CHAPTER 3

ADSORPTION OF VITAMIN E ON MESOPOROUS CARBON MOLECULAR SIEVES

3.1 VITAMIN E

Vitamin E (α-tocopherol) is a fat-soluble vitamin (Figure 3.1), which functions as an antioxidant that prevents the oxidation of cell membrane and low density lipoprotein by the free radical, which are formed in the normal metabolism and environmental factors such as smoking and pollution. Vitamin E also protects the lung tissue from nitrogen dioxide and ozone which will attack lungs and damaging polyunsaturated fatty acids in the lung cell membranes. Deficiency of vitamin E leads to blood clotting, which causes heart attack, strokes and phlebitis (inflammation of blood vessels). Vitamin E is administered to the heart attack patients after the attack in order to open the blood vessels when it is partially or totally blocked.

Figure 3.1 Structure of Vitamin E
Adsorption of vitamin E over the solid surfaces has attracted significant attention due to its importance in the field food industry and medical. Kavalenko and Kuznetsova (2000) reported the adsorption of vitamin E on carbon containing enterosorbents and proved that the vitamin molecules are oriented in such a way that the OH groups remain free and retain their biological activity.

3.2 CHARACTERISATION OF THE ADSORBENT

The powder X-ray diffraction patterns of CMK-3, CMK-1 and their corresponding silica templates are shown in Figure 3.2. CMK-3 possesses hexagonally ordered mesostructure as evident from the presence of at least three XRD peaks that can be indexed to (100), (110) and (200) reflections of two dimensional hexagonal space group (p6mm). Consequently, the synthesised material is the replica of the parent material SBA-15. CMK-1 exhibits three reflections in the region $2\theta = 2$ to 3.5, which is indexed to (110), (211) and (220) reflections of the cubic space group $I4_132$. Higher order reflections are observed in the region $2\theta = 3.5$ to 6.5 which are superposition of various reflections that are indexed according to $I4_132$ space group. It is interesting to note that the XRD pattern of CMK-1 material before the silica template removal is similar to that of MCM-48 which indicates an analogous structure. However, after the removal of the silica template, CMK-1 has an additional relatively narrow (110) diffraction line in its diffraction pattern confirming that the structure of MCM-48 is transformed into another structure. This indicates that the structure of CMK-1 is not the complete replica of MCM-48.
Figure 3.2  XRD powder patterns of CMK-3 and CMK-1 and their corresponding silica replica

Figure 3.3 shows the nitrogen adsorption isotherms of CMK-3, CMK-1 and the activated carbon. The isotherm of CMK-3 shows type IV isotherm according to the IUPAC classification and exhibits a H1 hysteresis loop whereas CMK-1 exhibits type IV isotherm with no hysteresis. As can be seen in Figure 3.3, the isotherms of CMK-3 and CMK-1 featured a narrow capillary condensation steps indicating high degree of mesopore size uniformity. Adsorption isotherm of activated carbon shows type I isotherm, which is the typical adsorption characteristics of microporous adsorbent. It can be inferred from the opening of the knee of the isotherm and the greater slope of the plateau that there was a wide pore size distribution in the activated carbon material used in this study. The textural properties of different micro and mesoporous carbon adsorbents is given in Table 3.1. The specific surface areas of CMK-1 and activated carbon are 1675 m²/g and 1629 m²/g respectively, which are higher than the specific surface area of
CMK-3 (1260 m²/g). However, the specific pore volume of activated carbon adsorbent is 0.7 cm³/g, which is lower than the specific pore volume of CMK-1 (1.05 cm³/g) and CMK-3 (1.1 cm³/g). Among the carbon materials studied, CMK-3 has large pore diameter and high specific pore volume (Table 3.1).

