Analysis of a one-component sorption in a single adsorbent particle by the orthogonal collocation method I. Isothermal models

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This paper is concerned with an analysis of four models of a one-component sorption in a single adsorbent particle under the isothermal process assumption. The transients of average values of dimensionless adsorbate concentration in particle have been calculated numerically by the orthogonal collocation method in connection with the Runge—Kutta—Merson technique for various values of model parameters. Some interesting features of the orthogonal collocation solutions are presented in this paper.

В статье описывается анализ четырех моделей однокомпонентной сорбции в одной частице адсорбента при изотермических условиях. Рассчитались временные зависимости средней безразмерной концентрации адсорбированного вещества в частице методом ортогональной колокации вместе с методом Рунге–Кутта–Мерсона для различных значений параметров моделей. В статье приводятся некоторые интересные варианты решения методом ортогональной колокации.

A detailed analysis of a nonisothermal one-component sorption in a single adsorbent particle is a necessary preliminary step if the adsorber model is to be refined. The adsorbent pellets dominate the dynamic behaviour of the packed bed adsorber with gas medium. In this paper we will in some detail consider the isothermal problem. The assumption of isothermal behaviour is a fair approximation when the adsorbable component is weakly adsorbed or present only in a very low concentration but in practice one is often concerned with the sorption of strongly adsorbed species at sufficiently high concentration for thermal effect to be important. However, some of the isothermal models can be tractable by analytical methods and we can obtain useful information from both simplified and linear versions of the more complicated nonlinear models.

Mathematical models

In the next text we shall visualize the adsorbent particle as a porous solid with twisting pores of different diameter and length, with crevices, dead end pores, and perhaps a micropore system imbedded in a system of larger pores. These large pores serve as main passages for the fluid adsorptive that penetrates the solid and catches on the pore walls.

The basic model (mass balance) for an isothermal one-component sorption in a single spherical adsorbent particle may be formally derived from the differential mass balance for the adsorbable component in a dilute binary mixture by dropping the convective term [1]

$$\varepsilon\frac{\partial c}{\partial t}=D_{ef}\left(\frac{\partial^2 c}{\partial x^2}+\frac{2}{x}\frac{\partial c}{\partial x}\right)-\frac{\partial a}{\partial t} \tag{1}$$

The effective diffusivity D_{ef}, which is considered to be constant, is a very composite property that reflects various transport mechanisms inside the complex pore structure. The initial and boundary conditions are

$$\begin{matrix} a=a_i \\ c=c_i^* \end{matrix} \quad \text{at } 0\leqq x\leqq R \quad \text{for } t=0 \tag{2}$$

$$\frac{\partial c}{\partial x}=0 \quad \text{at } x=0 \quad \text{for } t>0 \tag{3}$$

$$\frac{\partial c}{\partial x}=\frac{h_M}{D_{ef}}(c_b-c_{x=R}) \quad \text{at } x=R \quad \text{for } t>0 \tag{4}$$

c_b is the property of the bulk fluid phase, h_M is the mass transfer coefficient for the film that surrounds the pellets. For a general equilibrium isotherm $a=a(c)$, eqn *(1)* may be rewritten as

$$\varepsilon\frac{\partial c}{\partial t}=D_{ef}\left(\frac{\partial^2 c}{\partial x^2}+\frac{2}{x}\frac{\partial c}{\partial x}\right)-\frac{\partial a}{\partial c}\frac{\partial c}{\partial t} \tag{5}$$

Eqn *(5)* is seen to be a nonlinear parabolic partial differential equation, which is coupled to the fluid phase mass balance through the boundary condition *(4)*, c_b being in general the function of position in the adsorber and of time. For our purposes we shall regard it as the known constant value of $c_b=c_0$.

