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# Affinity adsorption of adsorbates into spherical monodisperse and bidisperse porous perfusive and purely diffusive adsorbent particles packed in a column

## Parameter estimation in the Laplace transform domain

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### Abstract

A novel mathematical method for parameter estimation is proposed and used to estimate in the Laplace transform domain the values of the parameters that characterize the mechanisms of intraparticle diffusion and convection in spherical perfusive or purely diffusive adsorbent particles with a monodisperse or with a bidisperse porous structure when the adsorbent particles are packed in a column. The parameter estimation method in the Laplace transform domain presented in this work is significantly simpler, easier to use and dramatically faster than the conventional parameter estimation procedure in the time domain, which requires the repeated numerical solution of the partial differential equations that describe the dynamic behaviour of the adsorption of an adsorbate in a column. Furthermore, since the value(s) of the parameter(s) that characterize the diffusional mass transfer mechanism(s) in the porous adsorbent particles is independent of the mode of operation, then the value(s) of the effective pore diffusion coefficient(s) determined by the mathematical method presented in this work could be used to describe the diffusional mass transfer rate of the adsorbate in operational modes other (finite bath (batch) operation, periodic countercurrent column operation, fluidized bed operation) than fixed-bed column operation.

*Keywords:* Adsorption; Adsorbents; Affinity adsorbents; Mathematical models; Simulation; Laplace transform domain

### 1. Introduction

In recent years, mathematical models describing adsorption in column systems [1–10] with perfusive [3–11] and purely diffusive adsorbent particles (perfusive adsorbent particles are defined to be porous adsorbent particles in which the intraparticle velocity,  $v_p$ , is non-zero [3–10] and purely diffusive adsorbent particles are defined to be porous adsorbent particles in which intraparticle fluid flow does not occur), as well as models describing adsorption in finite bath (batch) systems [12,13] with

purely diffusive adsorbent particles, have been presented and their theoretical implications studied. These models have provided significant information about the dynamic behaviour and the relative importance of the adsorption and mass transfer mechanisms occurring in the adsorption systems. The parameters that characterize the intraparticle mass transfer mechanisms can not presently be measured by independent experiments, and, thus, researchers and practitioners are interested in estimating them by matching the dynamic predictions in the time domain of appropriate mathematical models with the dynamic experimental data from the adsorption system of interest. Furthermore, the search for an appro-

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appropriate model to describe satisfactorily the dynamic behaviour of an adsorption system of interest in a column involves the process of model discrimination which requires the estimation of the parameters of a set of possible mathematical models employed in the model discrimination process. Parameter estimation and model discrimination in the time domain can require very time-consuming numerical computations and significant computer memory [14,15].

Liapis et al. [16] presented a novel method for estimating in the Laplace transform domain, the values of the parameters that characterize the film mass transfer and diffusional mechanisms of adsorption into purely diffusive porous adsorbent particles suspended in the liquid phase of a finite bath (batch) system. The parameter estimation method in the Laplace transform domain [16] was found to be significantly simpler, easier to use, and dramatically faster than the conventional parameter-estimation procedure in the time domain.

In this work, the method of Liapis et al. [16] for parameter estimation in the Laplace transform domain is extended to column systems having perfusive and purely diffusive adsorbent particles. Mathematical models describing adsorption in column systems having spherical perfusive and purely diffusive adsorbent particles are presented and solved in the Laplace transform domain for two different column systems: one in which the adsorbent particles packed in the column have a monodisperse porous structure, and one in which the adsorbent particles have a bidisperse porous structure. The parameters that characterize the intraparticle diffusional and convective (fluid flow) mechanisms of the adsorption process are estimated from simulated experimental data in the Laplace transform domain for both column systems, and the dynamic predictions, in the time,  $t$ , domain, of the appropriate model with the estimated parameters are compared with the simulated experimental data in the time,  $t$ , domain.

## 2. Mathematical models

Adsorption is considered to take place from a flowing liquid stream in a fixed bed of spherical adsorbent particles, under isothermal conditions. In the column system with monodisperse adsorbent

particles, the adsorbent particles are considered to be composed of one region in which intraparticle convection (fluid flow) and pore diffusion can occur [3]. In the column system with bidisperse porous adsorbent particles, the adsorbent particles are considered to be composed of two regions: a macroporous region made by macropores [3,5–11] in which intraparticle convection (fluid flow) and pore diffusion can occur, and a microporous [5–10] region made by spherical microparticles (microspheres [5–10]) in which pore diffusion occurs. The model expressions include the intraparticle mass transfer mechanisms of convection and diffusion and the mass transfer step involving the interaction between the adsorbate molecules and the active sites on the surface of the pores of the adsorbent particles. The mechanisms of external film mass transfer around the adsorbent particles and axial dispersion in the column are considered to have negligible contribution [2,17–19] to the overall mass transfer resistance for the systems studied in this work as well as for most practical systems, and they are not included in the model expressions; in future work, the magnitude of the effects of the external film mass transfer and axial dispersion mechanisms for a range of values of the system parameters will be presented.

### 2.1. Column system with adsorbent particles having a monodisperse porous structure

The differential mass balance for the adsorbate in the adsorbent particle is given by

$$\begin{aligned} & \frac{\partial C_p}{\partial t} + v_{pR} \frac{\partial C_p}{\partial R} + v_{p\theta} \left( \frac{1}{R} \right) \frac{\partial C_p}{\partial \theta} + \left( \frac{1}{\epsilon_p} \right) \frac{\partial C_s}{\partial t} \\ & = D_p \left[ \left( \frac{1}{R^2} \right) \frac{\partial}{\partial R} \left( R^2 \frac{\partial C_p}{\partial R} \right) \right. \\ & \quad \left. + \left( \frac{1}{R^2 \sin \theta} \right) \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial C_p}{\partial \theta} \right) \right] \end{aligned} \quad (1)$$

The initial and boundary conditions of Eq. (1) are as follows:

$$\text{at } t = 0, \quad C_p = 0, \quad 0 \leq R \leq R_p \quad (2)$$

$$\text{at } t = 0, \quad C_s = 0, \quad 0 \leq R \leq R_p \quad (3)$$

$$\text{at } R = R_p, \quad C_p = C_d(t, x), \quad t > 0, \quad 0 \leq \theta \leq \pi \quad (4)$$

$$\text{at } R = 0, C_p \text{ is finite, } t > 0, \quad 0 \leq \theta \leq \pi \quad (5)$$

$$\text{at } \theta = 0, \quad \left. \frac{\partial C_p}{\partial \theta} \right|_{\theta=0} = 0, \quad 0 \leq R \leq R_p \quad (6)$$

$$\text{at } \theta = \pi, \quad \left. \frac{\partial C_p}{\partial \theta} \right|_{\theta=\pi} = 0, \quad 0 \leq R \leq R_p \quad (7)$$

In this work, the interaction between the adsorbate molecules and the active sites on the surface of the pores of the adsorbent particle is taken to occur infinitely fast, and, therefore, local equilibrium between the adsorbate in the pore fluid and in the adsorbed phase at each point in the pores is considered to exist. Furthermore, the adsorbate concentration in the pore fluid is considered to be low enough so that the equilibrium adsorption isotherm is taken to be linear and its expression is given by

$$C_s = HC_p \quad (8)$$

The intraparticle velocity components  $v_{pR}$  and  $v_{p\theta}$  in Eq. (1) can be obtained from the following expressions [6,10,20,21]:

$$v_{pR} = FV_f \cos \theta \quad (9)$$

$$v_{p\theta} = -FV_f \sin \theta \quad (10)$$

The parameter  $F$  in Eqs. (9) and (10) may be considered to represent the fraction of the superficial fluid velocity in the column,  $V_f$ , that is flowing through the porous adsorbent particle [21], because the axial component of the intraparticle velocity,  $v_{px}$ , which is parallel to the flowing fluid stream along the axis of the column (see Fig. 1 in [6]), is obtained from the expression  $v_{px} = FV_f$  [6,7,10,21], when  $v_{pR}$  and  $v_{p\theta}$  are given by Eqs. (9) and (10). By using Eqs. (8)–(10) in the Laplace transform of Eq. (1), and introducing the dimensionless variables given by Eqs. (11) and (12)

$$\rho = \frac{R}{R_p} \quad (11)$$

$$\eta = \cos \theta \quad (12)$$

Eq. (1) takes, in the Laplace transform domain, the form given by Eq. (13)

$$\begin{aligned} & A_1 C'_p + \frac{Pe_{\text{intra}}}{2} \left[ \eta \frac{\partial C'_p}{\partial \rho} + \frac{(1-\eta^2)}{\rho} \frac{\partial C'_p}{\partial \eta} \right] \\ &= \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left( \rho^2 \frac{\partial C'_p}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial}{\partial \eta} \left[ (1-\eta^2) \frac{\partial C'_p}{\partial \eta} \right] \end{aligned} \quad (13)$$

where

$$A_1 = \frac{R_p^2 s}{D_p} \left( 1 + \frac{H}{\epsilon_p} \right) \quad (14)$$

and the intraparticle Peclet number,  $Pe_{\text{intra}}$ , is defined [6,7,10] as follows:

$$Pe_{\text{intra}} = \frac{FV_f 2R_p}{D_p} \quad (15)$$

By introducing the following variable transformation [22,23]

$$C'_p = X(s, \rho, \eta) \exp \left( \frac{Pe_{\text{intra}}}{4} \rho \eta \right) \quad (16)$$

