A generalized shrinking core model for multicomponent batch adsorption processes

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Abstract

A two resistance mass transfer model for multi component batch adsorption process has been developed including an external film mass transfer coefficient and an internal effective diffusivity that controls the internal mass transport process. The model is based on the shrinking core formulation. The developed model is more generalized, can accommodate wide range of initial adsorbate concentration in feed and the nature of the isotherm. The model is tested for two binary systems reported in the literature [Chem. Eng. Sci. 36 (1981) 731]. The model equations are solved numerically and optimized using nonlinear parameter estimation technique in order to match with the experimental kinetic data [Chem. Eng. Sci. 36 (1981) 731]. In this procedure, the process parameters, i.e. the external mass transfer coefficient and internal effective diffusivity are determined for a particular system. Using the estimated parameters, a parametric study has been carried out to observe the effects of initial adsorbate concentration, particle size of adsorbent, mass of adsorbent, etc. on the system kinetics.
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1. Introduction

Adsorption is an important unit operation in a number of natural and industrial systems such as, fundamental biological studies, separation and purification processes, recovery of chemical compounds, catalysis and waste treatment processes. It can substitute other separation processes and contribute effectively for removal of pollutants from aqueous solution.

The interactions and competitions between sorbates and sorbent in the system complicate the adsorption process. However, an efficient, accurate and cost effective design should account for the effects associated with the multicomponent adsorption [2]. Adsorption studies in agitated finite batch adsorbers yield important equilibrium and kinetic data useful for further fixed bed studies and for the prediction of industrial adsorber performance. The adsorber design is based on extensive pilot plant scale experiments [3], which supply the design parameters and such design is specific to system conditions. In order to estimate the parameters for wider operating conditions, mathematical modeling of process kinetics is required.

To develop a mathematical model that describes the multi-component adsorption dynamics, following information are generally required:

(i) a complete description of equilibrium behavior, i.e. the maximum level of adsorption attained in a sorbent/sorbate system as a function of the sorbate liquid phase concentration;
(ii) a mathematical representation of associated rate of adsorption, which is controlled by the resistances within the sorbent particles.

In adsorption, mainly two resistances prevail—the external liquid film resistance and the resistance in the adsorbent particle. The intraparticle diffusion resistance may be neglected for solutes those exhibit strong solid to liquid phase equilibrium solute distribution, in the initial period of operation. However, even for such systems, the above assumption leads to errors which are substantial beyond the first few minutes if the agitation is high [4]. So both the resistances are important for the kinetic study [5,6].

The external liquid film resistance is characterized by the external liquid film mass transfer coefficient (k_f). The mass transport within the adsorbent particles is assumed to be a pore diffusion [7,8] or homogeneous solid diffusion process [9,10].

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Nomenclature

a_i, a_{ij}	Freundlich isotherm constants
b_i, b_{ii}, b_{ij}	Freundlich isotherm constants
C_{0i}	initial liquid phase concentration of ith species (mmol/l)
C_{eit}	equilibrium concentration of ith species at time t (mmol/l)
C_{it}	liquid phase concentration of ith species at time t (mmol/l)
D_{pi}	effective diffusion coefficient of ith species in adsorbent (m²/s)
k_{fi}	liquid phase mass transfer coefficient of ith species (m/s)
K_{0i}	Langmuir isotherm constant
K_i	Redlich–Peterson isotherm constant
N	total number of components in the mixture
$N_i(t)$	adsorption rate of ith species at time t (mmol/s)
R	adsorbent particle radius (m)
R_{fi}	radius of concentration front due to ith species (m)
t	time (s)
V	volume of batch reactor (l)
W	weight of the adsorbent (g)
Y_e	solid phase concentration at a particular time (mg/g or mmol/g)
$\bar{Y}_{it}$	average solid phase concentration of ith species at time t (mmol/g)
Y_{si}	Langmuir isotherm constant

Greek letters

η_i, β_i	Redlich–Peterson isotherm constants
ρ	adsorbent density (g/cm³)

Dimensionless terms

Bi_i	Biot number of ith species
C_{it}^*	liquid phase concentration of ith species at any time t
C_{eit}^*	equilibrium liquid phase concentration
Ch_i	capacity factor for ith species
r	distance from center of the particle, $0 < r < 1$
Y_{eit}^*	equilibrium solid phase concentration
τ	dimensionless time

Subscripts

0	initial
i	component i in the mixture
t	at time, t

Superscript

*	non-dimensional

The pore diffusion model outlined in this paper is based on the unreacted shrinking core model [11,12] with pseudo steady-state approximation. This model has mostly been applied to gas–solid noncatalytic reactions [11], but a number of liquid–solid reactions also have been analyzed using this model [13,14]. The assumptions made in this model are as follows:

(i) the effective diffusivity in the adsorbent is independent of concentration;
(ii) pseudo steady-state approximation is valid;
(iii) the driving force in both film and particle mass transfer is linear;
(iv) the adsorbent particles are spherical and uniform.

The adsorption kinetic model based on this approach for single solute system is available in literature [8]. The major limitation of this model [8] is that it is specific to the nature of isotherm. This means that the model available in literature is most suitable for Langmuir type isotherm, i.e. formation of a monolayer of adsorbate on the adsorbent. Besides, this model is only applicable for higher initial adsorbate concentration in solution so that the batch process operating line intercepts the concentration invariant zone of isotherm. For example, for Astrazone blue—silica system, the literature model is applicable for $C_0 \gg 200$ mg/l [8]. Moreover, this model is for a single solute system. The present model, which is more generalized, overcomes the above limitations. The model proposed herein, can be applied to wide ranges of initial adsorbate concentrations for all possible nature of isotherms and it is applicable for a multicomponent system containing N number of solutes. The developed model is tested for a binary system available in literature [1]. The systems reported are: (i) adsorption of *para*-nitrophenol (PNP) and *para*-chlorophenol (PCP) on B10I activated carbon [1] and (ii) adsorption of 2,4-dichlorophenol and dodecyl benzene sulfonic acid on B10II activated carbon [1].

