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A new approach to evaluate kinetic parameters and mass transfer coefficients in continuous stirred tank reactors. Application to antibiotic separation

Sunil Nath *, Vivek Shukla

Department of Biochemical Engineering and Biotechnology, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

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Abstract

A new method is proposed to evaluate kinetic parameters and mass transfer coefficients for adsorption processes carried out in continuous stirred tank reactors. This method, employing a biphasic model, does not linearize *nonlinear* solute concentration versus time data, nor does it assume the existence of equilibrium in a typical *nonequilibrium* situation as is currently done. For a nonlinear adsorption isotherm, the coupled differential equations need to be solved numerically, but using an elegant analytical solution it is possible to determine rate constants and mass transfer coefficients in the case of nonlinear kinetics with a linear adsorption isotherm. This solution (biphasic model, linear isotherm) is obtained and compared with solutions incorporating (i) a linear model (linear isotherm) and (ii) a numerical solution (nonlinear isotherm) for recovery of the antibiotic novobiocin in stirred tank reactors. For novobiocin adsorption versus time data, use of the biphasic model results in a lower mean percentage error than either the linear model or the numerical simulation; further, it provides a far superior fit of short-time adsorption behavior. Hence, we strongly advocate that the biphasic model be routinely employed along with linear models and numerical simulations of Langmuir/Freundlich isotherms for interpretation of adsorption data.

Keywords: Continuous stirred tank reactors; Biphasic model; Antibiotic separation; Novobiocin adsorption; Nonequilibrium; Kinetic paramters; Mass transfer coefficient

1. Introduction

Separation processes carried out either in batch mode or in continuous stirred tank reactors or packed beds are of importance in the pharmaceutical and biotechnology industry [1,2]. For instance, adsorption in continuous stirred tank reactors is used effectively for separation of the antibiotic novobiocin from whole beer obtained by fermentation, thus bypassing the need for removal of insolubles by centrifugation or filtration [1]. The configuration of stirred tank reactors is also employed for recovery of the antibiotic bacitracin using a porous polystyrene resin with a yield of greater than 85% [2]. The adsorption kinetics, monitored by variation of the outlet antibiotic concentration ($\ln y$) with time, exhibits nonlinear behavior in most antibiotic separation processes. However, the rate constants are determined based on the assumption that the adsorption process follows first-order kinetics, i.e. the $\ln y$–time curve is fitted by a straight line [1,3]. Alternatively, the initial and final slopes of the data are taken [3]. These procedures lead to inaccurate values of the kinetic parameters as well as the mass transfer coefficients. Further, incorrect values of the adsorption equilibrium constant are obtained by falsely assuming the existence of equilibrium in a typical *nonequilibrium* situation. In fact, nonlinear kinetics have been observed in a wide variety of physical, chemical and biological processes: in the thermal inactivation of enzymes [4–7], in virus–cell fusion processes [8,9] and in the relaxation of polydisperse colloids/polymer solutions upon removal of the external field [10–13]. A method to accurately determine the kinetic parameters and the mass transfer coefficients from nonlinear kinetic data would therefore prove extremely useful, not only for antibiotic adsorption in stirred tank reactors but, in general, for analyzing the dynamics of nonequilibrium systems relaxing towards equilibrium.

We also note that concentration–time measurements are commonly made in small stirred tanks; these measurements are essential, because they characterize the kinetics of adsorption. Such kinetics cannot be inferred from equilibrium batch measurements made to determine the adsorption isotherm.

* Corresponding author. Fax: +91 11 6868521; e-mail: sunath@dbeb.iitd.ernet.in

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Moreover, measurements made in small stirred tanks are used to predict the behavior in large tanks, i.e. for process scale-up. Hence, accuracy in the small tank measurements and in data interpretation are of critical importance.

2. Theoretical model

2.1. Adsorption in a stirred tank

Adsorption in a continuous stirred tank reactor is diagrammatically depicted in Fig. 1. The tank initially contains no solute (i.e. pure solvent) and fresh unloaded adsorbent. At time zero, flow begins and feed enters the tank continuously at a flow rate Q and a constant solute concentration y_F. The concentration of solute on the adsorbent, q, varies with time. Solution steadily flows out of the tank with a concentration y that is time-variant. As adsorption occurs at a finite rate, y will rise. For rapid adsorption, y will increase at a low rate until the adsorbent capacity is exhausted, after which y will rise rapidly until it reaches y_F [1].

