

Adsorption of Dyes onto Bagasse Pith Using a Solid Diffusion Model

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Synopsis

The adsorption of four dyes (Basic Blue 69, Basic Red 22, Acid Blue 25, and Acid Red 114) onto bagasse pith has been studied using an agitated batch adsorber. The variables studied were initial dye concentration and pith mass. A mathematical model has been developed based on external mass transfer and solid-phase diffusion. The model has been used to generate theoretical concentration-time decay curves, and these results were adjusted to experimental data by a best fit approach. The external mass transfer coefficients are 2.0×10^{-3} , 1.5×10^{-3} , 8.0×10^{-4} , and 5.0×10^{-4} cm s⁻¹ and the solid diffusivities are 1.1×10^{-8} , 1.0×10^{-8} , 6.0×10^{-9} , and 3.0×10^{-9} cm² s⁻¹ for Basic Blue 69, Basic Red 22, Acid Blue 25, and Acid Red 114.

INTRODUCTION

Bagasse pith is abundantly available as a byproduct from the sugar industry. The equilibrium adsorption isotherms have been determined for the adsorption of four dyes, Basic Blue 69, Basic Red 22, Acid Blue 25, and Acid Red 114, onto pith.¹ Furthermore, details of the batch adsorber have been reported² together with experimental results.

The aim of the present paper is to apply a model based on external mass transfer and homogeneous diffusion to the adsorption of dyes on pith. Experiments have been undertaken to study the effects of initial dye concentration and pith mass on the rate of adsorption. Theoretical concentration-time decay curves were predicted by the model and compared with experimental results.

THEORY

Adsorption rate data from batch reactors have been analyzed using a model that includes the effects of external mass transfer, unsteady state intraparticle diffusion in the particle, and nonlinear adsorption isotherm. The theoretical model is based on the fundamental assumptions proposed by Mathews and Weber,³ in which the adsorbent particles are assumed to be identical spheres of radius R .

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Fundamental Equations

External mass transfer resistance in a completely mixed adsorber is principally in the hydrodynamic film surrounding the particle. Mass transfer from the fluid phase to the solid surface is expressed in terms of the time rate of change of the average solute concentration, \bar{q}_t , of the particle,

$$\frac{d\bar{q}_t}{dt} = \frac{k_f \cdot A_p}{V_p \cdot \rho_p} (C_t - C_s) \quad (1)$$

The average solute concentration of the particle is obtained by integrating the pointwise concentration over the volume of the particle.

$$\bar{q}_t = \frac{3}{R^3} \int_0^R q \cdot r^2 \cdot dr \quad (2)$$

The isotherm expression may be written in the general form of the three parameter Redlich-Peterson isotherm⁴

$$q_s = (K_R \cdot C_s) / (1 + a_R \cdot C_s^\beta) \quad (3)$$

where $\beta \leq 1.0$.

Transport within the solid phase for a spherical particle, assuming symmetry in two directions, is given by

$$\frac{\delta q}{\delta t} = D_s \left[\frac{\delta^2 q}{\delta r^2} + \frac{2}{r} \cdot \frac{\delta q}{\delta r} \right] \quad (4)$$

The material balance equation for a slurry adsorber is

$$V \cdot \frac{dC_t}{dt} = -W \cdot \frac{d\bar{q}_t}{dt} \quad (5)$$

The initial and boundary conditions for the fluid and solid phases are given as

$$C_t(0) = C_0 \quad (6)$$

$$\bar{q}_t(r, 0) = 0$$

$$q(R, t) = q_s(t) \quad (7)$$

$$\frac{\delta q}{\delta r}(0, t) = 0$$

The initial concentration of solute in the liquid phase is C_0 , and zero in the solid phase. The surface concentration in the solid phase is an unknown function of time, and the flux at the center of the particle is zero at all times.