2. Theory

The formulation of mathematical modeling considers both the equilibrium and kinetics for each component 'i' in a system of N number of components. The different types of multicomponent adsorptions are presented below.

Langmuir isotherm

$$Y_{ei} = \frac{Y_{si}C_{ei}}{1 + \sum_{i=1}^{i=N} K_{0i}C_{ei}} \tag{1}$$

Redlich–Peterson isotherm

$$Y_{ei} = \frac{Y_{si}C_{ei}}{1 + \sum_{i=1}^{i=N} K_i(C_{ei}/\eta_i)^{\beta i}} \tag{2}$$

Freundlich isotherm

$$Y_{ei} = \frac{a_i C_{ei}^{(bi+bii)}}{C_{ei}^{bii} + a_{ij}\sum_{j=1}^{j=N} C_{ej}^{bij}}, i \neq j \tag{3}$$

2.1. Adsorption kinetics

The following rate equations are developed considering the spherical adsorbent particles.

The mass transfer from external liquid phase to the adsorbent for the ith species can be written as

$$N_i(t) = 4\pi R^2 K_{fi}(C_{it} - C_{eit}) \tag{4}$$

The diffusion in pore liquid as per Fick's law can be written as for ith species

$$N_i(t) = \frac{4\pi D_{pi} C_{eit}}{[(1/R_{fi}) - (1/R)]} \tag{5}$$

The mass balance on a spherical element of adsorbent particle can be written as

$$N_i(t) = -4\pi R_{fi}{}^2 Y_{eit}\rho\left[\frac{dR_{fi}}{dt}\right] \tag{6}$$

The average concentration on adsorbent particle can be written as

$$\bar{Y}_{it} = Y_{eit}\left[1 - \left(\frac{R_{fi}}{R}\right)^3\right] \tag{7}$$

The differential mass balance over the system by equating the decrease in adsorbate concentration in the solution with the accumulation of the adsorbate in the adsorbent can be written as

$$N_i(t) = -V\left(\frac{dC_{it}}{dt}\right) = W\left(\frac{d\bar{Y}_{it}}{dt}\right) \tag{8}$$

The dimensionless terms are used for simplification as follows:

$$C_{it}^* = \frac{C_{it}}{C_{0i}}, \qquad r_i = \frac{R_{fi}}{R}, \qquad Bi_i = \frac{K_{fi}R}{D_{pi}},$$
$$Ch_i = \frac{W}{VC_{0i}}, \qquad C_{eit}^* = \frac{C_{eit}}{C_{0i}} \quad \text{and} \quad \tau = \frac{D_{p1}t}{R^2}$$

Combining Eqs. (4) and (5), the following expression is obtained:

$$C_{eit}^* = \frac{Bi_i(1 - r_i)C_{it}^*}{[r_i + Bi_i(1 - r_i)]} = g_{1i}(C_{it}^*, r_i) \tag{9}$$

Differentiating the above equation with respect to τ, the time variation of C_{eit}^* is obtained:

$$\frac{dC_{eit}^*}{d\tau} = \frac{Bi_i(1 - r_i)}{[r_i + Bi_i(1 - r_i)]}\frac{dC_{it}^*}{d\tau} - \frac{Bi_i C_{it}^*}{[r_i + Bi_i(1 - r_i)]^2}\frac{dr_i}{d\tau} \tag{10}$$

The equilibrium relationships can be presented as

$$Y_{eit} = g_{2i}(C_{e1t}, C_{e2t}\cdots C_{eNt}) \tag{11}$$

where g_{2i} is any equilibrium relationship as given in Eqs. (1)–(3).

Combining Eqs. (4) and (6) and after non-dimensionalization, the following expression is resulted:

$$\left(\frac{dr_i}{d\tau}\right) = \frac{-Bi_i D_{pi}(C_{0i}/\rho Y_{eit})(C_{it}^* - C_{eit}^*)}{D_{p1}r_i^2} \tag{12}$$

Combining Eqs. (7) and (8) and after non-dimensionalization the following expression is obtained:

$$\frac{dC_{it}^*}{d\tau} + Ch_i(1 - r_i^3)\frac{dY_{eit}}{d\tau} = 3Ch_i Y_{eit}r_i^2\left(\frac{dr_i}{d\tau}\right) \tag{13}$$

The derivative $dY_{eit}/d\tau$ is obtained from the equilibrium relationship. For an example, a Freundlich type of isotherm is considered. However, the same approach can be used for any other isotherms.