Eqns *(2—5)* are rendered dimensionless by the following substitutions [1]

$$q=\frac{a-a_i}{a_0^*-a_i} \quad Q=\frac{c-c_i^*}{c_0-c_i^*} \quad \tau=\frac{c_0-c_i^*}{a_0^*-a_i}\frac{D_{ef}t}{R^2}$$
$$\delta=\frac{\varepsilon(c_0-c_i)}{a_0^*-a_i} \quad \xi=\frac{x}{R} \quad Bi_M=\frac{h_M R}{D_{ef}} \tag{6}$$

$$\delta\frac{\partial Q}{\partial \tau}=\left(\frac{\partial^2 Q}{\partial \xi^2}+\frac{2}{\xi}\frac{\partial Q}{\partial \xi}\right)-\frac{\partial q}{\partial Q}\frac{\partial Q}{\partial \tau} \tag{7}$$

The initial and boundary conditions are

$$\begin{matrix} q=0 \\ Q=0 \end{matrix} \quad \text{at } 0\leqq\xi\leqq 1 \quad \text{for } \tau=0 \tag{8}$$

$$\frac{\partial Q}{\partial \xi}=0 \quad \text{at } \xi=0 \quad \text{for } \tau=0 \tag{9}$$

$$\frac{\partial Q}{\partial \xi}=Bi_{\mathrm{M}}(1-Q_{\xi=1}) \quad \text{at } \xi=1 \quad \text{for } \tau>0 \tag{10}$$

For the Langmuir isotherm

$$a=a_{\mathrm{s}}\frac{Kp}{1+Kp} \tag{11}$$

and using transformations (*6*) and transformation

$$\varkappa_1=\frac{a_0^*-a_{\mathrm{i}}}{a_{\mathrm{s}}-a_{\mathrm{i}}} \tag{12}$$

we obtain

$$q=\frac{Q}{1-\varkappa_1(1-Q)} \tag{13}$$

A simplification of this model is possible for the situation, in which the transfer coefficient for the film is large. It is equivalent to small changes in driving force across the film. Boundary condition (*10*) for large Bi_{M} has the form

$$Q_{\xi=1}=1 \quad \text{at } \xi=1 \quad \text{for } \tau\geqq 0 \tag{14}$$

Another simplification of the model is possible for a case of "weak" sorption, when linear equilibrium isotherm can be applicable. In this case $\varkappa_1=0$ and the model equations are linear. In Table 1 are listed mathematical formulations of four

Table 1

Mathematical formulation of four isothermal models

Model	Model equation	Equilibrium isotherm	Boundary condition
I1	$\delta\frac{\partial Q}{\partial \tau}=\nabla^2 Q-\frac{\partial q}{\partial \tau}$	$\varkappa_1\neq 0$	$\nabla Q(1)=Bi_{\mathrm{M}}(1-Q(1))$
I2		$\varkappa_1\neq 0$	$Q(1)=1$
I3		$\varkappa_1=0$	$\nabla Q(1)=Bi_{\mathrm{M}}(1-Q(1))$
I4		$\varkappa_1=0$	$Q(1)=1$

different models describing the "isothermal" sorption process. In model I1 it is assumed that intraparticle and film resistances against mass transport exist and that the equilibrium isotherm is nonlinear. In model I2 it is assumed that only the transport resistance in the particle is important. Models I3 and I4 are analogous but the equilibrium isotherm is linear, *i.e.* $\varkappa_1 = 0$. These two models are linear and are tractable by analytical methods. It is also possible to create further two models, in which only the film resistance against mass transport is included. These models are not interesting from the point of view of this work and we will not consider them.

Analysis of the isothermal models

The simplest linear models I3 and I4 are analytically treated in detail in papers [2, 3]. Models I1 and I2 are nonlinear and must be solved numerically. *Weisz* and *Hicks* [4] solved model I2 numerically. They presented a verification for the existence of only a limited range of sorption—diffusion behaviour. The first limiting case is one of "weak" sorption, *i.e.* of a linear isotherm — model I4. The second limiting case of "strong" sorption is the so-called shell- or zone-progressive process of sorption with the assumption of a quasi steady state for the concentration gradient between active shell and outer boundary. Various empirical rate equations giving the rate of the mean internal concentration change as a function of a linear or quadratic driving force were published in papers [5—8]. Equivalent relationship for nonconstant diffusivity has been developed in [9]. Some other models can be found in papers [10—12] and all these are discussed in detail in [13]. Analytical solution of models I3 and I4 is well known [2, 3]. Time dependence of mean internal concentration $\bar{Q}$ for model I3 is

$$\bar{Q} = 1 - \frac{6}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2} \exp(-k^2 \pi^2 \tau') \tag{15}$$

