A Liquid-Phase Adsorption Study of the Rate of Diffusion of Phenol from Aqueous Solution into Activated Carbon

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The differential equation for diffusion of a solute in a quasi-homogeneous, spherical, ion exchange particle, previously solved for time-dependent boundary conditions, is applied to an activated carbon adsorption system. This solution differs from the infinite volume solution which assumes constant boundary conditions. The result is applied to experimental data and yields effective adsorbent-phase diffusion coefficients. Equilibrium and rate studies were performed by using the aqueous phenol solution—activated carbon system. The rigorous solution to the diffusion equation is compared with a recently published frequency domain solution. Excellent agreement is obtained for values of the effective diffusion coefficient computed from the two rate equations.

It is recommended that the rigorous model be used for mechanism and diffusion coefficient determination. After the mass transfer parameters have been obtained, the simplified rate equation may be used for either lumped parameter or distributed parameter models for prediction of fixed-bed adsorber response. Further studies are required to determine if the simplified model adequately describes fixed-bed behavior.

Problems in design and operation of liquid-phase adsorption processes have two aspects, the adsorption equilibria and the rate mechanism involved in attaining these equilibria. Of fundamental importance is the determination of mass transfer parameters, that is, liquid film coefficients and effective adsorbent phase diffusion coefficients. After the design parameters have been obtained, one has the problem of simulating the transient response of a fixed-bed or batch process. In this work, a rigorous solution to the diffusion equation will be presented and used to determine an effective adsorbent-phase diffusion coefficient. A simplified rate equation will then be shown to be valid for the system studied. This simplified rate equation may be used in a simulation model for fixed-bed adsorbers.

PHASE EQUILIBRIA

Phenol was chosen as the adsorbate for two reasons: it is the primary reference solute used in liquid-phase adsorption studies, and it is a water pollutant in many industries, for example, the steel and pulp and paper industries.

The properties of aqueous phenol solutions and the activated carbon are discussed in detail because it is felt that this is an excellent reference solute and should be used to facilitate comparison of proposed rate equations in adsorption. In this manner, investigators exploring a new theoretical rate equation will have a standard system for comparison.

The concentration of phenol used for this study were approximately 1,000 μ g.-moles/liter of solution. It was determined that phenol exhibits a strong absorption of radiant energy at a wavelength of 270 mμ; therefore spectrophotometric analysis in the ultraviolet range was feasible. The concentrations were made up with a maximum error of about 5 μmoles/liter. The curve fit relation for the concentration—absorbance relationship is:

$$\text{Absorbance} = 0.0520 + 1.43 \times 10^{-3}\, C \qquad (1)$$

The adsorbent used in this study was type CAL activated carbon. The carbon was thoroughly screened, and fifty particles of the desired fraction were chosen at random and measured under the microscope. The minimum and maximum characteristic dimensions were recorded, and an average of these two dimensions was taken as the particle diameter. This value was found to be 1.57 ± 0.05 mm. The carbon had a total surface area (N_2 B.E.T. method) of about 1,000 sq. m./g. The molecular surface area of nitrogen is 16.2 sq. Å., while the molecular area for phenol is 41.2 sq. Å. Therefore, the effective surface area for phenol adsorption will be considerably less than 1,000 sq. m./g. because the phenol molecule is larger than the nitrogen molecule (*1*). In order to determine the effective surface area, a phenol B.E.T. plot was made by using the equilibrium data. The equilibrium data were obtained at 25°C. by placing varying amounts of adsorbent into flasks containing a given volume and concentration of aqueous phenol solution. After there was no change in concentration of phenol in the flasks, the amount of solute uptake was determined, and the adsorbent-phase concentration was computed. Approximately 3 hr. were required to reach equilibrium.

The B.E.T. adsorption isotherm may be written for liquid phase adsorption as

$$\frac{C^*}{\overline{C}^*(C_r - C^*)} = \frac{1}{\overline{C}_m a} + \frac{(a-1)C^*}{\overline{C}_m a C_r} \qquad (2)$$

Knowledge of the molecular area of the adsorbed specie allows computation of the surface area of the adsorbent from $\overline{C}_m$. $\overline{C}_m$ is calculated from the slope and intercept of a plot of Equation (2). The specific area of the adsorbent is computed from the following expression:

$$a_s = \overline{C}_m N \sigma \qquad (3)$$

The area determined for the adsorbent used in this study is 316 sq. m./g.

