Solution to the homogeneous surface diffusion model for batch adsorption systems using orthogonal collocation

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Abstract

A solution to the homogeneous surface diffusion model has been developed and incorporated into a batch adsorption model based on external boundary layer mass transport and homogeneous diffusion. The model has been extensively tested using three experimental adsorption systems, namely, phenol on carbon, basic yellow dye on carbon and basic blue dye on silica. The effect of initial solute concentration and adsorbent mass has been studied in 23 batch experiments, which have been modelled using the collocation solution method to solve the homogeneous surface diffusion equation. The theoretical concentration decay curves show a high degree of correlation with experimental data. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Adsorption may be defined as the selective removal of a component of a fluid mixture by contacting the fluid with a solid adsorbent. Applications include the purification of drinking water, removal of colourants and the removal of harmful pollutants from wastewater effluents. It also has application in air pollution control and many processes in chemical engineering.

Materials like activated carbon, silica, peat and wood/wood meal with their porous structure provide a large specific surface area for the adsorption of pollutant particles. Many types of adsorption plant exist e.g. batch, fixed bed, moving bed and development work on these systems is continuously going. Much research is also being done investigating the mechanisms and kinetics of adsorption. The adsorption process is complex and considerable use is made of mathematical models to describe the possible rate-controlling mechanisms. In addition computers are used to perform accurate and quick evaluation of the model solutions. One of the most widely used methods [1,2] for solving the diffusion equation is the numerical Crank–Nicolson method [3]. An alternative more simplified method [4,5] has been applied and is solved using the convolution theorem and a fourth order Runge–Kutta method. Orthogonal collocation

has been applied to solve the diffusion equation using one collocation point [6]. A number of workers, [7–9] using a linear driving force approximation, developed improved solutions to this particular case of homogeneous diffusion. Accuracy of the prediction was a problem for these approximate solutions but more accurate methods of solution were developed [10,11].

Several solutions are available in the literature for solving the homogeneous diffusion equation but the search for accuracy, simplicity and reducing the number of limiting assumptions continues. The present paper uses a single constant surface diffusivity to generate theoretical concentration decay curves for three sorption systems although it is feasible to correlate surface diffusivity with surface coverage [12–14]. The current paper restricts itself to using a single surface diffusivity to study the application of the collocation solution methodology. The model is simple and easy to use and the assumption of a single D_s provides accurate solutions for a wide range of adsorbents over a wide range of experimental conditions.

The basis of the collocation solution to be presented in this paper is the model proposed by Matthews and Weber [1] and extended by McKay et al. [2] and McKay and Walters [15].

This paper applies the collocation solution method to the following batch adsorption systems: phenol on activated carbon, Basic Yellow dye 21 on activated carbon and Basic Blue 69 on Sorbsil silica.

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Nomenclature

a, b	isotherm parameters
A_p	surface area of adsorbent particle (cm^2)
C	bulk liquid-phase concentration (mg/cm^3)
C_s	liquid-phase surface concentration (mg/cm^3)
D	diffusion coefficient (cm^2/s)
erf	error function
F, λ	trial solution functions
k_f	external mass transfer coefficient (cm/s)
n	number of integration steps
q	average solid-phase concentration (mg/g) or (mg/mg)
q_i	particle concentration (mg/g) or (mg/mg)
q_s	solid-phase surface concentration (mg/g) or (mg/mg)
r	distance within particle (cm)
R	radius of adsorbent particle (cm)
t	time period for adsorption (x)
ΔT	time step-length
u	integral solution f(x)
V	volume of solution (cm^3)
V_p	volume of adsorbent particle (cm^3)
W	weight of adsorbent material (g) or (mg)
x	dimensionless distance
x'	collocation point
Δx	distance step-length

Greek Symbols

β	isotherm exponent
ε	voidage of adsorbent particle
ρ	density of adsorbent particle (mg/cm^3)
τ	dimensionless time
λ	Crank–Nicholson parameter
λ_0	lamda zero parameter

2. Theory

A model has been developed to solve diffusional mass transport agitated batch adsorption systems. The present method by collocation is one of the weighted residual methods [6], and is closely allied to finite element theory [16]. The method of collocation has been applied successfully to solve a number of boundary-value problems [17,18] and has been used extensively to solve transport and chemical reactor problems where independent variables extend over a finite domain [19,20]. The method basically consists of choosing a trial solution containing several arbitrary constants (for ordinary differential equations) and functions (for partial differential equations) which are determined by requiring the differential of the integral equation to be satisfied according to some specified criteria. The method is simple and, at least for ordinary differential equations and some partial differential equations, has given accurate results for very few arbitrary constants/functions.

