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Surface Diffusion Kinetics in the Adsorption of Acetic Acid on Activated Carbon

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ABSTRACT

The recovery of acetic acid from industrial wastewaters is an important separation problem, and one of the routes suggested for this application is liquid phase adsorption on activated carbon adsorbents. Designing an adsorber for such applications requires knowledge of equilibrium isotherm as well as adsorption rate data. In the present work the kinetics of adsorption of acetic acid on activated carbon has been studied. A three-parameter isotherm model has been used to correlate the equilibrium data, and a combined external film transfer–surface diffusion model has been used to simulate the experimental adsorption rate data. The surface diffusivity values obtained range from 6 to 8.5 × 10^{-7} cm^2/s, and the values show a dependence on surface loading. These surface diffusivity values can be used in modeling the column breakthrough behavior for this system.

INTRODUCTION

Acetic acid is a typical pollutant present in industrial wastewaters at concentrations ranging from 0.1 to 5 wt%. Thus the wastewater from a DMT plant in the petrochemical industry contains around 3–4 wt% acetic acid. The recovery of acetic acid from such wastewaters is an important problem, particularly as acetic acid forms valuable feedstock for the manufacture of a wide variety of chemicals. Whereas the separation of acetic acid from water by conventional distillation is economic at concentrations exceeding 70 wt% (1), for low concentrations in water (below 5 wt%), adsorptive separations can provide a viable option.

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Generally, activated carbon adsorbents have been suggested for the removal of acetic acid from wastewater. A novel scheme has recently been patented for the simultaneous removal and recovery of acetic acid from water by concentration swing adsorption based on activated carbon adsorbent (2). For the design of an adsorber for such applications, it is necessary that accurate and reliable adsorption isotherm and adsorption rate data be available. The rate of adsorption in general may be controlled by a film resistance at the external surface of the adsorbent particle, or by diffusion within the adsorbent particle, or by both film and internal diffusional resistances. Kinetic models to describe the internal diffusional resistances in an adsorbent particle are generally based on pore diffusion, surface diffusion, or combined pore–surface diffusion models. Pore diffusion pictures the adsorbate as diffusing in the fluid-filled pores of the adsorbent and adsorbing on the internal walls. Adsorbed molecules are then immobilized and can only migrate by desorption. Surface diffusion visualizes the transport as occurring only on the surface of a pore wall by jumping of adsorbate molecules between adjacent sites (3). Such a model has been most frequently used to describe the kinetics of adsorption on activated carbon systems in terms of an effective surface diffusion coefficient (4).

The present work is part of our studies for the development of a liquid-phase adsorption process for the recovery of acetic acid from petrochemical plant wastewaters and describes the estimation of surface diffusion coefficient from batch kinetic data on acetic acid adsorption using a mathematical model.

MODEL DESCRIPTION

The mathematical model used to describe the kinetics of adsorption of acetic acid is basically a combined external film transfer surface diffusion model recently proposed by Chatzopoulos et al. (5). These workers had, however, modeled the kinetics of adsorption of toluene from water on activated carbon, both for the case of a constant surface diffusivity as well for the case of a concentration-dependant surface diffusivity. For the latter case they report that an excessive computational effort is required. A constant surface diffusivity has been used by several workers in modeling kinetics of batch adsorption in activated carbon systems (6–8). In the present work, this approach has been followed. For the equilibrium isotherm data correlation, we have used the three-parameter isotherm of the type proposed by Radke and Prausnitz (9).