Eq. (13) reduces to

$$A_2 X = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left( \rho^2 \frac{\partial X}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial}{\partial \eta} \left[ (1-\eta^2) \frac{\partial X}{\partial \eta} \right] \quad (17)$$

where

$$A_2 = \frac{sR_p^2}{D_p} \left( 1 + \frac{H}{\epsilon_p} \right) + \left( \frac{Pe_{\text{intra}}}{4} \right)^2 \quad (18)$$

and the boundary conditions given by Eqs. (4) and (5) become as follows:

$$\begin{aligned} \text{at } \rho = 1, \quad X &= C'_d \exp \left( -\frac{Pe_{\text{intra}}}{4} \eta \right), \\ -1 &\leq \eta \leq 1 \end{aligned} \quad (19)$$

$$\text{at } \rho = 0, \quad X \text{ is finite, } -1 \leq \eta \leq 1 \quad (20)$$

Solutions of equations with a structure similar to Eq. (17) have been presented [22,23]. Following a similar procedure as in [22,23], the solution of Eq. (17) with boundary conditions given by Eqs. (19) and (20) is found to be

$$X = C'_d \sum_{n=0}^{\infty} a_n P_n(\eta) \sum_{i=0}^{\infty} \frac{A_2^i \rho^{2i+n}}{b_{ni}} \quad (21)$$

where  $P_n(\eta)$  are the Legendre polynomials of first kind and

$$a_n = \frac{2n+1}{2} \frac{\int_{-1}^1 \exp\left(-\frac{Pe_{intra}}{4}\eta\right) P_n(\eta) d\eta}{\sum_{i=0}^{\infty} \frac{A_2^i}{b_{ni}}} \quad (22)$$

$$b_{n0} = 1; \quad b_{ni} = \prod_{j=1}^i 2j(2n+2j+1) \quad \text{for } i \geq 1 \quad (23)$$

Therefore, the solution to Eq. (1) in the Laplace transform domain is given by

$$C'_p = C'_d \exp\left(\frac{Pe_{intra}}{4}\rho\eta\right) \sum_{n=0}^{\infty} a_n P_n(\eta) \sum_{i=0}^{\infty} \frac{A_2^i \rho^{2i+n}}{b_{ni}} \quad (24)$$

The differential mass balance for the adsorbate in the flowing fluid stream in the column is given by

$$\frac{\partial C_d}{\partial t} + \frac{V_f}{\epsilon} \frac{\partial C_d}{\partial x} = -\frac{(1-\epsilon)}{\epsilon} \frac{\partial \bar{C}_p}{\partial t} \quad (25)$$

The average adsorbate concentration in the adsorbent particle,  $\bar{C}_p$ , is given by Eq. (26) as follows:

$$\bar{C}_p = \frac{3}{2R_p^3} \left[ \int_0^{\pi} \int_0^{R_p} \epsilon_p C_p R^2 \sin \theta dR d\theta + \int_0^{\pi} \int_0^{R_p} C_s R^2 \sin \theta dR d\theta \right] \quad (26)$$

The initial and boundary conditions of Eq. (25) are

$$\text{at } t=0, \quad C_d = 0, \quad 0 \leq x \leq L \quad (27)$$

$$\text{at } x=0, \quad C_d = C_{d,in}, \quad t > 0 \quad (28)$$

By using Eqs. (8) and (24) in the Laplace transform of Eq. (26), the following expression for the Laplace transform of  $\bar{C}_p$ , is obtained:

$$\bar{C}'_p = C'_d \frac{3}{2} (H + \epsilon_p) \sum_{n=0}^{\infty} a_n \sum_{i=0}^{\infty} \frac{A_2^i}{b_{ni}} \int_0^1 \int_{-1}^1 \rho^{2i+n+2} \times \exp\left(\frac{Pe_{intra}}{4}\rho\eta\right) P_n(\eta) d\eta dp \quad (29)$$

By employing Eq. (29) in the Laplace transform of Eq. (25), the following expression is obtained

$$\frac{dC'_d}{dx} + A_3 C'_d = 0 \quad (30)$$

where

$$A_3 = \frac{s}{V_f} \left( \epsilon + (1-\epsilon) \frac{3}{2} (H + \epsilon_p) \sum_{n=0}^{\infty} a_n \sum_{i=0}^{\infty} \frac{A_2^i}{b_{ni}} \int_0^1 \int_{-1}^1 \rho^{2i+n+2} \times \exp\left(\frac{Pe_{intra}}{4}\rho\eta\right) P_n(\eta) d\eta dp \right) \quad (31)$$

The boundary condition for Eq. (30) is obtained by taking the Laplace transform of Eq. (28), which gives the following expression:

$$\text{at } x=0, \quad C'_d = \frac{C_{d,in}}{s} \quad (32)$$

The solution to Eq. (30) with the boundary condition given by Eq. (32) is

$$C'_d = \frac{C_{d,in}}{s} \exp(-A_3 x) \quad (33)$$

Eqs. (24) and (33) represent the exact analytical solution in the Laplace transform domain of the problem involving the adsorption of an adsorbate from the flowing liquid stream into perfusive spherical monodisperse porous adsorbent particles packed in a column. If the monodisperse porous adsorbent particles are purely diffusive, then  $v_p = 0$  and this implies that  $F=0$ , and, thus, the analytical solution is obtained from Eqs. (24) and (33) by setting  $Pe_{intra} = 0$ .

## 2.2. Column system with adsorbent particles having a bidisperse porous structure

The differential mass balance for the adsorbate in the microporous region of the adsorbent particle is given by

$$\epsilon_{pm} \frac{\partial C_{pm}}{\partial t} + \left( \frac{1}{1-\epsilon_p} \right) \frac{\partial C_{sm}}{\partial t} = \epsilon_{pm} D_{pm} \left( \frac{\partial^2 C_{pm}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{pm}}{\partial r} \right) \quad (34)$$

and its initial and boundary conditions are as follows:

$$\text{at } t = 0, \quad C_{pm} = 0, \quad 0 \leq r \leq r_m \quad (35)$$

$$\text{at } t = 0, \quad C_{sm} = 0, \quad 0 \leq r \leq r_m \quad (36)$$

$$\text{at } r = r_m, \quad C_{pm} = C_p(t, R, \theta), \quad t > 0 \quad (37)$$

$$\text{at } r = 0, \quad \left. \frac{\partial C_{pm}}{\partial r} \right|_{r=0} = 0, \quad t > 0 \quad (38)$$

Again, local equilibrium between the adsorbate in the pore fluid and in the adsorbed phase at each point in the pores is considered to exist and the adsorbate concentration in the pore fluid is considered to be low enough that the equilibrium adsorption isotherm is taken to be linear and its expression is given by

$$C_{sm} = HC_{pm} \quad (39)$$

With these considerations, Eq. (34) can be written as

$$\frac{\partial C_{pm}}{\partial t} = D_{pm1} \left( \frac{\partial^2 C_{pm}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{pm}}{\partial r} \right) \quad (40)$$

where

$$D_{pm1} = \frac{D_{pm}}{1 + \frac{H}{\epsilon_{pm}(1 - \epsilon_p)}} \quad (41)$$

The solution of Eq. (40) in the Laplace transform domain is given by Eq. (42) as follows:

$$C'_{pm} = C'_p \left( \frac{r_m}{r} \right) \frac{\sinh \left( \sqrt{\frac{s}{D_{pm1}}} r \right)}{\sinh \left( \sqrt{\frac{s}{D_{pm1}}} r_m \right)} \quad (42)$$

The differential mass balance for the adsorbate in the macroporous region of the adsorbent particle is given by

$$\begin{aligned} \frac{\partial C_p}{\partial t} + v_{pR} \frac{\partial C_p}{\partial R} + v_{p\theta} \left( \frac{1}{R} \right) \frac{\partial C_p}{\partial \theta} + \left( \frac{1 - \epsilon_p}{\epsilon_p} \right) \frac{\partial \bar{C}_s}{\partial t} \\ = D_p \left[ \left( \frac{1}{R^2} \right) \frac{\partial}{\partial R} \left( R^2 \frac{\partial C_p}{\partial R} \right) \right. \\ \left. + \left( \frac{1}{R^2 \sin \theta} \right) \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial C_p}{\partial \theta} \right) \right] \quad (43) \end{aligned}$$