Table 1
Redlich–Peterson isotherm constants

Solute	Adsorbent	a (dm^3/g)	b (dm^3/mg)	β
Phenol	Carbon	11.3	0.069	0.920
Basic Yellow 21	Carbon	463.0	0.771	0.993
Basic Blue 69	Silica	0.43	0.020	0.990

The adsorption model assumes that the rate controlling processes are mass transport across the boundary layer and internal mass transport based on a homogeneous surface diffusion model (HSDM). The boundary layer mass transport, mass balance, homogeneous diffusion and equilibrium conditions are represented by Eqs. (1)–(3), respectively

$$V_p\rho(1 - \varepsilon)\frac{dq}{dt} = \frac{k_f A_p(C - C_s)}{1000} \tag{1}$$

$$\frac{\partial q_i}{\partial t} = D\left(\frac{\partial^2 q_i}{\partial r^2} + \frac{2}{r}\frac{\partial q_i}{\partial r}\right) \tag{2}$$

The Langmuir, Freundlich and Redlich–Peterson isotherms were analysed and the equation with the minimum error function was selected, namely, the Redlich–Peterson equation. The three parameter Redlich–Peterson [20] equation was selected to facilitate integration

$$q_s = \frac{aC_s}{1 + bC_s^\beta} \tag{3}$$

The values of the three constants a, b and β for each system are given in Table 1.

The average concentration in the particle q, is given by Eq. (4)

$$q = \frac{3\int_0^r q_i R^2 dr}{R^3} \tag{4}$$

The mass balance for the agitated batch adsorber is represented by

$$-V\frac{dC}{dt} = W\frac{dq}{dt} \tag{5}$$

Integrating,

$$\int_{C_n}^{C_{n+1}} dC = -\frac{W}{V}\int_{q_n}^{q_{n+1}} dq \tag{6}$$

Therefore

$$C_{n+1} = C_n - \frac{W}{V}(q_{n+1} - q_n) \tag{7}$$

where n signifies any point in time.

Eqs. (2) and (5) are subject to the following initial and boundary conditions:

$$q_i(r, 0) = 0; \ C(0) = C_0 \tag{8}$$

$$q_i(R, t) = q_s(t) \tag{9}$$

3. Model application and discussion

3.1. Solution implementation

The mathematical model necessitates the calculation of q, C, q_s and C_s in strict order and the collocation algorithm is set up to perform the analysis in the order.

Dimensionless variables τ and x are defined and introduced for the independent variables t and r in the equations

$$\tau = \frac{Dt}{R^2} \tag{10}$$

$$x = \frac{r}{R} \tag{11}$$

and defining

$$u = xq_i \tag{12}$$

Now Eqs. (1)–(9) become

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial x^2} \tag{13}$$

$$u(0, \tau) = 0 = u(x, 0) \text{ and } u(1, \tau) = q_s(\tau) \tag{14}$$

$$q(\tau) = 3\int_0^1 u(x, \tau)x\,dx \tag{15}$$

$$\frac{dq}{d\tau} = \frac{3k_f R(C - C_s)}{D\rho(1 - \varepsilon)} \tag{16}$$

$$C = C_0 - \left(\frac{W}{V}\right)q \tag{17}$$

The basis of the collocation method is to choose a trial solution for the differential equation under examination which is consistent with the physical and mathematical constraints imposed by the problem. In orthogonal collocation the trial solution is expanded as a sum of products. One term of the product is an arbitrary constant/function which is to be determined. The other term is an orthogonal polynomial; the trial solution is therefore expanded in terms of orthogonal polynomials. These polynomials must also comply with the constraints of the problem.

In the present work, it was therefore decided to apply the method of cartesian collocation. The method employed took as its trial solution the integral formulated exactly as in the analytical solution of McKay et al. [2].

$$u(x, \tau) = f(\tau)\left\{e^{-\lambda(1-x)^2} - e^{-\lambda(1+x)^2}\right\} \tag{18}$$

where $f(\tau)$ and $\lambda(\tau)$ are average time functions to be determined. Since there are two unknowns then two equations are required to solve for them. The first equation is the differential of u with respect to t and is obtained by substituting Eq. (18) into the diffusion Eq. (13) noting that

$$\frac{\partial u}{\partial \tau} = f'\left\{e^{-\lambda(1-x)^2} - e^{-\lambda(1+x)^2}\right\}$$
$$+ f\left\{-(1-x)^2\lambda' e^{-\lambda(1-x)^2} + (1+x)^2\lambda' e^{-\lambda(1+x)^2}\right\} \tag{19}$$

