A Branched Pore Kinetic Model for Activated Carbon Adsorption

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A branched pore kinetic model for aqueous phase activated carbon adsorption is presented in which the carbon particle is separated into rapidly and slowly diffusing regions. The model was developed to overcome problems arising from a single rate parameter analysis and is shown to describe experimental data well. In addition to very different rates of transport in the two regions, parameters estimated by regression analysis indicated differences in the adsorptive characteristics.

SCOPE

Activated carbon is gaining ever-increasing usage as a general purpose adsorbent for organics from the aqueous phase. However, the actual mechanisms of transport and adsorption within the activated carbon particle are not yet well understood. Because of the complexity of the internal pore structure, activated carbon kinetics have generally been modelled with a single effective diffusion parameter active throughout the particle (Fleck, 1973; Crittenden and Weber, 1978a; Fritz et al, 1979), even though it is accepted that activated carbons have heterogeneous surface properties and a wide range of pore sizes.

This single intraparticle parameter approach has led to inconsistencies between observed equilibrium and kinetic behavior. Consequently, it is the objective of this study to develop a model, based on present knowledge of the internal structure of activated carbon, which would enable a consistent treatment of both equilibrium and kinetic data. Such a model should give an accurate description of the adsorption process from initial contact through to equilibrium.

In the phenolic adsorption studies of Snoeyink (1969) and Zogorski (1976), among others, a rapid initial uptake phase followed by a slow approach to equilibrium was noted. Such behavior is not consistent with the single effective diffusion parameter model. In addition, several authors (Beck and Schultz, 1970; Satterfield et al., 1973) have demonstrated that the effective diffusion parameter in small pores is a strong function of the pore diameter to solute diameter ratio, and that diffusion rates decrease with decreasing pore size. Since activated carbons have a wide range of pore sizes, a corresponding range of diffusion rates should be expected. Rapid saturation of the fast diffusing pores would result in a net decrease in effective diffusion rate as adsorption proceeds.

As an approximation to the microscopic description of the diffusional process, a model has been developed in this work which divides the carbon particle into two regions of different diffusion rates. The regions are loosely termed *macropores* and *micropores*. (These terms should not be confused with their conventional uses to define certain pore size ranges.) Relatively rapid diffusion and adsorption occur in the macropores, and the remaining slow approach to equilibrium occurs in the micropores.

The micropores are assumed to be homogeneously distributed throughout the particle and to branch off the larger macropore network which is responsible for radial transport. A schematic diagram of the proposed model is shown in Figure 2. In many respects, the model is similar in form to the dual rate models developed for catalysts of pelletized microporous particles or for molecular sieves (Furusawa and Smith, 1973b; Ruckenstein et al., 1971; Shah and Ruthven, 1977). However, it is not possible to define the dimensions of the microporous sub-units when dealing with activated carbons. Thus, a lumped parameter approach was used to describe diffusion in the micropores. A surface diffusion mechanism was assumed to be responsible for transport in the macropores.

Batch kinetic experiments were conducted over extended periods using a closed system, liquid-phase Carberry reactor to obtain accurate data for evaluation of the model parameters.

CONCLUSIONS AND SIGNIFICANCE

Experimental data collected for the adsorption of phenolics onto activated carbon are accurately described by the proposed model. The data show that the observed behavior during a batch kinetic experiment, if followed for a sufficiently long period, is not consistent with a single intraparticle diffusion rate model. Furthermore, by viewing activated carbon adsorption as a dual mechanism rather than as a single mechanism process, equilibrium isotherms and relatively short-term batch kinetic data can be shown to be compatible. From the model parameters which were obtained by regression analysis of the data, several conclusions can be drawn.

Measured surface diffusion coefficients within the macropore network are comparable to previously reported coefficients obtained using a single parameter approach. This agreement occurs, because it is principally adsorption into the macropores which is observed in a typical, relatively brief kinetic experiment. For the phenols studied in this work, adsorption into the micropores is so slow that the macropore region is essentially saturated before significant micropore capacity is utilized.

The capacity in the micropore region constitutes about 30% of the total adsorptive capacity over the range of concentrations investigated. This slowly utilized capacity is neglected by the standard single intraparticle rate model; it constitutes the difference between the adsorptive capacity realized in a short batch kinetic experiment, and the capacity measured over an extended period in an isotherm evaluation.

Comparison of the calculated adsorption capacities within the micropore region at different equilibrium liquid-phase

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concentrations indicates that the micropore capacities are essentially constant, independent of liquid-phase concentration. Such behavior is indicative of very strong sorbate/sorbent interaction and suggests that adsorption within this region may be of a different type to that in the larger pores.

The experimental data clearly show the dual rate nature of adsorption onto activated carbon. Such behavior has been observed with molecular sieves and pelletized microporous catalysts, but has not previously been shown to apply to activated carbons. The proposed branch pore kinetic model describes the experimental data well and is able to describe the full course of adsorption from contact to equilibrium.