The independent variables in eqs. (3) and (2) can be transformed into dimensionless variables:

$$\tau = (D_s \cdot t) / R^2 \quad \text{and} \quad z = r / R \quad (8)$$

Subsequent change of variable with $u = z \cdot q$ and rearrangement gives the following set of equations for adsorption in a batch reactor:

$$\frac{\delta u}{\delta \tau} = \frac{\delta^2 u}{\delta z^2} \quad (9)$$

$$u(0, \tau) = 0 = u(z, 0) \quad (10)$$

$$u(1, \tau) = u_s(\tau) \quad (11)$$

$$\int_0^1 \frac{\delta u}{\delta \tau} \cdot z \cdot dz = \frac{3k_f \cdot R(C_t - C_s)}{D_s \cdot \rho_p} \quad (12)$$

$$\bar{q}_t = 3 \int_0^1 u \cdot z \cdot dz \quad (13)$$

$$V \cdot \frac{dC_t}{dt} = -W \cdot \frac{d\bar{q}_t}{dt} \quad (14)$$

Method of Solution

Equations (9)–(14) and (3) are difficult to solve analytically, and finite difference techniques must be employed. These equations were solved using the implicit finite difference scheme of Crank-Nicholson and are given elsewhere.⁵

A result $u(z, \tau)$ is a solution of eq. (9) and a general form of this solution is given by

$$u(z, \tau)_0 = \int_0^{\tau_n} d\tau f(\tau') \frac{1}{(\tau_n - \tau')^{0.5}} \left\{ \exp \left[\frac{-(z-1)^2}{4(\tau_n - \tau')} \right] - \exp \left[\frac{-(z+1)^2}{4(\tau_n - \tau')} \right] \right\} \quad (15)$$

The equations developed in this section can be used analytically with the aid of a computer to obtain the kinetic concentration decay curve, given the necessary mass transfer and equilibrium parameters.

DISCUSSION

A program was developed to give the theoretical concentration decay curve with corresponding surface equilibrium conditions using the two resistance approach. The principal parameters required for the use of the program were the external mass transfer coefficient and the solid phase diffusion coefficient. Initially the value of the external mass transfer coefficient k_f was taken from the single resistance analysis value. It is possible to obtain a theoretical decay curve using this k_f and an estimate of the solid phase diffusion coefficient D_s .

together with:

- (i) particle radius R (cm);
- (ii) solution volume V (dm^3);
- (iii) pith mass W (g);
- (iv) particle porosity ϵ_p ;
- (v) pith density ρ_p (g/cm^3);
- (vi) Redlich-Peterson constants k_R , a_R , and β ;

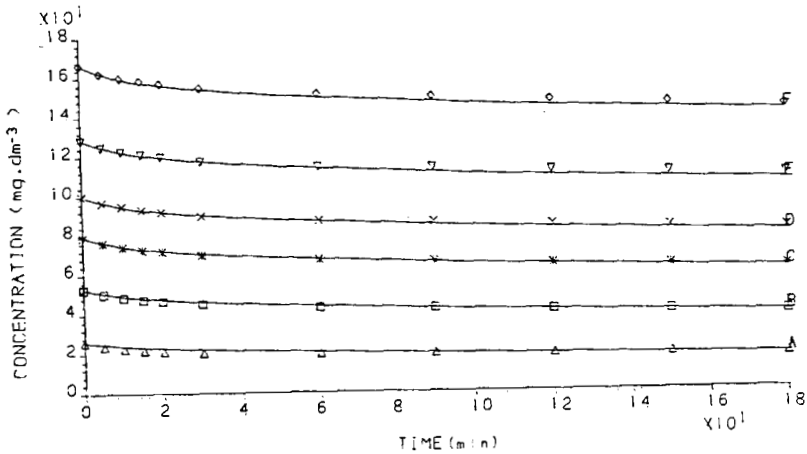


Fig. 1. Effect of initial dye concentration on adsorption of AB25 onto pith using solid-phase diffusion model: (A) CO = 25 ppm; (B) CO = 53 ppm; (C) CO = 79.3 ppm; (D) CO = 100 ppm; (E) CO = 128.6 ppm; (F) CO = 166.4 ppm.

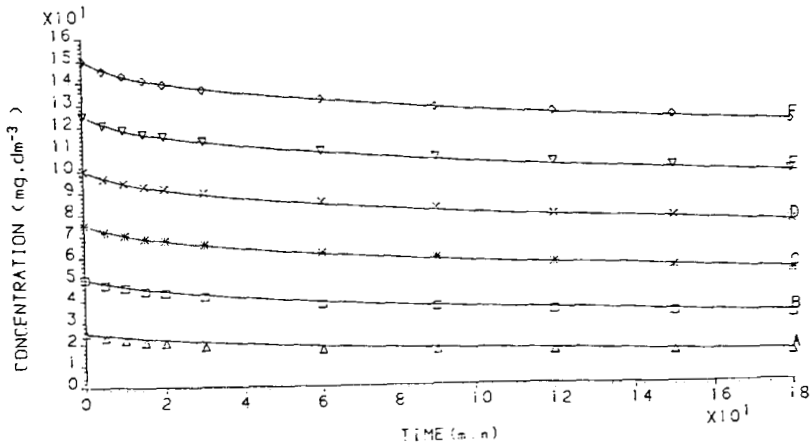


Fig. 2. Effect of initial dye concentration on adsorption of AR114 onto pith using solid-phase diffusion model: (A) CO = 25 ppm; (B) CO = 50 ppm; (C) CO = 75 ppm; (D) CO = 100 ppm; (E) CO = 125 ppm; (F) CO = 150 ppm.