The average adsorbate concentration in the microporous region,  $\bar{C}_s$ , is given by Eq. (44)

$$\bar{C}_s = \frac{3}{r_m^3} \left[ \int_0^{r_m} \epsilon_{pm} C_{pm} r^2 dr + \int_0^{r_m} \left( \frac{1}{1 - \epsilon_p} \right) C_{sm} r^2 dr \right] \quad (44)$$

and the initial and boundary conditions of Eq. (43) are given by Eqs. (2) and (4-7). By using Eqs. (39) and (42) in the Laplace transform of Eq. (44), the following expression for the Laplace transform of  $\bar{C}_s$  is obtained:

$$\begin{aligned} \bar{C}'_s = C'_p \left( \frac{3D_{pm1}}{sr_m^2} \right) \left( \frac{H}{1 - \epsilon_p} + \epsilon_{pm} \right) \\ \times \left[ \sqrt{\frac{s}{D_{pm1}}} r_m \coth \left( \sqrt{\frac{s}{D_{pm1}}} r_m \right) - 1 \right] \quad (45) \end{aligned}$$

By using Eq. (45), Eqs. (9) and (10) for the intraparticle velocity components, and the variable transformations given by Eqs. (11), (12) and (16) in the Laplace transform of Eq. (43), the following expression is obtained

$$A_4 X = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left( \rho^2 \frac{\partial X}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial}{\partial \eta} \left[ (1 - \eta^2) \frac{\partial X}{\partial \eta} \right] \quad (46)$$

where

$$\begin{aligned} A_4 = \frac{R_p^2 s}{D_p} + \left( \frac{3R_p^2 D_{pm1}}{\epsilon_p r_m^2 D_p} \right) (H + \epsilon_{pm}(1 \\ - \epsilon_p)) \left[ \sqrt{\frac{s}{D_{pm1}}} r_m \coth \left( \sqrt{\frac{s}{D_{pm1}}} r_m \right) - 1 \right] \\ + \left( \frac{Pe_{intra}}{4} \right)^2 \quad (47) \end{aligned}$$

Eq. (46) has the same form as Eq. (17); hence, the solution for  $C_p$  in the Laplace transform domain is

$$C'_p = C'_d \exp \left( \frac{Pe_{intra}}{4} \rho \eta \right) \sum_{n=0}^{\infty} d_n P_n(\eta) \sum_{i=0}^{\infty} \frac{A_4^i \rho^{2i+n}}{b_{ni}} \quad (48)$$

where

$$d_n = \frac{2n+1}{2} \frac{\int_{-1}^1 \exp \left( -\frac{Pe_{intra}}{4} \eta \right) P_n(\eta) d\eta}{\sum_{i=0}^{\infty} \frac{A_4^i}{b_{ni}}} \quad (49)$$

The differential mass balance for the adsorbate in the flowing fluid stream in the column is given by

$$\frac{\partial C_d}{\partial t} + \frac{V_f}{\epsilon} \frac{\partial C_d}{\partial x} = - \frac{(1 - \epsilon)}{\epsilon} \frac{\partial \bar{C}_{ps}}{\partial t} \quad (50)$$

The average adsorbate concentration in the adsorbent particle  $\bar{C}_{ps}$ , is given by

$$\bar{C}_{ps} = \frac{3}{2R_p^3} \left[ \int_0^{\pi} \int_0^{R_p} \epsilon_p C_p R^2 \sin \theta \, dR \, d\theta + \int_0^{\pi} \int_0^{R_p} (1 - \epsilon_p) \bar{C}_s R^2 \sin \theta \, dR \, d\theta \right] \quad (51)$$

and the initial and boundary conditions of Eq. (50) are given by the expressions in Eqs. (27) and (28). By using Eqs. (45) and (48) in the Laplace transform of Eq. (51), the expression for the Laplace transform of  $\bar{C}_{ps}$  is obtained and given by Eq. (52)

$$\bar{C}'_{ps} = C'_d A_5 \sum_{n=0}^{\infty} d_n \sum_{i=0}^{\infty} \frac{A_4^i}{b_{ni}} \int_0^1 \int_{-1}^1 \rho^{2i-n+2} \times \exp\left(\frac{Pe_{intra}}{4} \rho \eta\right) P_n(\eta) \, d\eta \, d\rho \quad (52)$$

where

$$A_5 = \frac{9}{2} \left( \frac{D_{pm1}}{sr_m^2} \right) (H + \epsilon_{pm}(1 - \epsilon_p)) \times \left[ \sqrt{\frac{s}{D_{pm1}}} r_m \coth\left(\sqrt{\frac{s}{D_{pm1}}} r_m\right) - 1 \right] + \frac{3}{2} \epsilon_p \quad (53)$$

By using Eq. (52) in the Laplace transform of Eq. (50), the expression given by Eq. (54) is obtained

$$\frac{dC'_d}{dx} + A_6 C'_d = 0 \quad (54)$$

where

$$A_6 = \frac{s}{V_f} \left( \epsilon + (1 - \epsilon) A_5 \sum_{n=0}^{\infty} d_n \sum_{i=0}^{\infty} \frac{A_4^i}{b_{ni}} \int_0^1 \int_{-1}^1 \rho^{2i+n+2} \exp\left(\frac{Pe_{intra}}{4} \rho \eta\right) P_n(\eta) \, d\eta \, d\rho \right) \quad (55)$$

The solution to Eq. (54) with the boundary condition given by Eq. (32) is

$$C'_d = \frac{C_{d,in}}{s} \exp(-A_6 x) \quad (56)$$

Eqs. (42), (48) and (56) represent the exact analytical solution in the Laplace transform domain of the problem involving the adsorption of an adsorbate from the flowing liquid stream into spherical perfusive bidisperse porous adsorbent particles packed in a column. If the bidisperse porous adsorbent particles are purely diffusive, then  $v_p = 0$  and this implies that  $F = 0$ , and, thus, the analytical solution is obtained from Eqs. (42), (48) and (56) by setting  $Pe_{intra} = 0$ .

### 3. Proposed mathematical method for parameter estimation in the Laplace transform domain

The prediction of the mathematical model for the breakthrough curve obtained from the exiting stream of a column adsorption system would be represented in the Laplace transform domain by the function

$$f'(s) = \frac{C'_d(s, L)}{C_{d,in}} \quad (57)$$

where  $C'_d(s, L)$  is given by Eq. (33) (with  $x=L$ ) for column systems with perfusive monodisperse porous adsorbent particles, and by Eq. (56) (with  $x=L$ ) for systems with perfusive bidisperse porous adsorbent particles. Eqs. (33) and (56) with  $x=L$  and  $Pe_{intra} = 0$  provide the expressions for  $C'_d(s, L)$  for column systems with monodisperse purely diffusive and bidisperse purely diffusive adsorbent particles, respectively. The function  $f'(s)$  in Eq. (57) is so complex (see Eqs. (33) and (56)) that it can not be inverted analytically to obtain  $f(t)$ , the exact solution in the time domain. However, we could consider that the experimental data of the breakthrough curve of a column adsorption system (the concentration of the adsorbate in the flowing fluid stream at the outlet of the column,  $C_d(t, L)$ , versus time,  $t$ , could be represented by a function

$$g(t) = \frac{C_d(t, L)}{C_{d,in}} \quad (58)$$

for which the Laplace transform,  $g'(s)$ , could be found. The parameters of the adsorption model could then be determined by fitting  $f'(s)$  to  $g'(s)$  over an appropriate range of the values of the Laplace variable  $s$ . Of course, the Laplace transform of the experimental data,  $g'(s)$ , could also be determined directly by the expression in Eq. (59)

$$g'(s) = \int_0^{\infty} \exp(-st) \frac{C_d(t, L)}{C_{d, \text{in}}} dt$$

$$\cong \sum_{j=0}^{\infty} \exp(-st_j) \frac{C_d(t_j, L)}{C_{d, \text{in}}} \Delta t \quad (59)$$

where  $C_d(t_j, L)$  represents the experimental value of  $C_d(t, L)$  at time  $t_j$  and  $\Delta t$  is the time interval between experimental measurements.