On the basis of this model, adsorption column models can be developed which may explain previous inconsistencies in the literature such as premature breakthrough, and tailing of the latter portions of experimental breakthrough curves. A better understanding of the mechanisms of adsorption onto activated carbon will enable improved process design of carbon contactors.

Existing Carbon Adsorption Models

Kinetic models, developed to describe the internal diffusional resistances within an activated carbon particle, range from the linear or quadratic driving force approximations noted by Vermeulen (1952), to the now widely used pore, solid, or pore/solid-combined diffusion models discussed by Fleck et al. (1973). All these models assume that a single effective diffusion parameter acts throughout the adsorption period and that all adsorption sites within the carbon particle are identical except for radial position. Consequently, a large diffusion parameter results in rapid attainment of equilibrium and a small coefficient in slow attainment.

The use of a single effective diffusion parameter has resulted in the past in a systematic lack of fit being evident in the batch kinetic analyses of many researchers (Crittenden, 1976; Di Giano, 1969; Fritz, 1979; Ying, 1973). This lack of fit is illustrated in Figure 1, where a single intraparticle parameter surface diffusion model has been fitted to data from a batch kinetic experiment using a nonlinear least squares procedure; the data are fitted three times using more of the available data each time. The model is seen to be able to describe only the very early data and in fact the fitted coefficient is a function of the time period over which data is regressed.

The observed lack of fit occurs, because the model is constrained to approach the equilibrium defined by the isotherm, whereas the experimental data show a rapid initial uptake but level off after this period to a slow rate. To match the rapid initial rate, a large diffusion coefficient is required and consequently the model also predicts a rapid approach to equilibrium which is not observed in practice. In the past, researchers faced with this problem have attempted to deal with it in one of the following ways:

(i) By accepting the lack of fit and obtaining a diffusion coefficient which only approximates the true behavior.

(ii) By collecting data only in the very early period where the model appears to fit the data reasonably well. The measured parameter is not then generally applicable throughout the adsorption period.

(iii) By introducing a pseudo-isotherm (Crittenden and Weber, 1978b; Wedin, 1976), which only includes that part of the total capacity obtained during the rapid initial uptake. In this way, the model prediction is constrained to level off at the same concentration as the experimental data and a reasonably good fit to the data can be obtained.

An additional approach has been suggested by Neretnieks (1976a) who proposed a concentration-dependent diffusion coefficient. This assumption has been applied by the author (Peel, 1979) and was found to be incapable of describing the observed behavior.

The slow approach to equilibrium following an initial rapid uptake period has been described previously by several authors (Snoeyink et al., 1969; Zogorski et al., 1976) in connection with isotherm and kinetic studies. Such a phenomenon is not unexpected, if the structure of activated carbons is taken into account.

Diffusion within Activated Carbon

The probability of a range or even a continuum of diffusion rates within an activated carbon particle can be anticipated, when consideration is given to the heterogeneity of the carbon surface and pore structure. The exact mechanisms of adsorption onto activated carbon are not yet well understood. Because of the wide range of pore sizes and surface properties, several mechanisms may act in parallel; thus, making analysis of observed behavior extremely complex. In pores larger than 2-nm radius (conventionally termed transitional and macropores), surface adsorption models including mono-and multilayer adsorption appear to have application and seem conceptually sound. In smaller pores (conventionally termed micropores), the radii of the pores become comparable to the radii of the adsorbing species and multi-dimensional sorbate-sorbent interactions will occur (Dubinin, 1966; Chen, 1973).

In addition, the proximity of the pore walls may reduce diffusion (Satterfield et al., 1973). Beck and Schultz (1970) measured effective diffusion coefficients of several molecules in small pores of precisely known dimensions and showed that the diffusion coefficient was strongly affected by the ratio of solute diameter to pore diameter. Even at ratios as large as 1:10, the effective diffusion coefficient was reduced by 40%.

No similar studies or theories have been presented for a surface diffusion mechanism. However, the same general behavior should be observed. For example, if the surface hopping mechanism discussed by Gilliland et al. (1974) is assumed to occur, decreasing pore radii would affect the energy barrier involved in the translation process and thus affect the rate of diffusion.