and for model I4

$$\bar{Q} = 1 - 6 \sum_{k=1}^{\infty} \frac{Bi_M^2 \exp(-\beta_k^2 \tau')}{\beta_k^2 [\beta_k^2 + Bi_M (Bi_M - 1)]} \tag{16}$$

where $\tau' = \tau/(1+\delta)$ and β_k are the roots of

$$\beta_k \operatorname{cotg} \beta_k + Bi_M - 1 = 0 \tag{17}$$

Solution and computing methods

In the present work the method of orthogonal collocation has been used for the solution of I1—I4 in connection with the Runge—Kutta—Merson technique to

solve the resulting ordinary differential equations. Orthogonal collocation is one of several Methods of Weighted Residuals. The differential equation is satisfied in N predetermined points of the variation interval of the independent variable ξ. A very efficient collocation method results when these collocation points are chosen as zeroes of certain orthogonal polynomials, the so-called Jacobi polynomials. The considered problem is symmetrical about $\xi=0$ so that an even set of Jacobi polynomials can be used. Gradient ∇Q and Laplace operator $\nabla^2 Q$ are found as weighted average of the values of the dependent variable at all collocation points and at the pellet surface

$$\nabla Q(I)=\sum_{J=1}^{N+1} A(I, J)\ Q(J) \tag{18}$$

$$\nabla^2 Q(I)=\sum_{J=1}^{N+1} B(I, J)\ Q(J) \tag{19}$$

Matrices **A** and **B** are dependent only on the chosen polynomials and can be found once for all. By choosing a suitable weighting function for the Jacobi polynomials it is possible to fix the zeroes at points where it is important to obtain an accurate solution. The weighting function is generally in the form $(1-\xi^2)^\alpha \xi^{2\beta}$ *Villadsen* and *Michelsen* discussed in [14] various weighting functions for solving the effectiveness factor problem with boundary condition (*10*) and presented Bi_M — dependent optimal collocation. However, for N greater than 1 or 2, this method is not significantly better than the standard method with $\alpha=0$, $\beta=1/2$ for sphere geometry. For our purposes it is important to study the transient of the mean internal concentration $\bar{Q}$ or $\bar{q}$ defined as the integral of the Q solution over the volume of the particle.

$$\bar{Q}=\frac{1}{V}\int_V Q(\xi)\,\mathrm{d}V=3\int_0^1 Q(\xi)\xi^2\,\mathrm{d}\xi \tag{20}$$

Integral (*20*) can be calculated *via* the summation formula of the Radau quadrature

$$\bar{Q}=\sum_{I=1}^{N+1} W(I)\ Q(I) \tag{21}$$

Model equations can be transformed, by using formulas (*18*) and (*19*), into a set of N ordinary differential equations for N internal collocation points

$$\mathrm{f}(I)\frac{\mathrm{d}Q(I)}{\mathrm{d}\tau}=\sum_{J=1}^{N+1} B(I, J)\ Q(J) \quad I=1, N \tag{22}$$

where

$$\mathrm{f}(I)=\delta+\frac{1-\varkappa_1}{[\varkappa_1 Q(I)+(1-\varkappa_1)]^2} \tag{23}$$

The boundary condition (*10*) is transformed into

$$\sum_{J=1}^{N+1} A(N+1, J)\, Q(J) = Bi_M(1 - Q(N+1)) \quad \text{for } \tau > 0 \tag{24}$$

and the boundary condition (*14*) is

$$Q(N+1) = 1 \quad \text{for } \tau \geqq 0 \tag{25}$$

The initial condition (*8*) is

$$Q(I) = 0 \quad \text{for } \tau = 0 \quad I = 1, \ldots, N \tag{26}$$

Models I1 and I3 are described by the set of N equations (*22*) and by eqn (*24*) for $N+1$ unknown Q values. Usually it is simpler to eliminate the unknown boundary ordinate from the system of equations

$$Q(N+1) = -\frac{\sum_{J=1}^{N+1} A(N+1, J)\, Q(J)}{Bi_M + A(N+1, N+1)} + \frac{Bi_M}{Bi_M + A(N+1, N+1)} \tag{27}$$

