

MINIMUM BED LENGTH TO OBTAIN "CONSTANT PATTERN" IN BI-COMPONENT FIXED-BED ADSORPTION

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A simple analytical solution is proposed to predict the minimum bed length, Z_{\min} , necessary to make two adsorption zones in bi-component fixed-bed adsorption separate from each other, by use of the so-called constant pattern concept and the linear driving force approximation. Values of Z_{\min} obtained from the analytical solution were compared with those from numerical breakthrough curves based on a rather rigorous mass balance as well as diffusion equations. The solution was found to be accurate enough. Experiments were performed for two monohydric alcohols-activated carbon and two monocarboxylic acids-activated carbon systems, respectively. Comparison of the predicted Z_{\min} based on the proposed equation gave larger values than the experimental values.

Introduction

To design a fixed-bed adsorber, breakthrough curves are not always necessary, and just a knowledge of the relationship between the break time and the bed length under certain operational conditions is enough. The relation will be a function of the length of the so-called adsorption zone.

For estimation of the adsorption zone length for single-component adsorption, Kawazoe and Fukuda proposed the so-called ($r-\zeta$) method⁶⁾ based on a linear-driving-force (LDF) approximation⁴⁾ and the constant pattern concept for the case of Langmuir-type isotherm systems and, later, Hashimoto and Miura⁵⁾ presented a very similar method for Freundlich isotherm systems.

A rather rigorous numerical calculation of fixed-bed breakthrough curves for non-linear isotherm systems was first proposed by Carter^{1,2)} for both single- and binary-component adsorption. He evaluated the resistance for intraparticle diffusion using differential mass balance equations and common fluid-to-particle rate equations. In the numerical calculation, finite difference equations were used. The authors used Carter's method to calculate breakthrough curves for single-component adsorption with Langmuir- and Freundlich-isotherm systems.^{3,10)} By use of the successive over-relaxation (SOR) method presented elsewhere,^{3,9)} the speed of convergence in the calculation became much higher. The authors' calculation procedure can be used in the calculation of binary component systems. In each iteration of the

calculation, adsorption equilibria can also be evaluated by use of the SOR method and thus the error in results become smaller than those with other numerical methods. In any case, the numerical solution will be useful for testing the validity of any simplified method.

On the other hand, the authors extended the constant pattern concept for single-component systems to multi-component systems and proposed a simple method to predict break times and the lengths of adsorption zones with respect to each component.¹²⁻¹⁴⁾ The calculation procedure for the breaktimes for respective components is presented elsewhere.¹³⁾ The method was proved to be useful in several cases.¹¹⁻¹⁴⁾

In the present paper, a simple method is derived to estimate the minimum bed length, Z_{\min} , required for the establishment of two adsorption zones, using the same assumptions as did Miura *et al.*⁷⁾ Then, the values of Z_{\min} estimated were compared with those obtained from breakthrough curves calculated numerically for binary-component systems. Furthermore, a comparison of Z_{\min} obtained by use of the simplified method with experimental results was performed for monohydric alcohols-activated carbon and monocarboxylic acids-activated carbon systems to show that the method gives a safe prediction.

1. Development of Basic Equations

Concentrations of solutes in the solid phase for binary-component adsorption on a fixed bed change with the time elapsed as shown in Fig. 1. Both components are adsorbed on the same portion of the bed, right after the operation starts (Fig. 1a), and

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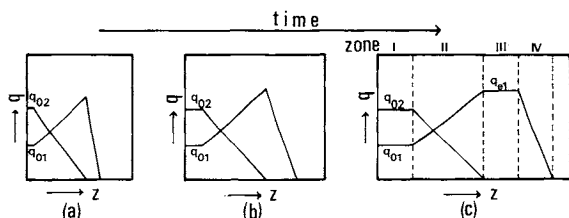


Fig. 1. Schematic history of amount adsorbed in a fixed bed and classification of four zones. I, second equilibrium-attained zone; II, second adsorption zone; III, first equilibrium-attained zone; IV, first adsorption zone.

