

Diffusion-Adsorption Problems in Macromolecular Systems: New Techniques for Parameter Estimation*

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Synopsis

It has been shown that the techniques used for estimation of diffusion-adsorption parameters in the past have certain basic flaws. New and efficient techniques for parameter estimation have been proposed. These have many advantages such as using the full concentration-time profile (rather than part of it), time saving, etc. The validity of these techniques has been demonstrated by the analysis of the data generated in our laboratory on adsorption of polyacrylamide and also the data on adsorption of dyes on chitin reported in the literature.

INTRODUCTION

We encounter the problem of adsorption of molecules on macromolecular substrates and adsorption of macromolecules on all types of substrates in a number of situations. The data on the rate of establishment of adsorption equilibrium of molecules or macromolecules at solid/liquid interfaces are of fundamental importance in many areas like flocculation of colloidal particles, adhesion, coating, effluent treatment for pollution control, etc. One of the most extensively studied case reported in this journal was the adsorption of dyes on chitin by McKay et al.,¹⁻⁵ the motivation being that the study of processes enables the design of dyestuff effluent plants. Another classic case is that of diffusion of humic acid,⁶ which is a macromolecule emanating out of the product of chemical and biological degradation of plant and animal residues and synthetic activities of microorganisms. Removal of humic acid substances by adsorption on activated carbon is an important problem, which has received a good deal of attention.

Apart from the above, there are many other instances where diffusion of macromolecules to substrates and their attachment to substrates assumes importance, and fairly fundamental investigations of such problems have been undertaken in the literature.

In order to make *a priori* prediction of the extent of adsorption on substrates, we require the knowledge of certain transport and equilibrium parameters related to external mass transport of the molecule to the adsorbing surface, intraparticle diffusion of the molecule through the pores of adsorbents, and finally the adsorption of the molecule at an interior site.

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We examined the mathematical techniques proposed in the past to evaluate these parameters, and we found that there were either inconsistencies or fundamental flaws in the methods proposed so far. We have reexamined these problems and propose a new technique which eliminates these flaws and enables rapid, unambiguous, and accurate estimation of the transport and adsorption parameters. We substantiate the validity of the technique by providing data on diffusion-adsorption of macromolecules generated by us and also by reanalyzing some of the data published in the literature.

Shortcomings of Previous Techniques of Analysis

In the early work of McKay et al.¹ published in this journal, the intraparticle diffusion and adsorption steps were neglected. The concentrations of adsorbate and adsorbents were assumed to be uniform due to the presence of rapid agitation. Therefore, the change in adsorbate concentration in solution C_t with respect to time t was given by

$$\frac{dC_t}{dt} = -k_f a_p (C_t - C_s) \quad (1)$$

Here k_f is the external mass transfer coefficient, a_p is the surface area of adsorbent particles per unit volume of solution, and C_s is the concentration of adsorbate on the surface of adsorbent particles. The equation was solved with the initial condition

$$t = 0, C_t = C_0 \quad (2)$$

Since the intraparticle diffusion was neglected by McKay et al., the concentration of adsorbate on the surface of adsorbent particles C_s could be assumed to be zero. Therefore, eq. (1) assumed the form

$$\left[\frac{d(C_t/C_0)}{dt} \right]_{t=0} = -k_f a_p \quad (3)$$

The external surface area a_p was evaluated as

$$a_p = \frac{3m}{R\rho_p(1 - \epsilon)} \quad (4)$$

Here m is the mass of adsorbent particles per unit volume of solution, R is the average radius of adsorbent particles, ϵ is the porosity of the adsorbent particles, and ρ_p is the density of adsorbent particles.

Equation (3) was used near $t = 0$ for obtaining external mass transfer coefficient k_f . Since the curves of (C_t/C_0) vs. t are very steep near $t = 0$, considerable error occurs in the estimation of the slopes. Hence the calculation of external mass transfer coefficient based on such analysis is in a sensitive region where small experimental error can cause a large change in the estimated value of the transfer coefficient.