A mass balance on the solute present in the liquid yields the following expression:

$$\epsilon V\frac{dy}{dt}=Q(y_F-y)-(1-\epsilon)V\frac{dq}{dt} \tag{1}$$

where V is the total tank volume, ϵ the void fraction (the fraction filled with solution), Q the feed rate, q the adsorbed solute concentration, and y_F and y the solute concentrations at the inlet and exit of the reactor, respectively.

A mass balance on the adsorbent gives

$$(1-\epsilon)V\frac{dq}{dt}=rV \tag{2}$$

where r is the rate of adsorption per unit volume of the tank.

If adsorption is controlled by diffusion from the solution to the adsorbent,

$$r=ka(y-y^*) \tag{3}$$

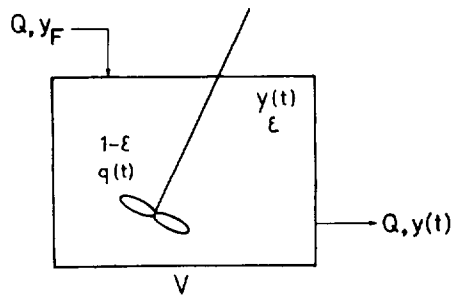

Fig. 1. Adsorption in a continuous stirred tank reactor. The reactor volume is V and initially it contains no solute. Feed enters the reactor continuously with flow rate Q and constant solute concentration y_F. The void fraction in the reactor (the fraction filled with solution) is ϵ. The solute concentration on the adsorbent, $q(t)$, varies with time. Solution flows out steadily from the reactor with a time-variant concentration, $y(t)$.

where k is the mass transfer coefficient, a the interfacial area per unit volume and y^* the solute concentration in equilibrium with the adsorbent.

If adsorption is controlled by diffusion and reaction within the adsorbent particle then for first-order, irreversible reaction, r takes the form

$$r=\sqrt{D\kappa}a(y-y^*) \tag{4}$$

with D the diffusion coefficient within the particle and κ a reaction rate constant for adsorption [1].

In principle, the exit concentration $y(t)$ and the adsorbent loading $q(t)$ can be determined by combining and integrating Eqs. (1) and (2) and either Eq. (3) or Eq. (4) along with an equilibrium adsorption isotherm (e.g. the Freundlich isotherm, $q=K(y^*)^n$, or the Langmuir isotherm, $q=q_0y^*/(K+y^*)$. For a nonlinear isotherm, these equations need to be solved numerically on a computer. This is carried out later; however, we initially explore the use of the linear isotherm

$$q=Ky^* \tag{5}$$

which leads to analytical results for the kinetic parameters and the mass transfer coefficient (see Section 3).

2.2. Biphasic model expression for determination of mass transfer coefficient and equilibrium constant

Combining Eqs. (2) and (3) and differentiating with respect to time, we have

$$(1-\epsilon)\frac{d^2q}{dt^2}=ka\frac{dy}{dt}-\frac{ka}{K}\frac{dq}{dt} \tag{6}$$

Now we must independently obtain relationships for dq/dt and d^2q/dt^2, which we shall then substitute in Eq. (6). From Eq. (1) we find that

$$\frac{dq}{dt}=\frac{\left[Q(y_F-y)-\epsilon V\frac{dy}{dt}\right]}{(1-\epsilon)V} \tag{7}$$

and differentiating Eq. (7) with time we obtain

$$\frac{d^2q}{dt^2}=\frac{1}{(1-\epsilon)V}\left[-Q\frac{dy}{dt}-\epsilon V\frac{d^2y}{dt^2}\right] \tag{8}$$

Substituting Eqs. (7) and (8) into Eq. (6) leads to

$$\epsilon\frac{d^2y}{dt^2}+\left[ka+\frac{Q}{V}+\frac{\epsilon ka}{(1-\epsilon)K}\right]\frac{dy}{dt}-\frac{ka}{K}\frac{Q}{(1-\epsilon)V}(y_F-y)=0 \tag{9}$$