The first differential of u with respect to x is given in Eq. (20)

$$\frac{\partial u}{\partial x} = f(\tau)\left\{2(1-x)\lambda e^{-\lambda(1-x)^2} + 2(1+x)\lambda e^{-\lambda(1+x)^2}\right\} \tag{20}$$

The second order differential of u with respect to x is given by Eq. (21)

$$\frac{\partial u^2}{\partial x^2} = f\left\{-2\lambda e^{-\lambda(1-x)^2} + 2\lambda e^{-\lambda(1+x)^2} + 4(1-x)^2\lambda^2 e^{-\lambda(1-x)^2} - 4(1+x)^2\lambda^2 e^{-\lambda(1+x)^2}\right\} \tag{21}$$

The equation must be satisfied at some $x=x'$, x' is the collocation point, giving

$$f'\left\{e^{-\lambda(1-x')^2} - e^{-\lambda(1+x')^2}\right\}$$
$$+ f\lambda'\left\{-(1-x')^2 e^{-1(1-x')^2} + (1+x')^2 e^{-\lambda(1+x')^2}\right\}$$
$$= 2f\lambda\left\{-e^{-\lambda(1-x')^2} + e^{-\lambda(1+x')^2} + 2(1-x')^2\lambda e^{-\lambda(1+x')^2}\right.$$
$$\left. -2(1+x)^2\lambda e^{-\lambda(1+x)^2}\right\} \tag{22}$$

For the second equation, Eqs. (16) and (17) are combined to give the condition

$$\int_0^1 \frac{\partial u(x, t)}{\partial t}x\,dx = \frac{k_f R(C - C_s)}{D\rho(1 - \varepsilon)} \tag{23}$$

$$f'\int_0^1\left\{xe^{-\lambda(1-x)^2} - xe^{-\lambda(1+x)^2}\right\}dx$$
$$+ \lambda'f\int_0^1\left\{-x(1-x)^2 e^{-\lambda(1+x)^2} + x(1+x)^2 e^{-\lambda(1+x)^2}\right\}$$
$$\times dx = \frac{k_f R(C - C_s)}{D\rho(1 - \varepsilon)} \tag{24}$$

At some small initial time τ_1 is taken for the initial condition for Eqs. (22) and (24). In order to run the program it is necessary to input an initial value for which has to provide a stable solution value. At the beginning of the adsorption process this criterion is most critical because the slope of the concentration decay curve is at its maximum and therefore most sensitive. The relationship shown in Eq. (25) was obtained by trial and error for several of the systems shown in this research

$$\lambda(\tau_1) = \frac{\lambda_0}{4\tau_1} \tag{25}$$

It is expected that λ_0 is a slowly varying function of τ_1, almost constant for sufficiently small τ_1.

The initial condition, $f(\tau_1)$ for (22) and (24) is obtained from (16) and (17) for sufficiently small τ_1

$$f(\tau_1) \int_0^1 x \left\{ e^{-\lambda(1-x)^2} - e^{-\lambda(1+x)^2} \right\} dx = \frac{\tau_1 k_f R C_0}{D\rho(1-\varepsilon)} \quad (26)$$

The integral in (26) is evaluated using standard methods giving

$$f(\tau_1) \left\{ \frac{\sqrt{\pi}}{2\sqrt{\lambda}} \mathrm{erf}(2\sqrt{\lambda}) - \frac{1}{2\lambda} + \frac{e^{-4\lambda}}{2\lambda} \right\} = \frac{\tau_1 k_f R C_0}{D\rho(1-\varepsilon)} \quad (27)$$

where erf is the error function.

The ordinary differential Eqs. (22) and (24) are solved simultaneously for $f(\tau)$ and $\lambda(\tau)$ and the boundary condition for the surface concentration using (24) becomes

$$q_s(\tau) = f(\tau) \left\{ 1 - e^{-4\lambda(\tau)} \right\} \quad (28)$$

The best fit data were those obtained by minimizing the error function, F, as defined in Eq. (29)

$$F = \frac{1}{m} \sum_{j=1}^{m} \left(\frac{q_{exp} - q_{theo}}{q_{exp}} \right)^2 \quad (29)$$

The set of equations are now ready for integration from $\tau = \tau_1$. The collocation algorithm now performs the solution analysis in the order (i) followed by (ii).

1. Eq. (18) must be solved first and this requires the solution of the pair of coupled ordinary differential collocation Eqs. (19) and (20). These provide values for $f(\tau)$ and $\lambda(\tau)$ in Eq. (18) at each time step. The function $f(\tau)$ is also used to determine the surface concentration in the solid phase using Eq. (28). Three methods were tested to solve the pair of differential collocation equations, namely a Gear Revision variable-order variable-step Adams method, a Runge–Kutta–Merson method and a variable-order variable-step Backward differentiation formulae method. It was found that in the first two methods the coupled equations were stiff, essentially having a solution which varied rapidly. On this basis, in order to make the solution stabilise quicker it was found that the Backward differentiation formulae was the most appropriate.