McKay et al.^{1,3} derived their equations by neglecting intraparticle diffusion, but they took into account instantaneous adsorption for both linear and nonlinear adsorption isotherms. The differential mass balance of adsorbate within the adsorbent particle was written as

$$D_e \left(\frac{\partial^2 C_r}{\partial r^2} + \frac{2}{r} \frac{\partial C_r}{\partial r} \right) - \rho_p \frac{\partial q_r}{\partial t} = \epsilon \frac{\partial C_r}{\partial t} \quad (5)$$

where D_e is the effective diffusivity of adsorbate within the adsorbent particles, C_r is the concentration of adsorbate within the adsorbent particle at radial distance r , and q_r is the amount of adsorbate adsorbed per unit weight of adsorbent at radial distance r . The initial and boundary conditions were given by eqs. (2), (6), (7), and (8):

$$t = 0, \quad C_r = 0 \quad \text{for } 0 < r < R \quad (6)$$

$$D_e \left(\frac{\partial C_r}{\partial r} \right)_{r=R} = k_f (C_t - C_s) \quad (7)$$

Due to symmetry,

$$r = 0, \quad \frac{\partial C_r}{\partial r} = 0 \quad (8)$$

The rate of adsorption for linear adsorption isotherm when adsorption is instantaneous was given as

$$\frac{\partial q_r}{\partial t} = K \frac{\partial C_r}{\partial t} \quad (9)$$

where K is the adsorption equilibrium constant.

Since the intraparticle diffusion was neglected, the analytical solution of eq. (5) can be obtained as

$$\frac{C_t}{C_0} = \frac{1}{1 + mK} + \frac{mK}{1 + mK} \exp \left(- \frac{1 + mK}{mK} k_f a_p t \right) \quad (10)$$

From the experimental data, the plot of $\ln[C_t/C_0 - 1/(1 + mK)]$ vs. t was made to give a straight line, the slope being $-[(1 + mK)/mK]k_f a_p$, from which the external mass transfer coefficient was evaluated.

In order that the above method can be reliably used, the slope should be *constant* and should not change with time as is implied in the basic assumptions made while defining the equations. However, in actual evaluation of the data made by McKay et al.¹ it was found that the slope did not remain constant and changed with time. This means that the external mass transfer coefficient estimated on the basis of such erroneous estimation procedure cannot be relied upon either.

In an effort to estimate the diffusion-adsorption parameters, McKay et al.² plotted the amount of dye adsorbed per gram of chitin particles against the

square root of time where two or three linear regions were apparent. The slope of first linear section was termed as rate parameter which included intraparticle diffusion. However, the approach used by them could not provide an unambiguous estimation of the individual rate parameter values.

Realizing these limitations of the prior efforts, later on McKay et al.⁴ proposed a two resistance model. Using this model, they obtained the individual rate parameters, namely, external mass transfer coefficient and effective diffusivity. However, since the external mass transfer coefficient is calculated independently, an error gets associated with the calculation of individual rate parameters. This is very much reflected in the large deviation between the experimental results and the model predictions shown by them especially at higher times.

When all the inconsistencies referred to in the foregoing are viewed together, it becomes apparent that the evaluation of diffusion and adsorption parameters carried out in the literature is fraught with uncertainties. We now propose a new technique that can be effectively used.

Development of a New Parameter Estimation Technique

We assume that solid particles capable of adsorbing polymeric molecules or ordinary molecules are placed in a stirred vessel containing the solution of these molecules. When the stirring is started, the ensuing diffusion-adsorption process will comprise the following three steps:

- (1) Mass transfer from the bulk fluid to the particle (adsorbent) surface.
- (2) Intraparticle diffusion.
- (3) Adsorption at an interior site in the porous adsorbent.

The mass balance for adsorbate in the liquid is given by

$$\frac{dC_t}{dt} = -k_f a_p (C_t - C_r|_{r=R}) \quad (11)$$

The mass balance for the adsorbate within the adsorbent particles follows as

$$D_e \left(\frac{\partial^2 C_r}{\partial r^2} + \frac{2}{r} \frac{\partial C_r}{\partial r} \right) - \rho_p \frac{\partial q_r}{\partial t} = \epsilon \frac{\partial C_r}{\partial t} \quad (12)$$

The rate of adsorption is given by

$$\frac{\partial n}{\partial t} = K_a \left(C_r - \frac{n}{K} \right) \quad (13)$$

where n is the amount of adsorbate per unit weight of adsorbent and K_a is the coefficient associated with the rate of adsorption.