Defining the fractional concentration difference $\{(y_F-y)/y_F\}$ as Y, we obtain

$$\frac{d^2Y}{dt^2}+\left[\frac{Q}{\epsilon V}+\frac{ka}{\epsilon}\left\{1+\frac{\epsilon}{(1-\epsilon)K}\right\}\right]\frac{dY}{dt}+\frac{kaQY}{K\epsilon(1-\epsilon)V}=0 \tag{10}$$

which is a linear second-order homogenous differential equation with general solution

$$Y=\frac{(y_F-y)}{y_F}=C_s\exp(-k_st)+C_l\exp(-k_lt) \quad (11)$$

The initial condition is:

$$t=0,\ y=0 \text{ or } Y=1 \quad (12)$$

Further, at $t=0$, $q=0$, i.e. $y^*=0$, and from Eqs. (2) and (3), $dq/dt=0$. Thus from Eq. (1) we have

$$\epsilon V\left(\frac{dy}{dt}\right)_{t=0}=Qy_F \quad (13)$$

or

$$\left(\frac{dY}{dt}\right)_{t=0}=-\frac{Q}{\epsilon V} \quad (14)$$

Differentiating Eq. (11) and restricting to $t=0$, we obtain

$$\left(\frac{dY}{dt}\right)_{t=0}=-C_sk_s-C_lk_l \quad (15)$$

From Eqs. (11) and (12) we have

$$C_s+C_l=1 \quad (16)$$

and combining Eqs. (14) and (15), we arrive at

$$C_sk_s+C_lk_l=\frac{Q}{\epsilon V} \quad (17)$$

Thus,

$$C_l=\frac{k_s-\frac{Q}{\epsilon V}}{k_s-k_l} \quad C_s=\frac{\frac{Q}{\epsilon V}-k_l}{k_s-k_l} \quad (18)$$

k_s and k_l are given by the solution of the characteristic equation obtained on substituting $Y=\exp(-k_st)$ or $Y=\exp(-k_lt)$ in Eq. (10). This characteristic equation works out to be

$$k_{s,l}^2-\left[\frac{Q}{\epsilon V}+\frac{ka}{\epsilon}\left\{1+\frac{\epsilon}{(1-\epsilon)K}\right\}\right]k_{s,l}+\frac{kaQ}{\epsilon(1-\epsilon)KV}=0 \quad (19)$$

On solving the above quadratic equation we finally arrive at the principal result

$$k_l=\frac{1}{2}\left[\left\{\frac{Q}{\epsilon V}+\frac{ka}{\epsilon}\left(1+\frac{\epsilon}{(1-\epsilon)K}\right)\right\}-\left\{\left(\frac{Q}{\epsilon V}+\frac{ka}{\epsilon}\right.\right.\right.$$
$$\left.\left.\left.\times\left(1+\frac{\epsilon}{(1-\epsilon)K}\right)\right)^2-\frac{4kaQ}{\epsilon(1-\epsilon)KV}\right\}^{1/2}\right] \quad (20a)$$

and

$$k_s=\frac{1}{2}\left[\left\{\frac{Q}{\epsilon V}+\frac{ka}{\epsilon}\left(1+\frac{\epsilon}{(1-\epsilon)K}\right)\right\}+\left\{\left(\frac{Q}{\epsilon V}+\frac{ka}{\epsilon}\right.\right.\right.$$
$$\left.\left.\left.\times\left(1+\frac{\epsilon}{(1-\epsilon)K}\right)\right)^2-\frac{4kaQ}{\epsilon(1-\epsilon)KV}\right\}^{1/2}\right] \quad (20b)$$

Thus, knowing k_s, k_l, C_s and C_l we can determine both the interfacial mass transfer coefficient, ka, and the equilibrium constant, K, using Eqs. (20a) and (20b).