Activated carbons such as the Filtrasorb F400 used in this study have a well-developed structure in the range less than 2-nm radius, with larger pores providing access to the interior of the particle. The high adsorptive capacity for many small organic molecules, such as phenols, has been related to this region which constitutes from 90-95% of the total surface area. Since phenols typically have molecular radii of approximately 0.35-0.5 nm (as calculated from the molar volume), all pores with radii

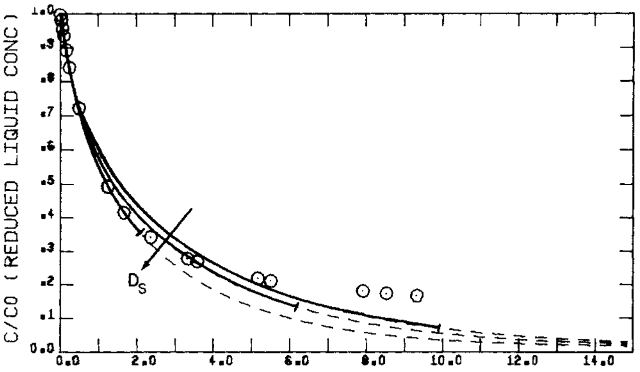

Figure 1. Single rate model applied to kinetic data.
——— extent of fitted data
– – – – – extrapolated curve.

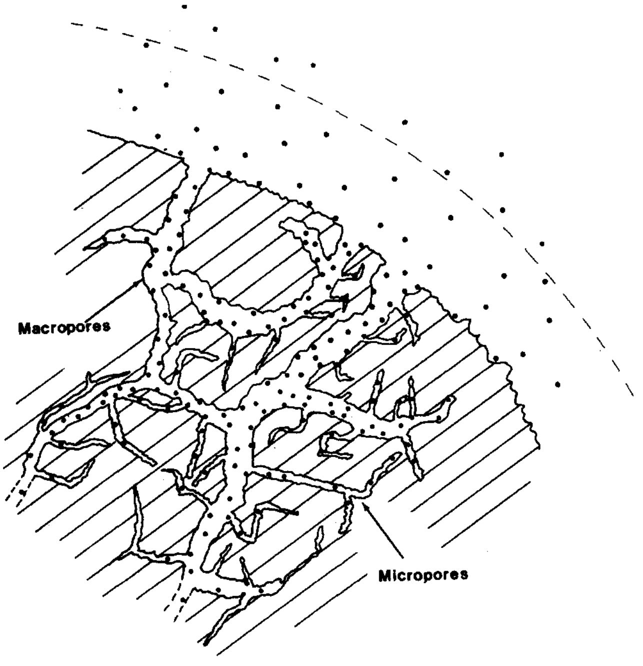

Figure 2. Idealized activated carbon pore structure.

larger than this should theoretically be available for adsorption. Thus, sorbate-micropore interactions are likely to be very important in adsorption of phenols onto activated carbon and are probably responsible for the previously discussed slow approach to equilibrium.

THEORY

On the basis of the above discussion a proper description of adsorption kinetics must involve at least two kinetic parameters which are active in different sections of the activated carbon particle. In this paper, the carbon particle has been partitioned into two main regions: macropores, in which the initial rapid adsorptive uptake is obtained; and micropores, in which restricted diffusion occurs and the remaining capacity to equilibrium is utilized.

The idealized physical representation is depicted in Figure 2. In this sense, macropores are pores large enough not to restrict diffusion of sorbate and micropores are pores in which diffusion is in some way restricted. The adsorption model for such a particle consists of three resistances in series: adsorbate first passing across the external liquid film; then diffusing and adsorbing in the macropores; and finally diffusing into and adsorbing in the micropores.

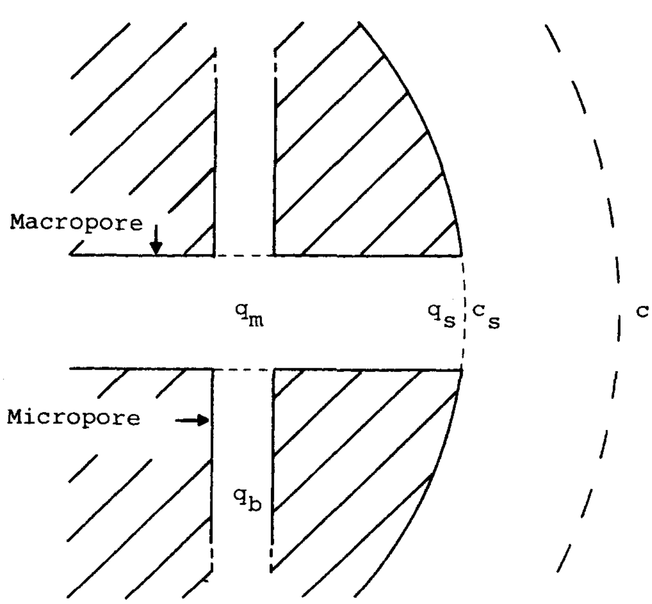

Figure 3. Conceptual diagram of adsorption system.

In clearly bidisperse adsorbents such as molecular sieves, dual rate models are widely used (Furusawa and Smith, 1973b; Ruckenstein et al., 1971; Shah and Ruthven, 1977). The situation is less complex, however, as the relative proportions and locations of the two regions are known. Activated carbons have either polydisperse or continuous pore size distributions and it is not possible to specify a *priori* either the dimensions or relative proportions of the macro- and micropore regions.