The initial and boundary conditions can be formulated as follows:

$$t = 0, \quad C_t = C_0 \tag{14}$$

$$t = 0, \quad C_r = 0, \quad n = 0 \tag{15}$$

$$k_f(C_t - C_r|_{r=R}) = D_e \frac{\partial C_r}{\partial r} \tag{16}$$

$$r = 0, \quad \frac{\partial C_r}{\partial r} = 0 \tag{17}$$

Taking Laplace transform of eq. (13) and using the boundary conditions given by eq. (15), we get

$$n(s) = \frac{K_a C_r(s)}{s + K_a/K} \tag{18}$$

Taking Laplace transform of eq. (12), substituting $n(s)$ from eq. (18), and utilizing the boundary conditions (16) and (17), we get

$$\frac{C(s)}{C_0} = \frac{1}{s + k_f \alpha_p \phi} \tag{19}$$

where

$$\phi = \frac{\theta - \tanh \theta}{\theta + (\text{Bi} - 1) \tanh \theta} \tag{20}$$

$$\theta = R \left[\frac{\epsilon s + \frac{\rho_p K_a s}{(s + k_a/K)}}{D_e} \right]^{1/2} \tag{21}$$

Since

$$\frac{C_\infty}{C_0} = \frac{1}{1 + \delta_0} \tag{22}$$

Taking Laplace transform of eq. (22), we get

$$\frac{C_\infty(s)}{C_0} = \frac{1}{s(1 + \delta_0)} \tag{23}$$

From eqs. (19) and (23), we get

$$\begin{aligned}
 F(s) &= \frac{C(s) - C_\infty(s)}{C_0 - C_\infty} \\
 &= \frac{1 + \delta_0}{\delta_0} \left[\frac{1}{s + k_f a_p \phi} - \frac{1}{s(1 + \delta_0)} \right] \quad (24)
 \end{aligned}$$

Usually the data are collected on C_t vs. t in a batch experiment. For such data a polynomial can be fitted between $[(C_t - C_\infty)/(C_0 - C_\infty)]$ and time t in the following form:

$$F(t) = \frac{C_t - C_\infty}{C_0 - C_\infty} = A + Bt + Ct^2 + Dt^3 + Et^4 + \dots \quad (25)$$

This can then be converted into Laplace domain with

$$F(s) = \frac{C(s) - C_\infty(s)}{C_0 - C_\infty}$$

giving

$$F(s) = \frac{A}{s} + \frac{B}{s^2} + \frac{2C}{s^3} + \frac{6D}{s^4} + \dots \quad (26)$$

By using eqs. (24) and (26) along with Marquardt's optimization routine,⁷ the three rate parameters, namely, the external mass transfer coefficient k_f , effective diffusivity D_e , and the rate coefficient for adsorption K_a , can be obtained.

The advantages of using this approach over the previous ones can now be enumerated. First, this approach enables us to calculate all the three transport resistances individually. Based on these individual values, one can decide which is the controlling step in the overall adsorption process. This will be useful in the design of efficient adsorbers. Second, this technique enables us to utilize the *entire* experimental data and therefore offers unique values of individual rate parameters, justifying the reliability of the technique. We do not have to split the C_t vs. t data in arbitrary time intervals as has been done in the past. Third, this approach requires less computer time compared to the other methods like curve fitting in the time domain.

Use of Moments Technique—Instantaneous Equilibrium Case

The moments technique for evaluating various transport parameters of the system is based on matching the experimental and theoretical moments. The moments technique is particularly attractive when the overall process is governed by several transport steps, since a simple analytical relation is usually obtained between the moments and the rate constants of each transport process (see Ramachandran and Smith⁸). Thus the rate parameters can be estimated accurately. In curve fitting technique in the time domain

excessive computer time is required, whereas the moments technique takes less computer time due to the simple analytical relations. In practice only the zeroth, first, and second moments are utilized, as the higher moments are difficult to determine accurately from the experimental data.