2.3. Method for analysis of nonlinear adsorption curves

Recently, a method has been described by one of us to analyze the thermal inactivation of enzymes exhibiting a nonlinear ln(activity)–time relationship [7]. As shown in Section 2.2, we obtain a similar nonlinear biphasic sum of exponentials type of decay for the fractional concentration difference $\{(y_F-y)/y_F\}$ for adsorption in a stirred tank with a linear adsorption isotherm. We can therefore write

$$\frac{y_F-y}{y_F}=A_s\exp(-k_st)+A_l\exp(-k_lt) \quad (21)$$

where subscripts s and l stand for the short-time phase and long-time phase respectively. Thus, k_s and k_l refer to the rate constants of the short-time and long-time phases, while A_s and A_l delineate the respective preexponential factors, which are functions of k_s, k_l, the reactor size and the operating parameters (flow rates). We need to determine k_s, k_l, A_s and A_l. At zero time Eq. (21) becomes

$$\frac{y_F-y}{y_F}=1=A_s+A_l \quad (22)$$

At sufficiently long times, the contribution of the fast decay can be neglected, i.e. $\exp(-k_st)\approx 0$. Thus, at long times

$$\frac{y_F-y}{y_F}=A_l\exp(-k_lt) \quad (23)$$

or

$$\ln\left[\frac{y_F-y}{y_F}\right]=\ln A_l-k_lt \quad (24)$$

Thus, a semilog plot of $\{(y_F-y)/y_F\}$ vs. t for long times yields k_l as slope and A_l as intercept. The short-time decay can now be readily interpreted:

$$\left[\frac{y_F-y}{y_F}-A_l\exp(-k_lt)\right]=A_s\exp(-k_st) \quad (25)$$

The left-hand side of Eq. (25) is known at every value of short time, because A_l and k_l have been determined from Eq. (24), and y and y_F are known from experimental solute concentration data as a function of time. Therefore, a modified plot of $\ln[(y_F-y)/y_F-A_l\exp(-k_lt)]$ vs. time for short times should have k_s as slope and A_s as intercept. Knowing A_s and A_l, we can verify whether their sum equals 1. This deconvolution procedure permits a rapid and accurate determination of the kinetic parameters from the experimental outlet solute concentration vs. time data for adsorption in continuous stirred tank reactors.

Table 1
Measured outlet solute concentration as a function of time for novobiocin adsorption in a continuous stirred tank reactor

Time/h	y/mg cm^{-3}
0.5	0.138
1.0	0.181
1.5	0.217
2.0	0.246
3.0	0.313
4.0	0.348
5.0	0.375
6.0	0.405
7.0	0.418

3. Results and discussion

3.1. Application to antibiotic separation

We now apply the biphasic model (Section 2.2, Section 2.3) to antibiotic separation and compare it with (i) the linear model (linear isotherm) and (ii) the numerical simulation (nonlinear isotherm). In particular, we consider the following problem of novobiocin adsorption [1].

A whole beer containing the antibiotic novobiocin is contacted with an ion-exchange resin suspended in a stirred tank (Fig. 1). The tank initially holds 0.876 l of liquid, which contains no antibiotic. The tank also holds 0.250 l of resin which initially contains 1.35 g l^{-1} antibiotic. Whole beer containing 0.640 mg antibiotic per cm^3 flows into the tank at a rate of 2.7 l h^{-1}. The outlet concentration (y) was measured by UV spectrophotometry (Table 1).

The temperature was constant at 35°C and the pH remained in the range 6.8–7.2. We need to estimate the interfacial mass transfer coefficient ka and the adsorption equilibrium constant K.

Table 2 shows the relative error in the outlet solute concentration for novobiocin adsorption in a stirred tank employing the linear model (linear isotherm), biphasic model (linear isotherm) and numerically simulated Freundlich isotherm. These results are also plotted in Fig. 2(a)–(c). By the linear model we mean a simple straight line fit of the experimental data on a semilog plot. For the biphasic model, $A_l = 0.82$, $A_s = 0.18$, $k_l = 0.126\ h^{-1}$ and $k_s = 5.044\ h^{-1}$ were determined by the method outlined in Section 2.3 (Eqs. (24) and (25)). As can be clearly seen from Table 2 and Fig. 2(a)–(c), the linear as well as the best fit for the nonlinear Freundlich model provides a very poor representation of short-time adsorption data in stirred tanks; the mean relative error for short times (0–2 h) works out at about 8% for the linear model and greater than 13% for the nonlinear model. In contrast, the biphasic model yields significantly superior results (relative error of only 3.5%). Moreover, the biphasic model results in a lower mean relative error of 4.36% (compared to 6.82 and 6.45% for the linear and nonlinear models, respectively) over the entire range of time values (0–7 h) (Table 2, Fig. 2(a)–(c)). Clearly, neither the linear model nor the nonlinear Freundlich model yields good fits of both short-time and long-time adsorption behavior. The biphasic model removes this difficulty and provides a superior simultaneous representation of both short-time and long-time behavior. Note that the Langmuir model does not provide a satisfactory representation of the novobiocin adsorption process.

