

Analysis of the Constant Molar Flow Method for Measurements of Kinetics Parameters in Porous Adsorbent Particles

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(Received 21 June 2002 • accepted 3 September 2002)

Abstract—The constant molar flow (CMF) method has been successfully applied to measure equilibrium and dynamic parameters in porous adsorbent particles. However, the application of this method is confined to a linear system without the external film resistance. The aim of the present study is two-fold: to derive the exact analytical solution of the linear CMF model with the external film resistance and to extend the theory of the CMF model to the nonlinear system. As time becomes sufficiently large, the solution of the linear CMF model asymptotes to a straight line, of which the slope is a function of the equilibrium parameters only and the intercept is a function of the dynamic parameters such as the effective diffusivity and the external film mass transfer coefficient. On the contrary, the solution of the nonlinear CMF model has two asymptotes: the early time asymptote and the late time asymptote. Numerical analysis using the orthogonal collocation in the radial domain of the particle phase is also used to interpret the behavior of the nonlinear CMF model.

Key words: Constant Molar Flow Method, Porous Adsorbent Particles, Effective Diffusivity

INTRODUCTION

Several techniques have been proposed for measuring the effective diffusivity in porous particles. The microbalance method [Gray and Do, 1991], the diffusion cell method [Dogu and Smith, 1976], the chromatography method [Schneider and Smith, 1968], the frequency response method [Yasuda, 1982; Park et al., 2000, 2001], the differential adsorption bed method [Do et al., 1991], the zero length column method [Eic and Ruthven, 1988] are used for this purpose. Each of these methods has advantages and disadvantages or limitations [Park et al., 1996].

As an alternative technique, the constant molar flow (CMF) method has been successfully applied to measure equilibrium and dynamic parameters in porous particles. The CMF method was first proposed by Do [1995]. Park and Do [1996] extended the theory of the CMF method to systems with bidisperse porous particles. Do and co-workers [Prasetyo and Do, 1998, 1999; Do et al., 2000] applied this technique to measure the effective diffusivity of several hydrocarbons in activated carbon particles. Do and Do [2001] compared the effective diffusivity obtained from the CMF method to the effective diffusivity from the differential adsorption bed and the differential permeation methods.

In the CMF method, a constant flow of adsorbate is introduced in a pre-evacuated adsorption reservoir. The pressure of the reservoir is monitored as a function of time and then analyzed to extract equilibrium and dynamic parameters such as the adsorption equilibrium constant and the effective diffusivity. Isothermal condition is assumed in this method. However, the application of this method is confined to a linear system without external film resistance. The aim of the present study is to extend the CMF method to account for the external film resistance. The exact solution for the linear sys-

tem with the external film resistance will be derived. A numerical solution using the orthogonal collocation in the radial domain within the particle phase is also used to interpret the behavior of the nonlinear CMF model.

MATHEMATICAL MODEL

The following assumptions are made to formulate the CMF model [Park and Do, 1996]:

- (1) ideal mixing in the reservoir
- (2) local adsorption equilibrium at the particle surface
- (3) homogeneous particle diffusion within the particle
- (4) isothermal condition
- (5) constant effective diffusivity
- (6) zero initial concentrations in the reservoir and in the particle.

The mathematical formulation based on the above assumptions is as follows [Do, 1995; Park and Do, 1996]:

Intraparticle Mass Balance:

$$\frac{\partial C_\mu}{\partial t} = D_e \frac{1}{r^\sigma} \frac{\partial}{\partial r} \left(r^\sigma \frac{\partial C_\mu}{\partial r} \right) \quad (1a)$$

$$\text{at } r=0, \quad \frac{\partial C_\mu}{\partial r} = 0 \quad (1b)$$

$$\text{at } r=R, \quad \left[\frac{\partial C_\mu}{\partial r} \right]_{r=R} = k_f (C_b - C_s) \quad (1c)$$

where C_μ is the concentration in the particle, C_b is the concentration in the reservoir outside the particles, C_s is the concentration in the gas phase at particle surface, D_e is the effective diffusivity, k_f is the external mass transfer coefficient, σ is the geometric factor of particle (0 for slab, 1 for cylinder and 2 for sphere) and r is the coordinate variable of particle. Note that the original boundary condi-

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tion at the particle surface of Do [1995] (i.e., at $r=R$, $C_\mu=KC_b$) is replaced by Eq. (1c) to account for the external film resistance.

