Liquid Phase Adsorption of α-Tocopherol by Activated Carbon

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Abstract: α-Tocopherol or commonly called vitamin E can be found in major commercial vegetable oils such as soya oil and palm oil. However, the existence in these oils is in low concentration. The recovery of low concentration of α-tocopherol from palm oils is increasingly popular. Adsorption technique for the recovery of α-tocopherol from palm oil is believed to be much lower in cost and more effective. As a case study in this work, activated carbon is chosen as the adsorbent and ethanol as the solvent. The adsorption equilibria of α-tocopherol onto activated carbon was conducted in batch and the concentration of α-tocopherol was identified by LCMS. Langmuirian monolayer adsorption theory was used for the analysis of the isotherm equilibria. The adsorptivity of α-tocopherol onto activated carbon was identified. The adsorption equilibria at low concentration found to be linear. The breakthrough curve was then generated using model assuming isothermal, single transition trace component with intraparticle diffusion. Sensitivity test on the curve indicated that the system is very sensitive to changes in diffusivity and passive to changes on the equilibrium constant.

Key words: Langmuir isotherm, α-tocopherol, Monolayer adsorption, sensitivity, dynamics

INTRODUCTION

Adsorption process is a popular process and widely applied in the field of separation processes (Farhad, 2003; Slisli and Jorg, 2003; Stuart and Neil, 1995). As an example, most of major industries using adsorption separation process for removal of contaminant from the polluted vapour before releasing it into the environment (Stuart and Neil, 1995, Schmutzer et al., 2003). Several researchers have also reported the use of adsorption to recover valuable component from vegetable oils (Chu et al., 2003; Chu et al., 2002, See, 2002).

The study of adsorption equilibria will provide a better understanding of the separation process and optimizing the separation efficiency. This work involves the study of the adsorption equilibria and the adsorptivity of α-tocopherol on activated carbon in liquid phase. Adsorption equilibria are the most important initial step in the analysis of adsorption process. The experimental and the analysis has to be considered carefully and the system has to be ensured that approaches an equilibrium. If this condition is not approached, it can lead to substantial errors in the dynamic loading ad breakthrough time (Bono, 1989, Bono et al., 2003; Chu et al., 2003; Farhadpour and Bono, 1996a, Farhadpour and Bono, 1996b). Here, the work presents the adsorption equilibria in liquid phase at ambient conditions. Break through curve is generated using Rosen’s plug flow model.

MATERIALS AND METHODOLOGY

The α-tocopherol and activated carbon used was purchased from Sigma Aldrich. Absolute ethanol (99.98%). The activated carbon purchased Sigma Aldrich. Prior experimental run, the activated carbon was grinded, sieved, washed and dried. The average size of grinded activated carbon was determined using Horiba particle size analyzer and found to be in the region of 16.9±0.1 µm.

The adsorption isotherm experiment technique was adopted from (Bono et al., 1989; Chu et al., 2003). Experiment was conducted by contacting a solution of α-tocopherol in ethanol with initial mass fractions, x0, a known mass of the dry activated carbon, W, in a closed vessel which then was filled up with nitrogen gas. The solution was continuously stirred for 1 hour and kept in a dark place for 24 h to be equilibrated in a thermally controlled environment. After 24 h, the equilibrium mass fraction in the liquid, x, was measured using Thermo Finnigan Liquid Chromatography Mass Spectrometer (LCMS). The setting condition of the LCMS was set to the condition as shown in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Detail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column type</td>
<td>C18</td>
</tr>
<tr>
<td>Mobile phase</td>
<td>5:95 Water: Methanol</td>
</tr>
<tr>
<td>Volume of injection</td>
<td>10 µl</td>
</tr>
<tr>
<td>Column temperature</td>
<td>40°C</td>
</tr>
<tr>
<td>UV detection wavelength</td>
<td>285 nm</td>
</tr>
<tr>
<td>Flowrate of the mobile phase</td>
<td>1 mL/min</td>
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</tbody>
</table>

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2080
RESULTS AND DISCUSSIONS

The relative adsorption of α-tocopherol onto activated carbon was calculated using Eq. 1 and the graph was plotted as adsorbed liquid mass per unit mass of adsorbent, $\Gamma_1$, versus the equilibrium liquid mole fraction $x_i$ as shown in Fig. 1.

$$ G_w = \frac{N_i(x_i - x_i^e)}{W_s} \quad (1) $$

Combining relative adsorption (Eq. 1) and the material balance will lead us to Eq. 2 (Bono et al., 2003; Farhadpour and Bono, 1996b).

$$ \Gamma_1 = \frac{N_i(x_i - x_i^e)}{W_s} = (1-x_i)n_i^e - n_i^e x_i \quad (2) $$