Differentiating Eq. (3) with respect to τ, the following expression of $dY_{eit}/d\tau$ is obtained:

$$\frac{dY_{eit}}{d\tau} = \frac{a_i(b_i + b_{ii})C_{eit}^{bi+bii-1}}{C_{eit}^{bii} + a_{ij}\sum_{j=1, j\neq i}^{N} C_{ejt}^{bij}}\frac{dC_{eit}}{d\tau}$$
$$- \frac{a_i C_{eit}^{bi+bii}(b_{ii}C_{eit}^{bii-1}(dC_{eit}/d\tau) + a_{ij}\sum_{j=1, j\neq i}^{N} b_{ij}C_{ejt}^{bij-1}(dC_{ejt}/d\tau))}{(C_{eit}^{bii} + a_{ij}\sum_{j=1 j\neq i}^{N} C_{ejt}^{bij})^2} \tag{14}$$

In the above equation, the concentrations C_{eit} can be expressed in its non-dimensional form by dividing and multiplying by C_{0i} in the right-hand side of Eq. (14). Therefore, Eq. (14) can be expressed in terms of C_{eit}^* as

$$\frac{dY_{eit}}{d\tau} = \frac{a_i(b_i + b_{ii})C_{0i}^{bi+bii}C_{eit}^{*bi+bii-1}}{C_{0i}^{bii}C_{eit}^{*bii} + a_{ij}\sum_{j=1, j\neq i}^{N} C_{0j}^{bij}C_{ejt}^{*bij}}\frac{dC_{eit}^*}{d\tau}$$
$$- \frac{a_i C_{0i}^{bi+bii}C_{eit}^{*bi+bii}(b_{ii}C_{0i}^{bii}C_{eit}^{*bii-1}(dC_{eit}^*/d\tau) + a_{ij}\sum_{j=1, j\neq i}^{N} b_{ij}C_{0j}^{bij}C_{ejt}^{*bij-1}(dC_{ejt}^*/d\tau))}{(C_{0i}^{bii}C_{eit}^{*bii} + a_{ij}\sum_{j=1 j\neq i}^{N} C_{0j}^{bij}C_{ejt}^{*bij})^2} \tag{15}$$

Now, C_{eit}^* can be expressed in terms of C_{it}^* and r_i using Eq. (9). Similarly $dC_{eit}^*/d\tau$ can be expressed in terms of $dC_{it}^*/d\tau$, $dr_i/d\tau$ and r_i using Eq. (10).

Therefore, using Eqs. (9) and (10), Eq. (15) can be written as

$$\frac{dY_{eit}}{d\tau} = f_{1i}\left(\frac{dC_{it}^*}{d\tau}, \frac{dr_i}{d\tau}, C_{it}^*, r_i\right) \tag{16}$$

Eq. (16) can be substituted in Eq. (13) and the resultant equation after simplification gives the governing equation for variation of bulk concentration of ith species (C_{it}^*) with time as expressed in the following form:

$$\left(\frac{dC_{it}^*}{d\tau}\right) = f_{2i}\left(\frac{dr_i}{d\tau}, C_{it}^*, r_i\right)$$

The derivative $dr_i/d\tau$ can be expressed as a function of C_{it}^* and r_i, using Eq. (9) and the equilibrium relationship,

Eq. (11) (as Freundlich isotherm is considered in this case, Eq. (11) should be replaced by Eq. (3)).

Therefore, the governing equation of the concentration profile for ith species, can be expressed as

$$\left(\frac{dC_{it}^*}{d\tau}\right) = f_{3i}(C_{it}^*, r_i) \tag{17}$$

Using Eq. (12) and the equilibrium relationship, Eq. (11), variation of r_i with time is given by

$$\left(\frac{dr_i}{d\tau}\right) = f_{4i}(C_{it}^*, r_i) \tag{18}$$

Eqs. (17) and (18) represent $2N$ coupled ordinary differential equations (N equations for $dC_{it}^*/d\tau$ and N equations for $dr_i/d\tau$ as the number of species is N).

The initial conditions that can be used to solve Eqs. (17) and (18) are, $C_{it}^* = 1.0$ and $r_i = 1.0$ at time, $\tau = 0.0$.

2.2. Case study for a binary system

For $N = 2$, the system is binary, i.e. there are two components in the liquid phase. The equilibrium relationship is given as

$$Y_{e1t} = \frac{a_1 C_{e1t}^{b_1+b_{11}}}{C_{e1t}^{b_{11}} + a_{12} C_{e2t}^{b_{12}}} \tag{19a}$$

and

$$Y_{e2t} = \frac{a_2 C_{e2t}^{b_2+b_{22}}}{C_{e2t}^{b_{22}} + a_{21} C_{e1t}^{b_{21}}} \tag{19b}$$

Using Eq. (9) we can write

$$C_{e1t}^* = \frac{Bi_1(1 - r_1)C_{1t}^*}{[r_1 + Bi_1(1 - r_1)]} = g_{11}(C_{1t}^*, r_1) \tag{20}$$

and

$$C_{e2t}^* = \frac{Bi_2(1 - r_2)C_{2t}^*}{[r_2 + Bi_2(1 - r_2)]} = g_{12}(C_{2t}^*, r_2) \tag{21}$$

Using Eq. (10), the time derivative of equilibrium concentrations are obtained as follows:

$$\frac{dC_{e1t}^*}{d\tau} = \alpha_{11}(r_1)\frac{dC_{1t}^*}{d\tau} - \beta_{11}(C_{1t}^*, r_1)\frac{dr_1}{d\tau} \tag{22a}$$

and

$$\frac{dC_{e2t}^*}{d\tau} = \alpha_{12}(r_2)\frac{dC_{2t}^*}{d\tau} - \beta_{12}(C_{2t}^*, r_1)\frac{dr_2}{d\tau} \tag{22b}$$

where $\alpha_{11}, \alpha_{12}, \beta_{11}, \beta_{12}$ are given in Appendix A.