2. The liquid surface concentration and the asymptotic concentration, that is, the concentration at which adsorption equilibrium has been achieved, were calculated using Newton's method for non-linear equations.

The objective now is to determine values for q, the average concentration of solute in the adsorbent particle, C, the concentration of solute in the solution, and q_s and C_s the surface concentrations in the solid and liquid phases, respectively. This enables two HSDM integrals to be solved and theoretical concentration versus time curves to be generated. The average particle concentration, q, the surface concentration in the solid phase, q_s and the solution concentration C at each time step are calculated numerically using Eqs. (16), (28) and (29), respectively. An internal check is made after

50 steps to see if the value of q_s is increasing. If it is not the program/run is halted. The check is made at 50 steps because it is possible for the q_s value to drop near the start and then rise again. A numerical technique for calculating the particle concentration over the particle's radius at selected times was also set up using the Eq. (18). The number of distance steps Δx, at which the concentration is evaluated is specified by an input variable. This will correspond to a set time interval, $\Delta \tau$, for integration. The distance step is progressively decreased automatically increasing the number of integration steps. This procedure is adopted until two consecutive sets of output data have converged to the same limiting values. An alternative method of establishing the accuracy of the integration to check the closure of the material balance, that is, moles adsorbed in solid phase versus moles removed from fluid phase.

3.2. Application of the model

The model has been developed to evaluate the integral in Eqs. (19) and (23) and to give the theoretical concentration decay curve with the corresponding surface equilibrium conditions using the two resistance approach, that is, external mass transfer and solid phase surface diffusion. Initially, the value of the external mass transfer coefficient was taken from single resistance analysis values. The independent estimation of the external mass transfer coefficient was obtained using established techniques [22–24]. All the techniques for determining k_f in batch adsorbers depend on some function related to the initial slope of the concentration versus time decay curve. Therefore, the accuracy in k_f is related to the severity of this slope. Application of the different techniques indicate the maximum k_f is $\pm 20\%$. Using this value of k_f and an estimate of the solid diffusivity, together with: (i) particle radius, (ii) solution volume, (iii) adsorbent mass, (iv) particle porosity, (v) adsorbent density, (vi) isotherm constants, (vii) the value of time relating to the extent of time allowed for adsorption and (viii) data relating to step length for integration; it is possible to obtain a theoretical decay curve. By iterating between various solid diffusivity coefficients it is possible to obtain a 'best' fit to the experimental decay curves for batch adsorption.

The isotherm data are used in the form of the Redlich–Peterson [21] isotherm Eq. (4) and the isotherm constants for the three adsorption systems are shown in Table 1.

3.2.1. Adsorption of phenol on activated carbon

The adsorption of phenol onto activated carbon is the most commonly used aqueous phase adsorption system reported in the literature [25–28]. The experimental results shown in Figs. 1 and 2 are based on work by Bino [29]. Fig. 1 shows the experimental points compared with the theoretical curves for three different initial phenol concentrations for an adsorption contact period of 1 h. A constant surface diffusivity was used for the modelling and the external mass transfer coefficient and diffusion coefficient are presented in Table 2.
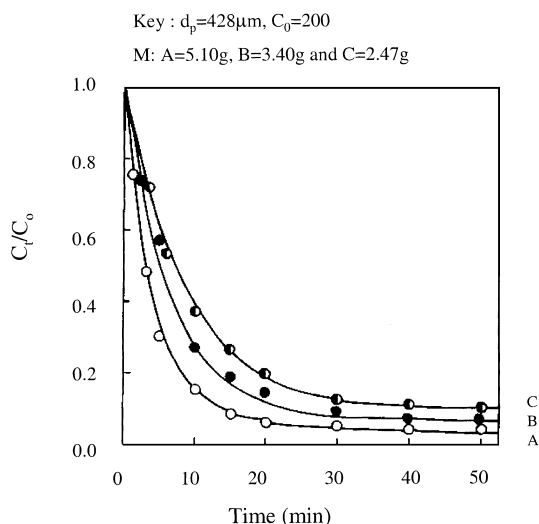
Key : d_p=428μm, C_0=200

M: A=5.10g, B=3.40g and C=2.47g

Fig. 1. Effect of carbon mass on uptake of phenol.