The model equations are

$$\frac{\partial q}{\partial t} = \frac{D_0}{r^2}\left[\frac{\partial}{\partial r} r^2 \left(\frac{\partial q}{\partial r}\right)\right] \tag{1}$$

$$\text{IC: } t = 0, \qquad 0 \leqslant r \leqslant R, \qquad q = 0 \tag{2}$$

$$\text{BC: } t > 0, \qquad \left.\frac{\partial q}{\partial r}\right|_{r=0} = 0 \quad \text{and} \quad D_0 \rho_S \left.\frac{\partial q}{\partial r}\right|_{r=R} = k_f(C - C_S) \tag{3}$$

External solute balance:

$$V_f \frac{dC}{dt} = \frac{3W}{\rho_S R} k_f (C - C_S) \tag{4}$$

$$\text{IC: } t = 0, \qquad C = C_0 \tag{5}$$

Adsorption isotherm:

$$q|_{r=R} = \frac{\alpha_1 C_S}{1 + \alpha_2 C_S^{\alpha_3}} \tag{6}$$

The equations have been nondimensionalized using the following quantities:

$$u = C/C_0, \qquad u_S = C_S/C_0, \qquad \eta = q/q_0, \qquad \rho = r/R, \qquad \tau = D_0 t/R^2$$

$$\text{Bi} = \frac{k_f R C_0}{\rho_S D_0 q_0}, \qquad A = \frac{3 W q_0}{V_f C_0}, \qquad K = \frac{1}{\alpha_2 C_0^{\alpha_3}} \tag{7}$$

A numerical procedure based on a finite difference scheme (10) was used to solve these equations.

EXPERIMENTAL

The adsorbent used in these studies was a granular activated carbon supplied by Industrial Carbons Pvt. Ltd., Baroda. The characteristics of this carbon are reported in Table 1. For equilibrium isotherm measurements, the granular carbon was crushed. Prior to its use in both equilibrium as well as rate experiments, the carbon was washed with dilute hydrochloric acid and boiled several times with distilled water until the water extract was neutral. The carbon was then dried at 150°C for 4 hours and stored in a dessicator.

TABLE 1
Physical Properties of ICA Grade Activated Carbon and System Properties Used in Simulation

Surface area (m^2/g)	1080
Skeletal density (kg/m^3)	2150
Apparent density (kg/m^3)	730
Particle size (m)	0.0017
Volume of feed phase (L)	0.8

Adsorption Isotherm Measurements

Weighed amounts of activated carbon was taken in glass-jacketed conical flasks containing aqueous solutions of acetic acid of known concentration. The flasks were securely stoppered, attached to a mechanical shaker, and the contents were maintained at 30 ± 0.05°C by circulation of thermostated liquid. The flasks were agitated for a period of 4 hours. Preliminary experiments had established that no change in concentrations could be detected after 2–3 hours. After equilibration, the aqueous phase was sampled, filtered, and analyzed for acetic acid content by titration with standard alkali.

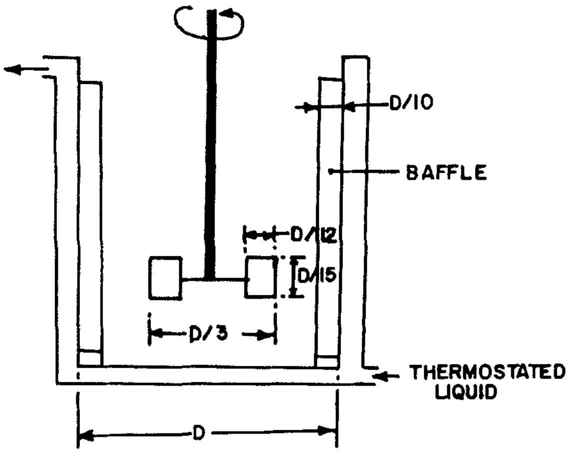

FIG. 1 Diagram of batch mixer.

Adsorption Rate Measurements

Adsorption rate measurements were carried out in a glass-jacketed baffled vessel with the dimensions shown in Fig. 1. In each experiment, 800 mL of aqueous acetic acid solution of known concentration was taken in the vessel and stirred by a turbine impeller of the dimensions also given in Fig. 1. The speed of the impeller was monitored by a digital tachometer. The vessel contents were maintained at 30 ± 0.05°C by circulation of thermostated liquid from a circulation bath. Weighed amount of granular activated carbon was then added, and the kinetic measurements were started. During the course of the experiments, small samples of the aqueous phase were withdrawn at fixed time intervals, filtered, and analyzed for their acetic acid content by titration with standard alkali.