In terms of non-dimensional concentrations, Eqs. (19a) and (19b) can be expressed as

$$Y_{e1t} = \frac{m_{11} C_{e1t}^{*n_{11}}}{m_{21} C_{e1t}^{*b_{11}} + m_{31} C_{e2t}^{*b_{12}}} \tag{23a}$$

and

$$Y_{e2t} = \frac{m_{12} C_{e2t}^{*n_{22}}}{m_{22} C_{e2t}^{*b_{22}} + m_{32} C_{e1t}^{*b_{21}}} \tag{23b}$$

where, $m_{11}, m_{21}, m_{12}, m_{22}, m_{31}, m_{32}, n_{11}, n_{22}$ are given in Appendix A.

Substituting, expressions of C_{e1t}^* and C_{e2t}^* from Eqs. (20) and (21) in Eqs. (23a) and (23b), Y_{eit} can be expressed in terms of C_{1t}^*, C_{2t}^*, r_1 and r_2 as

$$Y_{e1t} = \frac{m_{11} g_{11}^{n_{11}}}{m_{21} g_{11}^{b_{11}} + m_{31} g_{12}^{b_{12}}} = s_1(C_{1t}^*, C_{2t}^*, r_1, r_2) \tag{24a}$$

and

$$Y_{e2t} = \frac{m_{12} g_{12}^{n_{22}}}{m_{22} g_{12}^{b_{22}} + m_{32} g_{11}^{b_{21}}} = s_2(C_{1t}^*, C_{2t}^*, r_1, r_2) \tag{24b}$$

Differentiating Eqs. (24a) and (24b) and using Eqs. (20), (21), (22a) and (22b), the time derivatives of Y_{e1t} and Y_{e2t} are obtained as follows:

$$\frac{dY_{e1t}}{d\tau} = h_{11}\alpha_{11}\frac{dC_{1t}^*}{d\tau} - h_{12}\alpha_{12}\frac{dC_{2t}^*}{d\tau} - h_{11}\beta_{11}\frac{dr_1}{d\tau}$$
$$+ h_{12}\beta_{12}\frac{dr_2}{d\tau} \tag{25a}$$

and

$$\frac{dY_{e2t}}{d\tau} = -h_{21}\alpha_{11}\frac{dC_{1t}^*}{d\tau} + h_{22}\alpha_{12}\frac{dC_{2t}^*}{d\tau} + h_{21}\beta_{11}\frac{dr_1}{d\tau}$$
$$- h_{22}\beta_{12}\frac{dr_2}{d\tau} \tag{25b}$$

where $\alpha_{11}, \alpha_{12}, \beta_{11}, \beta_{12}, h_{11}, h_{12}, h_{21}$ and h_{22} are given in Appendix A.

From Eq. (12), the rate of shrinkage of the adsorbate particle due to both the species is written as

$$\left(\frac{dr_1}{d\tau}\right) = \frac{-Bi_1(C_{01}/\rho Y_{e1t})(C_{1t}^* - C_{e1t}^*)}{r_1^2} \tag{26a}$$

$$\left(\frac{dr_2}{d\tau}\right) = \frac{-Bi_2 D_{p2}(C_{02}/\rho Y_{e2t})(C_{2t}^* - C_{e2t}^*)}{D_{p1} r_2^2} \tag{26b}$$

Using Eqs. (20), (21), (23a) and (23b), $C_{e1t}^*, C_{e2t}^*, Y_{e1t}$ and Y_{e2t} can be expressed in terms of $C_{1t}^*, C_{2t}^*, r_1, r_2$ and Eqs. (26a) and (26b) can be expressed as

$$\left(\frac{dr_1}{d\tau}\right) = d_{11}(C_{1t}^*, C_{2t}^*, r_1, r_2) \tag{27a}$$

$$\left(\frac{dr_2}{d\tau}\right) = d_{22}(C_{1t}^*, C_{2t}^*, r_1, r_2) \tag{27b}$$

Using Eq. (13), following two governing equations of bulk concentrations are obtained:

$$X_{11}\frac{dC_{1t}^*}{d\tau} - X_{12}\frac{dC_{2t}^*}{d\tau} = Z_{11} \tag{28a}$$

$$-X_{21}\frac{dC_{1t}^*}{d\tau} + X_{22}\frac{dC_{2t}^*}{d\tau} = Z_{22} \tag{28b}$$

where X_{11}, X_{12}, X_{21}, X_{22}, Z_{11}, and Z_{22} are presented in Appendix A.

Eqs. (28a) and (28b) can be simplified as

$$\frac{\mathrm{d}C_{1t}^*}{\mathrm{d}\tau} = \frac{Z_{11}X_{22} + Z_{22}X_{12}}{X_{11}X_{22} - X_{12}X_{21}} \tag{29a}$$

$$\frac{\mathrm{d}C_{1t}^*}{\mathrm{d}\tau} = \frac{Z_{11}X_{22} + Z_{22}X_{12}}{X_{11}X_{22} - X_{12}X_{21}} \tag{29b}$$

The four equations, namely, Eqs. (27a), (27b), (29a) and (29b) are solved using fourth order Runge–Kutta method. The initial conditions used are, $C_{1t}^* = C_{2t}^* = 0.1$ and $r_1 = r_2 = 1.0$ at time, $\tau = 0$. Since four parameters, i.e. the mass transfer coefficients (k_{f1} and k_{f2}) and effective diffusivities (D_{p1} and D_{p2}) are unknown, they are determined by optimizing the experimental concentration decay data of both the components. The nonlinear parameter optimization technique Levenberg–Marquardt has been used along with fourth order Runge–Kutta method as ODEs solver for the parameter estimation. For this purpose, optimization subroutine UNLSF/DUNLSF from IMSL math Library has been used.