Key : d_p=428μm, M=0.85g
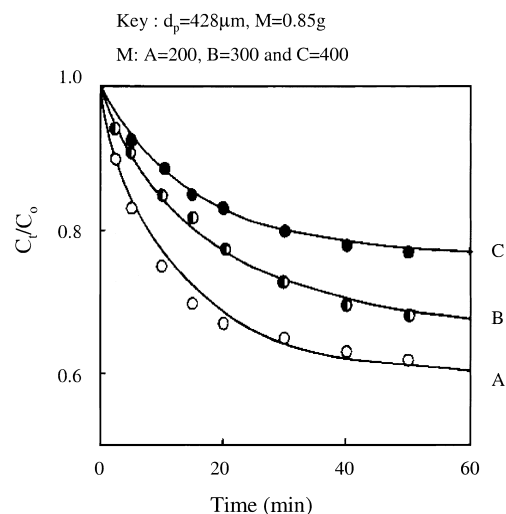
M: A=200, B=300 and C=400

Fig. 2. Effect of initial concentration for the adsorption of phenol on carbon.

The agreement between the experimental data and theoretically predicted curves is quite good. The main deviation is at the highest carbon mass where the carbon surface area to phenol mass ratio is very high. It is possible there may be some surface reaction with the most active sites on the carbon or an alternative, more likely, reason is that over 1 h the surface diffusion coefficient begins to change in magnitude.

Fig. 2 shows the effect of three different initial dye concentrations for the adsorption of phenol onto activated carbon. For the first 30 min the agreement is very good, except for the lowest initial dye concentration which by

implication means the highest carbon surface area to dye mass ratio, as in the data for varying carbon mass. However, as time increases it can be seen that the experimental points begin to decrease more rapidly than the theoretically predicted curves. It is possible that after an initial period during which homogeneous solid surface diffusion is rate controlling that the surface diffusion coefficient may become variable in the rate determining step, that is, when a significant fraction of the carbon surface is occupied.

Based on these observations it was decided that the orthogonal collocation solution should be tested using two

Table 2
External mass transfer coefficients and homogeneous solid diffusion coefficients

Solute	Adsorbent	C_0 (mg/dm^3)	M (g)	d_p (μm)	k_f (10^{-5} m/s)	D_s (10^{-14} m^2/s)
Phenol	Carbon	200	2.47	428	10±2	30±5
Phenol	Carbon	200	3.40	428	10±2	30±5
Phenol	Carbon	200	5.10	428	10±2	30±5
Phenol	Carbon	200	0.85	428	10±2	30±5
Phenol	Carbon	300	0.85	428	10±2	30±5
Phenol	Carbon	400	0.85	428	10±2	30±5
BY21	Carbon	100	0.108	428	3.0±0.5	2.5±0.5
BY21	Carbon	100	0.216	428	3.0±0.5	2.5±0.5
BY21	Carbon	100	0.316	428	3.0±0.5	2.5±0.5
BY21	Carbon	100	0.425	428	3.0±0.5	2.5±0.5
BY21	Carbon	100	0.425	428	3.0±0.5	2.5±0.5
BY21	Carbon	75	0.425	428	3.0±0.5	2.5±0.5
BY21	Carbon	50	0.425	428	3.0±0.5	2.5±0.5
BY21	Carbon	25	0.425	428	3.0±0.5	2.5±0.5
BY69	Silica	200	8.5	605	0.2±0.02	1.2±0.2
BY69	Silica	200	12.7	605	0.2±0.02	1.2±0.2
BY69	Silica	200	17.0	605	0.2±0.02	1.2±0.2
BY69	Silica	50	17.0	605	0.2±0.02	1.2±0.2
BY69	Silica	100	17.0	605	0.2±0.02	1.2±0.2
BY69	Silica	150	17.0	605	0.2±0.02	1.2±0.2
BY69	Silica	200	17.0	605	0.2±0.02	1.2±0.2
BY69	Silica	250	17.0	605	0.2±0.02	1.2±0.2
BY69	Silica	300	17.0	605	0.2±0.02	1.2±0.2

Fig. 3. Effect of carbon mass for the adsorption of Basic Yellow 21 dye onto activated carbon.
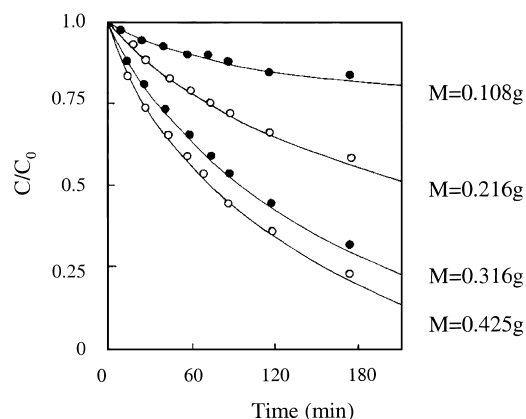

Fig. 4. Effect of initial dye concentration for the adsorption of Basic Yellow 21 dye onto activated carbon.

other adsorption systems. One system, using the same carbon adsorbent but the sorbate should be a larger adsorbing molecule, in the present case a dyestuff, Basic Yellow 21. The second system would be based on the adsorption of a dyestuff, Basic Blue 69, onto a different adsorbent, namely, Sorbsil silica. The experimental data for these two systems were available, Al-Duri [30] and Aga [31], respectively.