Based on these results, the biphasic model is explored further. Fig. 3 depicts the deconvoluted components of the fractional concentration difference $(y_F - y)/y_F$. Addition of the short-time and long-time components leads to the experimental curve, in accordance with Eq. (21). The percentage errors incurred in $\{(y_F - y)/y_F\}$, by considering (i) only the short-time phase of the biphasic model $\{A_s \exp(-k_s t)\}$, (ii) only the long-time phase of the biphasic model

Table 2
Relative error in outlet solute concentration (y) for novobiocin adsorption in a continuous stirred tank reactor employing the linear model (linear isotherm), biphasic model (linear isotherm) and numerically simulated Freundlich isotherm

Experimental / Calculated							
Time/h	y/mg cm^{-3}	Linear model		Biphasic model		Nonlinear model	
		y/mg cm^{-3}	E/%	y/mg cm^{-3}	E/%	y/mg cm^{-3}	E/%
0.0	0.0	0.10	–	0.0006	0.0	0.00	0.00
0.5	0.138	0.133	3.6	0.139	0.7	0.168	21.7
1.0	0.181	0.165	8.8	0.177	2.2	0.207	14.3
1.5	0.217	0.195	10.1	0.205	5.5	0.238	9.6
2.0	0.246	0.223	9.3	0.232	5.7	0.265	7.7
3.0	0.313	0.274	12.4	0.281	10.2	0.309	1.4
4.0	0.348	0.318	8.6	0.323	7.18	0.344	1.1
5.0	0.375	0.358	4.5	0.361	3.7	0.374	0.2
6.0	0.405	0.392	3.2	0.393	2.9	0.400	1.2
7.0	0.418	0.422	0.9	0.423	1.2	0.422	0.9
$\bar{E}$/%		6.82		4.36		6.45	
$\bar{E}_s$/%		7.95		3.53		13.32	