RESULTS AND DISCUSSION

The experimental adsorption isotherm data were correlated by the three-parameter isotherm model given in Eq. (6). A Nedler–Mead Simplex optimization procedure (11) was used to determine the isotherm parameters from the experimental data. Figure 2 portrays the extent of fit achieved using the model. The isotherm is

$$q\big|_{r=R} = \frac{0.2733C_S}{1 + 0.3816C_S^{0.7739}} \tag{8}$$

The batch kinetic studies have been carried out with three different initial concentrations of acetic acid in the feed and with three different dosages of carbon adsorbent. In all the experiments the impeller rpm was maintained at 650 ± 15. The experimental concentration decay curves are shown in Figs. 3 to 6.

In diffusion of adsorbate into the adsorbent particle, the external film resistance dominates during the initial stages of the process followed by increasing contribution from the internal (pore, surface) diffusional resistance as the adsorbate penetrates deeper inside the particle (12). The concentration decay curve for the first few minutes of the process can be used to estimate the external film transfer resistance (12). A typical curve for this system is shown in Fig. 7, and the external film transfer coefficient, which was determined from the slope of this curve for each data set following the procedure of Mathews and Weber (13), varies from 2.1×10^{-3} to 2.8×10^{-3} cm/s. A value of 2.5×10^{-3} cm/s was selected for the external film transfer coefficient of this system for use in the simulations. With this value and the system properties given in Table 1, the model equations were solved for each experimental condition. The best fit esti-

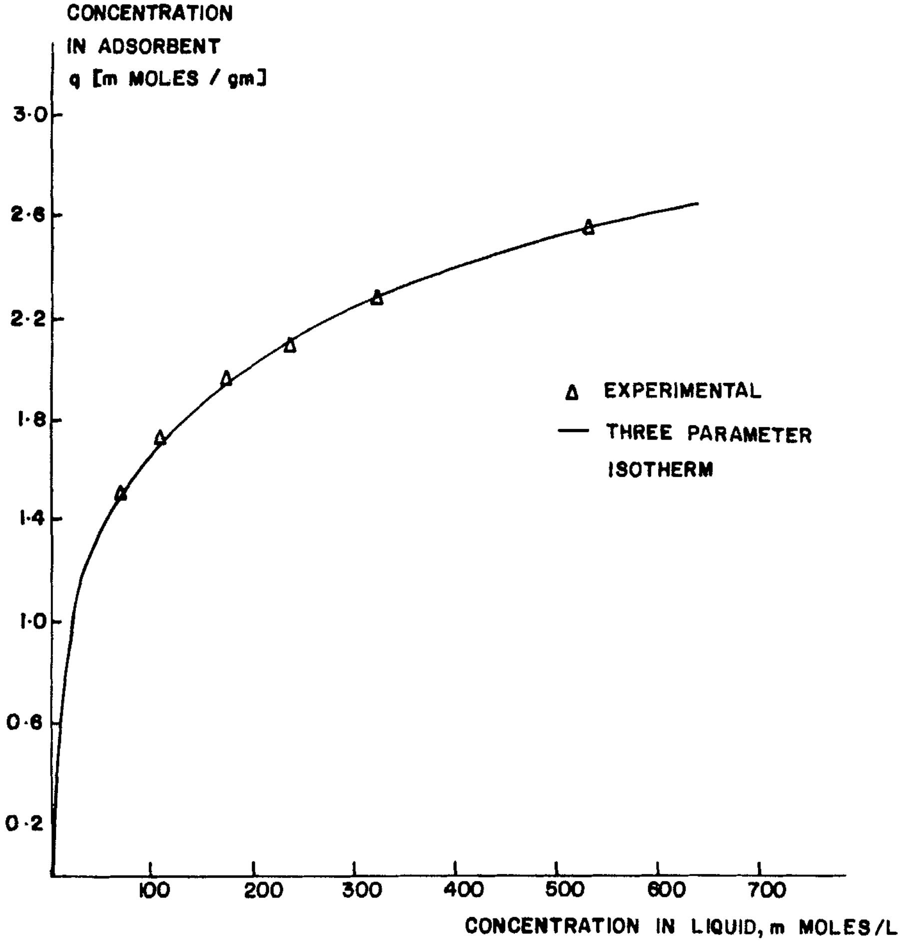

FIG. 2 Equilibrium isotherm for acetic acid adsorption on activated carbon at 30°C.