Mass Balance around the Reservoir:

$$V \frac{dC_b}{dt} + V_\mu \frac{d\langle C_\mu \rangle}{dt} = \dot{N}; \quad \langle C_\mu \rangle = \frac{(\sigma+1)}{R} \int_0^R r^\sigma C_\mu dr \quad (1d)$$

where V is the volume of reservoir outside particles, V_μ is the volume of particles, $\dot{N}$ is the constant molar flow-rate into reservoir, t is the time variable, and R is the particle radius.

Initial Conditions:

$$\text{at } t=0, \quad C_b=0, \quad C_\mu=0 \quad (1f)$$

Equilibrium at the Particle Surface:

$$\text{for the linear CMF model } C_\mu|_{r=R} = KC_s \quad (2a)$$

for the nonlinear CMF model with the Langmuir isotherm

$$C_\mu|_{r=R} = \frac{C_{\mu s} b C_s}{1 + b C_s} \quad (2b)$$

In Eq. (2a) K is Henry constant for the linear isotherm, and in Eq. (2b) $C_{\mu s}$ and b are the Langmuir isotherm parameters.

NONDIMENSIONALIZATION OF THE MODEL

With the dimensionless variables and parameters defined in Table 1, the model is rewritten in a dimensionless form as follows:

Intraparticle Mass Balance:

$$\frac{\partial y_\mu}{\partial \tau} = \left(\frac{\partial^2 y_\mu}{\partial x^2} + \frac{\sigma}{x} \frac{\partial y_\mu}{\partial x} \right) \quad (3a)$$

$$\text{at } x=0, \quad \frac{\partial y_\mu}{\partial x} = 0 \quad (3b)$$

$$\text{at } x=1 \quad \left[\frac{\partial y_\mu}{\partial x} \right]_{x=1} = \xi (y_b - y_s) \quad (3c)$$

Mass Balance around the Reservoir:

$$\frac{dy_b}{d\tau} + \beta \frac{d\langle y_\mu \rangle}{d\tau} = \Omega \quad \langle y_\mu \rangle = (\sigma+1) \int_0^1 x^\sigma y_\mu dx \quad (3d)$$

Initial Conditions:

Table 1. Definition of dimensionless variables and parameters

$$y_b = \frac{C_b}{C_0}; \quad y_s = \frac{C_s}{C_0}; \quad x = \frac{r}{R}; \quad \tau = \frac{D_e t}{R^2}$$

$$Bi = \frac{k_f R}{D_e}; \quad y_\mu = \frac{C_\mu}{C_{\mu 0}};$$

where C_0 is a reference concentration and $C_{\mu 0}$ is defined as

$C_{\mu 0} = KC_0$ for linear isotherm

$C_{\mu 0} = \frac{C_{\mu s} b C_0}{1 + b C_0}$ for Langmuir isotherm

Distribution parameter $\beta = \frac{V_\mu}{V} \left(\frac{C_{\mu 0}}{C_0} \right)$

Film resistance parameter $\xi = \frac{Bi}{C_{\mu 0}/C_0}$

Inlet molar flow rate parameter $\Omega = \frac{R^2/D_e}{V C_0/\dot{N}}$

$$\text{at } \tau=0, \quad y_b=0, \quad y_\mu=0 \quad (3e)$$

Adsorption Isotherm:

$$\text{for the linear CMF model} \quad y_\mu|_{x=1} = y_s \quad (4a)$$

$$\text{for the nonlinear CMF model} \quad y_\mu|_{x=1} = \frac{(1+bC_0)y_s}{1+bC_0 y_s} \quad (4b)$$

We note that the Langmuir isotherm of Eq. (4b) reduces to the linear isotherm of Eq. (4a) when $bC_0 \ll 1$.

ANALYTICAL SOLUTION OF THE LINEAR CMF MODEL

Eqs. (3a)-(3e) and Eq. (4a) give a set of linear equations, which can be solved by the Laplace transform technique.