In the proposed model a surface diffusion mechanism has been assumed to be responsible for transport in the macropore region. In working with strongly adsorbed solutes, several researchers have found surface diffusion to give a more rational description of transport than is given by a pore diffusion mechanism (Crittenden, 1976; Di Giano and Weber, 1969; Furusawa and Smith, 1973a; Neretnieks, 1976b).

To describe transport into the micropores, a lumped parameter approach has been used. Since neither the location (radius or length) nor the extent of the micropore region can be defined *a priori*, a simple approach which results in the minimum number of adjustable parameters has been taken. The carbon particle is partitioned into two regions: a fraction f consisting of macropores; a fraction (1-f) constituting the micropore region. Transport between the two regions, which are both distributed radially, is described by a linear driving force expression between the local macro- and micropore concentrations.

Equilibrium as described by the equilibrium isotherm holds at the interface between the liquid and solid phases. A conceptual diagram of the system is presented in Figure 3 from which the following mass balances can be written.

Liquid-Phase Mass Balance

A detailed discussion of the choice of this equation is given elsewhere (Peel, 1979). The equation used is:

$$V\frac{dc}{dt} = k_f A\,(c - c_s) \qquad (1)$$

Macropore Mass Balance

If the fraction f represents that part of the total adsorptive capacity which is utilized in the macropore region, the balance can be written:

$$f\frac{\partial q_m}{\partial t} = \frac{f D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q_m}{\partial r}\right) - R_b \qquad (2)$$

The introduction of the fraction f is equivalent to dividing the carbon volume or mass into two homogeneously distributed regions. R_b is the rate of transfer of sorbate from the macropore network to the micropores or branch pores.

Micropore Mass Balance

$$(1 - f)\frac{\partial q_b}{\partial t} = k_b(q_m - q_b) = R_b \qquad (3)$$

In addition, the following initial and boundary conditions apply:

$$q_m\,(r, o) = 0 \qquad (4)$$

$$q_b\,(r, o) = 0 \qquad (5)$$

$$c(o) = c_o \qquad (6)$$

$$q_m\,(R, t) = q_s(t) \qquad (7)$$

$$\frac{\partial q_m}{\partial r}\,(o, t) = 0 \qquad (8)$$

and coupling between the liquid and solid phases is achieved by equating the fluxes at the solid-liquid interface:

$$k_f A \,(c - c_s) = f \,D_s \,A \,\rho_c \frac{\partial q_m}{\partial r}\bigg|_R \tag{9}$$

The equations are first reduced to dimensionless form using the substitutions:

$$\begin{aligned} C &= c/c_o \\ Q &= q/q_o \\ \beta &= r/R \\ \theta &= D_s t/R^2 \end{aligned} \tag{10}$$

and the change of variable:

$$\eta = \beta^2 \tag{11}$$

is introduced to give a finer spatial grid near the surface of the particle where concentration gradients are highest (Svedberg, 1975). The resultant set of equations is:

$$\frac{\partial Q_m}{\partial \theta} = 4\eta \frac{\partial^2 Q_m}{\partial \eta^2} + 6\frac{\partial Q_m}{\partial \eta} - Bi_p(Q_m - Q_b) \tag{12}$$

$$\frac{\partial Q_b}{\partial \theta} = Bi_p \frac{f}{(1-f)} (Q_m - Q_b) \tag{13}$$

$$\frac{\partial C}{\partial \theta} = \frac{3 \,f \,Bi_f}{F} (C - C_s) \tag{14}$$

$$\frac{\partial Q_m}{\partial \eta}\bigg|_{\eta=1} = \frac{Bi_f}{2} (C - C_s) \tag{15}$$

in which the constants have the following meaning:

$$Bi_f = \frac{k_f \,c_o \,R}{\rho_c \,f \,D_s q_o} \tag{16}$$

$$Bi_p = \frac{k_b \,R^2}{f \,D_s} \quad \text{. . . . . modified Biot numbers} \tag{17}$$

$$F = \frac{V \,c_o}{W \,q_o} \quad \text{. . . . . separation factor} \tag{18}$$

The initial and boundary conditions become:

$$Q_m \,(\eta, o) = 0 \tag{19}$$

$$Q_b \,(\eta, o) = 0 \tag{20}$$

$$C(o) = 1 \tag{21}$$

$$Q_m \,(1, t) = Q_s \,(t) \tag{22}$$

and Eq. 8, the boundary condition at the center of the particle, is automatically satisfied by the change of variable (Eq. 11).

This set of Eqs. 12-22 was solved using Crank-Nicholson finite difference expansions and specifically for the case of a Freundlich isotherm, although the solution is adaptable for any general isotherm description.