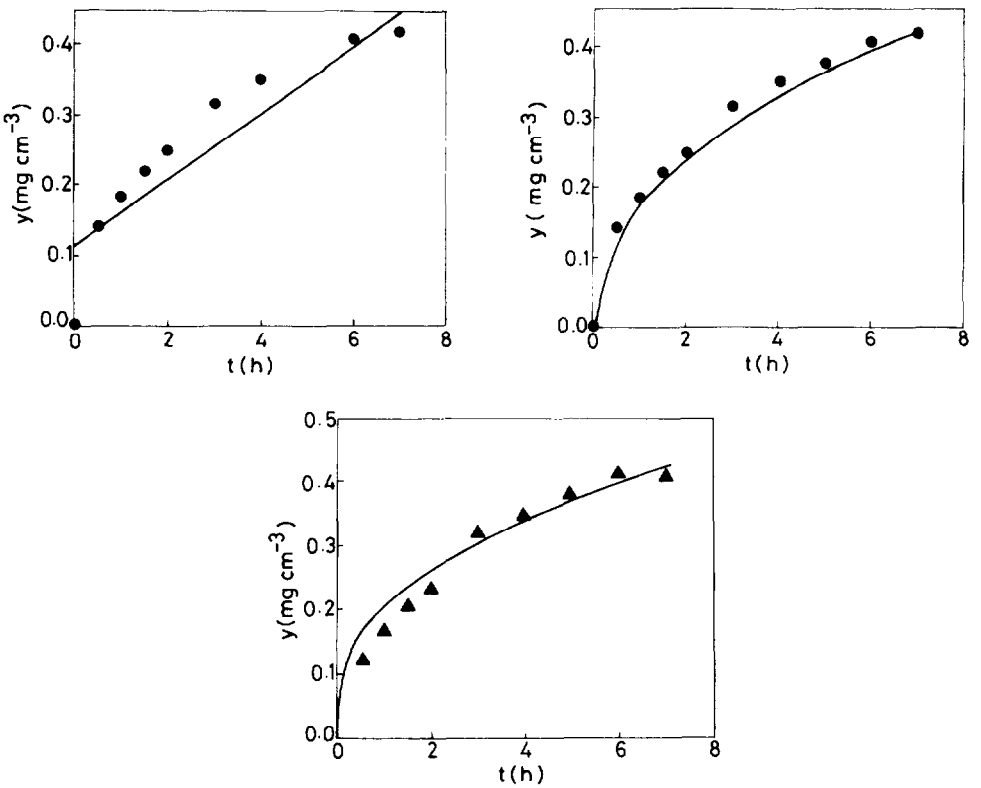

Fig. 2. Outlet solute concentration as a function of time for novobiocin adsorption in a continuous stirred tank reactor. Bold circles or triangles represent experimental data while the bold lines represent calculated values using (a) the linear model (linear isotherm), (b) the biphasic model (linear isotherm) and (c) numerical simulation, the Freundlich isotherm.

$\{A_1 \exp(-k_1 t)\}$, and (iii) both the phases of the biphasic model, are presented in Table 3 for novobiocin separation.

The above analysis provides us with the values of the rate constants k_1 and k_s for adsorption in a continuous stirred tank reactor. However, it is important to study how we determine the mass transfer coefficient ka and the adsorption equilibrium constant K in each model. For the linear model (linear isotherm) we have Eq. (20a) with k_1 known from the slope of the long-time data. However, there are two unknown parameters (ka and K) and an additional relationship is required to determine them. For the linear model, this additional relationship comes from the assumption of equilibrium for q–y data at long times. To calculate the resin loading $q(t)$, we integrate the solute mass balance (Eq. (1)) to obtain

$$q = q_0 + \frac{Qy_F t}{(1-\epsilon)V} - \frac{Q}{(1-\epsilon)V}\int_0^t y\,dt - \left(\frac{\epsilon}{1-\epsilon}\right)y(t) \tag{26}$$

which, for the conditions of our problem, yields

$$q = 1.35\ \text{g l}^{-1} + \left[2.7\ \text{l h}^{-1}\frac{0.640\ \text{mg cm}^{-3}}{0.25\ \text{l}}10^3\ \text{cm}^3\ \text{l}^{-1}\right]t - \frac{2.7\ \text{l h}^{-1}}{0.25\ \text{l}}\int_0^t y\,dt - \frac{0.876\ \text{l}}{0.250\ \text{l}}y(t) \tag{27}$$

For $t = 7$ h, Eq. (27) gives, after performing a graphical integration and simple calculations, a q value of 25 mg cm^{-3}. Therefore,

$$K = \frac{q}{y} = \frac{25\ \text{mg cm}^{-3}}{0.418\ \text{mg cm}^{-3}} = 60.0 \tag{28}$$

for the linear model, assuming equilibrium. This is not a particularly remarkable assumption in an intrinsically non-equilibrium situation; further, it gives undue weightage to a single long-time value. In any event, substituting $K = 60.0$ in Eq. (20a) yields a ka value of 3.95 h^{-1} (Table 4).

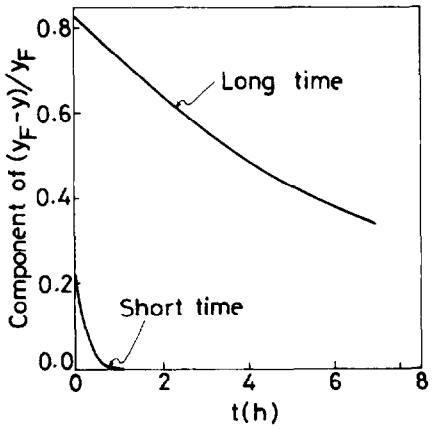

Fig. 3. Deconvolution of the experimental nonlinear biphasic fractional concentration difference curve into its short-time and long-time components for novobiocin separation. The values of the kinetic parameters are $k_1 = 0.126$ h^{-1}, $k_s = 5.044$ h^{-1}, $A_1 = 0.82$ and $A_s = 0.18$.