By employing monolayer Langmuir adsorption equilibria (Bono, 1989; Bono et al., 2003; Farhadpour and Bono, 1996b) the relative adsorption and Langmuir equilibria constant $k$ can be related as in Eq. 3.

$$ \frac{x_ix_i^e}{\Gamma_1} = \frac{1}{N_i} x_i + \frac{1}{N_i(k-1)} \quad (3) $$

The plot of $\frac{x_ix_i^e}{\Gamma_1}$ versus $x_i$ shown in Fig. 2 and the regression line indicates a good fit. This also exhibits the adsorption of α-tocopherol on activated carbon may obey the monolayer theory with the values of $N_i$ and $k$ as shown in Table 2.

The individual isotherm of α-tocopherol on activated carbon can be calculating using Langmuir monolayer adsorption isotherm as stated in equation 4 or mole basis in equation 5 (Bono, 1989, Bono et al., 2003; Farhadpour and Bono, 1996b).

$$ x_i^e = \frac{Kx_i}{1 + (K-1)x_i} \quad (4) $$

$$ n_i = N_i \frac{Kx_i}{1 + (K-1)x_i} \quad (5) $$

Figure 3, shows the individual adsorption isotherms of α-tocopherol on activated carbon. Result show that adsorption of α-tocopherol from ethanol by activated carbon at very low liquid concentration is linear and can be categorized as obeying Henry’s Law.

Fig. 1: Relative Adsorption for α-tocopherol onto activated carbon

Fig. 2: Adsorption of α-tocopherol-ethanol onto activated carbon according to Langmuir monolayer theory

Fig. 3: Individual adsorption isotherm for α-tocopherol on activated carbon at 25°C

Table 2: Saturation values $N_i$ and Langmuir isotherm constant, $k$

<table>
<thead>
<tr>
<th>$N_i$</th>
<th>$k$</th>
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<tbody>
<tr>
<td>0.002025</td>
<td>1.0043</td>
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</table>
SIMPLE MATHEMATICAL MODELING OF ADSORPTION COLUMN

A model correlated by Rosen was used to generate the breakthrough curve. For a system at low concentration, the differential fluid phase mass balance is given by equation 6 (Farhadpour and Bono, 1996a; Farhadpour and Bono, 1996b; Ruthven, 1984).

\[-D_e \frac{\partial^2 c}{\partial z^2} + \frac{\partial}{\partial z} (\nu c) + \frac{\partial c}{\partial t} + \frac{1 - e}{e} \frac{\partial q}{\partial t} = 0\]  \hspace{1cm} (6)

The above differential equation was then modeled by Rosen to give Eq. 7 (Faridah, 2003).

\[\frac{c}{c_e} = \frac{1}{2} + \frac{\pi}{4} \exp\left[-\xi H_1(\lambda) / 5\right] \sin\left[2\lambda^2 r / 15 - \xi H_2(\lambda) / 5\right] \frac{d\lambda}{\lambda}\]  \hspace{1cm} (7)

This assumes the condition to be isothermal, single transition trace component with intraparticle diffusion. Whereby,

\[H_1(\lambda) = \frac{\lambda [\sinh(2\lambda) + \sin(2\lambda)]}{[\cosh(2\lambda) - \cos(2\lambda)]} - 1\]  \hspace{1cm} (8)

\[H_2(\lambda) = \frac{\lambda [\sinh(2\lambda) - \sin(2\lambda)]}{[\cosh(2\lambda) - \cos(2\lambda)]}\]

and

\[\xi = \left(\frac{15D KZ}{R^2 \nu}\right) \left(1 - e\right), \quad t = \left(\frac{15D}{R^2} \right) \left(t - \frac{Z}{\nu}\right)\]  \hspace{1cm} (9)

Fig. 4: Influence of equilibrium constant, on the breakthrough curve

Fig. 5: Influence of diffusivity, D on the breakthrough curve

The K value was obtained from the Langmuirian equilibria isotherm above. Sensitivity tests of 25% variation on diffusivity and equilibrium constant was conducted and shown in Fig. 4 and 5, respectively.

Figure 4 show that the breakthrough curve is passive to changes on the equilibrium constant whereas Fig. 5 shows the breakthrough curve very sensitive to changes of diffusivity coefficient.

CONCLUSION

The adsorption of \( \alpha \)-tocopherol at low concentration it seem may be presented by monolayer adsorption theory analysis. Further work need to be done on the finding the effect of various solvents on the adsorption of \( \alpha \)-tocopherol. On the other hand, the breakthrough curve generated from the simple model shows the sensitivity toward the variation of diffusivity and the equilibrium constant.

REFERENCES