Eqn (*27*) is inserted into each of the N collocation equations (*22*) and a system of N equations for N interior Q values is obtained

$$\mathbf{f}\frac{\mathrm{d}\boldsymbol{Q}}{\mathrm{d}\tau} = \mathbf{C}\boldsymbol{Q} + \boldsymbol{d} \tag{28}$$

with the initial condition

$$\boldsymbol{Q} = 0 \quad \text{at} \quad \tau = 0 \tag{29}$$

where $\mathbf{f}$ is the diagonal matrix of functions $f(I)$, $\boldsymbol{Q}$ is the column vector of dimensionless concentrations $Q(I)$, $\mathbf{C}$ is the $N \times N$ matrix with the elements of

$$C(I, J) = B(I, J) - \frac{B(I, N+1)\, A(N+1, J)}{Bi_M + A(N+1, N+1)} \tag{30}$$

and $\boldsymbol{d}$ is the column vector with the elements of

$$d(I) = \frac{B(I, N+1)\, Bi_M}{Bi_M + A(N+1, N+1)} \tag{31}$$

Models I2 and I4 are simpler with boundary condition (*25*). The set of N equations in matrix notation is similar to formula (*28*), but with the elements of $\mathbf{C}$ and $\boldsymbol{d}$ slightly different from the corresponding elements in eqns (*30*) and (*31*)

$$\begin{aligned} C(I, J) &= B(I, J) \\ d(I) &= B(I, N+1) \end{aligned} \tag{32}$$

Elements $A(I, J)$, $B(I, J)$, $W(I)$ were computed by programs listed in [14]. The

set of ordinary differential equations was integrated by the Runge—Kutta—Merson method with a variable step size, adjustment being made by calculating the truncation error.

Results and discussion

Figs. 1—4 graphically compare the collocation solution with the corresponding exact solution of I3 and I4 and that of I1 and I2 with the collocation solution for $N=25$. Fig. 1 presents the collocation approximations of I4 together with the exact solution (*15*) for $N=1, 2, 3$. Some dependence of average value of dimensionless sorbate concentration $\bar{q}$ is drawn against the root of dimensionless time. Fig. 1 shows the effect of the increasing number of collocation points on the precision of the collocation approximation. Fig. 2 shows the effect of various values of parameter Bi_M on the approximations of I3 solution (*16*) for $N=1$ and $Bi_M=1.100$. In all these cases the errors of collocation solution have a maximum for $\tau=0$, but the error decreases with increasing N and decreasing Bi_M. From eqns (*21*) and (*27*) it follows that for $\tau=0$

$$\bar{Q}=W(N+1)\frac{Bi_M}{Bi_M+A(N+1,\,N+1)}$$

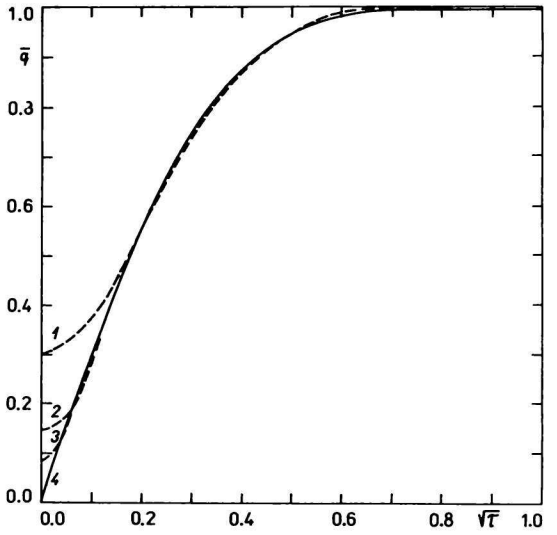

Fig. 1. Collocation approximation of model I4.
——— Exact solution; – – – – collocation solutions for $N=1, 2, 3$.