3. Results and discussion

The theoretical model developed herein is applicable for a solutions containing N number of solutes. However, the model is tested against a two component system. The binary systems considered are (i) *para*-nitrophenol (component 1) and *para*-chlorophenol (component 2) on B10I activated carbon and (ii) 2,4-dichloro phenol (component 1) and dodecyl benzene sulfonic acid (component 2) on B10II activated carbon [1]. Both of these systems follow Freundlich type isotherms. The experimental data on kinetics and the isotherm constants have been reported in literature [1,15]. The values of the isotherm constants are presented in Table 1. Using the nonlinear optimization technique, four unknown process parameters, namely, the external mass transfer coefficients for both the components (k_{f1} and k_{f2}) and the effective diffusivities of the components in the adsorbent (D_{p1} and D_{p2}) are estimated after the concentration decay profile

Table 1
Isotherm constants for different components [1]

Sl. no.	1	2
Activated carbon	B10I	B10II
Solutes	PNP(1)/PCP(2)	DCP(1)/DBS(2)
$a1$	3.25	3.86
$b1$	0.13	0.12
$b11$	0.96	0.39
$a12$	0.29	0.23
$b12$	1.00	0.60
$a2$	3.10	1.08
$b2$	0.15	0.06
$b22$	0.90	0.24
$a21$	1.90	0.70
$b21$	0.93	0.41

matching for both the components. For the system, PNP and PCP on B10I activated carbon, the experimental data on concentration decay has been considered for the following conditions [1], $C_{01} = 10.1$ mmol/l, $C_{02} = 2.12$ mmol/l, $W/V = 2.0$ g/l, $\rho = 2.05$ g/cm^3 and $R = 0.66$ mm. The estimated values of the parameters are: $k_{f1} = 21.3 \times 10^{-5}$ m/s; $k_{f2} = 29.8 \times 10^{-5}$ m/s; $D_{p1} = 6.4 \times 10^{-9}$ m^2/s and $D_{p2} = 7.2 \times 10^{-9}$ m^2/s. Fig. 1 shows the model fit of the experimental data on the kinetics under above conditions.

Similarly, for the system DCP and DBS on B10II activated carbon, the experimental data on concentration decay are considered for the following conditions [1]: $C_{01} = 5.1$ mmol/l, $C_{02} = 5.0$ mmol/l, $W/V = 2.0$ g/l, $\rho = 2.05$ g/cm and $R = 0.66$ mm. The estimated values of the parameters are: $k_{f1} = 11.96 \times 10^{-5}$ m/s; $k_{f2} = 5.49 \times 10^{-5}$ m/s; $D_{p1} = 1.77 \times 10^{-9}$ m^2/s and $D_{p2} = 0.081 \times 10^{-9}$ m^2/s. Fig. 2 shows the model fit of the experimental data on the kinetics under above conditions.

Using the estimated parameters, a parametric study has been carried out to observe the effects of the mass of adsorbent, adsorbent particle size, etc. on the bulk concentration decay.

3.1. Parametric study

The various parameters that affect the adsorption kinetics are—the initial adsorbate concentration in liquid, the mass of adsorbent, the particle size of adsorbent, the volume of the adsorbate solution, etc.

3.1.1. Effect of initial adsorbate concentration
The effects of the initial adsorbate concentrations on the bulk concentration profiles of both the solutes are presented in Fig. 3. In Fig. 3, the initial concentrations of both the solutes are taken as 10 mmol/l in first case (curves 1 and 3) and in the second case both the concentrations are considered ten times less, i.e. 1 mmol/l (curves 2 and 4). Two trends are observed from this figure. First, DCP is adsorbed more in both the levels of the initial concentrations. Second, with decrease in the initial concentrations, the adsorption of the solutes increases. It is clear from the figure that at any point of time, the concentration of DCP in the bulk liquid is less than that of DBS. Therefore, DCP is adsorbed more on activated carbon due to interactions and competitions with DBS. With the decrease in initial adsorbate concentration in the solution, the rate of concentration decay in the liquid phase increases resulting in an increase in the adsorption rate.

3.1.2. Effect of the ratio of the mass of adsorbent to the solution volume
Fig. 4 shows the effects of mass of adsorbent to the solution volume ratio on the concentration decay in liquid phase for both the species. In one case (curves 1 and 3), the W/V ratio is taken as 1 g/l and in the other one (curves 2 and 4), the W/V ratio is taken five times, i.e. 5 g/l. In both the
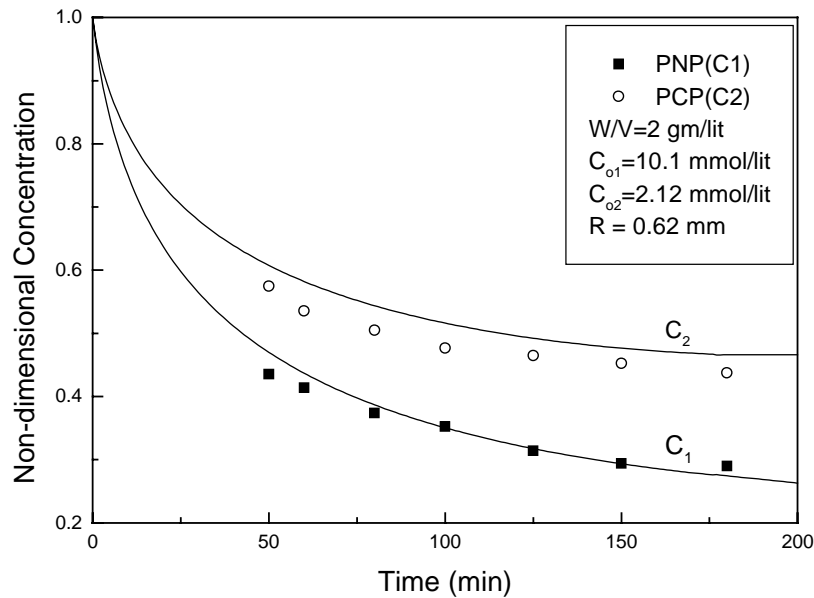
Fig. 1. Bulk concentration profile of PNP and PCP on B10I activated carbon.