Since there is no direct correspondence between a value of  $t$  and a value of  $s$ , an approximate range for the values of  $s$  could be determined by using the following relationships:

$$\lim_{s \rightarrow 0} (sg'(s)) = \lim_{t \rightarrow \infty} g(t) = 1 \quad (60)$$

$$\lim_{s \rightarrow \infty} (sg'(s)) = \lim_{t \rightarrow 0} g(t) = 0 \quad (61)$$

A lower value of  $s$ ,  $s_l$ , could be determined by letting

$$s_l g'(s_l) = 0.9999 \quad (62)$$

Likewise, an upper value of  $s$ ,  $s_u$ , could be determined by letting

$$s_u g'(s_u) = 0.0001 \quad (63)$$

The values of 0.9999 and 0.0001 in Eqs. (62) and (63) are chosen to give finite values of  $s_l$  and  $s_u$ , since, in the Laplace transform domain, the limits in Eqs. (60) and (61) are approached asymptotically; values other than 0.9999 and 0.0001 that are close to the limits of one and zero could also be used in Eqs. (62) and (63). After the appropriate range of the values of  $s$  has been determined through the use of Eqs. (62) and (63), the values of the parameters of the mathematical model could be determined directly in the Laplace transform domain by fitting  $f'(s)$  to a dataset generated from  $g'(s)$  at a sufficient number of values of  $s$  in the range  $s_l \leq s \leq s_u$ . The function  $g'(s)$  that is used in Eqs. (62) and (63) to establish the range of the values of  $s$  and to generate the dataset in

that range, could be the Laplace transform of an analytical function that represents the experimental data, or it could be determined directly by Eq. (59).

#### 4. Results and discussion

Simulated experimental data of  $C_d(t, L)$  versus time,  $t$ , for adsorption in column systems with monodisperse porous adsorbent particles were obtained from the numerical solution of the mathematical model described by Eqs. (1)–(8) and (25)–(28), and simulated experimental data of  $C_d(t, L)$  versus time,  $t$ , for adsorption in column systems with bidisperse porous adsorbent particles were obtained from the numerical solution of the mathematical model described by Eqs. (2), (4)–(7), (27), (28), (34)–(39), (43), (44), (50) and (51). The numerical solution procedure that was employed has been presented elsewhere [6,24]. The values of the parameters used to generate the simulated experimental data are presented in Table 1; these parameter values are for systems involving the adsorption of bovine serum albumin (BSA) into anion-exchange porous adsorbent particles. Also listed in Table 1 for each case is the value of the intraparticle Peclet number,  $Pe_{\text{intra}}$ , calculated from Eq. (15). Cases 1, 2 and 3 in Table 1 are systems with monodisperse porous particles that differ only in the amount of intraparticle fluid flow. Case 1 has a relatively large value of  $F$  (and, therefore,  $Pe_{\text{intra}}$ ), and, thus, the perfusive adsorbent particles in case 1 have a relatively large amount of intraparticle fluid flow, whereas case 2, with relatively small values of  $F$  and  $Pe_{\text{intra}}$ , is a perfusive system in which there is very little intraparticle fluid flow. Case 3 has  $F = Pe_{\text{intra}} = 0$  and the adsorbent particles in case 3 are purely diffusive. Likewise, cases 4, 5 and 6 in Table 1 are systems with bidisperse porous particles that differ only in the amount of intraparticle fluid flow. Case 4 has relatively large values of  $F$  and  $Pe_{\text{intra}}$ , case 5 has relatively small values of  $F$  and  $Pe_{\text{intra}}$ , and case 6 has  $F = Pe_{\text{intra}} = 0$ ; the adsorbent particles in case 6 are purely diffusive.

The form of the function  $g(t)$  that was used to represent the simulated experimental data in the time,  $t$ , domain was one composed of segments of polynomials, as follows:

Table 1

Values of the parameters of the adsorption models that were used to generate the simulated experimental data

Parameter	Case					
	1	2	3	4	5	6
$D_p$ (m <sup>2</sup> /s)	$1.622 \times 10^{-11}$	$1.622 \times 10^{-11}$	$1.622 \times 10^{-11}$	$1.327 \times 10^{-11}$	$1.327 \times 10^{-11}$	$1.327 \times 10^{-11}$
$D_{pm}$ (m <sup>2</sup> /s)	n/a	n/a	n/a	$7.08 \times 10^{-12}$	$7.08 \times 10^{-12}$	$7.08 \times 10^{-12}$
$F$	$8.00 \times 10^{-3}$	$1.00 \times 10^{-3}$	0	$7.236 \times 10^{-3}$	$1.00 \times 10^{-4}$	0
$H$	628.4	628.4	628.4	628.4	628.4	628.4
$L$ (m)	0.01	0.01	0.01	0.01	0.01	0.01
$r_m$ (m)	n/a	n/a	n/a	$3.5 \times 10^{-7}$	$3.5 \times 10^{-7}$	$3.5 \times 10^{-7}$
$R_p$ (m)	$7.5 \times 10^{-6}$	$7.5 \times 10^{-6}$	$7.5 \times 10^{-6}$	$7.5 \times 10^{-6}$	$7.5 \times 10^{-6}$	$7.5 \times 10^{-6}$
$V_f$ (m/s)	$2.778 \times 10^{-3}$	$2.778 \times 10^{-3}$	$2.778 \times 10^{-3}$	$2.778 \times 10^{-3}$	$2.778 \times 10^{-3}$	$2.778 \times 10^{-3}$
$\epsilon$	0.35	0.35	0.35	0.35	0.35	0.35
$\epsilon_p$	0.55	0.55	0.55	0.45	0.45	0.45
$\epsilon_{pm}$	n/a	n/a	n/a	0.50	0.50	0.50
$Pe_{intra}$	22.7	0.3	0	20.6	0.3	0

n/a: not applicable.

$$g(t) = \begin{cases} 0 & \text{for } t \leq t_0 \\ \sum_{j=0}^{n_i} a_{ij} t^j & \text{for } t_{i-1} < t \leq t_i, \quad i = 1, 2, \dots, m \\ 1 & \text{for } t_m < t \end{cases} \quad (64)$$

The six sets of simulated experimental data considered in this work were each fitted to Eq. (64) with  $m=4$  and  $n_1=n_2=n_3=n_4=3$ . The values of  $t_i$  that were used are presented in Table 2. Also listed in Table 2 are the values of the coefficients  $a_{ij}$  that provide the best fit with the simulated experimental data.

The Laplace transform of the function  $g(t)$  in Eq. (64) is given by the following expression:

$$g'(s) = \frac{e^{-st_m}}{s} - \sum_{i=1}^m \left[ a_{i0} \frac{e^{-st}}{s} + \sum_{j=1}^{n_i} a_{ij} e^{-st} \left( \frac{t^j}{s} + j! \sum_{k=1}^j \frac{t^{j-k}}{(j-k)! s^{k+1}} \right) \right]_{t=t_{i-1}}^{t=t_i} \quad (65)$$

The expression for  $g'(s)$  in Eq. (65) and the values of

$t_i$  and  $a_{ij}$  in Table 2 were used in Eqs. (61) and (62) to obtain the values of  $s_1$  and  $s_u$  presented in Table 3 and to generate the values of  $g'(s)$  at 451 values of  $s$ , evenly spaced on a logarithmic scale, in the range  $s_1 \leq s \leq s_u$  for each of the six cases. The parameters of the model that characterize the mass transfer mechanisms were estimated by fitting the function  $f'(s)$  in Eq. (57) to these datasets using the ODRPACK [25] software package. For cases 1 and 2, systems with perfusive monodisperse porous adsorbent particles, the parameters that were estimated are the effective pore diffusion coefficient,  $D_p$ , and the parameter  $F$ . For case 3, a system with purely diffusive monodisperse porous adsorbent particles, only the effective pore diffusion coefficient,  $D_p$ , was estimated. For cases 4 and 5, systems with perfusive bidisperse porous adsorbent particles, the parameters that were estimated are the effective pore diffusion coefficient in the micropores,  $D_{pm}$ , the effective pore diffusion coefficient in the macropores,  $D_p$ , and the parameter  $F$ . For case 6, a system with purely diffusive bidisperse porous adsorbent particles, the effective pore diffusion coefficient in the micropores,  $D_{pm}$ , and the effective pore diffusion coefficient in the macropores,  $D_p$ , were estimated.