The solution in the Laplace domain can be obtained as:

$$\bar{y}_b = \frac{1}{\Omega s^2 [1 + \beta F(s)]} \quad (5)$$

where the function $F(s)$ is defined as

$$\text{for } \sigma=0 \quad F(s) = \left(\frac{1}{1 + \frac{\sqrt{s}}{\xi} \tanh(\sqrt{s})} \right) \left(\frac{\tanh(\sqrt{s})}{\sqrt{s}} \right) \quad (6a)$$

$$\text{for } \sigma=1 \quad F(s) = 2 \left(\frac{1}{1 + \frac{\sqrt{s}}{\xi} \tanh\left(\frac{I_1(\sqrt{s})}{I_0(\sqrt{s})}\right)} \right) \left(\frac{I_1(\sqrt{s})}{\sqrt{s} I_0(\sqrt{s})} \right) \quad (6b)$$

$$\text{for } \sigma=2 \quad F(s) = 3 \left(\frac{1}{1 + \frac{1}{\xi} [\sqrt{s} \coth(\sqrt{s}) - 1]} \right) \left(\frac{\sqrt{s} \coth(\sqrt{s}) - 1}{s} \right) \quad (6c)$$

By taking the inverse transform of Eq. (5) using the method of residues, the analytical solution for the reservoir concentration can be obtained as follows:

$$y_b(\tau)/\Omega = \frac{1}{1+\beta} \tau + \frac{1}{(\sigma+1)(\sigma+3)(1+\beta)^2} \left(1 + \frac{\sigma+3}{\xi} \right) - 2(\sigma+1)\beta \sum_{n=1}^{\infty} \frac{\exp(-\lambda_n^2 \tau)}{\lambda_n^2 \left[\left(1 - \frac{(\sigma-1)}{\xi} \right) \lambda_n^2 + (\sigma+1)^2 \beta^2 \left(1 - \frac{\lambda_n^2}{(\sigma+1)\beta\xi} \right)^2 + (\sigma+1)^2 \beta \right]} \quad (7)$$

where the eigenvalues λ_n of the infinite series are obtained by the following transcendental equations:

$$\text{for } \sigma=0 \quad 1 + \beta \left(1 - \frac{\lambda^2}{\beta\xi} \right) \frac{\tan\lambda}{\lambda} = 0 \quad (8a)$$

$$\text{for } \sigma=1 \quad 1 + 2\beta \left(\frac{1}{1 - \frac{\lambda}{\xi} \left(\frac{J_1(\lambda)}{J_0(\lambda)} \right)} \right) \left(\frac{J_1(\lambda)}{\lambda J_0(\lambda)} \right) = 0 \quad (8b)$$

$$\text{for } \sigma=2 \quad 1 + 3\beta \left(1 - \frac{\lambda^2}{3\beta\xi} \right) \left(\frac{1 - \lambda \cot\lambda}{\lambda^2} \right) = 0 \quad (8c)$$

Note that the analytical solution given by Eq. (7) reduces to the solution of Do [1995] when ξ is infinity.

NUMERICAL SOLUTION

For the nonlinear CMF model, the set of governing equations Eqs. (3a)-(3e), (4b) are nonlinear partial differential equations, which are solved by the collocation analysis in the radial domain within the particle.

Selecting N interior collocation points for the radial domain within the particle, N ordinary differential equations (ODEs) of the initial value type can be obtained [Villadsen and Michelsen, 1978]. These N ODEs and Eq. (3d), together with the initial condition of Eq. (3e), make a set of $(N+1)$ ODEs of the initial value type to be solved numerically. Eight interior collocation points (i.e., $N=8$) for the radial domain are used. The built-in function "ODE15S.M" of MATLAB is used as the integration routine to solve the initial value problem of the $(N+1)$ coupled ODEs.

We note that the Langmuir isotherm of Eq. (4b) reduces to the linear isotherm of Eq. (4a) when $bC_0 \ll 1$. Thus, the numerical solution of the nonlinear model should reduce to the solution of the linear model when $bC_0 \ll 1$.