mates for the surface diffusion coefficient required for the simulation of the concentration decay curves are tabulated in Table 2, and the model predictions are compared with experiment in Figs. 3 to 6. It is seen that the model predictions which have been made over a range of carbon dosages and feed concentrations are reasonably good. The surface diffusion coefficient varies from 6 to 8.5 × 10^{-7} cm^2/s. It may be pointed out that Suzuki and Kawazoe (14) had given the following correlation for surface diffusion coefficient of organic solutes adsorbing from the aqueous phase onto activated carbon:

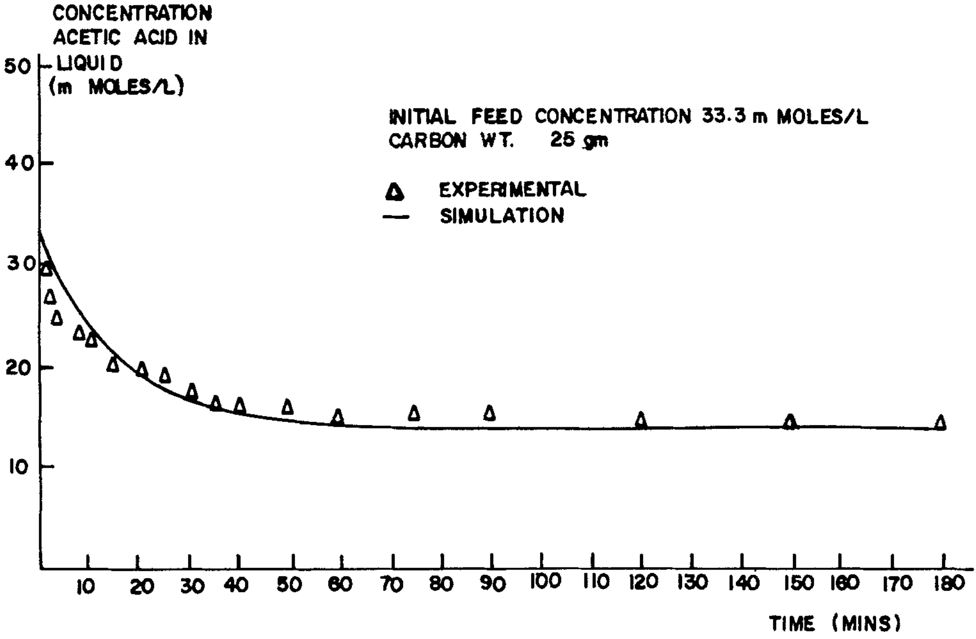

FIG. 3 Batch adsorption of acetic acid on activated carbon. Concentration decay curve.