afterwards each adsorption zone is established (Fig. 1b). Next, the two adsorption zones separate from each other with the progress of time and then become constant in length (Fig. 1c). From the mass balance for less-adsorbable and more-adsorbable components (component 1 and 2), respectively, under the constant pattern condition, the exhaustion time for component 1, t_{E1} , is described by Eq. (1) in the same way as in the authors' previous paper.¹³⁾

$$t_{E1} = \frac{c_e \{z + (1/2)Z_{IV}\}}{U_1 c_{01} + \{1 - (q_{01}/q_e)\} U_2 c_e} \quad (1)$$

$$U_1 = u c_e / \gamma q_e, \quad U_2 = u c_{02} / \gamma q_{02}$$

$$z = Z_I + Z_{II} + Z_{III} \quad \text{at} \quad t = t_{E1}$$

where u and γ denote linear flow rate of fluid and bulk density of the fixed bed, q_{01} and q_{02} are amount adsorbed of components 1 and 2, respectively, in equilibrium with c_{01} and c_{02} , q_e is the amount adsorbed in equilibrium with the maximum concentration c_e of component 1, i.e., the concentration of equilibrium-attained zone (Z_{III}), z denotes the whole bed length and Z_{IV} corresponds to the length of the first adsorption zone, and U_1 and U_2 denote traveling velocities of the first and the second adsorption zones, respectively.

The break time of component 2, t_{B2} , is given as follows from the mass balance for component 2.¹³⁾

$$t_{B2} = \frac{z - (1/2)Z_{II}}{U_2} \quad (2)$$

$$z = Z_I + Z_{II} \quad \text{at} \quad t = t_{B2}$$

Therefore, the difference between the exhaustion time and the break time, Δt ($= t_{B2} - t_{E1}$), can be written as:

$$\Delta t = \left[\frac{1}{U_2} - \frac{c_e}{U_1 c_{01} + \{1 - (q_{01}/q_e)\} U_2 c_e} \right] z - \frac{1}{2} \left[\frac{Z_{II}}{U_2} + \frac{c_e Z_{IV}}{U_1 c_{01} + \{1 - (q_{01}/q_e)\} U_2 c_e} \right] \quad (3)$$

It is clear from the equation that the difference, Δt , is a function of bed length z under the condition that a

constant pattern is established. When the value of z is the same as the minimum bed length Z_{min} , required for the separation of Zone IV from Zone II, Δt should be equal to zero. Therefore, replacing the left-hand side of Eq. (3) with 0, Z_{min} can be given as follows:

$$Z_{min} = \frac{1}{2} \left[\frac{U_2 c_e}{U_1 c_{01} - (q_{01}/q_e) U_2 c_e} (Z_{II} + Z_{IV}) + Z_{II} \right] \quad (4)$$

The amount adsorbed, q_{01} and q_{02} , can be estimated from adsorption equilibria for a binary system and for given concentrations, c_{01} and c_{02} , respectively. The equilibrium amount adsorbed of component 1 (q_e) for concentration (c_e) at Zone II, can be also estimated as described elsewhere.^{8,11,13)} The length of Z_{IV} can easily be given by use of well-known procedures^{3,5,6,10)} for a single-component system with the values of c_e and q_e , and Z_{II} can be estimated from an apparent adsorption isotherm as described elsewhere.¹³⁾ Therefore, all of the variables on the right-hand side of Eq. (4) are known.

2. Determination of Minimum Bed Length from Breakthrough Curves

For numerical calculation of breakthrough curves for binary adsorption on a fixed bed, the calculation procedure is essentially similar to that for single component systems. As is well known, dimensionless equations of fixed-bed adsorption for component i (where $i = 1$ or 2) can be written as Eqs. (5) to (8) by use of the assumptions of plug flow, constant influent flow rate, surface diffusion controlling, and establishment of adsorption equilibrium momentarily at the particle-to-fluid interface.

Material balance in the bed:

$$\frac{\partial \bar{C}_i}{\partial Z_i} + \frac{\partial \bar{Q}_i}{\partial T_i} = 0 \quad (5)$$

Rate equations

for fluid film transfer:

$$\frac{\partial \bar{Q}_i}{\partial T_i} = \bar{C}_i - C_{s,i} \quad (6)$$

for transfer at interface:

$$\frac{\partial \bar{Q}_i}{\partial T_i} = -(N_s K_0)_i \left(\frac{\partial Q_i}{\partial R} \right)_{R=1} \quad (7)$$

for intraparticle diffusion:

$$\frac{\partial Q_i}{\partial T_i} = \frac{(N_s K_0)_i}{3} \left(\frac{\partial^2 Q_i}{\partial R^2} + \frac{2}{R} \frac{\partial Q_i}{\partial R} \right) \quad (8)$$

where C_i denotes fluid concentration of component i , Q_i is the amount adsorbed of component i , Z_i and T_i are respectively bed length and contact time regarding component i , R means radial length in a particle, and $N_s K_0$ ($= k_f a_v / \beta k_s a_v$) is the diffusional parameter.