Moments of Concentration Decay Curve

The n^{th} moment μ_n of the concentration decay curve in the time domain is defined as

$$\mu_n = \int_0^\infty \frac{C_t - C_\infty}{C_0 - C_\infty} t^n dt \tag{27}$$

In Laplace domain the moments are related to concentration as

$$F(s) = \frac{C(s) - C_\infty(s)}{C_0 - C_\infty}$$

i.e.,

$$F(s) = \mu_0 - \mu_1 s + \mu_2 \frac{s^2}{2!} + \dots + \frac{(-1)^n \mu_n s^n}{n!} \tag{28}$$

Therefore, the n th moment in Laplace domain can be obtained as

$$\mu_n = \lim_{s \rightarrow 0} (-1)^n \frac{d^n F(s)}{ds^n} \tag{29}$$

MOMENT ANALYSIS FOR INSTANTANEOUS EQUILIBRIUM CASE

The mass transport of adsorbate from the bulk fluid to the interior site of the porous adsorbent is governed by eqs. (11) and (12) with the following equation for instantaneous adsorption equilibrium:

$$\frac{\partial q_r}{\partial t} = K \frac{\partial C_r}{\partial t} \tag{30}$$

The initial and boundary conditions are the same as those described in the case of eqs. (14)-(17).

The zeroth and first moments for this case are obtained as (see Furusawa and Suzuki⁹)

$$\mu_0 = \frac{T_D}{15(1 + \delta_0)} \left(1 + \frac{5}{\text{Bi}} \right) \tag{31}$$

$$\mu_1 = \mu_0^2 + \frac{1}{525(1 + \delta_0)} T_D^2 \tag{32}$$

where

$$T_D = \frac{R^2(\epsilon + \rho_p K)}{D_e} \quad (33)$$

and

$$\text{Bi} = \text{Biot number} = \frac{k_f R}{D_e} \quad (34)$$

EXPERIMENTAL

The adsorption experiments were carried out using aqueous solutions of polyacrylamide (Separan AP-30, Dow Chemicals) and benzoic acid. The range of concentration used in this work was 100–500 ppm. Activated carbon (High Abrasion Furnace Black, HAF N-330) of Phillips Carbon Black Ltd. was used as an adsorbent. Experiments were carried out in a cylindrical glass vessel (0.085 m diameter and 0.1 m height) with a Teflon coated magnetic stirrer;

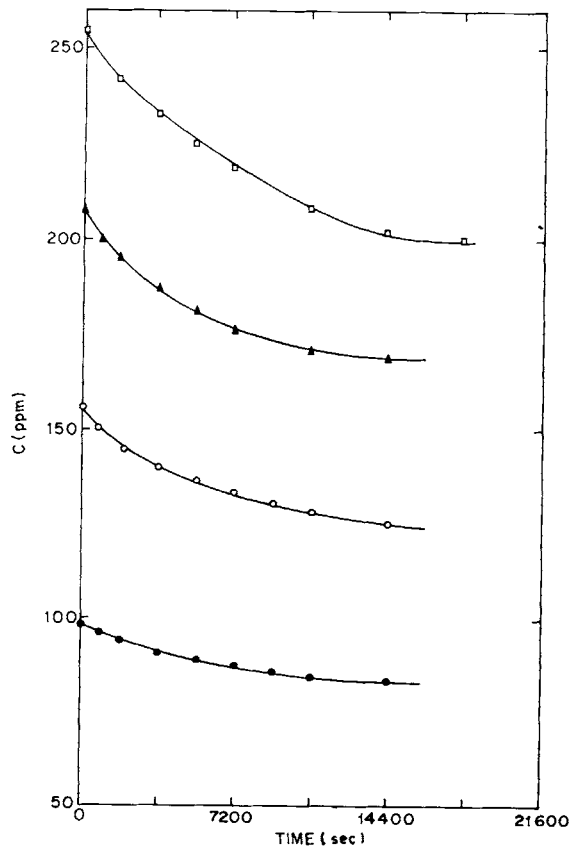


Fig. 1. Kinetics of adsorption for polyacrylamide (Separan AP-30) adsorbed on carbon black. Concentration (ppm): (●) 99; (○) 156; (▲) 208; (□) 255.