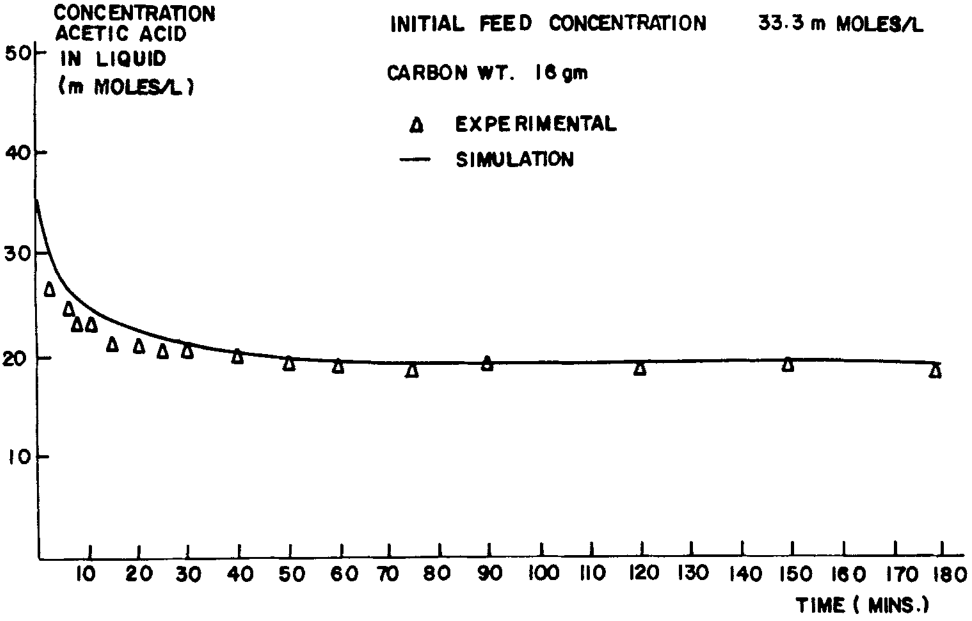

FIG. 4 Concentration decay curve for batch adsorption of acetic acid.

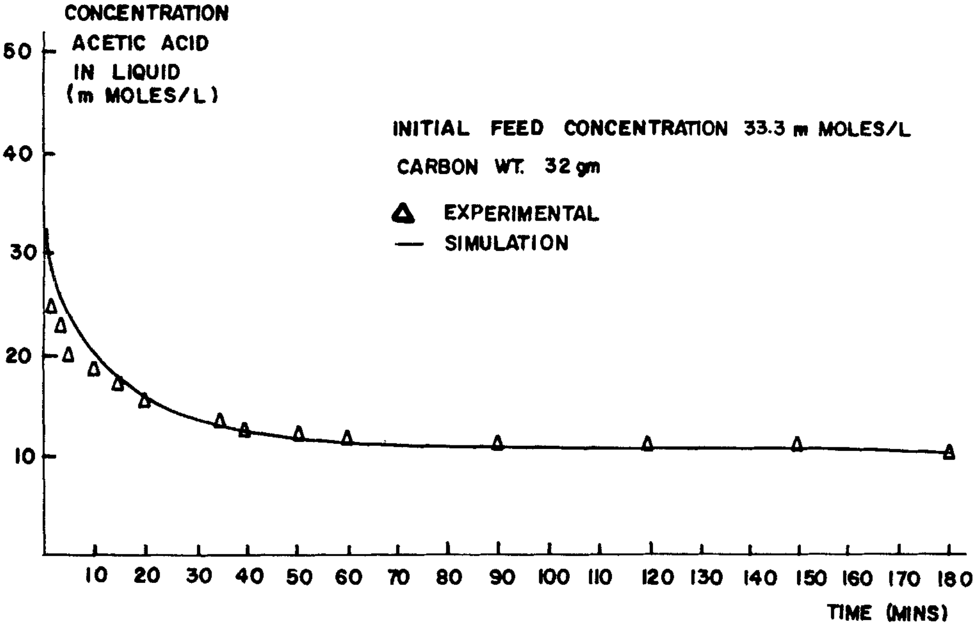

FIG. 5 Kinetics of adsorption of acetic acid on activated carbon.

$$D_0 = 1.1 \times 10^{-4} \exp(-5.32T/T_b) \quad (9)$$

From this correlation the surface diffusion coefficient of acetic acid at 30°C works out to be 1.4×10^{-7} cm^2/s. However, we point out that this correlation does not take into account the concentration dependence of the surface diffusion coefficient. It is known that surface diffusivity in-

TABLE 2
Concentration Dependence of Surface Diffusivity

Initial feed concentration (mmol/L)	Carbon weight (g)	Surface diffusivity (cm^2/s)	Equilibrium liquid concentration (mmol/L)	Surface loading (mmol/g)
33.3	32	7.0	10.5	0.7615
33.2	16	8.1	19.1	0.9802
33.2	25	6.0	13.8	0.8586
49.0	16	8.5	32.2	1.1860
16.9	16	7.3	7.3	0.6395