The values of the parameters that were estimated are presented in Table 4 for each of the six cases of simulated experimental data. The values of the estimated parameters,  $D_p$  and  $F$ , for case 1 are very



Table 2

Values of the parameters of the function  $g(t)$  in Eq. (64) used to represent the simulated experimental data

Parameter	Case					
	1	2	3	4	5	6
$a_{10}$	$4.166 \times 10^{-4}$	$1.168 \times 10^{-3}$	$1.168 \times 10^{-3}$	$1.314 \times 10^{-4}$	$1.943 \times 10^{-3}$	$1.944 \times 10^{-3}$
$a_{11}$	$-7.175 \times 10^{-4}$	$-2.156 \times 10^{-3}$	$-2.156 \times 10^{-3}$	$-9.086 \times 10^{-4}$	$-8.375 \times 10^{-3}$	$-8.377 \times 10^{-3}$
$a_{12}$	$6.534 \times 10^{-5}$	$2.248 \times 10^{-4}$	$2.248 \times 10^{-4}$	$1.623 \times 10^{-4}$	$3.582 \times 10^{-3}$	$3.583 \times 10^{-3}$
$a_{13}$	$1.073 \times 10^{-4}$	$1.404 \times 10^{-4}$	$1.404 \times 10^{-4}$	$2.442 \times 10^{-4}$	$-5.597 \times 10^{-5}$	$-5.602 \times 10^{-5}$
$a_{20}$	$6.330 \times 10^{-2}$	$-1.082 \times 10^{-1}$	$-1.083 \times 10^{-1}$	$-4.072 \times 10^{-2}$	$-1.808 \times 10^{-1}$	$-1.809 \times 10^{-1}$
$a_{21}$	$-2.249 \times 10^{-2}$	$1.291 \times 10^{-2}$	$1.292 \times 10^{-2}$	$9.436 \times 10^{-3}$	$4.225 \times 10^{-2}$	$4.226 \times 10^{-2}$
$a_{22}$	$2.922 \times 10^{-3}$	$1.439 \times 10^{-3}$	$1.438 \times 10^{-3}$	$1.033 \times 10^{-3}$	$-3.019 \times 10^{-4}$	$-3.025 \times 10^{-4}$
$a_{23}$	$-4.876 \times 10^{-5}$	$-3.298 \times 10^{-5}$	$-3.298 \times 10^{-5}$	$-1.684 \times 10^{-5}$	$-4.448 \times 10^{-6}$	$-4.441 \times 10^{-6}$
$a_{30}$	$-9.240 \times 10^{-1}$	$-6.404 \times 10^{-1}$	$-6.401 \times 10^{-1}$	$-3.890 \times 10^{-1}$	$-2.711 \times 10^{-1}$	$-2.712 \times 10^{-1}$
$a_{31}$	$8.971 \times 10^{-2}$	$7.896 \times 10^{-2}$	$7.894 \times 10^{-2}$	$5.012 \times 10^{-2}$	$5.438 \times 10^{-2}$	$5.439 \times 10^{-2}$
$a_{32}$	$-1.375 \times 10^{-3}$	$-1.409 \times 10^{-3}$	$-1.409 \times 10^{-3}$	$-4.658 \times 10^{-4}$	$-8.925 \times 10^{-4}$	$-8.929 \times 10^{-4}$
$a_{33}$	$6.795 \times 10^{-6}$	$9.304 \times 10^{-6}$	$9.299 \times 10^{-6}$	$-7.430 \times 10^{-8}$	$5.538 \times 10^{-6}$	$5.541 \times 10^{-6}$
$a_{40}$	$-4.031 \times 10^{-1}$	$2.270 \times 10^{-1}$	$2.269 \times 10^{-1}$	$-1.868 \times 10^{-1}$	$4.279 \times 10^{-1}$	$4.281 \times 10^{-1}$
$a_{41}$	$6.204 \times 10^{-2}$	$2.631 \times 10^{-2}$	$2.631 \times 10^{-2}$	$4.627 \times 10^{-2}$	$1.585 \times 10^{-2}$	$1.584 \times 10^{-2}$
$a_{42}$	$-9.189 \times 10^{-4}$	$-3.003 \times 10^{-4}$	$-3.003 \times 10^{-4}$	$-6.043 \times 10^{-4}$	$-1.474 \times 10^{-4}$	$-1.473 \times 10^{-4}$
$a_{43}$	$4.548 \times 10^{-6}$	$1.146 \times 10^{-6}$	$1.146 \times 10^{-6}$	$2.636 \times 10^{-6}$	$4.579 \times 10^{-7}$	$4.574 \times 10^{-7}$
$t_0$	2.604	2.810	2.810	1.533	2.160	2.160
$t_1$	8.000	8.000	8.000	5.000	8.000	8.000
$t_2$	25.00	25.00	25.00	20.00	25.00	25.00
$t_3$	40.00	45.00	45.00	40.00	50.00	50.00
$t_4$	74.80	100.2	100.2	86.64	125.1	125.1

Table 3

Values of the lower and upper limits of the Laplace transform variable,  $s$ , determined by Eqs. (62) and (63)

	Case					
	1	2	3	4	5	6
$s_l$	$1.1 \times 10^{-5}$	$1.0 \times 10^{-5}$	$1.1 \times 10^{-5}$	$1.1 \times 10^{-5}$	$6.0 \times 10^{-6}$	$6.0 \times 10^{-6}$
$s_u$	1.2	1.3	1.3	1.8	1.8	1.8

Table 4

Values of the parameters estimated in the Laplace transform domain

Parameter	Case					
	1	2	3	4	5	6
$D_p$ ( $m^2/s$ )	$1.615 \times 10^{-11}$	$1.614 \times 10^{-11}$	$1.621 \times 10^{-11}$	$1.345 \times 10^{-11}$	$1.322 \times 10^{-11}$	$1.336 \times 10^{-11}$
$D_{pm}$ ( $m^2/s$ )	n/a	n/a	n/a	$4.70 \times 10^{-12}$	$7.72 \times 10^{-12}$	$5.84 \times 10^{-12}$
$F$	$8.03 \times 10^{-3}$	$6.54 \times 10^{-4}$	n/a	$7.29 \times 10^{-3}$	$7.51 \times 10^{-4}$	n/a

n/a: not applicable

nearly the same (less than 0.5% difference) as the values that were used to generate the simulated experimental data of case 1. The value of the intraparticle Peclet number for case 1, using the estimated value of  $F = 8.03 \times 10^{-3}$ , is  $Pe_{\text{intra}} = 22.8$ , nearly the same as the value of  $Pe_{\text{intra}} = 22.7$  in Table 1. The large value of  $Pe_{\text{intra}}$  for case 1 indicates that intraparticle fluid flow contributes significantly to the intraparticle mass transfer [6,7].

For case 2, there is less than 0.5% difference between the estimated value of  $D_p$  and the value used to generate the simulated experimental data, whereas the estimated value of  $F$  is more than 500% larger than the value of  $F$  used to generate the data. Figs. 1 and 2 compare the prediction of the mathematical model for column systems with monodisperse porous adsorbent particles using the estimated parameter values of  $D_p = 1.614 \times 10^{-11} \text{ m}^2/\text{s}$  and  $F = 6.54 \times 10^{-4}$  from Table 4 with the simulated experimental data of case 2, in the Laplace transform domain and in the time domain, respectively. The results in Figs. 1 and 2 clearly show that the solution of the mathematical model using the estimated parameter values describes the simulated experimental data very well, even though the estimated value of  $F$  is different from that used to generate the data. The value of the intraparticle Peclet number for case 2, using the value of  $F = 1.00 \times 10^{-4}$  that was used to

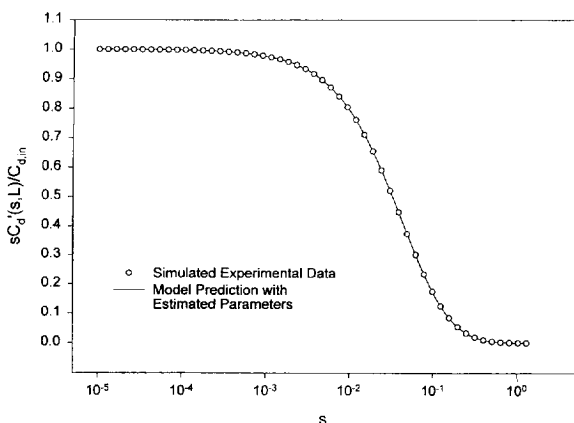


Fig. 1. Comparison in the Laplace transform domain of the simulated experimental data for case 2 with the prediction of the model for systems having monodisperse porous adsorbent particles (Eq. (33)) using the estimated parameter values of  $D_p = 1.614 \times 10^{-11} \text{ m}^2/\text{s}$  and  $F = 6.54 \times 10^{-4}$  from Table 4.