0.25 dm³ solution was used in each experiment with activated carbon loading of 1–5 g. The concentration of the solution was measured at definite time intervals. The quantity of polymer adsorbed was determined by the method of analysis described by Scoggins and Miller.¹⁰ This method is used for the determination of concentration of partially hydrolyzed, water-soluble polyacrylamide in aqueous solution. The method consists of reacting bromine (at pH 3.5) with polyacrylamide to give a product that oxidized iodide ion to iodine. The iodine liberated was measured spectrophotometrically as the starch tri-iodide complex. Actual concentration measurements were carried out by using Shimadzu UV 240 spectrophotometer at the wavelength 610 nm. The concentrations of benzoic acid were determined by measuring absorbance at 228 nm wavelength using Shimadzu UV 240 spectrophotometer.

Application of the New Technique for Parameter Estimation

We shall now demonstrate the application of the technique described here to analyze the data obtained by us and also those previously reported in the literature.

First consider our experimental investigation on diffusion-adsorption in dilute solutions of benzoic acid and polyacrylamide. Typical concentration vs time curves are shown in Figures 1 and 2. Also the equilibrium adsorption data were obtained by doing a long time experiment. These are shown in Figures 3 and 4. Based on these data, the parameters were estimated by using eqs. (24) and (26). Table I shows the estimated values of the parameters.

Consider the values of K_a first, which is expected to be independent of the concentration. We see that, within the limits of the experimental error, an

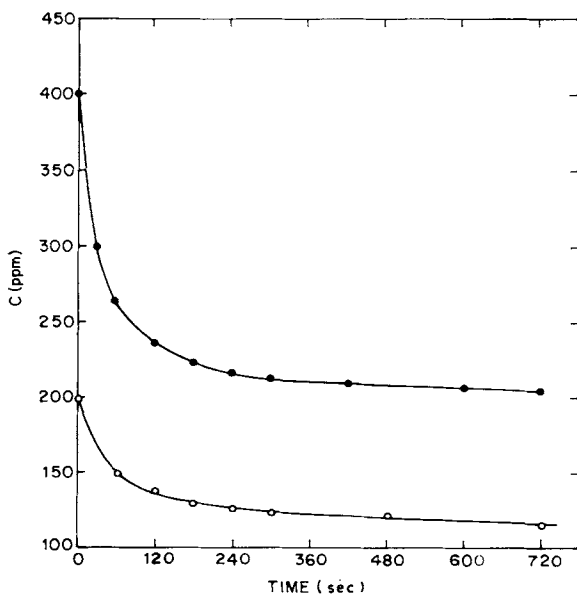


Fig. 2. Kinetics of adsorption for benzoic acid adsorbed on carbon black. Concentration (ppm): (○) 200; (●) 400.

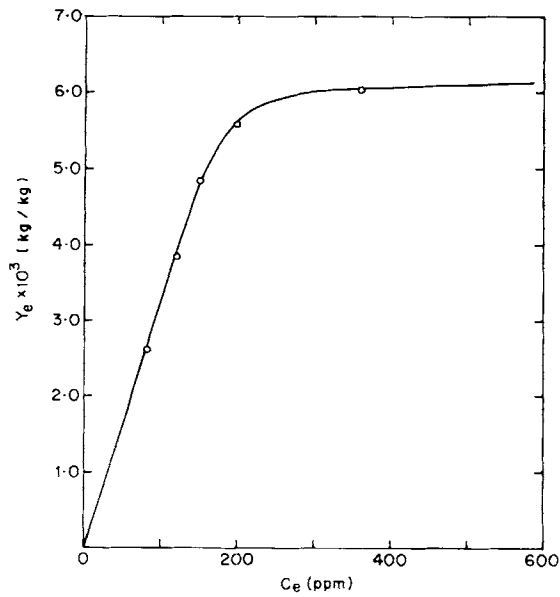


Fig. 3. Equilibrium data on adsorption of polyacrylamide (Separan AP-30) on carbon black.

average value of about $2.52 \times 10^{-5} \text{ m}^3/\text{kg s}$ obtained for polyacrylamide, whereas it is about $5 \times 10^{-3} \text{ m}^3/\text{kg s}$ for benzoic acid.