- (vii) the time value, related to the extent of time allowed for adsorption;
- (viii) data related to step length for integration.

By iterating between the external mass transfer coefficient k_f and the solid phase diffusion coefficient D_s , it is possible to obtain a "best fit" to the experimental decay curves for batch adsorption.

The model has been applied extensively for the adsorption of AB25, AR114, BB69, and BR22 onto pith. The variables studied were (i) initial dye concentration and (ii) pith mass.

The effect of initial dye concentration is shown in Figures 1-4 for a wide range of initial dye concentrations. The correlation between experimental and theoretical results is excellent, and the fitted parameters k_f and D_s are given in Table I. It was found that the parameters k_f and D_s were constant and were sufficient to fit a wide range of experimental conditions for each system.

For high initial dye concentrations the surface concentrations q_s and C_s rise very rapidly, and Figures 5 and 6 show the variation of surface solid-phase concentration q_s and the liquid-phase concentration C_s at the surface of the particle for the adsorption of BB69 onto pith.

In Figures 7 and 8 the bulk liquid concentration C_t decreases with time, and it approaches the equilibrium curve along the operating line. The tie lines are drawn between the bulk liquid values of (C_t, \bar{q}_t) and the surface equilibrium values (C_s, q_s) . As time increases, the tie lines move up the operating line and round the equilibrium curve. The solution of the problem involves calculating a surface liquid-phase equilibrium concentration C_s from the surface solid-phase concentration q_s .

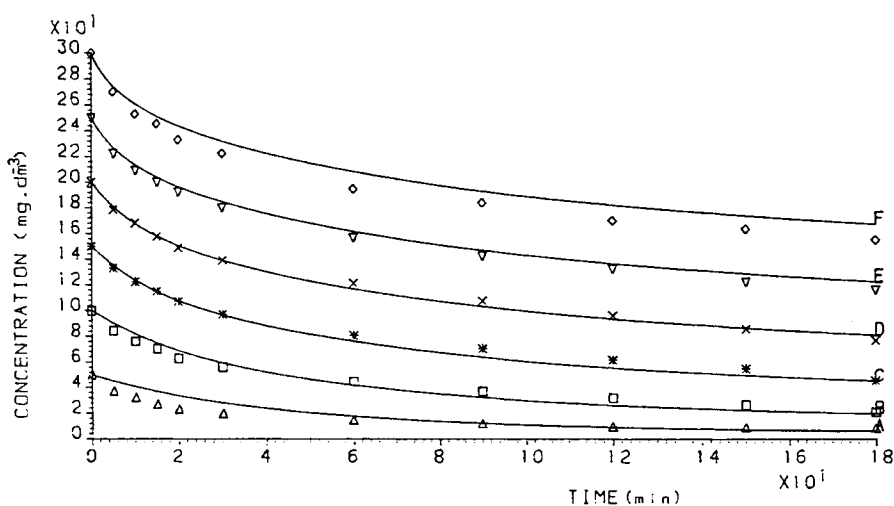


Fig. 3. Effect of initial dye concentration on the adsorption of BB69 onto pith using solid-phase diffusion model: (A) CO = 50 ppm; (B) CO = 100 ppm; (C) CO = 150 ppm; (D) CO = 200 ppm; (E) CO = 250 ppm; (F) CO = 300 ppm.