Figure 3.3 Nitrogen adsorption isotherms of different carbon adsorbents: (●) CMK-3, (■) CMK-1 and (▲) Activated carbon
Table 3.1  Textural parameters of the CMK-1, CMK-3 and activated carbon

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>d spacing (nm)</th>
<th>$A_{BET}$ (m$^2$/g)</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>$D_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMK-1</td>
<td>5.14</td>
<td>1675</td>
<td>1.05</td>
<td>2.3</td>
</tr>
<tr>
<td>CMK-3</td>
<td>8.72</td>
<td>1260</td>
<td>1.10</td>
<td>3.3</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>-</td>
<td>1629</td>
<td>0.70</td>
<td>-</td>
</tr>
</tbody>
</table>

3.3  ADSORPTION OF VITAMIN E

Figure 3.4 shows the equilibrium adsorption isotherms of vitamin E onto CMK-1, CMK-3 and activated carbon in $n$-heptane, a non-polar solvent. Each isotherm shows a sharp initial rise, suggesting a high affinity between vitamin E molecules and the adsorbent surface. All the three adsorbents show type IV isotherm with three well defined stages. The first stage is indicative of monolayer adsorption of vitamin E at lower final solution concentration and the second stage at the intermediate final concentration corresponds to layer by layer adsorption in the mesopores. The plateau at the end of the each isotherm associates with the saturation level of adsorption of vitamin E on the adsorbents. It can be seen from the Figure 3.4 that the amount of vitamin E adsorption increases with increasing initial concentration of vitamin E solution. This can be explained as follows: when the vitamin E concentration in the bulk is low, vitamin E may be adsorbed perpendicular to the surface with comparable probabilities. However, when the vitamin E concentration is high, the vitamin E molecules land close to each other with the long axis, yielding a higher adsorbed amount. Moreover, the high concentration of vitamin E also favors surface crystallisation and thus the vitamin E crystallised on the surface may yield more closely packed arrangements than the randomly deposited one occurring at low bulk concentration.
It is evident from Figure 3.3 that each isotherm exhibits pore filling step within the range of final solution concentration and this pore filling step is consistent with different pore diameter of each adsorbent. CMK-3 shows a huge shift in the pore filling step to higher final solution concentration and an upward movement of the plateau. It is also important to note that CMK-3 exhibits a huge amount of vitamin E adsorption (5.94 mmol/g) which is comparatively higher as compared with CMK-1 and activated carbon which register the amount of vitamin E adsorption of 5.01 mmol/g and 4.10 mmol/g respectively. It has been reported by Noll et al (1992) that the BET surface area of adsorbent is a crucial factor in determining the adsorption capacities of the adsorbent. In the range of final solution concentrations of vitamin E shown in Figure 3.4, the adsorption capacities of the carbon adsorbents is in the following order: CMK-3 > CMK-1 > activated carbon, although activated carbon has more specific surface area as compared with other carbon
adsorbents used in this study. However, upto the initial solution concentration of vitamin E of ca. 2 g/l, all the three adsorbents show almost similar amount of vitamin E adsorption and should be attributed to the monolayer adsorption, which is decided by the specific surface area of each adsorbent. By contrast, when the initial solution concentration of vitamin E is above 2 g/l, there is lot of changes in the pore filling step and the adsorption capacities are different for all the three carbon adsorbents. This obviously indicates that textural parameters of the porous adsorbents other than BET surface area such as pore volume and pore diameter also play an important role in determining the adsorption capacity of vitamin E on each adsorbent.

It should also be noted that though the difference in the pore volume of CMK-1 and CMK-3 is very small, there is huge difference in their amount of vitamin E adsorption. We surmised that this could be due to the difference in the pore structure and diameter of CMK-1 and CMK-3. It has been recently reported by Teng and Hsieh (1998) that the surface of the pores with smaller pore diameter can not be utilised in adsorption and the fractional coverage of the small pore surface may depend on the length of the diffusion path. During the diffusion process in the adsorbent with smaller pores (CMK-1), pore blockage may occur due to aggregation of two or more vitamin E molecules (Mckay et al 1985). Consequently, a longer diffusion path of smaller mesopores will result in a greater probability for the pore blockage to occur and thus a smaller coverage is obtained in CMK-1. However, in the case of CMK-3, the existence of large pores may enhance the diffusion of the vitamin E molecules from the mesopore to the interior part of the carbon without any blockage. Hence, it is assumed that the high vitamin E adsorption capacities of the CMK-3 can be thus explained by the fact CMK-3 contain large pore diameter, which enhance the access of interior part of the mesopores of carbon adsorbent for vitamin E molecules.
In order to study the effect of solvent polarity on the amount of vitamin E adsorption, adsorption measurements were carried out on CMK-3 and activated carbon in n-butanol, a polar solvent and the results are given in Figure 3.5. In contrast to the results obtained in the vitamin E adsorption capacities in n-heptane solvent, Figure 3.5 shows that CMK-3 and activated carbon exhibiting the lowest vitamin E adsorption when the solvent was n-butanol. Moreover, the difference in the adsorption capacities of vitamin E with respect to CMK-3 and activated carbon in n-butanol is lower compared to the difference in the adsorption capacities of vitamin E in CMK-3 and activated carbon in n-heptane.