ASYMPTOTIC BEHAVIOR

When time is large enough, the solution of the linear CMF model approaches a straight line (i.e., asymptote), the slope of which is dependent on β only, but the intercept is a strong function of ξ , as we can see in Eq. (7).

As a matter of fact, a quasi-equilibrium condition prevails in the adsorption system after long time of operation of the CMF semi-batch adsorber. This quasi-equilibrium condition can be achieved at any time of the course of the adsorption if the inlet molar flow rate into the adsorber is slow enough. In such a condition the number of moles fed into the adsorber is equal to the total number of moles in the reservoir and in the particles, and the concentrations in the two phases are in equilibrium to each other [Do and Do, 2001]. Thus, the overall mass balance at the quasi-equilibrium is

$$\Omega\tau = y_b + \beta y_\mu^* \quad (9)$$

where y_μ^* is the equilibrium concentration in the particle, which is given by

$$\text{for linear isotherm } y_\mu^* = y_b \quad (10a)$$

$$\text{for Langmuir isotherm } y_\mu^* = \frac{(1+bC_0)y_b}{1+bC_0y_b} \quad (10b)$$

Substituting Eqs. (10) into Eq. (9), we obtain

for linear isotherm

$$\left. \frac{y_b(\tau)}{\Omega} \right|_{\text{equilibrium}} = \frac{1}{1+\beta} \tau \quad (11a)$$

for Langmuir isotherm

$$\left. \frac{y_b(\tau)}{\Omega} \right|_{\text{equilibrium}} = \frac{-m + \sqrt{m^2 + 4bC_0\tau/\Omega}}{2bC_0}; \quad m = \frac{1+\beta(1+bC_0)}{\Omega} - bC_0\tau \quad (11b)$$

This quasi-equilibrium solution gives information about the slope

of the asymptote of the model. For the linear CMF model, the slope of the asymptote is the same as the slope of the quasi-equilibrium solution. For the quasi-equilibrium solution of the nonlinear CMF model, the following asymptotic equations for the early time and for the late time can be obtained:

$$\left. \frac{y_b(\tau)}{\Omega} \right|_{\text{equilibrium}} = \frac{1}{1+\beta(1+bC_0)} \tau \quad \text{for } \tau \ll \tau_c \quad (12a)$$

$$\left. \frac{y_b(\tau)}{\Omega} \right|_{\text{equilibrium}} = \tau - \frac{1+\beta(1+bC_0)}{bC_0\Omega} \quad \text{for } \tau \gg \tau_c \quad (12b)$$

where τ_c is defined as the time for $m=0$, which is given by

$$\tau_c = \frac{1+\beta(1+bC_0)}{bC_0\Omega} \quad (13)$$

Thus, the asymptote of the nonlinear CMF model is

$$\text{Early time asymptote: } \frac{y_b(\tau)}{\Omega} = \frac{1}{1+\beta(1+bC_0)} \tau + c_1 \quad \text{for } \tau \ll \tau_c \quad (14a)$$

$$\text{Late time asymptote: } \frac{y_b(\tau)}{\Omega} = \tau + c_2 \quad \text{for } \tau \gg \tau_c \quad (14b)$$

where the intercepts of the asymptotes (i.e., c_1 and c_2) for the nonlinear CMF model could not be determined analytically because of the nonlinearity of the model. However, the information of asymptotes for the quasi-equilibrium solution should be important for the nonlinear CMF model to correlate the experimental data. Typical values of parameters of the CMF experiment [Prasetyo and Do, 1988] are: $\beta=10$, $\Omega=0.001-10$. Thus, we obtain $\tau_c=1-100$ (by taking $bC_0=1$) in order of magnitude calculation.

SIMULATION OF THE MODEL

For the simulation of the model, we use the representative values of $\beta=10$ and $\Omega=0.1$. To show the effects of adsorption affinity and the external film resistance, we use some different values of bC_0 (i.e., $bC_0=1, 0.1$, and 0.001) and ξ (i.e., $\xi=1, 10, 100, 1000$).