cases, it may be observed the bulk concentration decay of DCP is more rapid compared to that of DBS, i.e. DCP is adsorbed more on the activated carbon as observed earlier. With the increase in mass of adsorbent, the concentration decay of a particular component is sharper. This is due to the fact that with increase in adsorbent amount, the adsorption sites increase leading to a rapid decrease in the liquid phase concentration.

3.1.3. Effect of the Biot number (Bi)

k_f, D_p, R, or their combinations can change the Biot number for a system. With constant D_p and R values, for different external mass transfer coefficient values, the model is simulated to observe the effect of Biot number on the concentration decay. This is shown in Fig. 5. The figure shows that for a particular component, the rate of concentration decay increases with Biot number. This simply signifies that the external mass transfer resistance decreases with increase in the film mass transfer coefficient (in this case, Biot numbers are varied by changing the film mass transfer coefficient only, keeping the effective diffusivity and the particle radius values constant) and therefore more solutes are available to the potent sites of the adsorbent for adsorption. This leads to a decrease in the bulk solute
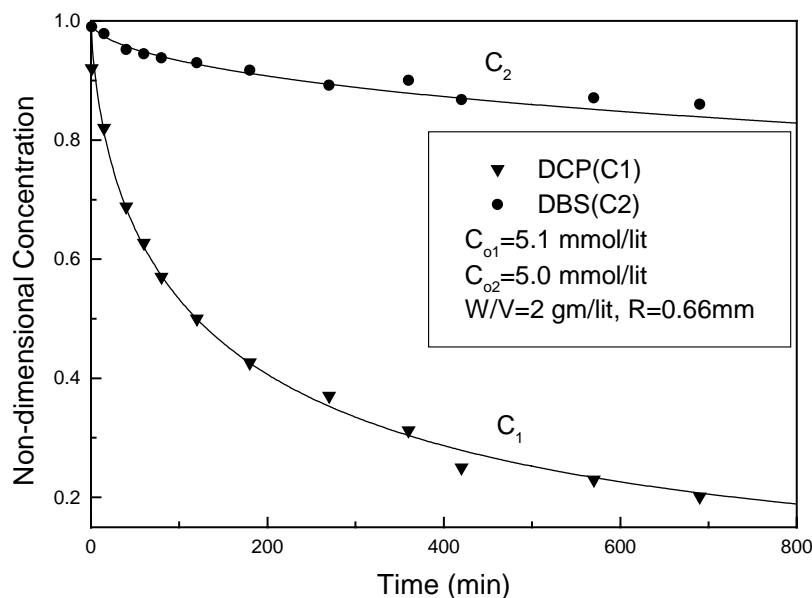

Fig. 2. Bulk concentration profile of DCP and DBS on B10II activated carbon.
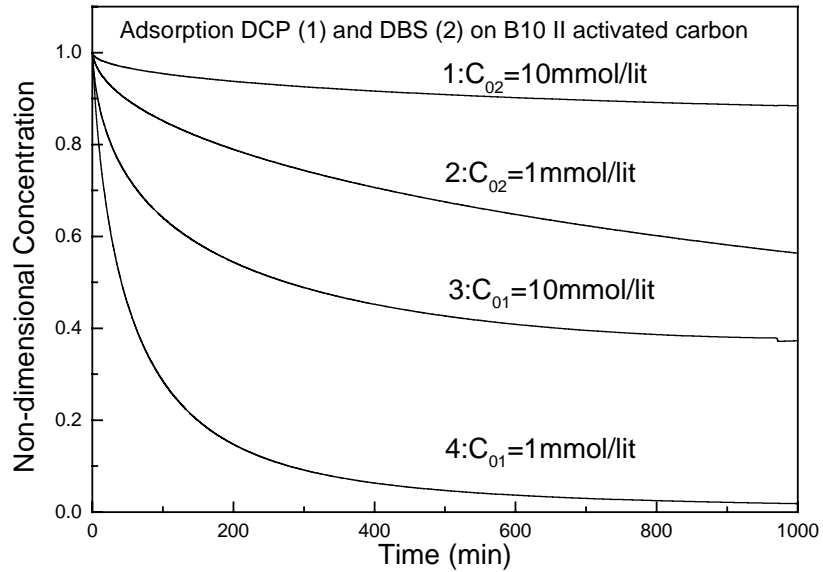
Fig. 3. Effect of initial adsorbate concentration on concentration decay.

concentration with the Biot number. It is also interesting to note that the bulk concentration decay profiles remain almost unaltered for both the solutes at higher Biot numbers. For DBS, Biot number beyond 224 and for DCP, Biot number beyond 22 are not going to improve the adsorption of these solutes because beyond the above values of Biot numbers, the concentration profiles remain almost unchanged. This indicates that there exists a critical external energy requirement, which causes turbulence (either by stirring or imposing flow in the system and thereby increasing the film mass transfer coefficient) corresponding to which a critical Biot number for the system is obtained. Further increase in

external energy leading to increase in the Biot number (or increase in the film mass transfer coefficient) will not result a significant improvement of the adsorption of the species.