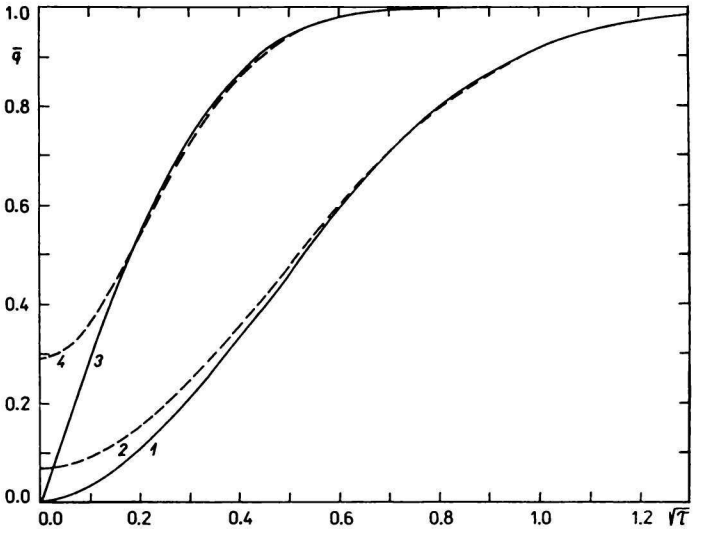

Fig. 2. Collocation approximation of model I3 for various Bi_M.
——— Exact solution; - - - - collocation solution for $N=1$.
1, 2. $Bi_M=1$; *3, 4.* $Bi_M=100$.

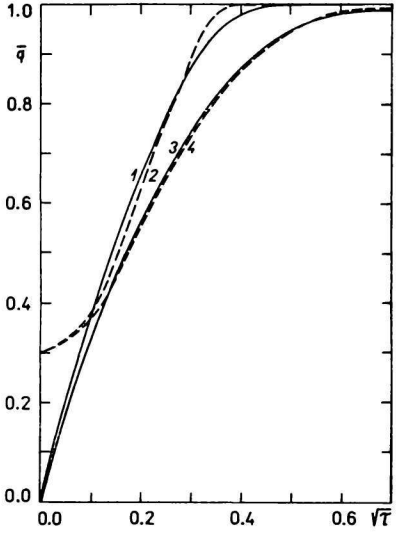

Fig. 3. Collocation approximation of model I2 for various $\varkappa_1$.
——— Exact solution ($N=25$); - - - - collocation solution for $N=1$.
1, 2. $\varkappa_1=0$; *3, 4.* $\varkappa_1=0.9$.

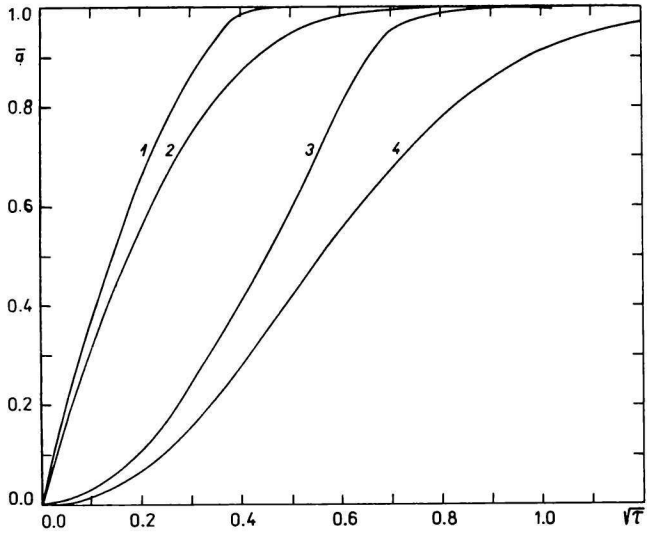

Fig. 4. Transients of $\bar{q}$ for model I1.
1. $Bi_M = 1000$, $\varkappa_1 = 0.908$; *2.* $Bi_M = 1000$, $\varkappa_1 = 0.0$; *3.* $Bi_M = 1$, $\varkappa_1 = 0.908$; *4.* $Bi_M = 1$, $\varkappa_1 = 0.0$.