The low vitamin E adsorption capacities of CMK-3 and activated carbon in n-butanol can be explained by the low affinity of adsorption of vitamin E on the carbon surfaces. In the presence of n-butanol, there will be preferential formation of hydrogen bond between the OH groups of n-butanol molecules and the active hydroxyl and ether group of vitamin E molecules. This may develop the stronger vitamin E and n-butanol interaction and reduce the interaction between the carbon surface and the vitamin E molecules. Consequently, we assume that the lower vitamin E adsorption capacities of carbon adsorbents in n-butanol resulted from the increased formation of n-butanol solvent clusters on hydroxyl and ether groups of vitamin E molecule, that reduced access to the surface of carbon, thereby reducing the interaction energy between vitamin E and adsorbent surface and/or blocked the pores. On the other hand, when n-heptane was used as the solvent, the interaction between the hydrophobic tail group of vitamin E molecule and the hydrophobic carbon surface will be higher and their interaction may not be affected by the non-polar solvent. Hence, the vitamin E adsorption capacity in n-heptane solvent is higher as compared with the polar solvent n-butanol. Thus it can be concluded that polar solvent,
n-heptane is good choice for getting the highest amount of vitamin E adsorption in carbon adsorbents.

![Graph showing adsorption isotherm of vitamin E onto different carbon adsorbents in n-butanol and n-heptane solvents.](Figure 3.5)

**Figure 3.5** The adsorption isotherm of vitamin E onto different carbon adsorbents in *n*-butanol and *n*-heptane solvents

### 3.4 CHARACTERISATION OF THE ADSORBENT AFTER VITAMIN E ADSORPTION

In order to know whether the vitamin E molecules filled inside the mesopores of CMK-3 adsorbent, the adsorbent was characterised by XRD and nitrogen adsorption before and after vitamin E adsorption. Figure 3.6 shows the changes in the powder XRD patterns of CMK-3 carbon materials before and after the vitamin E adsorption experiment at three different initial vitamin E concentrations such as 1 g/l, 4 g/l and 40 g/l in *n*-heptane solvent. It can be seen from the Figure 3.6 that all the CMK-3 samples display a strong (100) reflection at low angle and two very small peaks at higher angles, which is typical for CMK-3 mesoporous carbon. However, with increase in the initial
concentration of vitamin E solution in \( n \)-heptane in the adsorption medium, the intensity of all three low angle peaks decreases as compared to the CMK-3 carbon before vitamin E adsorption. This is probably due to the larger contrast in density of the carbon walls and empty pores relative to that of the carbon walls and pores filled with vitamin E molecules (Marler et al 1996). Moreover, the reduction in the intensity of higher angle peaks are much higher when a higher vitamin E loading was achieved. The reduction in the intensity of XRD peaks of CMK-3 with increasing amount of vitamin E adsorption supports the fact that vitamin E molecules are filled inside the mesopores of CMK-3 without affecting its structure.