Table 3
Relative error in fractional concentration difference $\{(y_F - y)/y_F\}$ using short-time phase, long-time phase and biphasic model for novobiocin separation

Time/h	Experimental	Short-time phase		Long-time phase		Biphasic model	
	$\frac{(y_F - y)}{y_F}$	$A_s \exp(-k_s t)$	% error	$A_l \exp(-k_l t)$	% error	(3) + (5)	% error
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
0.0	1.0	0.179	82.1	0.820	18	0.999	0.10
0.5	0.784	0.014	76.5	0.769	1.9	0.783	0.13
1.0	0.717	0.001	99.7	0.723	0.8	0.724	0.97
1.5	0.661	–	99.98	0.679	2.7	0.679	2.70
2.0	0.616	–	–	0.637	3.4	0.637	3.40
3.0	0.511	–	–	0.561	9.7	0.561	9.70
4.0	0.456	–	–	0.495	8.5	0.495	8.50
5.0	0.414	–	–	0.436	5.3	0.436	5.30
6.0	0.367	–	–	0.385	4.9	0.385	4.90
7.0	0.347	–	–	0.339	2.3	0.339	2.30

Table 4
Comparison of the calculated values of the equilibrium constant (K) and the interfacial mass transfer coefficient (ka) by various methods for adsorption in stirred tank reactors

Model	K	ka/h^{-1}
Linear model–linear isotherm	60.0	3.95
Biphasic model–linear isotherm	32.0	1.46
Nonlinear model ($n = 1.54$)	102.7	18.70

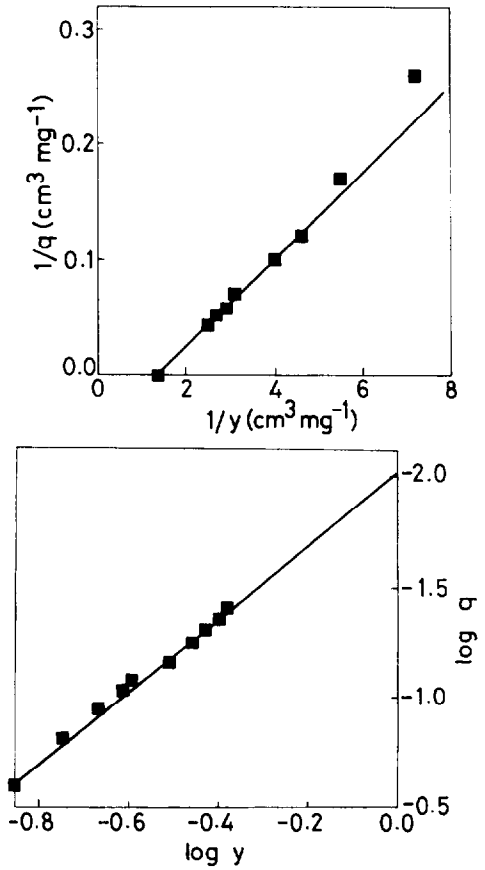

Fig. 4. Fitting of novobiocin adsorption data using: (a) the Langmuir isotherm; (b) the Freundlich isotherm.

The biphasic model removes the above deficiencies. We utilize the value of k_l as well as k_s, determined from experimental data, and simultaneously solve for K and ka using Eqs. (20a) and (20b). Thus, we avoid linearizing nonlinear y vs. time data; nor do we assume the existence of equilibrium in a nonequilibrium situation. The values of K and ka are found to be 32.0 and 1.46 h^{-1} respectively using the biphasic model (Table 4). The values of the equilibrium constant and the mass transfer coefficient (102.7 and 18.70 h^{-1} respectively) obtained from a best fit of the Freundlich model are also presented in Table 4. We thus find that for novobiocin separation, the values of the "equilibrium" constant and the mass transfer coefficient determined using the biphasic model are significantly different from the values obtained on employing linear/nonlinear models.