For large Bi_M $(Bi_M \to \infty)$ and $\tau = 0$

$$\bar{Q} = W(N+1)$$

and for small Bi_M $(Bi_M \to 0)$ and $\tau = 0$

$$\bar{Q} = 0$$

Fig. 3 presents the effect of nonlinearity of the adsorption isotherm on the precision of collocation solution for I2. The dependence of the average value of dimensionless sorbate concentration $\bar{q}$ is drawn against $\sqrt{\tau}$ for $\varkappa_1 = 0$ and 0.9 for $N = 1$ along the precise solution curve for $N = 25$. From Fig. 3 it is seen that for linear isotherm $\varkappa_1 = 0$ the precision of collocation solution for small N is better. Fig. 4 shows the transients of $\bar{q}$ for I1 for various values of $\varkappa_1$ and Bi_M and $N = 8$. From Fig. 4 it is obvious that there exists a large range of the saturation time $\bar{q} = 0.99$ depending on the parameters of models.

Conclusion

Computation results showed that the method of orthogonal collocation is suitable for solving this type of equations. The accuracy of collocation solution increases rapidly with the increasing number of collocation points N and also with

increasing time. For the first rapid steps of adsorption process 8 collocation points are needed, but further a smaller number of points $N=2, 3$ is satisfactory. The decrease of values $\varkappa_1$ and Bi_M has also favourable influence on the accuracy of collocation solution. In all models the approximation error for $\tau=0$ has a maximum value. In general, the approximations of collocation solution are better for a less rapid process, when the concentration profiles in the particle are not very steep. The most general isothermal model is I1 and it is applicable in all cases of isothermal adsorption discussed in this text. In the next paper the application of the orthogonal collocation method will be reported for solving nonisothermal sorption models.

Symbols

a	adsorbate concentration in particle	$\mathrm{mol\,m^{-3}}$
a_i	initial adsorbate concentration in particle	$\mathrm{mol\,m^{-3}}$
a_s	monolayer capacity in the Langmuir isotherm	$\mathrm{mol\,m^{-3}}$
a_0^*	equilibrium adsorbate concentration	$\mathrm{mol\,m^{-3}}$
$A(I, J)$	differentiation weight from eqn (*18*)	
A	$(N+1)\times(N+1)$ matrix of $A(I, J)$ elements	
$B(I, J)$	differentiation weight from eqn (*19*)	
B	$(N+1)\times(N+1)$ matrix of $B(I, J)$ elements	
Bi_M	Biot number for mass transfer	
c	adsorptive concentration in the gaseous phase	$\mathrm{mol\,m^{-3}}$
c_b	adsorptive concentration in the bulk flow	$\mathrm{mol\,m^{-3}}$
c_i^*	equilibrium initial adsorptive concentration	$\mathrm{mol\,m^{-3}}$
$c_{x=R}$	adsorptive concentration at the particle surface	$\mathrm{mol\,m^{-3}}$
c_0	constant adsorptive concentration in the bulk flow	$\mathrm{mol\,m^{-3}}$
$C(I, J)$	matrix elements defined by eqns (*30*) or (*32*)	
C	$N\times N$ matrix with $C(I, J)$ elements	
$d(I)$	vector elements defined by eqns (*31*) or (*32*)	
d	column vector with $d(I)$ elements	
D_{ef}	effective diffusivity	$\mathrm{m^2\,s^{-1}}$
$\mathrm{f}(I)$	function defined by eqn (*23*)	
f	diagonal matrix of functions $\mathrm{f}(I)$	
h_M	film mass transfer coefficient	$\mathrm{m\,s^{-1}}$
K	equilibrium parameter in the Langmuir equation	$\mathrm{Pa^{-1}}$
N	number of internal collocation points	
p	partial pressure of adsorptive	Pa
q	dimensionless adsorbate concentration in particle	
$Q_{\xi=1}=Q(1)=Q(N+1)$	dimensionless concentration at the particle surface	
$\bar{Q}$	average dimensionless adsorptive concentration defined by eqns (*20*) or (*21*)	

$Q(I)$	dimensionless concentration at I-th collocation point	
$\boldsymbol{Q}$	column vector with $Q(I)$ elements	
R	radius of particle	m
t	time	s
V	volume of particle	m^3
$W(I)$	Radau quadrature weight from eqn (*21*)	
x	space coordinate	m
α, β	weight parameters for Jacobi polynomials	
β_k	k-th root of eqn (*17*)	
δ	dimensionless parameter defined by eqn (*6*)	
ε	porosity of particle	
$\varkappa_1$	dimensionless parameter defined by eqn (*12*)	
ξ	dimensionless space coordinate	
τ	dimensionless time	

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