Fig. 1 shows the solutions of the linear CMF model for the three

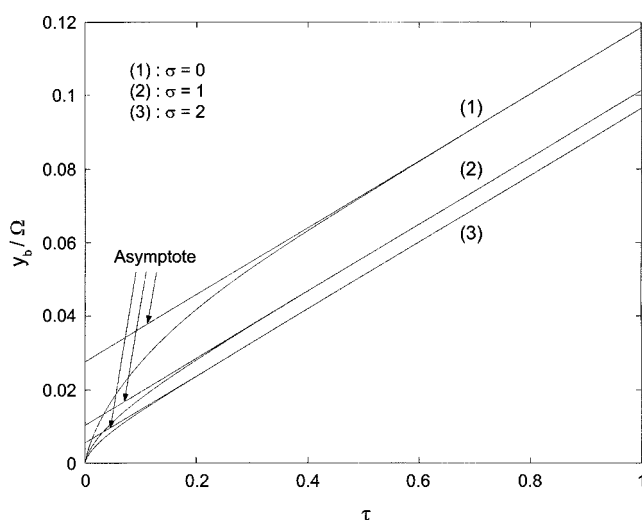


Fig. 1. Effect of the particle shape factor σ on the response of the linear CMF model ($\beta=10$, $\xi=1000$).

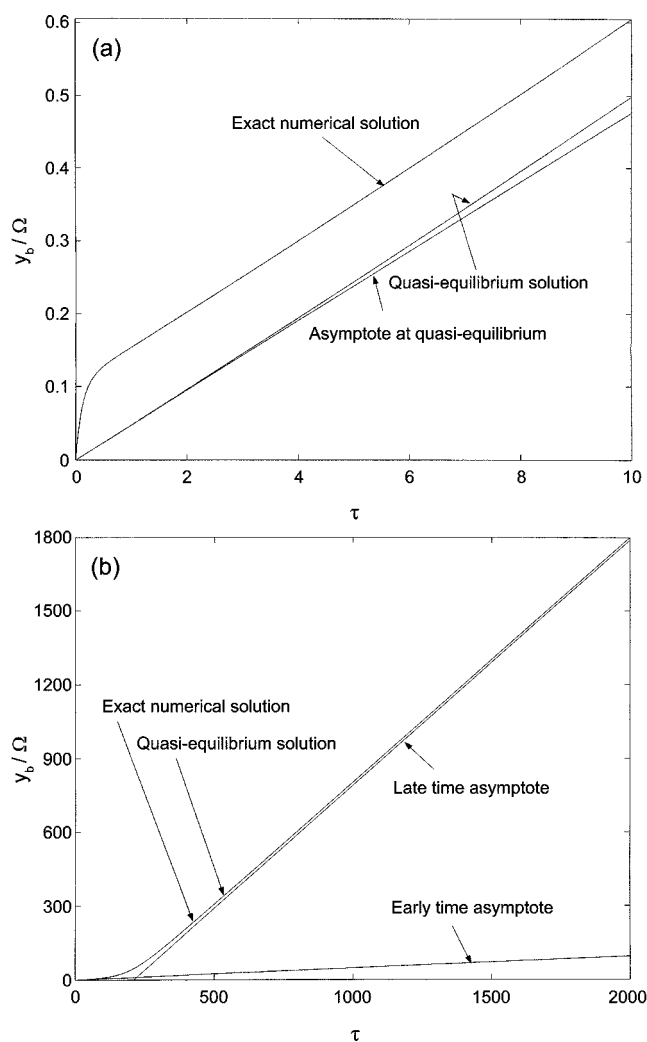


Fig. 2. Asymptotic behavior of the solution of the nonlinear CMF model ($\sigma=0$, $\beta=10$, $\xi=1$, $\Omega=0.1$, $bC_0=1$): (a) Early time asymptote, (b) Late time asymptote.

different particle shapes, that is, slab, cylinder, and sphere. The slopes of the asymptotes are all the same, but the intercepts are different from one another. The response time to reach the long time solution is large for slab particles and small for spherical particles. The response time for cylindrical particles lies between those of slab and spherical particles.

Fig. 2 shows the existence of the early time asymptote and the late time asymptote for the nonlinear CMF model. Since the collection of data in the typical CMF experiment are completed in the early time (e.g., in the region $\tau < 1$), the practically useful asymptote should be the early time asymptote rather than the late time asymptote.