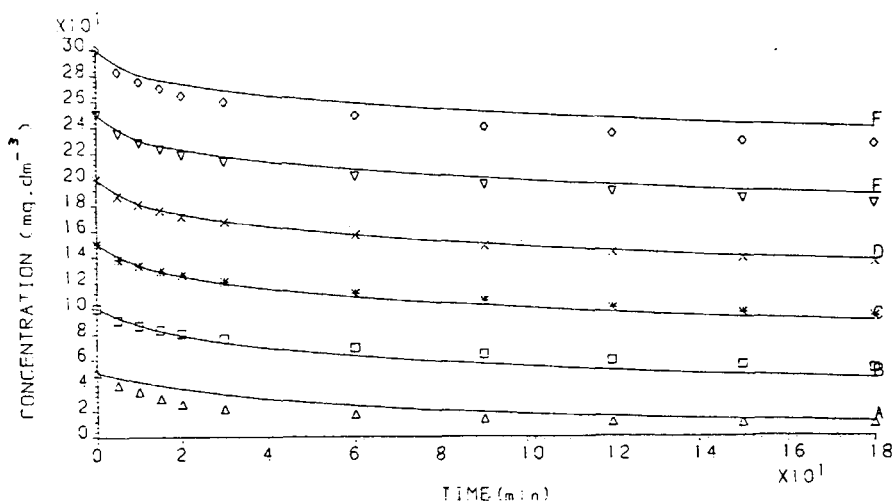


Fig. 4. Effect of initial dye concentration on the adsorption of BR22 onto pith using solid-phase diffusion model: (A) $C_0 = 50.0$ ppm; (B) $C_0 = 100.0$ ppm; (C) $C_0 = 150.0$ ppm; (D) $C_0 = 200.0$ ppm; (E) $C_0 = 250.0$ ppm; (F) $C_0 = 300.0$ ppm.

TABLE I
External Mass Transfer and Solid-Phase Diffusion Coefficients
For the Adsorption of Acid Dyes onto Pith^a

Run no.	Dye	Redlich-Peterson constants			C_0 (mg dm ⁻³)	M (g)	$k_f \times 10^{-4}$ (cm s ⁻¹)	$D_s \times 10^{-9}$ (cm ² s ⁻¹)
		K_R (dm ³ g ⁻¹)	a_R (dm ³ mg ⁻¹)	β				
1	AB25	0.50	0.036	0.88	26	3.4	8.0	6.0
2					53	3.4	8.0	6.0
3					79	3.4	8.0	6.0
4					100	3.4	8.0	6.0
5					129	3.4	8.0	6.0
6					166	3.4	8.0	6.0
7					100	0.85	8.0	6.0
8					100	1.275	8.0	6.0
9					100	1.70	8.0	6.0
10					100	2.125	8.0	6.0
11					100	2.55	8.0	6.0
12					100	3.40	8.0	6.0
1	AR114	1.1	0.032	0.99	25	3.4	5.0	3.0
2					50	3.4	5.0	3.0
3					75	3.4	5.0	3.0
4					100	3.4	5.0	3.0
5					125	3.4	5.0	3.0
6					150	3.4	5.0	3.0
7					100	0.85	5.0	3.0
8					100	1.275	5.0	3.0
9					100	1.70	5.0	3.0
10					100	2.125	5.0	3.0
11					100	2.55	5.0	3.0
12					100	3.40	5.0	3.0

^a $d_p = 605 \times 10^{-4}$ cm, agitation speed = 400 rpm, $T = 20^\circ\text{C}$, $V = 1.7$ dm³ and $\rho_p = 0.804$ g cm⁻³.

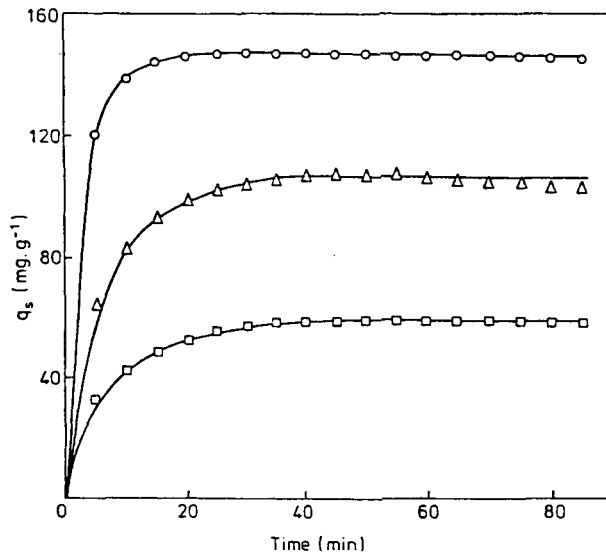


Fig. 5. Solid phase concentration at particle surface q_s against contact time during the adsorption of BB69 onto pith. C_0 (mg dm^{-3}): (\circ) 200; (Δ) 100; (\square) 50.