The Freundlich isotherm can be written:

$$q_s = M \,c_s^n \tag{23}$$

or alternatively

$$Q_s = C_s^n \tag{24}$$

Due to the nonlinearity of the isotherm, the coupling equation (Eq. 15) is nonlinear and the solution must be iterative at each point in time. Initial guesses of the future concentrations were calculated by linearly extrapolating the change over the previous time interval and were used in the first iteration. The newly calculated values were then directly substituted and the solution repeated until a converged solution was obtained. In practice, only two iterations were found to be necessary to achieve the required accuracy.

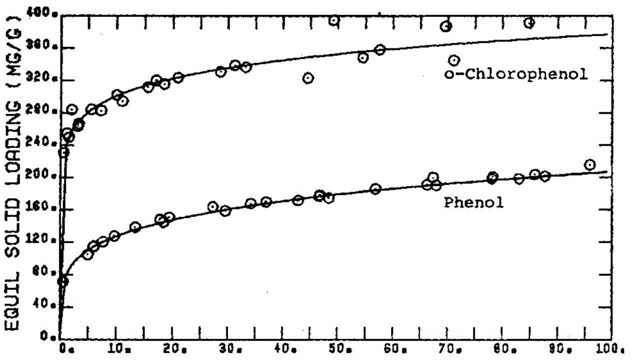

Figure 4. Phenol and o-chlorophenol isotherms.

TABLE 1. FREUNDLICH ISOTHERM PARAMETERS

Substrate	M	n
Phenol	78.1 (±3.3)	0.212 (±0.011)
o-Chlorophenol	240.2 (±2.1)	0.098 (±0.003)

±: approximate 95% confidence limits on linear hypothesis.

The solution was compared to the analytical solution of Patterson (1947) for the simplified case of very large k_f and a linear isotherm with the fraction f set equal to unity. The solution under these conditions was identical to the analytical solution.

EXPERIMENTAL

Sorbate-Sorbent System

All studies were conducted using reagent grade phenol and o-chlorophenol (OCP) as adsorbates, and Filtrasorb F400 (Calgon Corp.) was used as the adsorbent. The carbon was sieved to 16 × 30 mesh from the 12 × 40 mesh supplied to give a more uniform sample size. All carbon samples were boiled in distilled water and washed three times in distilled, deionized water before being dried in a 103°C oven. Some of the carbon was ground to −200 mesh for use in the powdered carbon isotherm studies.

Both isotherms and batch kinetics were carried out at 20°C. Ultraviolet spectrophotometry was used to measure adsorbate concentrations, phenol at 270 nm and OCP at 274 nm, using a 1-cm path length cell on a Beckman Model 25 Spectrophotometer. Duplicate and multiple analyses indicated a standard deviation of 0.065 mg/L for both adsorbates in the 0.5-200 mg/L range investigated.

Isotherms

Three isotherms were evaluated for each adsorbent using granular and powdered carbon and different initial concentrations of adsorbate. The isotherms were run for extended periods (Peel and Benedek, 1979), and periodically checked until equilibrium attainment was assured. For a given adsorbate, the measured isotherms were essentially indistinguishable, verifying the existence of a single unique isotherm for the system, and the combined isotherms for each adsorbate were well described by the Freundlich equation. The isotherms are shown in Figure 4 and the fitted parameters and confidence limits are given in Table 1.

Batch kinetics

The kinetic runs were conducted in a water jacketed, baffled and sealed, liquid-phase Carberry reactor in which the activated carbon was held in wire baskets and rotated through the liquid phase. This system allowed close control of temperature and external film transfer coefficient in a zero attrition closed environment, and thus allowed accurate data to be obtained over extended periods of time. Runs in the absence of activated carbon showed no observable concentration change over four-day periods.

In each run, an accurately weighd quantity of the activated carbon was placed in the wire baskets and the reactor filled with distilled water. The

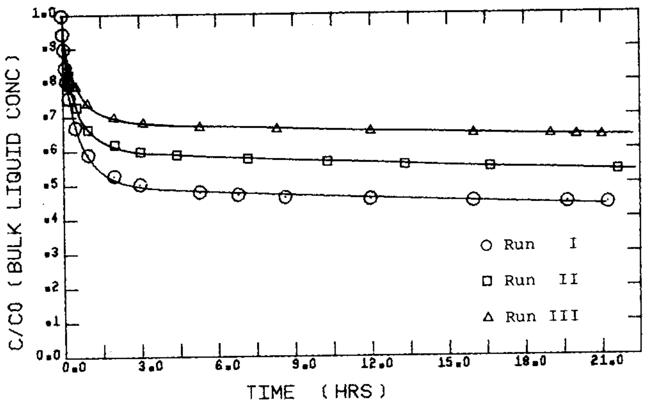

Figure 5. Batch kinetic experiments: phenol.

rotational speed was set and the system allowed to come to thermal equilibrium before a concentrated amount of the adsorbate was injected through a septum. Measurements were taken at 30 s intervals for the first 3 or 4 min to enable an accurate calculation of the external film transfer coefficient. Thereafter, concentration measurements were made at gradually increasing intervals until the experiment was terminated. All samples were reinjected immediately after UV measurement to eliminate errors due to sampling losses.