3.2.2. Adsorption of Basic Yellow 21 dye onto carbon

The homogeneous solid phase diffusion model has been used to simulate the results for the adsorption of Basic Yellow 21 onto activated carbon. Fig. 3 shows the effect of varying carbon mass on the adsorption concentration versus time decay curve for four carbon masses. The experimental data points are plotted as dimensionless concentration, C_t/C_0, against contact time. The theoretical concentration decay curve shows excellent correlation up to almost 2 h, at which time the experimental data points begin to fall more rapidly at the two higher dye concentrations. As in the case of phenol adsorption, it is likely that the surface diffusivity begins to change as the adsorbent surface becomes saturated or even pore diffusion starts to contribute to the adsorption mechanism and the deviation between experimental and theoretical data occurs.

Fig. 4 shows the effect of initial dye concentration on the concentration versus time decay curves. In all cases the correlation between experimental and theoretical data is good. This agreement is probably due to the fact that all the dye concentrations are relatively low compared to the maximum saturation capacity of 543 mg/g for activated carbon for Basic Yellow 21 [21]. All the concentration versus time concentration decay curves have been modelled using a constant solid phase diffusivity as shown in Table 2.

3.2.3. Adsorption of Basic Blue 69 on Sorbsil silica

Sorbsil silica was selected as an alternative adsorbent to activated carbon. Its structure is substantially different in that it has only limited micropores, less than 20%, whereas carbon has over 80% of its surface area in micropores. The
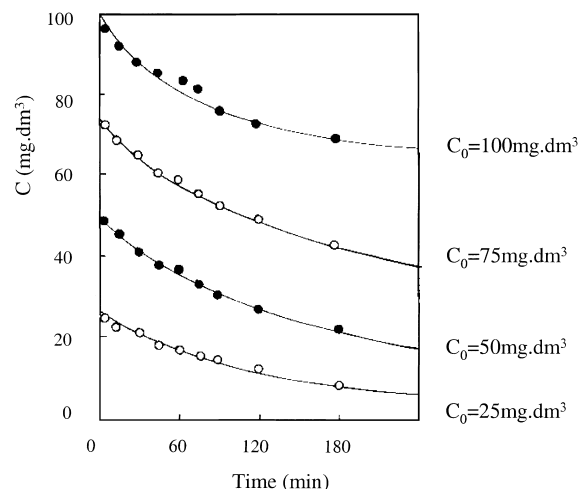
model has been applied to the adsorption of Basic Blue 69 dye onto Sorbsil silica using the experimental data of Aga [31]. Fig. 5 shows the effect of varying silica mass on the concentration decay curves. The correlation between experimental data points and the theoretical curves is very good, particularly at lower contact times and higher silica masses. After approximately 100 min, the trend is similar to the previous two systems at lower silica surface area to dye mass ratios, there is a slight deviation between the solid line theoretical decay curve and the experimental data points. The theoretical decay curves decrease slower than the experimental data points. Figs. 6 and 7 show the effect of six initial dye concentrations. The agreement between experimental data points and theoretical concentration de-
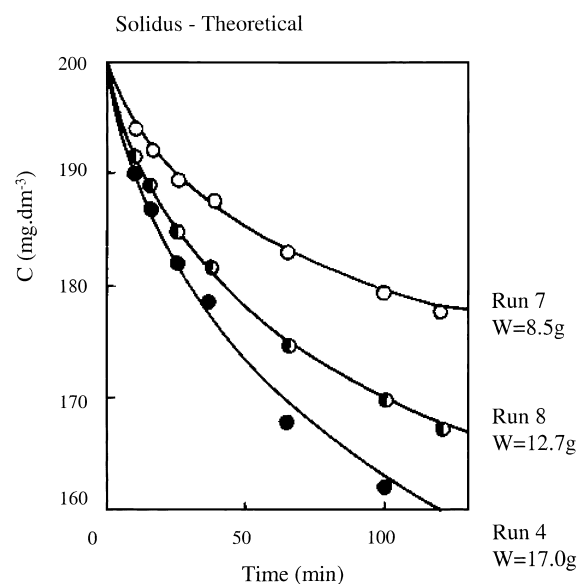

