they follow linear relationship with following equations.

\[ y = -1.319x + 1.388, \quad R^2 = 0.953 \quad (\text{log P vs } q_e) \]  \hspace{1cm} (4.18)

\[ y = 6.839x - 10.44, \quad R^2 = 0.983 \quad (\text{dipole moment vs } q_e) \]  \hspace{1cm} (4.19)

\[ y = 6.568x + 7.371, \quad R^2 = 0.971 \quad (\text{electron affinity vs } q_e) \]  \hspace{1cm} (4.20)

\[ y = -19.44x - 114.1, \quad R^2 = 0.988 \quad (\text{ionization potential vs } q_e) \]  \hspace{1cm} (4.21)
\[ y = -0.102x + 2.767, \quad R^2 = 0.963 \text{ (molar refractivity vs } q_e) \] 

(4.22)

**Figure 4.58:** Adsorptive affinity as a function of different physical properties 1: Methanol, 2: Ethanol, 3: Butanol.

### 4.3.5. Correlation of Adsorptive Affinity with interaction Energy

The adsorptive interaction energies between adsorbate and adsorbent, \( \Delta E_{\text{int}} \) were correlated with adsorption affinity (**Figure 4.59**). The figure indicates the relationship between adsorptive affinity and adsorptive interaction for all three tested alcohols in this work. Thus, adsorption equilibrium is a function of solute-sorbent binding interaction. This observation is similar to some other adsorption processes reported elsewhere [31].

**Figure 4.59:** Adsorptive affinity as a function of interaction energy, 1: Methanol, 2: Ethanol, 3: Butanol (0.865 mol L\(^{-1}\) for methanol, 0.6 mol L\(^{-1}\) for ethanol, 0.382 mol L\(^{-1}\) for butanol).
4.3.6. Correlation of Adsorptive Enthalpy with Interaction Energy

A plot of adsorption enthalpies ($\Delta H^\circ$) of the three alcohols against interaction energies ($\Delta E_{\text{int}}$) gives a linear relationship (Figure 4.60), indicating the dependency of enthalpies of adsorption on adsorptive interaction energy. The enthalpy determines the strength of the solute-sorbent binding interaction and thus solute-sorbent binding interaction significantly affects the adsorption affinity of the process which may be considered as an enthalpic process.

![Graph showing correlation between $\Delta E_{\text{int}}$ and $\Delta H$](image)

**Figure 4.60:** $\Delta E_{\text{int}}$ as a function of change in enthalpy, 1: Methanol, 2: Ethanol, 3: Butanol.

4.4. Conclusion

The adsorption of alcohols onto the membranes was studied for adsorption of acetic acid and alcohols from dilute aqueous solution. It was observed that adsorption process was affected by parameters such as pH, initial concentration of the alcohol, and temperature. The kinetics and adsorption isotherms were investigated. The adsorption behavior of the systems was best fitted with the Langmuir isotherm and the kinetics of
adsorption followed the pseudo second order reaction, where the adsorption rate is proportional to the concentration of adsorbate and the remaining number of vacant sites of adsorbent. The adsorptive affinity follows the order methanol > ethanol > butanol onto the β-CD membrane. The adsorption intensity is weakly dependent on the aqueous phase pH. Adsorptive interaction is strongly related to the interaction energy between adsorbent and adsorbate.
4.5. References