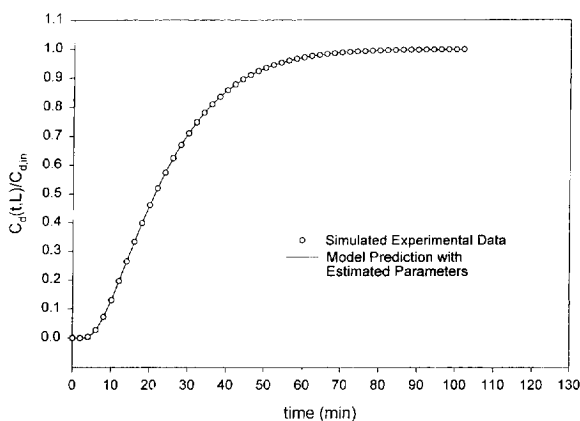


Fig. 2. Comparison in the time domain of the simulated experimental data for case 2 with the prediction of the model for systems having monodisperse porous adsorbent particles (numerical solution of Eqs. (1)–(8) and (25)–(28)) using the values of the parameters estimated in the Laplace transform domain ( $D_p = 1.614 \times 10^{-11} \text{ m}^2/\text{s}$  and  $F = 6.54 \times 10^{-4}$  from Table 4).

generate the simulated experimental data, is  $Pe_{\text{intra}} = 0.3$ , while a value of  $Pe_{\text{intra}} = 1.7$  would be obtained using the estimated value of  $F = 6.54 \times 10^{-4}$ . The results of earlier work [6,7] have indicated that when the value of  $Pe_{\text{intra}}$  is this small, intraparticle fluid flow does not significantly affect the mass transfer resistance in perfusive adsorbent particles (the adsorbent particles behave almost as purely diffusive adsorbent particles), and, therefore, the performance of column adsorption systems with perfusive adsorbent particles is insensitive to the value of  $F$  when  $Pe_{\text{intra}}$  is small.

The estimated value of  $D_p$  in Table 4 for case 3, a system having purely diffusive monodisperse porous adsorbent particles, is almost identical to the value of  $D_p$  that was used to generate the simulated experimental data of case 3.

There is less than 2% difference between the estimated values of  $D_p$  and  $F$  in Table 4 and the values of  $D_p$  and  $F$  that were used to generate the simulated experimental data of case 4, whereas the difference between the estimated value of  $D_{\text{pm}}$  and the value that was used to generate the data is 34%. The value of the intraparticle Peclet number for case 4, using the estimated value of  $F = 7.29 \times 10^{-3}$ , is  $Pe_{\text{intra}} = 20.8$ , nearly the same as the value of  $Pe_{\text{intra}} = 20.6$  in Table 1. The large value of  $Pe_{\text{intra}}$  for case 4 indicates that intraparticle fluid flow

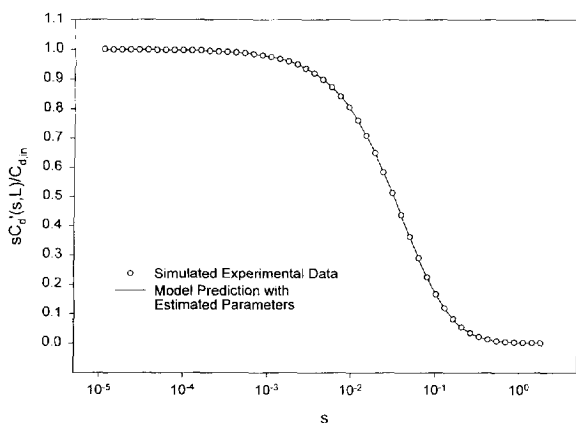


Fig. 3. Comparison in the Laplace transform domain of the simulated experimental data for case 4 with the prediction of the model for systems having bidisperse porous adsorbent particles (Eq. (56)) using the estimated parameter values of  $D_p = 1.345 \times 10^{-11} \text{ m}^2/\text{s}$ ,  $D_{pm} = 4.70 \times 10^{-12} \text{ m}^2/\text{s}$  and  $F = 7.29 \times 10^{-3}$  from Table 4.

contributes significantly to the intraparticle mass transfer [6,7]. Figs. 3 and 4 compare the prediction of the mathematical model for column systems with bidisperse porous adsorbent particles using the estimated parameter values of  $D_p = 1.345 \times 10^{-11} \text{ m}^2/\text{s}$ ,  $D_{pm} = 4.70 \times 10^{-12} \text{ m}^2/\text{s}$ , and  $F = 7.29 \times 10^{-3}$  from Table 4 with the simulated experimental data of case

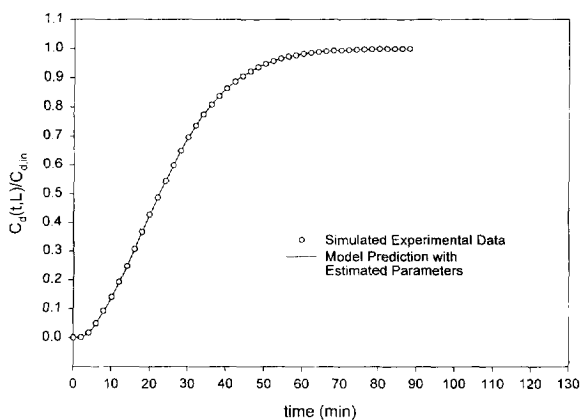


Fig. 4. Comparison in the time domain of the simulated experimental data for case 4 with the prediction of the model for systems having bidisperse porous adsorbent particles (numerical solution of Eqs. (2), (4)–(7), (27), (28), (34)–(39), (43), (44), (50), (51)) using the values of the parameters estimated in the Laplace transform domain ( $D_p = 1.345 \times 10^{-11} \text{ m}^2/\text{s}$ ,  $D_{pm} = 4.70 \times 10^{-12} \text{ m}^2/\text{s}$  and  $F = 7.29 \times 10^{-3}$  from Table 4).

4 in the Laplace transform domain and in the time domain, respectively. Even though the estimated value of  $D_{pm}$  is different from the value that was used to generate the simulated experimental data, the solution of the mathematical model using the estimated parameter values describes the simulated experimental data very well. The results of earlier work [10] have indicated that the mass transfer resistance in the microporous region of bidisperse porous adsorbent particles is smaller than the mass transfer resistance in the macroporous region when the size of the microparticle is significantly smaller than the size of the adsorbent particle, which implies that in such cases the performance of column adsorption systems with bidisperse porous adsorbent particles is relatively insensitive to the value of  $D_{pm}$ .

For case 5, while the estimated value of  $D_p$  in Table 4 is very nearly the same as the value of  $D_p$  that was used to generate the simulated experimental data, the estimated value of  $D_{pm}$  is 9% larger and the estimated value of  $F$  is 650% larger than the values used to generate the data. The value of  $Pe_{intra}$  for the simulated experimental data of case 5, using the value of  $F = 1.00 \times 10^{-4}$ , is  $Pe_{intra} = 0.3$ , whereas a value of  $Pe_{intra} = 2.4$  would be obtained using the estimated value of  $F = 7.51 \times 10^{-4}$  from Table 4. These values of  $Pe_{intra}$  are small enough so that the performance of the column system is not sensitive to the value of  $F$ , for the reason presented in the discussion of case 2. Also, the system performance is relatively insensitive to the value of  $D_{pm}$ , for the reason presented in the discussion of case 4, so that the mathematical model for column systems with bidisperse porous adsorbent particles using the estimated parameter values in Table 4 describes very well the simulated experimental data of case 5. This is shown by the results in Figs. 5 and 6, which compare the prediction of the mathematical model for column systems with bidisperse porous adsorbent particles using the estimated parameter values of  $D_p = 1.322 \times 10^{-11} \text{ m}^2/\text{s}$ ,  $D_{pm} = 7.72 \times 10^{-12} \text{ m}^2/\text{s}$ , and  $F = 7.51 \times 10^{-4}$  from Table 4 with the simulated experimental data of case 5 in the Laplace transform domain and in the time domain, respectively.

The estimated value of  $D_p$  in Table 4 for case 6, a system having purely diffusive bidisperse porous adsorbent particles, is less than 1% different than the value of  $D_p$  used to generate the simulated ex-

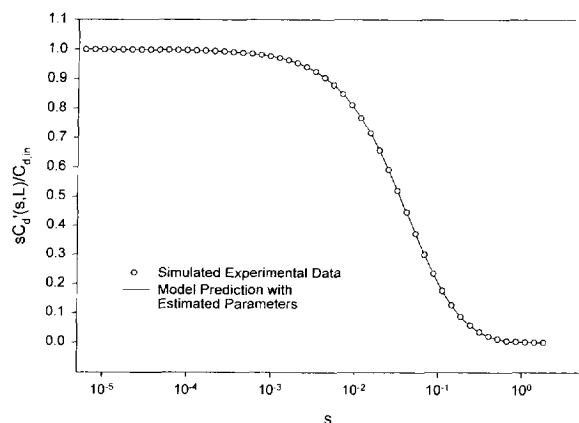


Fig. 5. Comparison in the Laplace transform domain of the simulated experimental data for case 5 with the prediction of the model for systems having bidisperse porous adsorbent particles (Eq. (56)) using the estimated parameter values of  $D_p = 1.322 \times 10^{-11} \text{ m}^2/\text{s}$ ,  $D_{pm} = 7.72 \times 10^{-12} \text{ m}^2/\text{s}$  and  $F = 7.51 \times 10^{-4}$  from Table 4.