Fig. 5. Effect of varying silica mass for the adsorption of Basic Blue 69 on silica (500–710 μm).
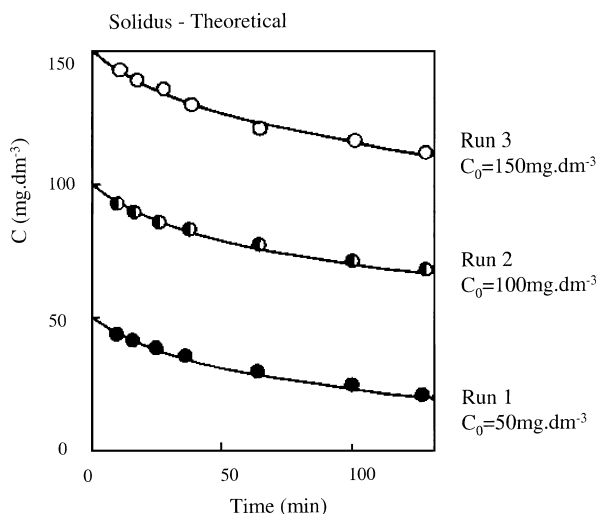
Solidus - Theoretical

Fig. 6. Effect of initial dye concentration for the adsorption of Basic Blue 69 on silica.

cay curves is excellent and for the two highest initial dye concentrations, that is the lowest silica surface area to dye mass ratios, the experimental data points decrease faster than the theoretical decay curves.

The rapid build up of solid surface phase concentration with time has created problems in solving previous homogeneous surface diffusion models in handling small increments in the driving force for mass transfer resulting in unstable output. However, this problem can be overcome in the present model by careful selection of the collocation parameters and suitably small integration time increments.

Values of solid diffusivities have been given in Table 2 literature values include 8.9×10^{-14}, $2.5 \times 10^{-12}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ for sodium laurylsulphonate and phenol, respectively [32];
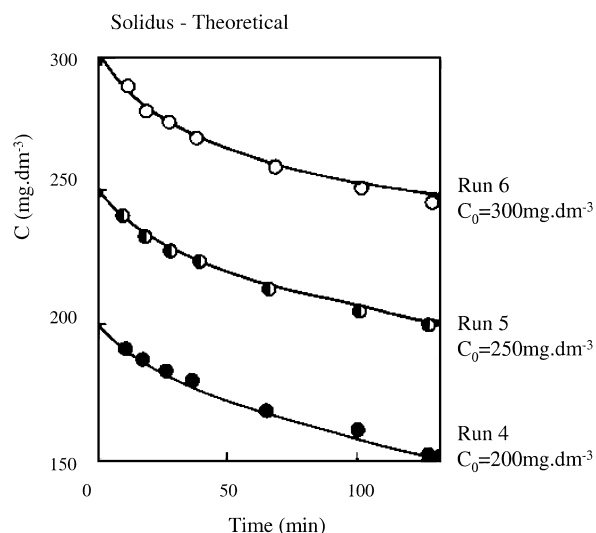
Solidus - Theoretical

Fig. 7. Effect of initial dye concentration for the adsorption of Basic Blue 69 on silica.

1.58×10^{-12}, 1.7×10^{-12}, 0.99×10^{-13} and 1.38×10^{-12} $\mathrm{m}^2\,\mathrm{s}^{-1}$ for p-bromophenol, p-toluene sulphonate, dodecyl benzene sulphonate and phenol, respectively [1]; 1.7×10^{-11}–1.9×10^{-11}, 2.0×10^{-12}–8.0×10^{-12}, 4.0×10^{-12} -28×10^{-12}, 5×10^{-12}–11×10^{-12}, 1.8×10^{-12}–3.1×10^{-12}, and 0.1×10^{-8}–$0.3 \times 10^{-8}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ for p-nitrophenol, phenol, p-chlorophenol, 2,4-dichlorophenol and dodecyl benzene sulphonate, respectively [33]. All the previous results were based on carbon adsorption and the range of values given in the last reference are due to the effect of different initial solute concentrations influencing the surface diffusion component. A value of $1.8 \times 10^{-11}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ was obtained by Rice [34] for the adsorption of sodium chloride solution on resin using a solid diffusion mechanism. However, the value of the effective solid diffusivity obtained in this work for a range of silica masses and initial dye concentrations was $1.2 \pm 0.2 \times 10^{-14}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ which is of a similar order of magnitude to the result for dodecyl benzene sulphonate, a large organic molecule with some ionic character. The adsorption rate is controlled by external mass transfer and homogeneous surface diffusion. The experimental decay curves were tested using film resistance models only [22,24] during the analysis and evaluation of the external mass transfer coefficient. In all cases, the adsorption rate was only controlled by film mass transfer for the initial 2–5 min. After this short initial period of theoretical film only concentration decay curve decreased much more rapidly that the experimental concentration decay curve. The effectiveness factor technique [35] was also used to confirm this phenomenon. It is therefore apparent that surface diffusion is the predominant rate controlling mechanism for the majority of the adsorption process.