Now consider the value of k_f , the external mass transfer coefficient. Most correlations on mass transfer coefficients pertaining to mass transfer to particles in agitated systems are in the following form:

$$\text{Sh} = 2 + K'(\text{Re}^{1/2}\text{Sc}^{1/3}) \quad (35)$$

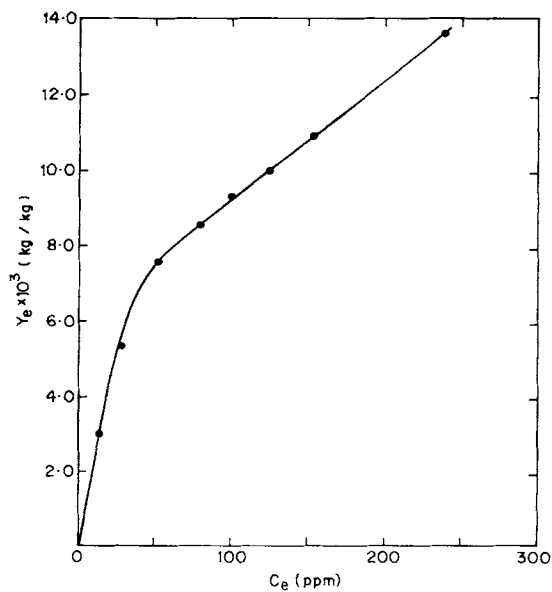


Fig. 4. Equilibrium data on adsorption of benzoic acid on carbon black.

TABLE I
Transport and Adsorption Parameters Calculated by Our Technique

No.	System	K_f (m/s)	D_e (m ² /s)	K_a (m ³ /kg s)
<u>Polyacrylamide</u>				
1	99 ppm	1.49×10^{-7}	3.2×10^{-12}	1.99×10^{-5}
2	156 ppm	1.89×10^{-7}	2.99×10^{-12}	2.65×10^{-5}
3	208 ppm	1.20×10^{-7}	2.60×10^{-12}	2.89×10^{-5}
4	255 ppm	1.026×10^{-7}	2.059×10^{-12}	2.52×10^{-5}
<u>Benzoic acid</u>				
5	200 ppm	4.49×10^{-5}	5.59×10^{-11}	6.00×10^{-3}
6	400 ppm	3.99×10^{-5}	5.085×10^{-11}	5.05×10^{-3}

where the Reynolds number (Re) is appropriately defined (see, e.g., Levins and Glastonbury¹¹). We used a magnetic stirrer with mild intensity of agitation and so the influence of second term is likely to be negligible. Considering $Sh = 2$ gives us by definition

$$k_f = 2D/d \quad (36)$$

where d is the diameter of the adsorbent particles. Equation (36), in actual fact, provides a lower bound on the mass transfer coefficient. The average size of the particles was 50 μm . The diffusivity of benzoic acid in water at 30°C is $1.06 \times 10^{-9} \text{ m}^2/\text{s}$.¹² Substituting in the above, we find that $k_f = 4.24 \times 10^{-5} \text{ m/s}$, which should be a lower bound. Comparing this value with the experimental value of $k_f = 4.49 \times 10^{-5}$ shows that the estimation procedure used by us is indeed reasonable.

A similar exercise can be repeated with our data on polyacrylamide solution. We need the data on diffusivity of polyacrylamide in water, which was taken from the work of Scholtan.¹³ Those data were correlated by us in the following empirical form

$$D = D_0(1 + 1.5C) \quad (37)$$

$$D_0 = 8.46 \times 10^{-4} M^{-0.69} \quad (38)$$

where C is the concentration in weight percent and M is the molecular weight of polyacrylamide.

TABLE II
Physical Properties of Adsorbents

Mesh size	300/325
Average particle diameter (μm)	50
Total surface area (m ² /kg) ^a	84,720
Apparent particle density ^b (kg/m ³)	1800
Porosity	0.60

^aMercury porosimetry data.

^bDetermined by mercury displacement.