The complete equilibrium curve is shown in Figure 1. Because the B.E.T. equation only describes a portion of the total relationship, that is, that portion required for the surface area determination, the equations describing the total curve may be written in the following least-squares form:

$$C^* = 4.786 \times 10^{-6}\,\overline{C}^{*2.624} \qquad 400 \geqq C^* \geqq 0 \qquad (4)$$

$$C^* = -\,2255.6 + 2.593\overline{C}^* \qquad 700 \geqq C^* > 400 \qquad (5)$$

$$C^* = 57.51 + 0.699\overline{C}^* - 1.331 \times 10^{-4}\overline{C}^{*2} \qquad 975 \geqq C^* > 700 \qquad (6)$$

RATE EQUATION FOR THE QUASI-HOMOGENEOUS MODEL

The prediction of diffusion rates in solid-liquid systems is difficult, even if the diffusion coefficients of the species in pure solvent are known. The theory of adsorption kinetics may be approached in such a way as to bypass the problems of describing the pore liquid and the pore structure (matrix) of the adsorbent. There are two basic approaches to this problem: the pore diffusion model and the quasi-homogeneous model. The pore diffusion model is considered elsewhere (6).

The pore liquid and matrix are considered as a single quasi-homogeneous phase in the second model. The diffusion rate given by this model for a sphere is

$$\frac{\partial \overline{C}_i}{\partial t} = \overline{D}\left[\frac{\partial^2 \overline{C}_i}{\partial r^2} + \frac{2}{r}\frac{\partial \overline{C}_i}{\partial r}\right] \qquad (7)$$

Miller (3) and Tien and Thodos (5) have used the following analysis for describing adsorption and ion exchange systems, respectively. Consider the following system: adsorbent particles are placed in a well-stirred solution of a given solute (the solution is of finite volume). The following assumptions are involved:

1. The spherical, uniform adsorbent particles are quasi-homogeneous in structure.
2. The adsorbent particle is isotropic in nature.
3. The diffusion coefficient $\overline{D}$ is independent of radial distance.
4. The adsorption process is irreversible; that is, the rate of desorption is negligible.
5. The term *well stirred* implies the following: the concentration of the solute in solution is uniform; the liquid film resistance, surrounding each particle, has been removed by high agitation; and there is equilibrium at the solid-liquid interface.

Although the assumption of spherical particles discounts a rigorous interpretation of Equation (7) for systems of irregular particles, an effective diffusion coefficient can still be determined for these systems.

The following conditions apply to Equation (7):

Initial condition $\quad \overline{C} = 0 \quad \text{for} \quad t < 0, \; 0 < r < R \qquad (8)$

Boundary condition $\quad \overline{C} = \overline{C}_s \quad \text{at} \quad r = R, \; t > 0 \qquad (9)$

Equation (7) can be solved analytically if $\overline{C}_s$ can be determined as function of time. It will be assumed that $\overline{C}_s$ can be approximated as a polynomial function of time:

$$\overline{C}_s = \overline{C}_s(t) = \sum_{i=0}^{m} P_i t^i \qquad (10)$$

For this particular study, the polynomial is a second-order function of time:

$$\overline{C}_s = \overline{C}^* = A + Bt + Ct^2 \qquad (11)$$

The final solution that satisfies Equations (8), (9), and (11) is

$$\begin{aligned}\overline{C}_i = A &+ \frac{2AR}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\exp\left[-\overline{D}\left(\frac{n\pi}{R}\right)^2\right]t \cdot \sin\frac{n\pi}{R}r + B\left[t - \frac{R^2 - r^2}{6\overline{D}}\right] - \frac{2BR^3}{\pi^3\overline{D}r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^3} \\ &\cdot \exp\left[-\overline{D}\left(\frac{n\pi}{R}\right)^2\right]t \cdot \sin\frac{n\pi}{R}r \\ &+ C\left[t^2 - \left(\frac{R^2 - r^2}{\overline{D}}\right)\cdot\left(\frac{t}{3} + \frac{3r^2 - 7R^2}{180\overline{D}}\right)\right] \\ &+ \frac{4CR^5}{\pi^5\overline{D}^2 r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^5}\cdot\exp\left[-\overline{D}\left(\frac{n\pi}{R}\right)^2\right]t \cdot \sin\frac{n\pi}{R}r\end{aligned} \qquad (12)$$

In view of the fact that the medium is granular, $\overline{C}_i$ cannot be interpreted as a quantity having meaningful value at a point. The quantity $\overline{C}_i$ should be interpreted as an average over a small neighborhood of the point in question, small with respect to R but large with respect to the dimensions of the passages within the porous particle.