Fig. 3 shows the effect of the adsorption affinity on the response curve. The response curves of the nonlinear systems are obtained from the numerical solution, and those of the linear system are obtained from the analytical solution. As the value of bC_0 decreases, the response curve of the nonlinear model approaches to that of the corresponding linear model. The curve for $bC_0=0.001$ nearly coincides with the response curve of the linear model, which is obtained from the analytical solution of Eq. (7). This coincidence suggests that the accuracy of the numerical calculation is excellent.

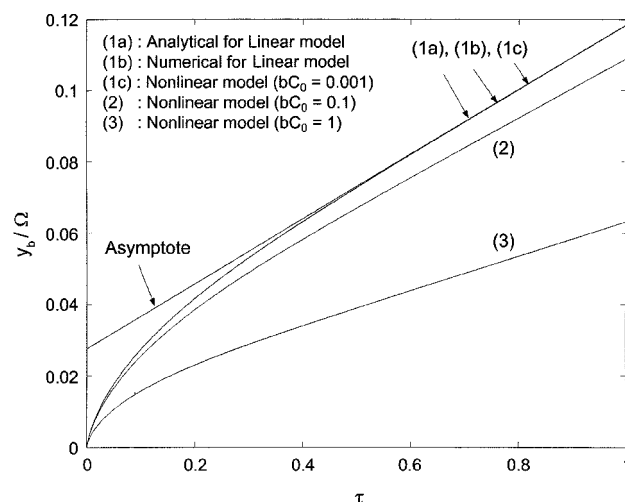


Fig. 3. Effect of the adsorption affinity bC_0 on the response of the nonlinear CMF model ($\sigma=0$, $\beta=10$, $\xi=1000$, $\Omega=0.1$).

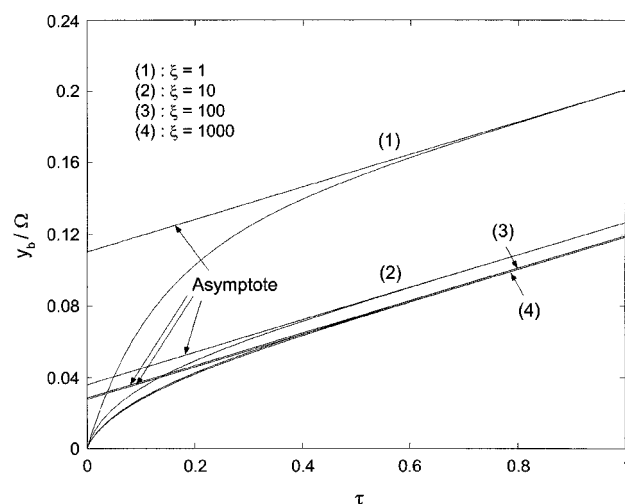


Fig. 4. Effect of the external film resistance parameter ξ on the response of the linear CMF model ($\sigma=0$, $\beta=1000$).

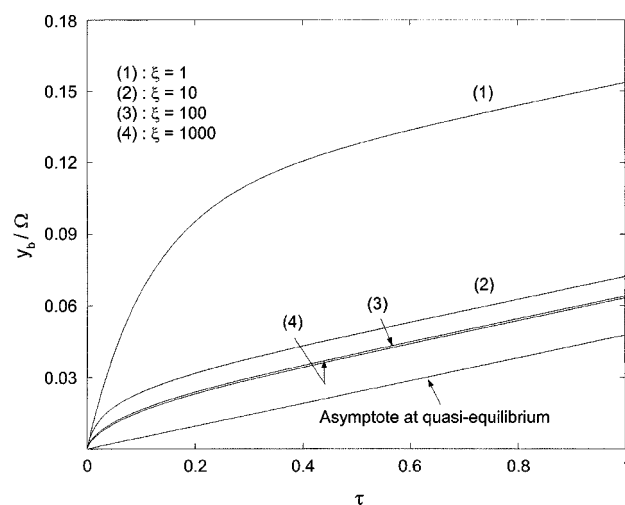


Fig. 5. Effect of the external film resistance parameter ξ on the response of the nonlinear CMF model ($\sigma=0$, $\beta=1000$, $\Omega=0.1$, $bC_0=1$).