perimental data; however, there is an 18% difference between the estimated value of  $D_{pm}$  and the value used to generate the data. The performance of the adsorption system of case 6, like those of cases 4 and 5, is relatively insensitive to the value of  $D_{pm}$  and the results in Figs. 7 and 8, which compare the prediction of the mathematical model for column systems with bidisperse porous adsorbent particles using the

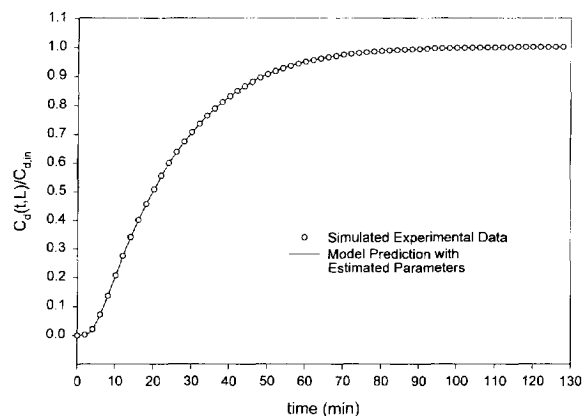


Fig. 6. Comparison in the time domain of the simulated experimental data for case 5 with the prediction of the model for systems having bidisperse porous adsorbent particles (numerical solution of Eqs. (2), (4)–(7), (27), (28), (34)–(39), (43), (44), (50) and (51)) using the values of the parameters estimated in the Laplace transform domain ( $D_p = 1.322 \times 10^{-11} \text{ m}^2/\text{s}$ ,  $D_{pm} = 7.72 \times 10^{-12} \text{ m}^2/\text{s}$  and  $F = 7.51 \times 10^{-4}$  from Table 4).

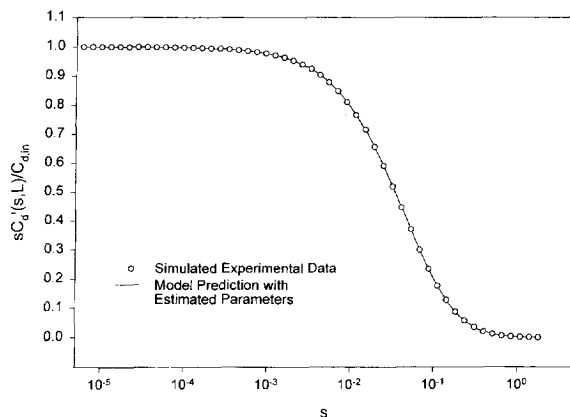


Fig. 7. Comparison in the Laplace transform domain of the simulated experimental data for case 6 with the prediction of the model for systems having bidisperse porous adsorbent particles (Eq. (56)) using the estimated parameter values of  $D_p = 1.336 \times 10^{-11} \text{ m}^2/\text{s}$  and  $D_{pm} = 5.84 \times 10^{-12} \text{ m}^2/\text{s}$  from Table 4.

estimated parameter values of  $D_p = 1.336 \times 10^{-11} \text{ m}^2/\text{s}$  and  $D_{pm} = 5.84 \times 10^{-12} \text{ m}^2/\text{s}$  from Table 4 with the simulated experimental data of case 6 in the Laplace transform domain and in the time domain, respectively, showing that the mathematical model using the estimated parameter values describes very well the simulated experimental data.

In all of the cases considered in this work, systems

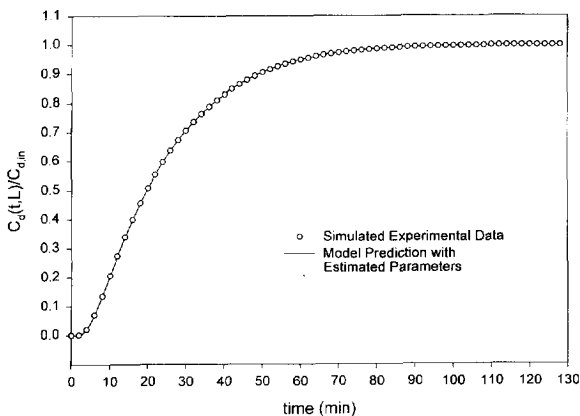


Fig. 8. Comparison in the time domain of the simulated experimental data for case 6 with the prediction of the model for systems having bidisperse porous adsorbent particles (numerical solution of Eqs. (2), (4)–(7), (27), (28), (34)–(39), (43), (44), (50) and (51)) using the values of the parameters estimated in the Laplace transform domain ( $D_p = 1.336 \times 10^{-11} \text{ m}^2/\text{s}$  and  $D_{pm} = 5.84 \times 10^{-12} \text{ m}^2/\text{s}$  from Table 4).

with perfusive and purely diffusive adsorbent particles with a monodisperse and with a bidisperse porous structure, the value of the parameter  $D_p$  that was estimated in the Laplace transform domain is nearly identical to the value of  $D_p$  that was used to generate the simulated experimental data. The estimated value of the parameter  $F$  is almost the same as the value of  $F$  that was used to generate the simulated experimental data for systems with perfusive adsorbent particles with a monodisperse and with a bidisperse porous structure for which the value of  $Pe_{intra}$  is relatively large. For systems having perfusive adsorbent particles for which the value of  $Pe_{intra}$  is small, the value of  $F$  is not estimated accurately; however, the estimated value of  $F$  does result in a value of  $Pe_{intra}$  small enough that intraparticle fluid flow does not affect the performance of the adsorption system. For all systems with bidisperse porous adsorbent particles, the difference between the estimated value of the parameter  $D_{pm}$ , which represents the effective pore diffusion coefficient of adsorbate in the micropores, and the value of  $D_{pm}$  that was used to generate the simulated experimental data is substantially larger than the corresponding difference for the parameter  $D_p$ ; the difference between the value of  $D_{pm}$  used to generate the simulated experimental data and that estimated in the Laplace transform domain has an insignificant effect on the dynamic performance of the adsorption system because the performance of column systems with bidisperse porous adsorbent particles in which the size of the microparticle is significantly smaller than the size of the adsorbent particle is relatively insensitive to the value of  $D_{pm}$ .

The parameters that can be estimated most accurately ( $D_p$  in all systems and  $F$  in systems with perfusive particles for which the value of  $Pe_{intra}$  is large) are those that characterize the mass transfer mechanisms that have the greatest effect on the overall performance of the adsorption system. The parameters that characterize mass transfer mechanisms that have little effect on system performance ( $D_{pm}$  in systems with bidisperse porous particles and  $F$  in systems with perfusive particles for which the value of  $Pe_{intra}$  is small) were not estimated as accurately. The use of multiresponse data (multiple breakthrough curves at different values of the superficial velocity,  $V_r$ , in the column) could possibly

improve the accuracy of the estimated values of the parameters for which the adsorption system is relatively insensitive. It should be noted that the results presented in this work indicate that when the dynamic behaviour of an adsorption system that employs the bidisperse model for the porous particles becomes insensitive to variations in the value of the parameter  $D_{pm}$ , this could suggest that the mass transfer resistance in the microspheres does not contribute significantly to the overall mass transfer resistance in the porous adsorbent particles, and, therefore, a monodisperse model for the porous adsorbent particles could also be employed to describe the dynamic behaviour of the adsorption system. Furthermore, if the dynamic behaviour of an adsorption system employing either a monodisperse or a bidisperse model for the porous adsorbent particles becomes insensitive to variations in the value of  $F$ , this could suggest that the value of  $F$  is low enough that the perfusive porous adsorbent particles behave almost as purely diffusive adsorbent particles.

## 5. Conclusions and remarks

Mathematical models describing adsorption in column systems having spherical perfusive or purely diffusive adsorbent particles with a monodisperse porous structure or with a bidisperse porous structure were presented and solved in the Laplace transform domain. Then a novel mathematical method was proposed and used to estimate in the Laplace transform domain the values of the parameters that characterize the mechanisms of intraparticle diffusion and convection. The parameter estimation method in the Laplace transform domain presented in this work is significantly simpler, easier to use and dramatically faster than the conventional parameter estimation procedure in the time domain, which requires the repeated numerical solution of the partial differential equations that describe the dynamic behaviour of the adsorption of an adsorbate in a column.