Figure 3.6 XRD powder patterns of CMK-3 adsorbent before and after vitamin E adsorption at different initial solution concentration in \( n \)-heptane
Figure 3.7 shows the nitrogen adsorption isotherms of CMK-3 adsorbents before and after the vitamin E adsorption in \(n\)-heptane. Table 3.2 summarizes the textural parameters of the carbon adsorbents before and after vitamin E adsorption with different initial solution concentration. It can be seen from Figure 3.7 that the amount of nitrogen adsorbed decreases with increasing vitamin E loading. Moreover, the specific surface area and pore volume are concomitantly reduced with increasing vitamin E loading. The specific pore volume of CMK-3 adsorbent after vitamin E adsorption decreases from 1.1 to 0.19 cm\(^3\)/g which is almost 82.8 % reduction in the total specific pore volume whereas the specific surface area is reduced from 1260 to 178 m\(^2\)/g which is 85.87 % reduction in the total specific surface area.

![Figure 3.7](image)

Figure 3.7  Nitrogen adsorption isotherms of CMK-3 before and after vitamin E adsorption at different initial solution concentration in \(n\)-heptane: (open symbols: desorption; closed symbols: adsorption): (●) CMK-3, (■) CMK-3 (1 g/l), (▲) CMK-3 (4 g/l) and (♦) CMK-3 (40 g/l)
Table 3.2 The textural parameters of CMK-3 materials after vitamin E adsorption in different solvents at various initial solution concentrations

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Initial Concentration (g/l)</th>
<th>$A_{BET}$ (m$^2$/g)</th>
<th>$V_p$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-heptane</td>
<td>1</td>
<td>733</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>501</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>178</td>
<td>0.19</td>
</tr>
<tr>
<td>n-butanol</td>
<td>1</td>
<td>786</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>647</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>298</td>
<td>0.30</td>
</tr>
</tbody>
</table>

In addition, it is interesting to note from the nitrogen adsorption isotherm that when 40 g/l initial concentration of vitamin E in n-heptane is used, there is no capillary condensation step found in the nitrogen adsorption isotherm. These results should be attributed to the tight packing of vitamin E molecules inside the mesopores of CMK-3 adsorbent. Similar reduction in the specific pore volume and specific surface area was also found in the case of other adsorbents such as CMK-1 and activated carbon. Moreover, the information concerning the textural parameters of CMK-3 adsorbent after adsorption of different concentration of vitamin E in n-butanol has been obtained. This information is important in comparing the packing of vitamin E molecules inside the mesopores of CMK-3 in n-butanol. Figure 3.8 compares the nitrogen adsorption isotherms of CMK-3 adsorbent after vitamin E adsorption in both n-heptane and n-butanol solvent system with different concentration. It is quite interesting to note that the amount of nitrogen adsorbed in the vitamin E adsorbed CMK-3 in n-butanol is always higher compared to the vitamin E adsorbed CMK-3 in n-heptane at low and high initial concentration of vitamin E (1 g/l, 4 g/l and 40 g/l). The specific
pore volume of CMK-3 adsorbent after vitamin E adsorption in \textit{n}-butanol (initial concentration of 40 g/l) decreases from 1.1 to 0.31 cm$^3$/g, which is only 71.8 \% reduction in the total specific pore volume whereas the specific surface area is reduced from 1260 to 300 m$^2$/g, which is 76.2 \% reduction in the total specific surface area. As can be seen from Figure 3.8, the capillary condensation step in the nitrogen adsorption isotherm is visible after vitamin E adsorption using initial concentration of vitamin E in \textit{n}-butanol of 40 g/l, whereas the capillary condensation is totally absent after the vitamin E adsorption using the same concentration of vitamin E in \textit{n}-heptane. This confirms the tight packing of the vitamin E molecules inside the mesopores of CMK-3 adsorbent when we used the non-polar solvent such as \textit{n}-heptane is used.

![Figure 3.8](image)

\textbf{Figure 3.8} Comparison of the nitrogen adsorption isotherms of CMK-3 after vitamin E adsorption at different initial solution concentration in \textit{n}-heptane and \textit{n}-butanol: (●) CMK-3 (4 g/l-\textit{n}-butanol), (■) CMK-3 (40 g/l-\textit{n}-butanol), (▲) CMK-3 (4 g/l-\textit{n}-heptane) and (♦) CMK-3 (40 g/l-\textit{n}-heptane)