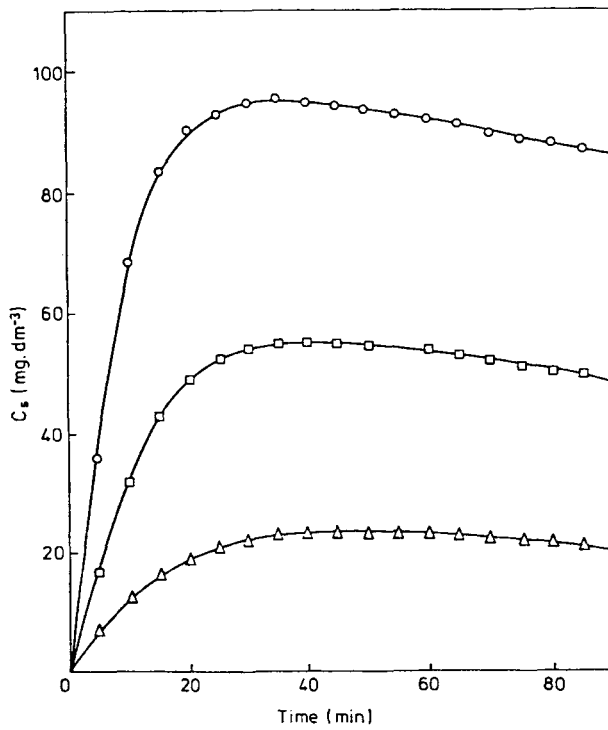


Fig. 6. Liquid phase concentration at particle surface C_s against contact time during the adsorption of BB69 onto pith. C_0 (mg dm^{-3}): (\circ) 200; (\square) 150; (Δ) 100.

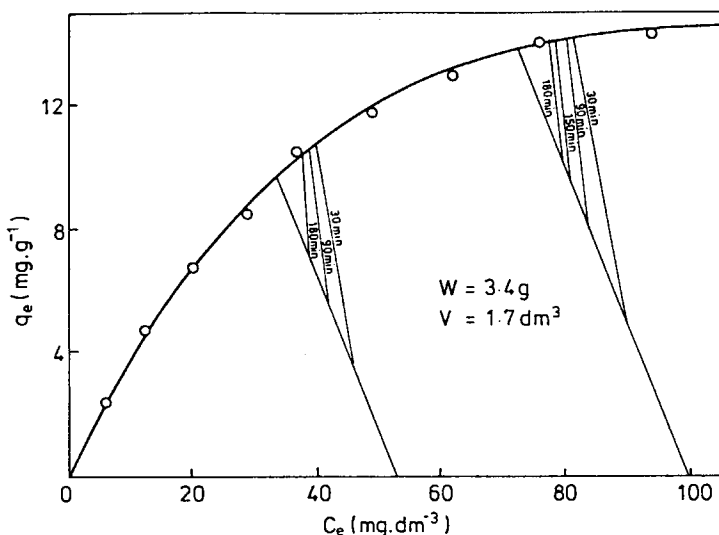


Fig. 7. Equilibrium isotherm for AB25 onto pith showing operating lines and tie lines.

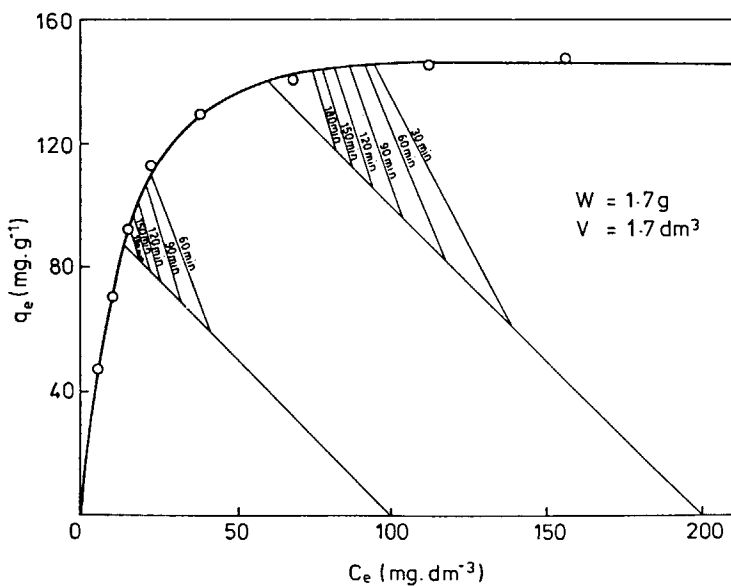


Fig. 8. Equilibrium isotherm for BB69 onto pith showing operating lines and tie lines.