If the equilibrium adsorption isotherm is nonlinear for a certain practical range of values of the concentration of the adsorbate, and if the values of the parameters  $D_p$ ,  $D_{pm}$  and  $F$  that characterize the

mechanisms of intraparticle diffusion and convection are independent of the concentration of the adsorbate (for many systems of practical interest, the values of  $D_p$ ,  $D_{pm}$  and  $F$  are independent of the concentration of the adsorbate), then adsorption experiments could be performed in the range of values of the concentration of the adsorbate where the equilibrium isotherm is linear and the values of the parameters  $D_p$ ,  $D_{pm}$  and  $F$  could be efficiently determined in the Laplace transform domain. These values of  $D_p$ ,  $D_{pm}$  and  $F$  could then be used in the mathematical models of Liapis et al. [6], Heeter and Liapis [7] and Heeter [26] that consider adsorption systems having nonlinear equilibrium isotherms, and the numerical solution of those models [6,7,26] could describe the dynamic behaviour of nonlinear adsorption systems in a column; the mode of operation could be fixed-bed operation in a column [6,7,26] or periodic countercurrent column operation [7,26]. Furthermore, since the value(s) of the parameter(s) that characterize(s) the diffusional mass transfer mechanism(s) in the porous adsorbent particles is independent of the mode of operation, then the value(s) of the effective pore diffusion coefficient(s) determined by the mathematical method presented in this work could be used to describe the diffusional mass transfer rate of the adsorbate in operational modes other (finite bath (batch) operation, periodic countercurrent column operation, fluidized bed operation) than fixed-bed column operation.

## 6. Symbols

$a_n$	parameter defined by Eq. (22) (dimensionless)		fluid stream of the column ( $\text{kg}/\text{m}^3$ of bulk fluid)
$A_1$	parameter defined by Eq. (14) (dimensionless)	$C_{d,in}$	concentration of adsorbate at $x=0$ ( $\text{kg}/\text{m}^3$ of bulk fluid)
$A_2$	parameter defined by Eq. (18) (dimensionless)	$C_p$	concentration of adsorbate in the fluid of the pores of adsorbent particles with a monodisperse porous structure or in the fluid of the macropores of adsorbent particles with a bidisperse porous structure ( $\text{kg}/\text{m}^3$ of pore volume)
$A_3$	parameter defined by Eq. (31) ( $\text{m}^{-1}$ )	$\bar{C}_p$	average concentration of adsorbate in an adsorbent particle with a monodisperse porous structure given by Eq. (26) ( $\text{kg}/\text{m}^3$ of adsorbent particle)
$A_4$	parameter defined by Eq. (47) (dimensionless)	$C_{pm}$	concentration of adsorbate in the fluid of the micropores ( $\text{kg}/\text{m}^3$ of micropore volume)
$A_5$	parameter defined by Eq. (53) (dimensionless)	$\bar{C}_{ps}$	average concentration of adsorbate in an adsorbent particle with a bidisperse porous structure given by Eq. (51) ( $\text{kg}/\text{m}^3$ of adsorbent particle)
$A_6$	parameter defined by Eq. (55) ( $\text{m}^{-1}$ )	$C_s$	concentration of adsorbate in the adsorbed phase in an adsorbent particle with a monodisperse porous structure ( $\text{kg}/\text{m}^3$ of adsorbent particle)
$b_{ni}$	parameter defined by Eq. (23) (dimensionless)	$\bar{C}_s$	average concentration of adsorbate in the microparticles given by Eq. (44) ( $\text{kg}/\text{m}^3$ of microparticle)
$C_d$	concentration of adsorbate in the flowing	$C_{sm}$	concentration of adsorbate in the adsorbed phase of the microparticles ( $\text{kg}/\text{m}^3$ of adsorbent particle)
		$d_n$	parameter defined by Eq. (49) (dimensionless)
		$D_p$	effective pore diffusion coefficient of adsorbate in the pores of an adsorbent particle with a monodisperse porous structure or in the macropores of an adsorbent particle with a bidisperse porous structure ( $\text{m}^2/\text{s}$ )
		$D_{pm}$	effective pore diffusion coefficient of adsorbate in the micropores ( $\text{m}^2/\text{s}$ )
		$D_{pm1}$	parameter defined by Eq. (41) ( $\text{m}^2/\text{s}$ )
		$f(t)$	breakthrough curve predicted by model (dimensionless)
		$F$	parameter in Eqs. (9) and (10) (dimensionless)
		$g(t)$	breakthrough curve from experimental data (dimensionless)
		$H$	equilibrium adsorption constant for linear isotherm (dimensionless)

$L$	length of column (m)
$Pe_{\text{intra}}$	intraparticle Peclet number (dimensionless)
$P_n$	Legendre polynomials of first kind
$r$	radial distance in microparticle (m)
$r_m$	radius of microparticle (m)
$R$	radial distance in adsorbent particle (m)
$R_p$	radius of adsorbent particle (m)
$s$	Laplace variable
$s_l$	lower value of Laplace variable
$s_u$	upper value of Laplace variable
$t$	time (s)
$v_p$	intraparticle velocity vector (m/s)
$v_{pR}$	intraparticle velocity component along the $R$ direction (m/s)
$v_{p\theta}$	intraparticle velocity component along the $\theta$ direction (m/s)
$v_{px}$	axial component of the intraparticle velocity (m/s)
$V_f$	column fluid superficial velocity (m/s)
$x$	axial distance in column (m)
$X$	variable defined by Eq. (16) ( $\text{kg}/\text{m}^3$ )

## 7. Greek letters

$\epsilon$	void fraction of column
$\epsilon_p$	void fraction of adsorbent particles with a monodisperse porous structure or macropore void fraction of adsorbent particles with a bidisperse porous structure
$\epsilon_{pm}$	micropore void fraction
$\eta$	cosine of polar coordinate angle (dimensionless)
$\theta$	polar coordinate angle (radians)
$\rho$	dimensionless radial distance in adsorbent particle

## 8. Superscript

variable in the Laplace transform domain

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## References

- [1] B.H. Arve and A.I. Liapis, *Biotechnol. Bioeng.*, 30 (1987) 638.
- [2] B.H. Arve and A.I. Liapis, *Biotechnol. Bioeng.*, 32 (1988) 616.
- [3] A.I. Liapis and M.A. McCoy, *J. Chromatogr.*, 599 (1992) 87.
- [4] M.A. McCoy, A.I. Liapis and K.K. Unger, *J. Chromatogr.*, 644 (1993) 1.
- [5] A.I. Liapis and M.A. McCoy, *J. Chromatogr. A*, 660 (1994) 85.
- [6] A.I. Liapis, Y. Xu, O.K. Crosser and A. Tongta, *J. Chromatogr. A*, 702 (1995) 45.
- [7] G.A. Heeter and A.I. Liapis, *J. Chromatogr. A*, 711 (1995) 3.
- [8] Y. Xu and A.I. Liapis, *J. Chromatogr. A*, 724 (1996) 13.
- [9] G.A. Heeter and A.I. Liapis, *J. Chromatogr. A*, 734 (1996) 105.
- [10] G.A. Heeter and A.I. Liapis, *J. Chromatogr. A*, 743 (1996) 3.
- [11] N.B. Afeyan, N.F. Gordon, I. Mazsaroff, L. Varady, S.P. Fulton, Y.B. Yang and F.E. Regnier, *J. Chromatogr.*, 519 (1990) 1.
- [12] B.H. Arve and A.I. Liapis, *AIChE J.*, 33 (1987) 179.
- [13] B.H. Arve and A.I. Liapis, *Biotechnol. Bioeng.*, 31 (1988) 240.
- [14] A. Tongta, A.I. Liapis and D.J. Siehr, *J. Chromatogr. A*, 686 (1994) 21.
- [15] G.A.F. Seber and C.J. Wild, *Nonlinear Regression*, Wiley, New York, NY, 1989.
- [16] A.I. Liapis, A. Tongta and O.K. Crosser, *Math. Model. Sci. Comput.*, 5 (1995) 1.
- [17] M.A. McCoy and A.I. Liapis, *J. Chromatogr.*, 548 (1991) 25.
- [18] F.H. Arnold, H.W. Blanch and C.R. Wilke, *Chem. Eng. J.*, 30 (1985) B9.
- [19] F.H. Arnold, H.W. Blanch and C.R. Wilke, *Chem. Eng. J.*, 30 (1985) B25.
- [20] G. Neale, N. Epstein and W. Nader, *Chem. Eng. Sci.*, 28 (1973) 1865.
- [21] G.A. Heeter and A.I. Liapis, *J. Chromatogr. A*, in press.
- [22] G. Stephanopoulos and K. Tsvieriotis, *Chem. Eng. Sci.*, 44 (1989) 2031.
- [23] G. Carta, M.E. Gregory, D.J. Kirwan and H.A. Massaldi, *Sep. Technol.*, 2 (1992) 62.
- [24] Y. Xu, Ph.D. Dissertation, Department of Chemical Engineering, University of Missouri-Rolla, Rolla, MO, 1995.
- [25] P.T. Boggs, R.H. Byrd, J.E. Rogers and R.B. Schnabel, *User's Reference Guide for ODRPACK Version 2.01*, National Institute of Standards and Technology, Gaithersburg, MD, 1992.
- [26] G.A. Heeter, Ph.D. Dissertation, Department of Chemical Engineering, University of Missouri-Rolla, Rolla, MO, 1997.