The results of the application of the orthogonal collocation model, presented in this paper, applying a constant solid phase diffusivity to a range of sorption systems, produces excellent agreement between the theoretical model and experimental data. At high surface coverage in Figs. 2, 3 and 5, the results of the present work suggest a variable surface diffusivity may be applicable [36,37] or even contribution from pore diffusion may be appropriate to several experiments. In this case an effective diffusivity combining pore and surface diffusion may be involved in the rate controlling process.

Surface diffusion, studied in a 'film-solid diffusion' model was found to be concentration dependent [30]. Komiyama and Smith [28] found that surface diffusion contributed 20 times as much as pore volume diffusion. The maximum pore diffusion contribution is 20%; in most cases it is 10% [39]. Therefore, surface diffusion has an inevitable effect on the observed effective diffusivity which can be considered as a 'lumped' diffusivity that includes solid and pore diffusion effects. This means that the internal diffusion rate for the combined mechanism is given by

$$\frac{\partial q}{\partial t} = D_{\mathrm{p}}\frac{\partial C}{\partial r} + \rho_{\mathrm{s}}D_{\mathrm{s}}\frac{\partial q}{\partial r} \tag{30}$$

that is

$$\frac{\partial q}{\partial t} = \left(D_{\mathrm{p}} + \rho_{\mathrm{s}} D_{\mathrm{s}} \frac{\partial q}{\partial C} \right) \frac{\partial C}{\partial r} \qquad (31)$$

However, for the 'film-solid diffusion' model the rate of internal mass transfer is given by

$$\frac{\partial q}{\partial t} = D_{\mathrm{eff}} \frac{\partial C_{\mathrm{t}}}{\partial r} \qquad (32)$$

Hence

$$D_{\mathrm{eff}} = D_{\mathrm{p}} + \rho_{\mathrm{s}} D_{\mathrm{s}} \frac{\partial q}{\partial C} \qquad (33)$$

where D_{p} gives the pore diffusion contribution and $\rho_{\mathrm{s}} D_{\mathrm{s}}(\partial q / \partial C)$ represents the contribution of surface diffusion. $\partial q / \partial C$ is the slope of the adsorption isotherm. It is a function of the initial sorbate concentration and the V/m ratio. Following from the shape of isotherm it decreases as initial concentration increases or V/m increases because both lead to a higher equilibrium sorbate concentration [33]. This leads to the following deductions:

1. D_{eff} decreases with increasing initial solute concentration, as $\partial q / \partial C$ decreases, it also decreases as V/m increases for the same reason. This was obtained by Fritz et al. [33] and possibly in the present study.
2. The relative importance of surface diffusion decreases as the initial solute concentration increases. This was also obtained by Komiyama and Smith [38], who found that the ratio $D_{\mathrm{s}} q_{\mathrm{e,t}} / D_{\mathrm{p}} \varepsilon_{\mathrm{p}} C_{\mathrm{e,t}}$ decreases as the initial sorbate concentration increases. Also the surface-pore contribution decreases from 5 to 1.2 as the initial concentration changes from 25–100% saturation [39]. This confirms the above point on the relative contributions from different mechanisms.

Currently work is being carried out to develop a pore-surface diffusion model. In addition a detailed technical comparison is being made between a number of solution methods to the homogeneous solid phase diffusion model by comparing outputs generated from the solution models directly, rather than direct testing against experimental data where the mechanism of adsorption is a major source of controversy.

4. Conclusions

The collocation method has proved successful in solving the homogeneous diffusion model for three adsorption systems. Experimental data points and theoretically predicted concentration decay curves are in good agreement within the constraints imposed of the model, which are: firstly, only homogeneous solid phase diffusion is taking place, secondly, the solid phase diffusion coefficient has been maintained constant for any particular sorption system.

The model has successfully been applied to three adsorption systems. The adsorption of phenol, a reasonably small organic molecule onto activated carbon and the adsorption of a much larger dye molecule onto carbon both give excellent correlation between the experimental data and theoretical predictions. The third system is a large organic dye molecule also but the adsorbent, silica, is not as heterogeneous as the activated carbon and also not as microporous, but the model still provides excellent correlation to the experimental data. Therefore, this orthogonal collocation solution for HSD can be applied to a range of different solutes and adsorbents.

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