The effect of varying pith mass is shown in Figures 9–12 for a wide range of pith masses. The same values for the external mass transfer coefficients and the solid phase diffusion coefficients were obtained as in the initial dye concentration results. The correlation between experimental and theoretical results is again excellent except at high masses. At high masses there is low surface coverage and consequently heterogeneity at pith sites is probably important. This will result in D_s not being constant in certain cases, whereas

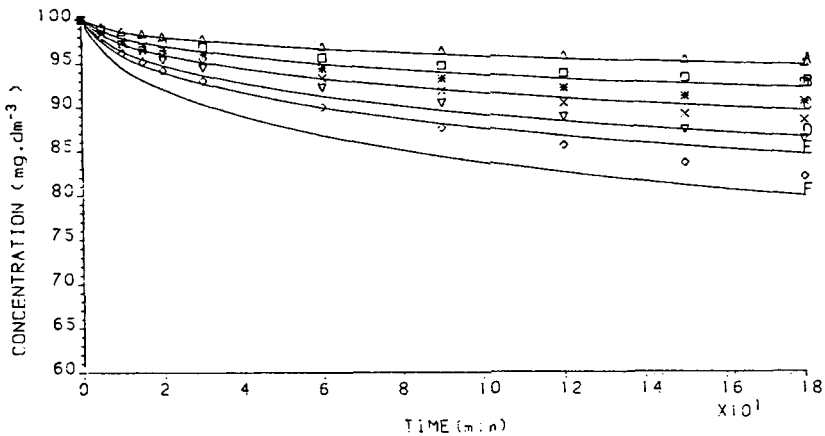


Fig. 9. Effect of pith mass on the adsorption of AB25 using solid-phase diffusion model: (A) M = 0.85 g; (B) M = 1.275 g; (C) M = 1.7 g; (D) M = 2.125 g; (E) M = 2.55 g; (F) M = 3.4 g.

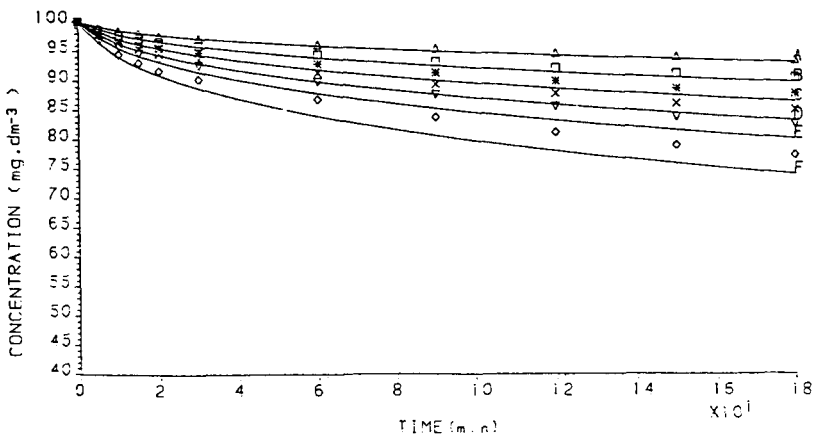


Fig. 10. Effect of pith mass on the adsorption of AR114 using solid-phase diffusion model: (A) M = 0.85 g; (B) M = 1.275 g; (C) M = 1.7 g; (D) M = 2.125 g; (E) M = 2.55 g; (F) M = 3.4 g.

for high loadings the effects of heterogeneous surface diffusion are swamped to a certain extent. An alternative explanation is that the rate controlling step is dependent on pore and surface diffusion whereby the apparent diffusivity D_{app} is given by⁶

$$D_{app} = \frac{D_{mol} \cdot \epsilon_p}{\mu} + \rho_p \cdot D_s \frac{\delta q_e}{\delta C_e} \tag{16}$$

where μ is the tortuosity factor.