Finally, Fig. 4 depicts the fit of the Langmuir and Freundlich isotherms to novobiocin adsorption data. The Langmuir isotherm leads to a negative intercept on the $1/q$ vs. $1/y$ plot and has therefore been rejected. The Freundlich isotherm fits reasonably, but (as is clearer from Table 2) does not fit both long-time (high y) and short-time (low y) data equally well. We also recommend that a large number of experimental points be taken at short times to enable accurate deconvolution of the faster decay.

Discussion of an interesting point is now in order. Analysis of the novobiocin adsorption data based on the method outlined in Section 2.3 gives the values $k_l = 0.126$ h^{-1}, $k_s = 5.044$ h^{-1}, $A_l = 0.82$ and $A_s = 0.18$ for the biphasic model. On the other hand, on substituting these values of k_l and k_s into Eq. (18) we obtain $C_l = 0.40$ and $C_s = 0.60$. Why do the values of C_l and C_s not match the A_l and A_s values for the biphasic model? The answer lies in the principal assumption made in the theoretical analysis: that of a linear adsorption isotherm. For a linear isotherm we could rigorously prove several results (Eqs. (11), (18)–(20)), such as the sum of exponentials type of decay. Plotting q vs. y for novobiocin adsorption reveals that the isotherm is close to but not perfectly linear. These results indicate that even a nonlinear

isotherm may lead to a sum of exponentials type of expression (Eq. (11)) for the exit solute concentration vs. time behavior in a stirred tank; however, $A_l = C_l$ and $A_s = C_s$ only for a perfectly linear isotherm. Thus the method of analysis developed here for the determination of kinetic parameters may be applicable to linear as well as nonlinear isotherms but, needless to say, a numerical analysis has to be carried out to determine the mass transfer coefficient for a nonlinear isotherm.

4. Conclusions

A new method, incorporating a biphasic model, is developed to determine kinetic parameters and mass transfer coefficients for adsorption in continuous stirred tank reactors and applied to antibiotic recovery processes. The method does not linearize outlet solute concentration versus time data, nor does it assume the existence of equilibrium in a typical non-equilibrium situation. It is simple, self-checking and offers an additional equation so that an extra parameter can be evaluated. It yields superior results to the use of either the first-order linear model or even the numerical simulation of nonlinear adsorption isotherms in the case of novobiocin adsorption in stirred tank reactors. For the linear adsorption isotherm, closed-form analytical solutions have been obtained; however, the method may also be applied profitably to nonlinear isotherms. The parameters K and ka will take on different values depending on the model employed for data analysis; for novobiocin adsorption in a stirred tank reactor, the predictions of K and ka using the biphasic model are more accurate and are therefore to be preferred. We strongly advocate that the biphasic model be routinely employed along with linear models and numerical simulations of Langmuir/Freundlich isotherms for interpretation of adsorption data.

Appendix A. Nomenclature

A_l	Preexponential factor for long times (Eq. (21))
A_s	Preexponential factor for short times (Eq. (21))
a	Interfacial area ($m^2\ m^{-3}$)
C_l	Constant in Eq. (11)
C_s	Constant in Eq. (11)
D	Diffusion coefficient ($m^2\ s^{-1}$)
K	Adsorption equilibrium constant
k	Mass transfer coefficient ($m\ s^{-1}$)
ka	Interfacial mass transfer coefficient (s^{-1})
k_l	Long-time rate constant (s^{-1})
k_s	Short-time rate constant (s^{-1})
Q	Volumetric flow rate ($m^3\ s^{-1}$)
q	Adsorbed solute concentration ($kg\ m^{-3}$)
r	Adsorption rate ($kg\ m^{-3}\ s^{-1}$)
t	Time (s)
V	Volume of stirred tank (m^3)
Y	Fractional solute concentration difference $\{(y_F - y)/y_F)\}$
y	Solute concentration at the outlet of the stirred tank ($kg\ m^{-3}$)
y_F	Solute concentration at the inlet of the stirred tank ($kg\ m^{-3}$)
y^*	Equilibrium solute concentration ($kg\ m^{-3}$)

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