The next step is to incorporate the mass balance and put Equation (12) into a form that will yield an expression from which the effective adsorbent-phase diffusion coefficient may be determined. This expression, given in

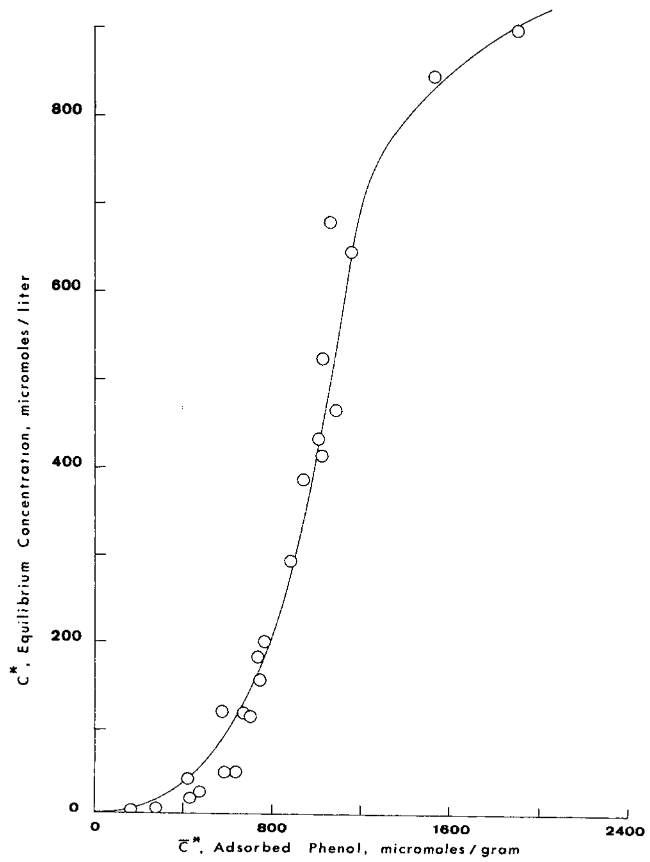

Fig. 1. Equilibrium relationship for the adsorption of phenol on activated carbon at 25°C.

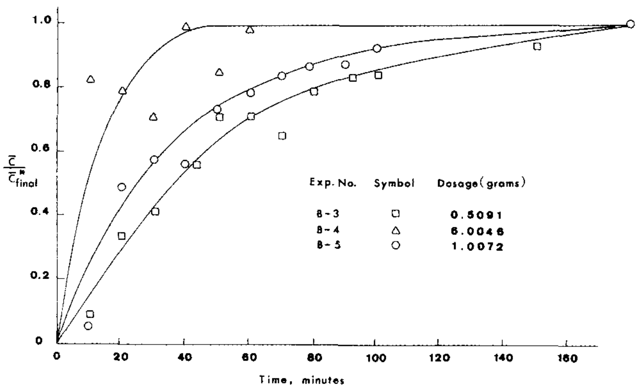

Fig. 2. The effect of carbon dosage on uptake of phenol from 1 liter of solution at high agitation: 1,000 rev./min.

final form, is

$$\frac{\overline{W} \quad \frac{4}{3}\pi R^2 \rho_p}{A + Bt + Ct^2} = \frac{\overline{C}}{\overline{C}_s} = 1$$

$$- \left\{ \frac{6}{\pi^2}\Phi_1 \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[\frac{-n^2\pi^2}{\psi}\right] \right.$$

$$+ \Phi_2 \left[\frac{\psi}{15} - \frac{6\psi}{\pi^4} \sum_{n=1}^{\infty} \frac{1}{n^4} \exp\left[\frac{-n^2\pi^2}{\psi}\right]\right]$$

$$\left. + \Phi_3 \left[\frac{2\psi}{15} - \frac{12\psi^2}{945} + \frac{12\psi^2}{\pi^6} \sum_{n=1}^{\infty} \frac{1}{n^6} \exp\left[\frac{-n^2\pi^2}{\psi}\right]\right] \right\} \tag{13}$$

where

$$\Phi_1 = \frac{A}{A + Bt + Ct^2}$$

$$\Phi_2 = \frac{Bt}{A + Bt + Ct^2}$$

$$\Phi_3 = \frac{Ct^2}{A + Bt + Ct^2}$$

The rate parameter is defined in Equation (14) and has the units of reciprocal time (*5*):

$$\psi = \frac{R^2}{\overline{D}t} \tag{14}$$

Equation (13) is a function of Φ_1, Φ_2, and Φ_3 for a specified value of ψ. The Φ's are functions of time; therefore, it is possible to plot $\overline{C}/\overline{C}_s$ vs. t with ψ as a parameter.