RESULTS AND DISCUSSION

The results of three kinetic experiments with phenol using varying carbon masses but otherwise identical conditions are shown in Figure 5. The conditions under which the experiments were run are given in Table 2. The data from each of the runs, numbered I to III, were regressed using the branched pore kinetic model in a nonlinear least squares routine and the fitted parameters (D_s, k_b, and f) are given in Table 2 also. The external film transfer coefficient, k_f, was measured directly from the first few-minutes data when intraparticle diffusional resistance is negligible. Figure 6 shows a typical set of data with external film transfer controlling for the first 2 min and the deviation from the straight line thereafter being due to developing intraparticle diffusion resistance. The figure shows that the film transfer coefficient, which is proportional to the initial slope of the plot of Log C vs. time, can be accurately measured by this technique.

The apparent dependence of the measured k_f values on the mass of carbon, Table 2, was attributed to varying hydraulic flow patterns with different amounts of carbon in the baskets. Other runs with lesser quantities of carbon did not show such a dependence indicating that adjacent particles were probably causing flow interference in runs with large carbon masses.

The ability of the model to adequately fit the experimental data, Figure 5, is clearly excellent. The calculated D_s and k_b values in Table 2 are reasonably constant. The measured values of D_s are comparable to previously reported values obtained using a single intraparticle parameter model (Crittenden and Weber, 1978a; Fritz et al., 1979; Sudo et al., 1978). This correspondence is to be expected as the micropore uptake is only significant in the latter stages of adsorption, a region not normally investigated in a batch kinetic study. The parameter f appeared to increase with increasing liquid-phase equilibrium concentration C_e and this observation led to further investigation.

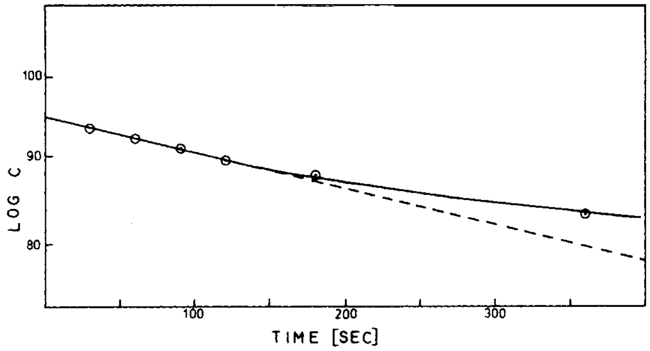

Figure 6. Initial uptake rate data in batch system.

In Figure 7 the results of the kinetic runs I to III have been plotted on the phenol isotherm. For each run the calculated capacity within the branch or micropore region [equal to $(1-f)q_e$] was determined and is shown on the figure, the capacities appearing to be virtually constant, independent of the equilibrium concentration. This result indicates that the capacity in the micropore region has an upper bound, and that this capacity was saturated over the concentration range investigated. The behavior is consistent with the earlier proposal that micropore adsorption would involve multidirectional sorbate-sorbent interactions and that the micropore region would therefore exhibit a higher affinity for the adsorbate than would the macropore region. As a consequence, the micropore region would saturate at lower liquid-phase concentrations.

In adsorption-desorption studies of activated carbon using supercritical CO_2 as a regenerant fluid, Modell (1978) found that only 70% of the initial adsorptive capacity could be recovered when using phenol adsorbed on Filtrasorb F300. He attributed this lost capacity to irreversible adsorptive interactions with surface oxide groups. He also obtained higher regeneration recoveries when systems were regenerated after short adsorption periods, suggesting much of the lost capacity was related to the slow adsorption mechanism.

Additionally, Snoeyink (1968) was able to desorb only about 50% of adsorbed phenol from a Columbia LC carbon even after five months of contact.

The existence of an irreversibly or strongly bound fraction of the total capacity is thus well established, and the limited results of the present study appear to associate this fraction with the slow diffusing or micropore region.

An understanding of the relative importance of each parameter can be seen from the sensitivity analyses presented in Figures 8, 9, and 10, where typical phenol kinetic parameters have been used in the simulations. As shown in Figure 8, the model is very sensitive to the parameter f throughout the adsorption period. Figures 9 and 10 show D_s to be a function of the

TABLE 2. DATA OF PHENOL KINETIC RUNS I, II, AND III.