As for the adsorption equilibria, isotherms for the

respective single-component adsorption were assumed to obey Freundlich-type equation.

$$q_i = k_i c_i^{1/n_i} \quad (9)$$

Solving simultaneously Eqs. (5) to (8) by using adsorption equilibria, breakthrough curves were calculated. The SOR method^{3,9)} was used for various calculation conditions. Since the values of $k_F a_v$ were estimated to be 0.1 s^{-1} from Wilson's equation¹⁵⁾ and the experimentally observed values of $k_S a_v$ were almost $0.1 \text{ g/cm}^3 \text{ s}$ for the butyric acid-valeric acid-activated carbon system, the values of $k_F a_v$ and $k_S a_v$, adopted in the calculation were 0.05, 0.1 and 0.2 in respective units. The values of the equilibrium parameters, k and $1/n$, changed from 2 to 7 and from $1/2$ to $1/4$, respectively, when the unit of amount adsorbed was expressed in terms of mmol/g and that of fluid concentration in terms of mmol/l.

Figure 2 shows some examples of breakthrough curves calculated by use of the numerical method including Eq. (8) (i.e., neither LDF approximation nor the so-called constant pattern concept was used).

It is obvious that a bed length of 5.5 cm is not enough to make Zones II and IV separate from each other. The results for bed lengths of 25.5 and 45.5 cm show that the maximum concentration of component 1 reaches c_e . As shown in Fig. 2, Δt can be obtained from numerical breakthrough curves for the respective bed lengths.

From the values of Δt with respect to various operational conditions, Z_{\min} values were calculated as shown in **Fig. 3** and some of the results are listed in **Table 1**. It seems that the value of minimum bed length required to make Zone II and Zone IV separate from each other is dependent on the travelling velocities of the two zones, U_1 and U_2 , as well as the lengths of the zones, Z_{II} and Z_{IV} . The results can also be estimated from Eq. (4).

3. Comparison of Z_{\min} from Numerical Results with Those from the Simplified Method

When the second term in brackets of the right-hand side of Eq. (4) is negligible, the ratio of Z_{\min} to $(Z_{II} + Z_{IV})$ is dependent on the ratio of travelling velocities, U_2/U_1 . Therefore, values of $Z_{\min}/(Z_{II} + Z_{IV})$ and U_2/U_1 were evaluated from the values presented in Table 1 and are listed in columns 6 and 7 of the table.

With respect to various equilibria parameters and diffusional resistance within the particles for realistic cases, Z_{II} and Z_{IV} were determined by use of the procedures mentioned above and then Z_{\min} was obtained from Eq. (4). Furthermore, these values were also obtained from the numerical breakthrough curves. The ratios of Z_{\min} to $(Z_{II} + Z_{IV})$ are plotted in **Fig. 4** against the ratio of travelling velocities, U_2/U_1 .

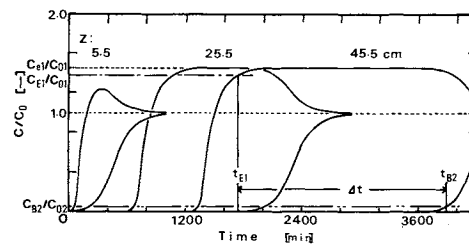


Fig. 2. Numerical breakthrough curves.

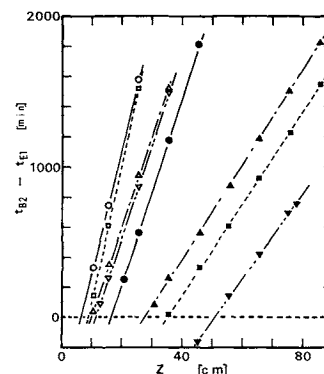


Fig. 3. Plots of $(t_{B2} - t_{E1})$ from numerical breakthrough curves versus bed length z . (Keys refer to Table 1.)

Figure 4 shows that the relations between the values of $Z_{\min}/(Z_{II} + Z_{IV})$ and the values of U_2/U_1 from the simplified method and from the numerical breakthrough curves can be expressed by a single curve irrespective of the values of equilibrium parameter, because the effect of the equilibrium is included in the ratio U_2/U_1 .