Experimental values of $\overline{C}/\overline{C}_s$ are plotted against time and intersect the calculated curves corresponding to different values of ψ. This plot is shown in Figure 3. The effective adsorbent-phase diffusion coefficient is calculated by determining the intersection of the curves shown in Figure 3. The times are read from the abscissa, and Equation (15) is used to compute the coefficient:

$$\overline{D} = \frac{R^2}{\psi t} \tag{15}$$

BATCH RATE EXPERIMENTS: DETERMINATION OF ADSORBENT-PHASE EFFECTIVE DIFFUSION COEFFICIENTS

The experiment design consists of a batch rate determination. The experimental apparatus consisted of a reaction flask (volume slightly greater than 1 liter) and a motor-impeller assembly which enabled agitation of the solid-fluid system. One liter of phenol solution was placed in the flask, the agitator was turned on, a given amount of adsorbent was added, and the timer was started. A tachometer was used to determine the shaft speed of the agitator assembly. Approximately 1,000 rev./min. is required to eliminate the liquid film surrounding each adsorbent particle. The effect of removing samples from the finite volume of solution yields an error of 0.5% for every sample taken. The highest error in the experimental determinations, due to removal of samples, was 8%. In many of the experiments the error was less than this. All determinations were at 25°C.

The three curves plotted in Figure 2 to show the effect of carbon dosage on the rate process are the result of three experiments: B-3, B-4, and B-5. It can be seen that the batch rate increases with increasing carbon dosage.

The following illustrates the steps required in computing $\overline{C}_s$ and in preparing a grapical plot such as Figure 3 to determine the effective diffusion coefficient:

1. From the fluid-phase concentration as a function of time (direct observation), compute the adsorbent phase concentration as a function of time.
2. For a given fluid-phase concentration, the adsorbent phase concentration in equilibrium with the solution is determined from the adsorption isotherm.
3. The value obtained in step 2 is $\overline{C}_s$.
4. The ratio of $\overline{C}/\overline{C}_s$ is then plotted vs. time.

The previous discussion yields the experimental plot. The theoretical curves are now superimposed upon the experimental curve.

Several experiments were performed following this procedure. One such experiment is illustrated in Figure 3. Three separate experiments were performed yielding plots such as Figure 3. Nine points were analyzed to determine an average diffusion coefficient of 0.69 × 10^{-7} sq. cm./sec. The nine values were in good agreement with each other, with an average deviation of 3.62%.

SIMPLIFIED RATE EQUATION

The fundamental reason for the previous analysis is to give the investigator an insight into the mechanism and magnitude of the mass transfer process for a particular system of interest. Also of importance to the engineer is the prediction of the transient response of a fixed-bed adsorber. Many investigations have been made in this area. Of particular interest is a recent work (*4*) which is

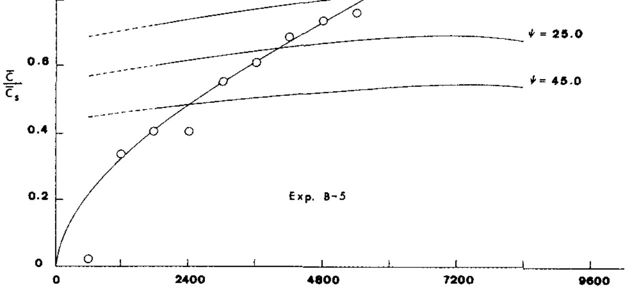

Fig. 3. Analysis of data for the determination of effective adsorbent-phase diffusion coefficients.

a thorough analysis of the continuity and rate equations for adsorber. The only disadvantage of this analysis is the excessive computing times required. Whether the fixed-bed adsorber is simulated by a lumped or distributed parameter model, the advantage of a simple yet effective rate equation is obvious.