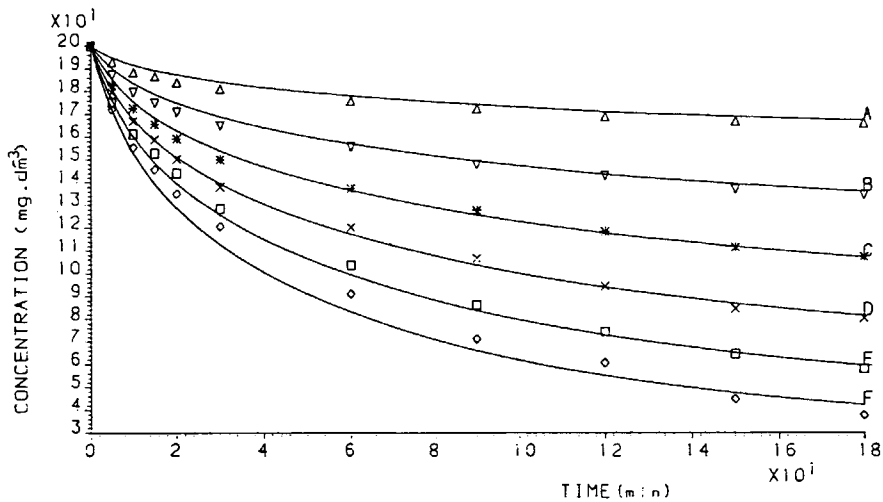


Fig. 11. Effect of pith mass on the adsorption of BB69 using solid-phase diffusion model: (A) $M = 0.425$ g; (B) $M = 0.850$ g; (C) $M = 1.275$ g; (D) $M = 1.70$ g; (E) $M = 2.125$ g; (F) $M = 2.55$ g.

From this equation it is apparent that the term $\delta q_e / \delta C_e$ will change rapidly with high masses which means operating lines terminating at low C_e values on the isotherms, i.e., higher gradients for $\delta q_e / \delta C_e$.

There are only limited data available in the literature reporting external mass transfer coefficients for the adsorption of dye ions. However, there are several papers in which external mass transfer coefficients, in well agitated batch adsorbers, have been determined for small organic molecules. These values, all using activated carbon, include values of 2.12×10^{-3} , 5.4×10^{-3} , 5.1×10^{-3} , and 4.8×10^{-2} cm s^{-1} for dodecyl benzene sulfonate, *p*-bromophenol, phenol, and *p*-toluene sulfonate, respectively;⁷ 2.0×10^{-3} and 1.0×10^{-3} cm s^{-1} for AB25 and Basic Yellow 11 respectively.⁵ Other values of 0.45×10^{-4} and 3.5×10^{-3} cm s^{-1} were obtained by Allen⁸ for the adsorption of AB25 and BB69 onto peat, respectively. McKay⁹ obtained a value of 2.0×10^{-4} cm s^{-1} for the adsorption of BB69 onto silica. The values of external mass transfer coefficients obtained in this work are 8.0×10^{-4} , 5.0×10^{-4} , 2.0×10^{-3} , and 1.5×10^{-3} cm s^{-1} for the adsorption of AB25, AR114, BB69, and BR22 onto pith, respectively. Hence, these values of external mass transfer coefficients are of a similar order of magnitude to those previously obtained by other workers for large organic molecules/ions.

Values of solid phase diffusion coefficients have been given in the literature based on different initial solute concentrations and different adsorbent mass/solution volume ratios. These include 1.58×10^{-8} , 2.0×10^{-8} , 0.99×10^{-9} , and 1.38×10^{-8} $\text{cm}^2 \text{s}^{-2}$ for *p*-bromophenol, *p*-toluene sulfonate, dodecyl benzene sulfonate, and phenol, respectively;³ 2.0×10^{-9} and 3.0×10^{-10} $\text{cm}^2 \text{s}^{-1}$ for AB25 and Basic Yellow 11, respectively.⁵ All the previous results were based on carbon adsorption. Other values of 1.5×10^{-9} and 2.1×10^{-9} $\text{cm}^2 \text{s}^{-1}$ were obtained by Allen⁸ for the adsorption of AB25 and BB69 onto peat respectively. McKay⁹ obtained a value of 1.2×10^{-9} $\text{cm}^2 \text{s}^{-1}$ for the