3.1.4. Effect adsorbent particle size

The effects of the adsorbent particle size on the concentration decay curves are shown in Fig. 6. It may be observed from this figure that the concentration decay curve is sharper for lower particle diameter. This indicates the rate of adsorption increases with the decrease of the adsorbent particle size. With smaller particle size, the surface area available is more for constant mass of adsorbent. Therefore, the
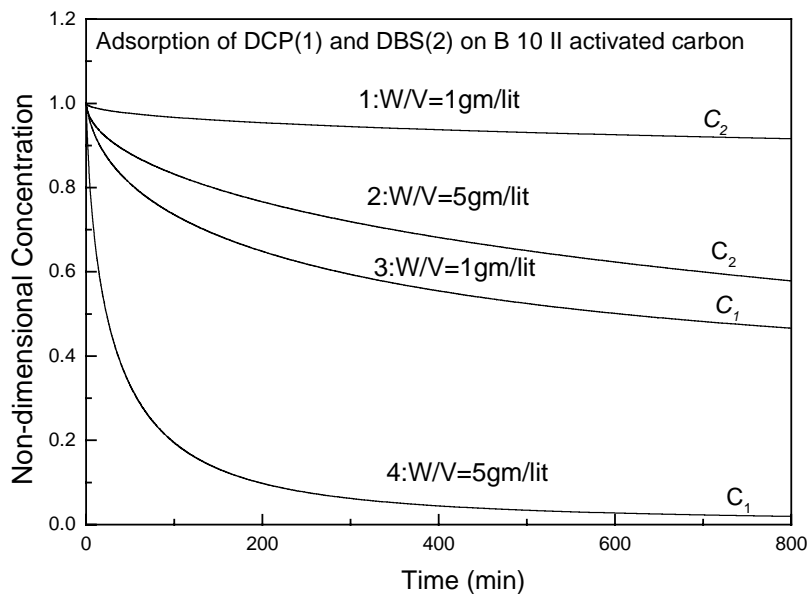

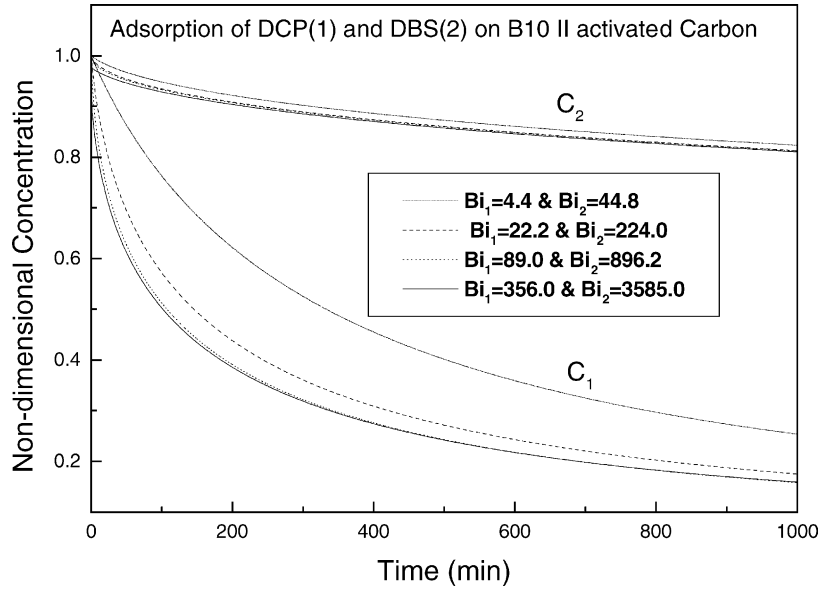Fig. 4. Effect of the adsorbent mass to volume ratio on concentration decay.

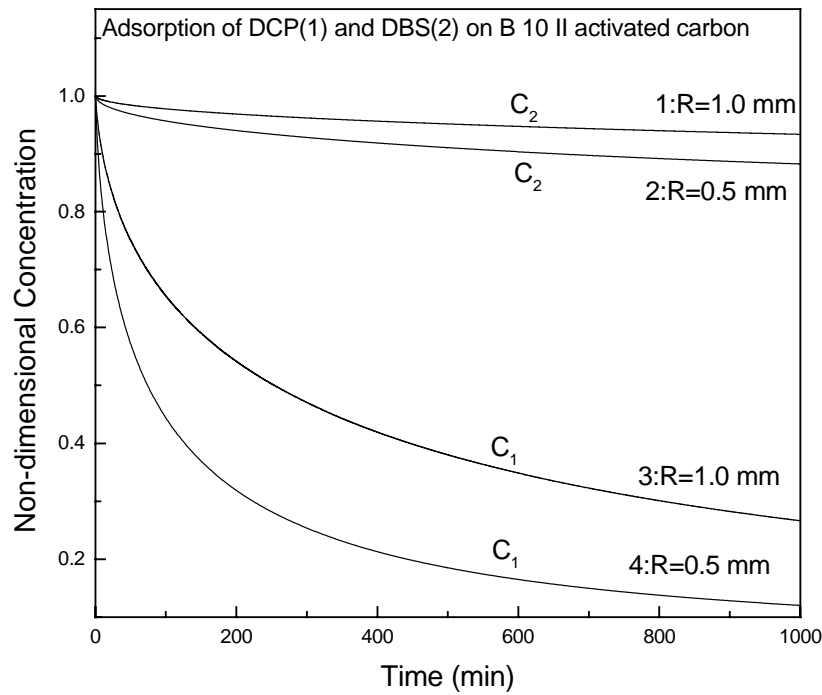Fig. 5. Effect of Biot number on concentration decay.