4. Application of the Simplified Method to Practical Cases

For adsorption from binary monocarboxylic acid solution and binary monohydric alcohol solutions on a fixed bed of carbon particles, experiments were performed at 25°C for various bed lengths.

Since the experimental procedure is almost the same as that described elsewhere,¹³⁾ only the results are presented here. Experimental breakthrough curves are shown in **Fig. 5** for the system butyric acid-valeric acid-activated carbon. It seems from the figure that the breakthrough curves with respect to the 43.3 and 61.3 cm long beds, respectively, can be used to evaluate Z_{\min} .

The difference, Δt (see Fig. 2), between the exhaustion time t_{E1} and the break time t_{B2} , which correspond to $c_{E1} = 0.9c_e$ and $c_{B2} = 0.1c_{02}$, respectively, is plotted against bed length, z , as shown in **Fig. 6**. Also shown in the figure are the results for other monocarboxylic acid systems. For monohydric alcohol systems, the results are shown in **Fig. 7**.

The values of Z_{\min} obtained from Figs. 6 and 7 are

Table 1. Minimum bed length Z_{\min} obtained from numerical breakthrough curves

| Keys in Fig. 3 | U_1 [cm/h] | U_2 [cm/h] | Z_{II} [cm] | Z_{IV} [cm] | Z_{\min} [cm] | U_2/U_1 [—] | $Z_{\min}/(Z_{II} + Z_{IV})$ [—] |
|-------------------|-----------------|-----------------|------------------|------------------|--------------------|------------------|-------------------------------------|
| ○ | 1.75 | 0.505 | 11.8 | 5.8 | 6.5 | 0.289 | 0.369 |
| △ | 1.83 | 0.651 | 12.0 | 7.5 | 10.0 | 0.356 | 0.513 |
| □ | 0.941 | 0.385 | 7.5 | 6.9 | 9.0 | 0.409 | 0.625 |
| ▽ | 1.27 | 0.548 | 9.1 | 8.5 | 11.5 | 0.432 | 0.653 |
| ● | 0.791 | 0.430 | 6.6 | 11.3 | 16.5 | 0.543 | 0.922 |
| ▲ | 1.33 | 0.780 | 9.5 | 17.2 | 27.5 | 0.584 | 1.030 |
| ■ | 1.02 | 0.661 | 7.7 | 19.9 | 35.0 | 0.645 | 1.268 |
| ▼ | 0.693 | 0.508 | 6.2 | 22.3 | 50.5 | 0.733 | 1.772 |

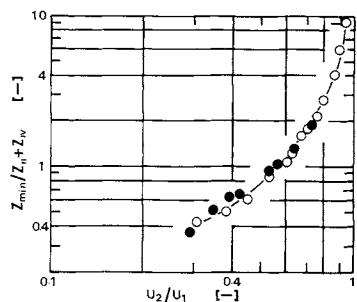


Fig. 4. $Z_{\min}/(Z_{II} + Z_{IV})$ versus ratio of travelling velocities, U_2/U_1 . ○, from simplified method; ●, from numerical breakthrough curves.

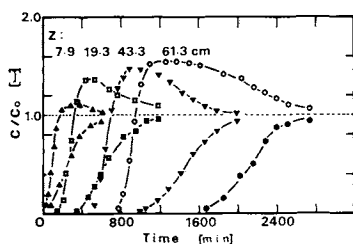


Fig. 5. Experimental breakthrough curves for butyric acid-valeric acid system.

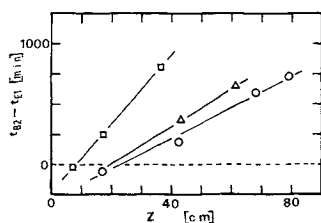


Fig. 6. $\Delta t (= t_{B2} - t_{E1})$ from experimental results versus bed length z for monocarboxylic acid systems. (Keys refer to Table 2.)

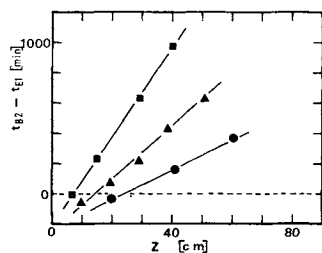


Fig. 7. $\Delta t (= t_{B2} - t_{E1})$ from experimental results versus bed length z for monohydric alcohol systems. (Keys refer to Table 2.)