Figs. 4 and 5 show the effect of the film resistance parameter ξ on the response for the linear CMF and nonlinear CMF models, respectively. In a nonlinear CMF model as well as a linear CMF model the slope of the asymptote is independent of the film resistance parameter, but the intercept is a strong function of the film resistance parameter when $\xi < 100$. Hence, we can extract the equilibrium parameters (e.g., adsorption affinity) from the slope and the dynamic parameters (i.e., D_e and k_f) from the intercept. To separate one of the dynamic parameters from another, experiments of different particle sizes should be required. The straight lines starting from the origin in Fig. 5 are the early time asymptote of the quasi-equilibrium solutions, which is independent of ξ . This asymptote is included in Fig. 5 to visualize the asymptotic behavior of the actual response of the model.

CONCLUSIONS

In the CMF method, a constant flow of adsorbate is introduced in a pre-evacuated adsorption reservoir. The response of the reservoir concentration is monitored as a function of time to extract equilibrium and dynamic parameters such as the adsorption equilibrium constant and the effective diffusivity.

In the present study, the exact analytical solution of an linear CMF model is presented to account for the external film resistance. As time increases, the solution approaches to a straight line, the intercept of which is a function of dynamic parameters such as effective diffusivity and film mass transfer coefficient and the slope is a function of the equilibrium parameter only. Experiments of different particle sizes should be required to separate one of dynamic parameter from another.

A numerical solution using orthogonal collocation is presented to simulate the nonlinear CMF model with the Langmuir isotherm. As a result of simulation, it is shown that the response of the nonlinear CMF model as well as the linear CMF model approaches to a straight line as time increases.

ACKNOWLEDGMENT

This work was supported by the Kyungnam University Research Fund, 2002.

NOMENCLATURE

b	: Langmuir isotherm parameter, defined in Eq. (2b)
C_b	: concentration in the fluid phase [mol/cm ³]
C_0	: reference concentration, on which dimensionless concentration is based [mol/cm ³]
C_s	: concentration in the fluid phase at the particle surface [mol/cm ³]
C_μ	: concentration in the particle phase [mol/cm ³]
$C_{\mu 0}$	: reference concentration, defined in Table 1 [mol/cm ³]
$C_{\mu s}$	: Langmuir isotherm parameter, defined in Eq. (2b) [mol/cm ³]
D_e	: effective diffusivity, defined by Eq. (1a) [cm ² /s]
$F(s)$	: function of s , defined by Eqs. (6)
k_f	: external film mass transfer coefficient, defined by Eq. (2d) [cm/s]
K	: dimensionless Henry constant of the linear isotherm, defined by Eq. (2a)

N	: number of interior collocation points in radial domain
$\hat{N}$	: molar flow rate of adsorbate into reservoir [mol/sec]
r	: radial variable within the particle [cm]
R	: equivalent radius of the particle [m]
s	: laplace domain variable [s ⁻¹]
t	: time variable [s]
V, V_μ	: volume of free space and particles within the reservoir, respectively [cm ³]
x	: dimensionless radial variable within the particle, defined in Table 1
y_b	: dimensionless concentration in the fluid phase, defined in Table 1
y_s	: dimensionless concentration in the fluid phase at the particle surface, defined in Table 1
y_μ	: dimensionless concentration in the particle phase at the particle surface, defined in Table 1
$\langle y_\mu \rangle$	: mean value of y_μ
$y_{\mu s}$	: dimensionless Langmuir isotherm parameter, defined in Table 1

Greek Letters

β	: dimensionless distribution parameter, defined in Table 1
λ	: independent variable of transcendental equation for eigenvalues, defined in Eqs. (8)
λ_n	: the n -th eigenvalue, defined in Eq. (7)
σ	: shape factor of macroparticle (0 for slab, 1 for cylinder and 2 for sphere)
τ	: dimensionless time variable, defined in Table 1
ξ	: dimensionless film resistance parameter, defined in Table 1
Ω	: dimensionless inlet molar flow rate parameter, defined in Table 1

Mathematical Functions

I_n	: modified Bessel function of the first kind of order n
J_n	: Bessel function of the first kind of order n

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