Run No.	N (r/min)	W (g)	C_o (mg/L)	C_e (mg/L)	k_f (cm/s)	D_s (cm^2/s)	k_b (s^{-1})	f
I	250	0.9898	96.3	27.0	1.33E-02 (±5%)	7.78E-08 (±10%)	1.44E-06 (±27%)	0.63 (±2%)
II	250	0.7216	96.3	41.0	1.82E-02 (±5%)	9.01E-08 (±9%)	1.87E-06 (±18%)	0.66 (±2%)
III	250	0.5393	94.7	55.0	2.01E-02 (±5%)	7.75E-08 (±7%)	1.80E-06 (±16%)	0.68 (±2%)

±95% confidence limits on linear hypothesis.
Reactor volume equal to 2.3L in each case.

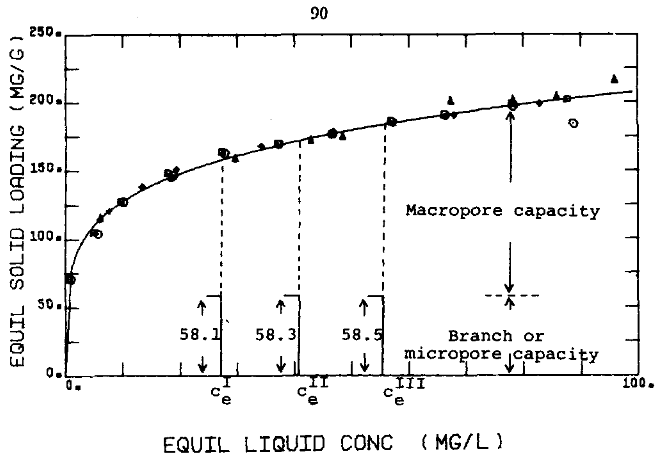

Figure 7. Postulated distribution of phenol isotherm.

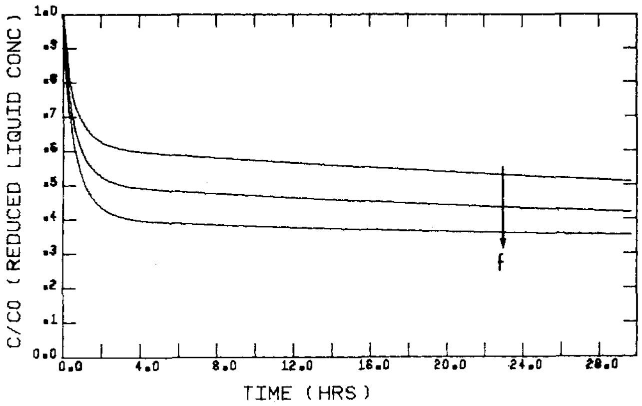

Figure 8. Sensitivity analysis: f parameter.
D_s = 7.5×10^{-8} cm²/s
k_b = 1.8×10^{-6} cm/s
k_f = 0.01 cm/s
f = (0.525, 0.700, 0.875)

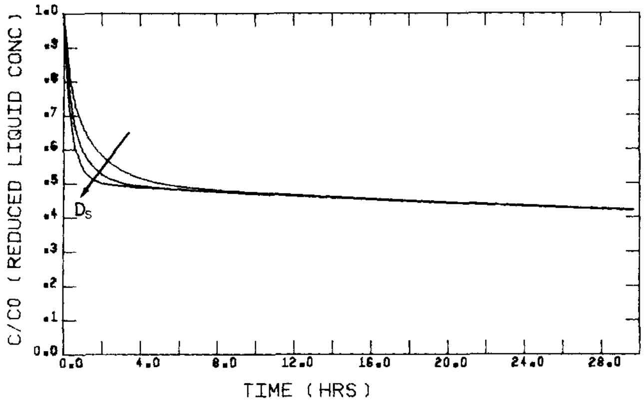

Figure 9. Sensitivity analysis: D_s parameter.
D_s = (3.75, 7.5, 15.) $\times 10^{-8}$ cm²/s
k_b = 1.8×10^{-6} cm/s
k_f = 0.01 cm/s
f = 0.7

initial rapid uptake period only and k_b to be a function of the slow, long-term uptake. Thus, for parameter values typical of a phenolic adsorption system, the rates of rapid and slow diffusion are so different that the two processes occur almost successively.

A shell-type model in which a rapidly adsorbing macropore shell surrounds a slowly adsorbing core was initially investigated in the present work and has also been presented recently by Famularo (1978). This model is satisfactory as long as the two rates are very different, but it is not physically representative of activated carbon in which pores are homogeneously dispersed throughout the particle. Consequently, it was not expected to be correct, if it were to be applied to systems in which the adsorption rates in the two regions were more similar. Hence, the more general branched pore model was used throughout this study.