For 100 ppm solution, we obtain $D = 2.849 \times 10^{-12} \text{ m}^2/\text{s}$. Substituting for D in eq. (36) and with $d = 50 \times 10^{-6} \text{ m}$, we obtain $k_f = 1.14 \times 10^{-7} \text{ m/s}$. Our experimentally deduced mass transfer coefficients in Table I are in the range of $1.026\text{--}1.89 \times 10^{-7} \text{ m/s}$. Again the theoretical value gives a fairly good agreement with the mass transfer coefficient obtained by us experimentally, thereby substantiating the reliability.

We now turn to the estimation of D_e , the intraparticle diffusivity. The recent exhaustive review on hindered transport of large molecules in liquid-filled pores by Deen⁴ provides the necessary background. Indeed in well-characterized cylindrical pores, it is possible to estimate the intraparticle diffusivity from fundamental considerations. But due to the variation in pore shapes, sizes, and also shape and size distribution of pores in our carbon black sample, it is very difficult to estimate D_e with any degree of certainty. The physical properties of adsorbent particles are given in Table II. The molecular

TABLE III
Different Parameter Values Estimated by Moments Technique
(Analysis of Data by McKay et al.^{1,2})

No.	System	$\frac{C_\infty}{C_0}$	$\mu_0 \times 10^{-3}$ (s)	$\mu_1 \times 10^{-6}$ (s ²)	$T_D \times 10^{-4}$ (s)	$D_e \times 10^{10}$ (m ² /s)	Bi	$k_f \times 10^5$ (m/s)
<u>MY5/chitin</u>								
1	0.2 kg/m ³ 3.33 rps	0.4	1.01	1.369	2.139	7.24	6.49	1.56
2	0.2 kg/m ³ 6.67 rps	0.4	0.900	1.220	2.320	6.68	10.98	2.43
3	0.2 kg/m ³ 8.33 rps	0.4	0.750	0.847	1.932	8.0	10.97	2.90
4	0.15 kg/m ³ 6.67 rps	0.17	0.405	0.380	2.582	6.0	12.98	2.58
<u>AB25/chitin</u>								
5	0.15 kg/m ³ 6.67 rps	0.71	5.259	35.308	7.518	3.91	10.599	1.37
6	0.20 kg/m ³ 6.67 rps	0.75	5.210	35.472	7.635	3.21	13.475	1.43
<u>AB158/chitin</u>								
7	0.20 kg/m ³ 6.67 rps	0.64	4.24	22.105	5.819	7.1	7.115	1.67
8	0.20 kg/m ³ 10 rps	0.64	3.96	20.055	5.989	6.9	9.206	2.10
<u>DR84/chitin</u>								
9	0.20 kg/m ³ (302 μm diameter particles)	0.74	3.577	18.315	6.22	0.417	33.3	0.92
10	0.20 kg/m ³ (605 μm diameter particles)	0.772	4.374	25.200	6.42	1.43	15.23	0.72
11	0.20 kg/m ³ (925 μm diameter particles)	0.816	5.136	34.238	7.11	2.30	15.28	0.76

diffusivity in free solution D should provide an upper bound on D_e , since when hindrance factor (λ) approaches the value of zero in the free solution we have $D = D_e$. Otherwise, D will be always greater than D_e . The values of D_e reported in Table I appear to be consistent with these physical considerations.

We will now consider the data in the literature and show how the moments technique can be applied to make a reliable parameter estimation. The experimental concentration time curves reported by McKay et al.^{1,2} were used for this purpose. We evaluated the zeroth and first moments using eq. (27). C_∞ was taken as the steady state concentration and moments were evaluated up to that time. The equilibrium data on adsorption was taken from the literature.⁵ Equations (31) and (32) were solved simultaneously for obtaining the external mass transfer coefficient k_f and the effective diffusivity D_e . Table III gives the estimated values of different parameters. The mass transfer coefficients calculated by us are always about 30% lower than those calculated by McKay et al.¹

We believe that the values of external mass transfer coefficients calculated by McKay et al.¹ are less reliable for various reasons. First, while using eq. (10), McKay et al.¹ have determined the slopes between $t = 0$ and $t = 30$ s. These slopes unfortunately *change with time*; therefore, any external mass transfer coefficient calculated on the basis of time-dependent slope is contrary to the physics underlying eq. (3), which assumes k_f to be independent of time. Second, in using the present method of estimation, we have accounted for both external mass transport and intraparticle diffusion. The moments technique used by us utilizes the entire experimental data and not only part of the data as done by McKay et al.¹ The external mass transfer coefficients calculated by us are therefore more reliable.