A recent mathematical treatment of Equation (7) has shown that for large values of time, a simplified rate equation may be obtained (2):

$$\frac{d\overline{C}}{dt} = k_p(\overline{C}^* - \overline{C}) \tag{16}$$

where

$$k_p = \frac{15\overline{D}}{R^2} \tag{17}$$

In order to verify this result, the data previously presented were used to prepare Figures 4 and 5. Although only one experiment is presented here (B-5), other data were also analyzed. It is realized that data obtained by investigations of many different systems will be necessary to completely verify the simplified model. From Figure 4 it is interesting to note that $d\overline{C}^*/dt$ does indeed approach zero at long times according to Jury's argument (2). In Figure 5, the data were represented with a least-squares linear relationship to yield a value of 1.18×10^{-2} min.$^{-1}$ for the adsorbent-phase mass transfer coefficient. Use of the diffusion coefficient determined in the rigorous analysis and application of Equation (17) yields a value of 1.00×10^{-2} min.$^{-1}$ for the mass transfer coefficient. There is excellent agreement between the two methods.

CONCLUSIONS

It was determined that both rate equations presented yield essentially the same effective adsorbent-phase diffusion coefficient for the aqueous phenol—activated carbon system. It is recommended that more systems be studied to substantiate the simplified model. The simplified rate equation is of a form amenable to simulation of fixed-bed adsorber systems and should be examined as a possible rate model for such a system.

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NOTATION

a = a constant in the B.E.T. equation
a_s = specific surface area of the adsorbent, sq. m./g.

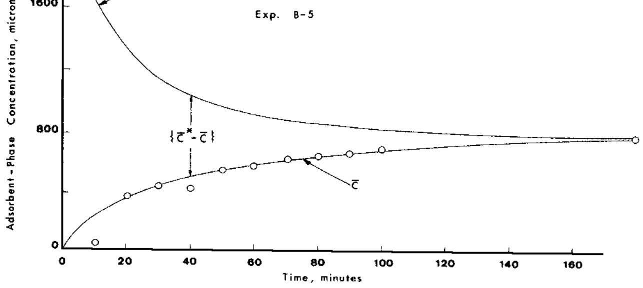

Fig. 4. Adsorbent-phase approach to equilibrium.

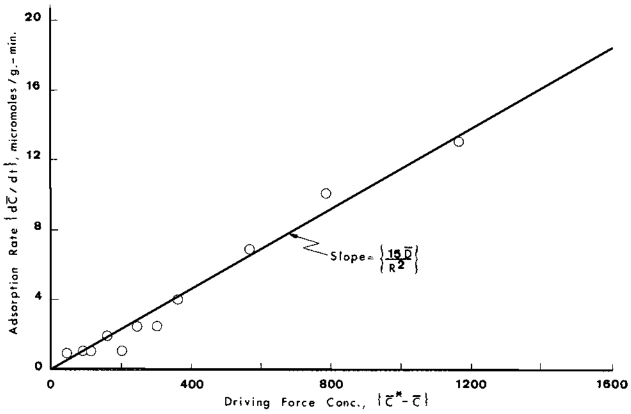

Fig. 5. Determination of the effective adsorbent-phase mass transfer coefficient.

A, B, C = empirical curve fit constants
C = concentration of the solute in solution, µmoles/liter
C^* = concentration of the solute in solution at equilibrium, µmoles/liter
$\overline{C}$ = average concentration of solute in adsorbent, µmoles/g.
$\overline{C}_i$ = point concentration of solute in adsorbent. µmoles-g.
$\overline{C}_m$ = value of $\overline{C}$ for complete monolayer coverage, µmoles-g.
C_r = residual concentration in solution at saturation level of adsorbent (8.995×10^5 µmoles/liter for phenol), µmoles/liter
$\overline{C}_s$ = concentration on the adsorbent surface at $r = R$, µmoles/g.
$\overline{C}^*$ = concentration of solute in adsorbent at equilibrium, µmoles/g.
$\overline{D}$ = effective adsorbent-phase diffusion coefficient, sq. cm./sec.
k_p = adsorbent-phase mass transfer coefficient, min.$^{-1}$
n = integer value in the infinite series
N = Avogadro's number, 6.023×10^{17} molecules/µmole
r = radial space coordinate, cm.
R = radius of an adsorbent particle, cm.
t = time, sec.
$\overline{W}$ = amount of solute adsorbed, µmoles

Greek Letters

ρ_p = particle density, g./cc.
σ = molecular surface area of a molecule of adsorbate (area of adsorbent occupied by one molecule of solute), sq. Å.

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