The small slopes of the tails of the uptake curves in Figure 10 give an indication of the necessity of obtaining accurate data over an extended period. The slow uptake rate coefficient k_b is important in the modelling of carbon adsorption columns. Because the rate of change of concentration is small, adequate parameter discrimination requires data over many hours. Such data can

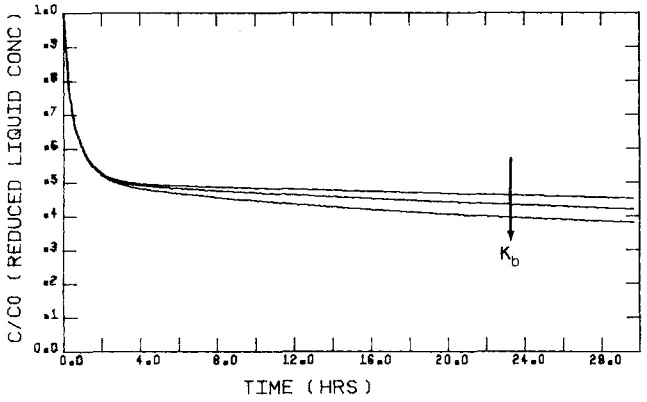

Figure 10. Sensitivity analysis: k_b parameter.
D_s = 7.5×10^{-8} cm²/s
k_b = (0.9, 1.8, 3.6) $\times 10^{-6}$ cm/s
k_f = 0.01 cm/s
f = 0.7

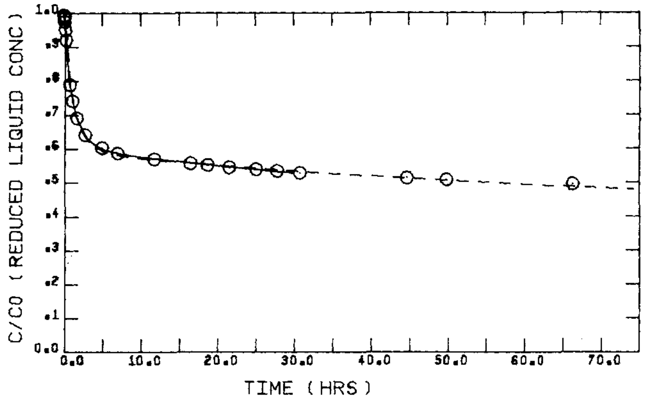

Figure 11. OCP kinetic run—0 to 30 and 75 h.
V = 2.3 L, W = 0.3920 g, c_o = 96.9 mg/L
0-30 hours: D_s = 4.18×10^{-8},
k_b = 1.56×10^{-6},
f = 0.659
0-75 hours: D_s = 3.81×10^{-8},
k_b = 1.14×10^{-6},
f = 0.678

only be satisfactorily obtained in a closed, zero-attrition system as used in the present study.

Data from a three-day OCP run are shown in Figure 11, in which the solid line represents the model prediction when only the first 30 hours of data were regressed and the dashed curve represents the model best fit when all 75 hours of data were regressed. The fitted parameters given on the figure show that although D_s and f changed by less than 10% and 5% respectively, the value of k_b fell by over 25%. Column adsorption runs reported elsewhere (Peel, 1979) indicated that the smaller value was more representative of an operating system.

The rate of transport in the micropores is likely to decrease as smaller pores are penetrated. Thus, the measured k_b is actually an average of a continuum of different rates. Consequently, the measured coefficient becomes a better estimate of the overall mean rate as data obtained over longer time spans are used. Nevertheless, the lumped parameter approach for the micropore transport appeared to be quite adequate for describing adsorptive behavior, and a more complex treatment does not appear justified at the present time.

NOTATION

A = total interfacial surface area, m^2
Bi_f = modified film Biot number, $k_f\, c_o\, R/\rho_c\, f\, D_s\, q_o$
B_{ip} = modified particle Biot number, $k_b\, R^2/f\, D_s$
c = liquid-phase concentration, kg/m^3
c_o = initial liquid-phase concentration, kg/m^3
C = reduced liquid-phase concentration, c/c_o
D_s = surface diffusion coefficient, m^2/s
f = fraction of total adsorptive capacity in macropores
F = separation factor, $V\, c_o/W\, q_o$
k_f = external liquid film mass transfer coefficient, m/s
k_b = branch pore rate coefficient, s^{-1}
M, n = Freundlich equation parameters
q = solid-phase concentration, kg/kg carbon
q_o = solid-phase concentration in equilibrium with c_o, kg/kg carbon
Q = reduced solid-phase concentration, q/q_o
r = radial variable, m
R = carbon particle radius, m
t = time variable, s
V = liquid-phase volume, m^3
W = mass of activated carbon, kg

Greek Letters

β = reduced radial variable, r/R
η = transformed radial variable, $\eta = \beta^2$
ρ_c = carbon particle density, kg/m^3
θ = dimensionless time variable, $D_s\, t/R^2$

Subscripts

b = branch or micropore
e = equilibrium
m = macropore
s = liquid-solid interface

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