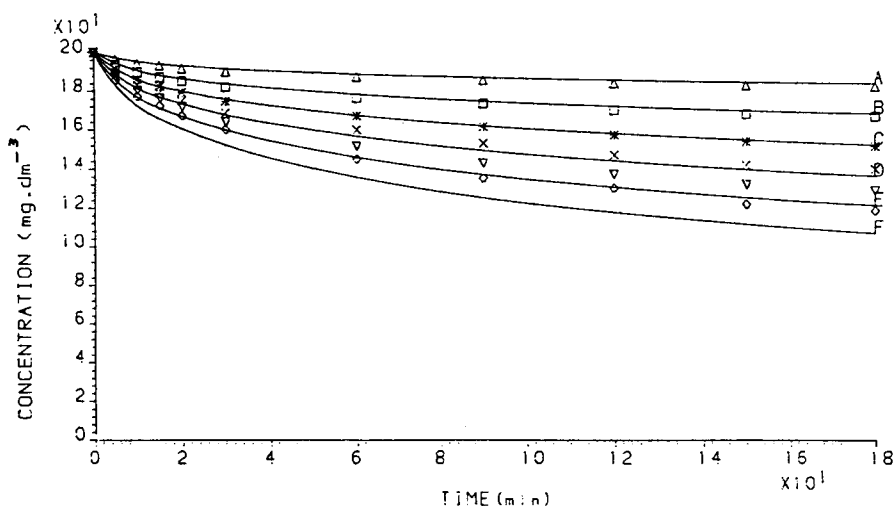


Fig. 12. Effect of pith mass on adsorption of BR22 using solid-phase diffusion model: (A) $M = .425$ g; (B) $M = .85$ g; (C) $M = 1.275$ g; (D) $M = 1.7$ g; (E) $M = 2.125$ g; (F) $M = 2.55$ g.

adsorption of BB69 onto silica. The values of solid phase diffusion coefficients obtained in this work are 6.0×10^{-9} , 3.0×10^{-9} , 1.1×10^{-8} , and 1.0×10^{-8} $\text{cm}^2 \text{s}^{-1}$ for the adsorption of AB25, AR114, BB69, and BR22 onto pith, respectively.

Certain general points may be deduced from fitting the experimental and theoretical concentration time profiles:

(1) From the model, a single external mass transfer coefficient and a single solid phase diffusion coefficient were obtained to predict concentration profiles for the variation of initial dye concentration and pith mass.

(2) The model shows that the solid surface concentrations q_s and C_s rise very rapidly to the equilibrium values and then slowly decrease due to the inward diffusion of the adsorbate into the adsorbent pellet.

(3) The program can be used to describe experimental data with a high degree of accuracy up to 3 h of contact time.

SUMMARY

A homogeneous solid phase diffusion model has been developed using a computer to predict the performance of a batch adsorber. The computer program utilizes a semianalytical solution for a two-resistance model based on external mass transfer and homogeneous solid phase diffusion. The model has been successfully applied to four adsorption systems, namely, the adsorption of AB25, AR114, BB69, and BR22 onto pith. The method produces excellent correlations between experimental and theoretical concentration decay curves in batch adsorbers. The model developed presents a solution using a single solid diffusion coefficient and a single external mass transfer coefficient which are sufficient to characterize the system within a range of initial dye concentrations, 25–300 mg dm^3 and solid/liquid ratios, W/V , 0.25–2.

APPENDIX: NOMENCLATURE

α_R	modified isotherm constant ($\text{dm}^3 \text{mg}^{-1}$) ^{β} m
C_0	initial solute concentration (mg dm^{-3})
C_s	equilibrium liquid-phase solute concentration (mg dm^{-3})
$C_{s,t}$	surface liquid-phase solute concentration at time t (mg dm^{-3})
C_t	adsorbate concentration at time t (mg dm^{-3})
d_p	adsorbent particle size (m)
D_{mol}	molecule diffusivity ($\text{cm}^2 \text{s}^{-1}$)
D_{app}	apparent pore diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
D_s	surface diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
k_f	external mass transfer coefficient ($\text{cm}^2 \text{s}^{-1}$)
K_R	modified isotherm constant ($\text{dm}^3 \text{g}^{-1}$)
$q_{r,t}$	solid-phase solute concentration at radial distance r and t (mg g^{-1})
q_s	equilibrium solid-phase solute concentration (mg g^{-1})
\bar{q}_t	average solid-phase solute concentration (mg g^{-1})
r	radial distance (cm)
\bar{r}	separation factor
R	particle radius (cm)
t	time (min, s)
u	transformed solid-phase solute concentration (mg g^{-1})
V	volume of batch reactor (dm^3)
V_p	volume of adsorbent particle (cm^3)
W	weight of solid adsorbent (g)
z	r/R , dimensionless radial distance

Greek Symbols

ϵ_p	adsorbent particle porosity
β	isotherm constant in modified isotherm expression
ρ_p	adsorbent particle density on solid base
τ	$D_p t/R^2$, dimensionless time
μ	tortuosity

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