Table 2. Minimum bed length for monocarboxylic acid and for monohydric alcohol systems

| Keys in Figs. 6 and 7 | System | Z_{\min} [cm] | | U_2/U_1 [—] |
|-----------------------------|-----------------------------------------|-----------------|-----------|------------------|
| | | Observed | Estimated | |
| ○ | Propionic acid–butyric acid | 22.7 | 24.3 | 0.38 |
| □ | Propionic acid–valeric acid | 8.5 | 13.2 | 0.25 |
| △ | Butyric acid –valeric acid | 20.1 | 27.1 | 0.61 |
| ● | <i>n</i> -Propanol – <i>n</i> -butanol | 23.8 | 38.4 | 0.87 |
| ■ | <i>n</i> -Propanol – <i>n</i> -pentanol | 7.9 | 11.5 | 0.88 |
| ▲ | <i>n</i> -Butanol – <i>n</i> -pentanol | 14.8 | 21.9 | 0.87 |

listed in **Table 2** as $Z_{\min \text{ obs.}}$ along with those estimated by use of Eq. (4), expressed as $Z_{\min \text{ est.}}$. An error in estimation of Z_{\min} by the simplified method, which included all estimation errors of Z_{II} , Z_{IV} and equilibrium amount adsorbed for binary system, was found to be about 35%, except for the propionic acid-butyrac acid system. In this case, although adsorption zones II and IV separate from each other they seem not to be constant in length.

The values obtained from Eq. (4), however, were larger than the experimental values for almost all systems studied. Therefore, it can be concluded that this simple method gives a safe prediction of minimum bed length.

Conclusion

For binary component systems, the minimum bed length required for separation of each adsorption zone, Z_{\min} , was calculated with the aid of the constant pattern concept and linear-driving-force approximation. The results obtained agreed fairly well with those determined from the numerical breakthrough curves based on rather rigorous differential equations. From comparison of both results with experimental results for the systems monocarboxylic acid-activated carbon and monohydric alcohol-activated carbon, it became clear that the above simple procedure gave a safe prediction of the minimum bed length required to achieve separation of two adsorption zones in the fixed bed.

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Nomenclature

| | | |
|------------|-------------------------------------------------------------------------------------|-----------------------|
| b | = mean particle radius | [m] |
| C | = c/c_0 | [—] |
| c | = fluid concentration | [kg/m ³] |
| c_B | = fluid concentration at break-point | [kg/m ³] |
| c_E | = fluid concentration at exhaustion-point | [kg/m ³] |
| c_e | = maximum concentration of less-adsorbable component | [kg/m ³] |
| c_{0i} | = initial concentration of component i | [kg/m ³] |
| $k_F a_v$ | = fluid-film volumetric mass transfer coefficient | [kg/m ³ s] |
| $k_S a_v$ | = intraparticle volumetric mass transfer coefficient | [s ⁻¹] |
| $N_S K_0$ | = $\beta k_S a_v / S k_F a_v$ | [—] |
| $1/n$ | = Freundlich exponent | [—] |
| \bar{Q} | = mean value of q/q_0 | [—] |
| Q | = local value of q/q_0 within particles | [—] |
| q | = amount adsorbed in equilibrium with c | [kg/kg] |
| q_e | = amount adsorbed in equilibrium with c_e for single-component system | [kg/kg] |
| q_{0i} | = amount adsorbed in equilibrium with c_{0i} for binary-component system | [kg/kg] |
| R | = r/b | [—] |
| r | = radial length | [m] |
| T | = $(t - z\epsilon/u)k_F a_v / \beta\gamma$ | [—] |
| t | = time | [s] |
| t_{B2} | = break time for more-adsorbable component, corresponding to $c_{B2} = 0.1c_{02}$ | [s] |
| t_{E1} | = exhaustion time for less-adsorbable component, corresponding to $c_{E1} = 0.9c_e$ | [s] |
| Δt | = refer to Eq. (3) and Fig. 2 | [s] |
| U_i | = travelling velocity of adsorption zone | [m/s] |
| u | = linear flow rate | [m/s] |
| Z | = $z k_F a_v / u$ | [—] |

| | | |
|------------|-------------------------------------------------------------------------|----------------------|
| z | = bed length | [m] |
| Z_{\min} | = minimum bed length required for establishment of two adsorption zones | [m] |
| Z_{II} | = length of second adsorption zone | [m] |
| Z_{IV} | = length of first adsorption zone | [m] |
| β | = slope of operational line | [m ³ /kg] |
| γ | = bed bulk density | [kg/m ³] |

<Subscript>

i = component

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