Fig. 6. Effect of adsorbent particle size on concentration decay.

adsorption front progresses rapidly with smaller particle size of adsorbent.

4. Conclusion

The pore diffusion model based on shrinking core formulation is developed for a multi component system and successfully tested with the literature data. The model can be used for a wider range of initial adsorbate concentrations with all possible types of isotherms. The rate of adsorption increases with decrease in initial adsorbate concentration, increase in mass of adsorbent, decrease in adsorbent particle size. The model is useful to estimate k_f and D_p values, which are required for the design of fixed bed adsorber.

Appendix A

The terms in Eqs. (22a) and (22b) are

$$\alpha_{11} = \frac{Bi_1(1-r_1)}{[r_1 + Bi_1(1-r_1)]}, \qquad \alpha_{12} = \frac{Bi_2(1-r_2)}{[r_2 + Bi_2(1-r_2)]},$$

$$\beta_{11} = \frac{Bi_1 C_{1t}^*}{[r_1 + Bi_1(1-r_1)]^2}$$

and

$$\beta_{12} = \frac{Bi_2 C_{2t}^*}{[r_2 + Bi_2(1-r_2)]^2}$$

The terms in Eqs. (23a) and (23b) are

$$m_{11} = a_1 C_{01}^{b_1+b_{11}}, \qquad n_{11} = b_1 + b_{11}, \qquad m_{21} = C_{01}^{b_{11}},$$
$$m_{31} = a_{12} C_{02}^{b_{12}}$$
$$m_{12} = a_2 C_{02}^{b_2+b_{22}}, \quad n_{22} = b_2 + b_{22}, \qquad m_{22} = C_{02}^{b_{22}},$$
$$m_{32} = a_{21} C_{01}^{b_{21}}$$

The terms in Eqs. (25a) and (25b) are

$$h_{11} = \frac{p_{11} g_{11}^{q_{11}}}{p_{12} g_{11}^{b_{11}} + p_{13} g_{12}^{b_{12}}} - \frac{p_{14} g_{11}^{q_{12}}}{(p_{12} g_{11}^{b_{11}} + p_{13} g_{12}^{b_{12}})^2},$$

where

$$p_{11} = a_1(b_1 + b_{11}) C_{01}^{b_1+b_{11}}, \qquad p_{12} = C_{01}^{b_{11}},$$
$$p_{13} = a_{12} C_{02}^{b_{12}}, \qquad p_{14} = a_1 b_{11} C_{01}^{b_1+2b_{11}}$$
$$q_{11} = b_1 + b_{11} - 1 \quad \text{and} \quad q_{12} = b_1 + 2b_{11} - 1$$

$$h_{12} = \frac{p_{15} g_{11}^{q_{13}} g_{12}^{q_{14}}}{(p_{12} g_{11}^{b_{11}} + p_{13} g_{12}^{b_{12}})^2}$$

where

$$p_{15} = a_1 a_{12} b_{12} C_{01}^{b_1+b_{11}} C_{02}^{b_{12}}, \qquad q_{13} = b_1 + b_{11},$$
$$q_{14} = b_{12} - 1$$

$$h_{21} = \frac{p_{25} g_{12}^{q_{13}} g_{11}^{q_{24}}}{(p_{21} g_{12}^{b_{11}} + p_{23} g_{11}^{b_{21}})^2}$$

where

$$p_{25} = a_2 a_{21} b_{21} C_{02}^{b_2+b_{22}} C_{01}^{b_{21}}, \qquad q_{24} = b_{21} - 1,$$
$$p_{21} = C_{02}^{b_{22}}$$
$$p_{23} = a_{21} C_{02}^{b_{21}}$$

$$h_{22} = \frac{p_{22} g_{12}^{q_{22}}}{p_{21} g_{12}^{b_1} + p_{23} g_{11}^{b_{21}}} - \frac{p_{24} g_{12}^{q_{21}}}{(p_{21} g_{12}^{b_1} + p_{23} g_{12}^{b_{21}})^2},$$

where

$$p_{22} = a_2(b_2 + b_{22}) C_{02}^{b_2+b_{22}}, \qquad p_{24} = a_2 b_{22} C_{02}^{b_2+2b_{22}},$$
$$q_{11} = b_2 + b_{22} - 1 \quad \text{and} \quad q_{21} = b_2 + 2b_{22} - 1$$

The terms in Eqs. (28a) and (28b) are

$$X_{11} = 1 + Ch_1(1 - r_1^3) h_{11} \alpha_{11}$$

$$X_{12} = Ch_1(1 - r_1^3) h_{12} \alpha_{12}$$

$$Z_{11} = [Ch_1(1 - r_1^3) h_{11} \beta_{11} + 3 Ch_1 Y_{e1t} r_1^2] d_{11}$$
$$\qquad - Ch_1(1 - r_1^3) h_{12} \beta_{12} d_{22}$$

$$X_{21} = Ch_2(1 - r_2^3) h_{21} \alpha_{11}$$

$$X_{22} = 1 + Ch_2(1 - r_2^3) h_{22} \alpha_{22}$$

$$Z_{22} = [Ch_2(1 - r_2^3) h_{22} \beta_{12} + 3 Ch_2 Y_{e2t} r_2^2] d_{22}$$
$$\qquad - Ch_2(1 - r_2^3) h_{21} \beta_{11} d_{11}$$

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