The external mass transfer coefficient increases with an increase in the speed of agitation. Figure 5 gives the plot of $\ln k_f$ vs. speed of agitation, N .

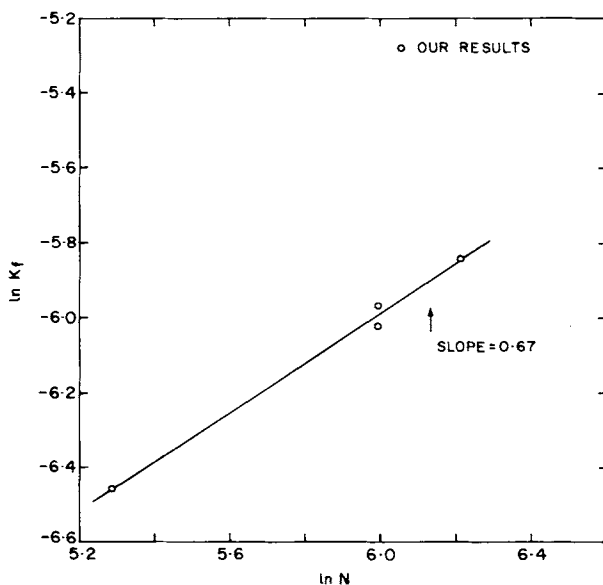


Fig. 5. Effect of speed of agitation on external mass transfer coefficient. Data for MY5 on chitin.

This indicates that k_f is proportional to $N^{0.67}$. This is quite consistent with the reports in the literature on variation of external mass transfer coefficient with speed,¹¹ which shows that k_f is proportional to $N^{0.5-0.75}$.

CONCLUDING REMARKS

We have shown that the methods used in the past in the literature for diffusion-adsorption parameter estimations from batch data are unnecessarily cumbersome and also have certain inherent flaws. We have proposed some new techniques for analyzing the concentration time data in adsorption-diffusion systems for parameter estimation and shown how a very reliable estimate of the parameters could be made. We have demonstrated the usefulness of these techniques by using both our own experimental data as well as data in the literature. We have specifically enumerated the advantages of using our technique in the hope that they will be widely used in the future.

APPENDIX: NOMENCLATURE

a_p	specific surface of the adsorbent (m^{-1}) particles
Bi	Biot number, $K_f R/D_e$
C_t	bulk concentration of adsorbate in liquid phase at time t (kg/m^3)
C_0	initial concentration of adsorbate in liquid phase (kg/m^3)
C_∞	steady-state concentration of adsorbate in liquid phase (kg/m^3)
C_r	concentration of adsorbate within particle at radial distance r (kg/m^3)
C_s	concentration of adsorbate at particle surface (kg/m^3)
$C(s)$	Laplace transform of $C(t)$
D_e	effective diffusivity of adsorbate in adsorbent particles (m^2/s)
$F(s)$	Function defined by eq. (24)
K	adsorption equilibrium constant (m^3/kg)
K_a	coefficient of rate of adsorption ($m^3/kg\ s$)
k_f	mass transfer coefficient for liquid phase to the particle surface (m/s)
K'	constant of eq. (35)
m	adsorbent concentration in liquid (kg/m^3)
n	concentration of adsorbate on adsorbent particles (kg/kg)
q	amount adsorbed in adsorbent particles (kg/kg)
R	radius of adsorbent particles (m)
Re	Reynolds' number for particles
r	radial distance from the centre of the adsorbent particle (m)
s	transform variable (s^{-1})
Sc	Schmidt number
T_D	parameter defined by eq. (33) (s)
t	time (s)

Greek

δ_0	ratio of adsorption capacity of particle to liquid
ϵ	adsorbent particle porosity
μ_n	n th moment (s^n)
ρ_p	adsorbent particle density (kg/m^3)
ϕ	function defined by eq. (20)
θ	Thiele modulus defined by eq. (21)

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