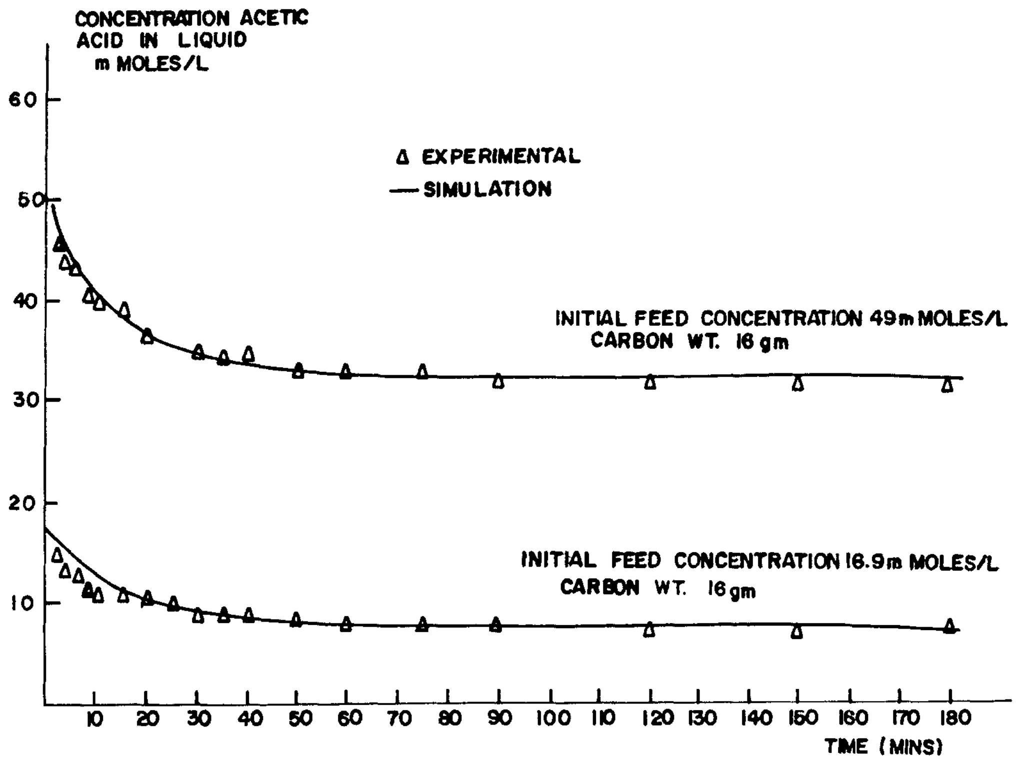

FIG. 6 Kinetics of adsorption of acetic acid on activated carbon.

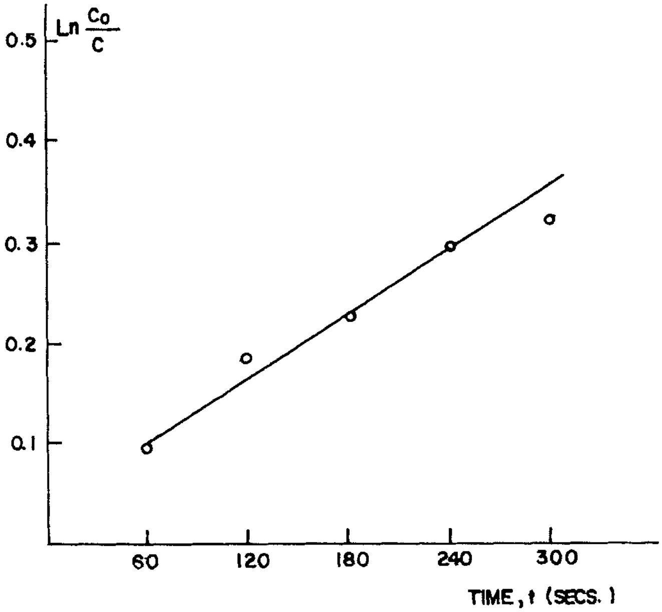

FIG. 7 Initial uptake rate data in batch systems.

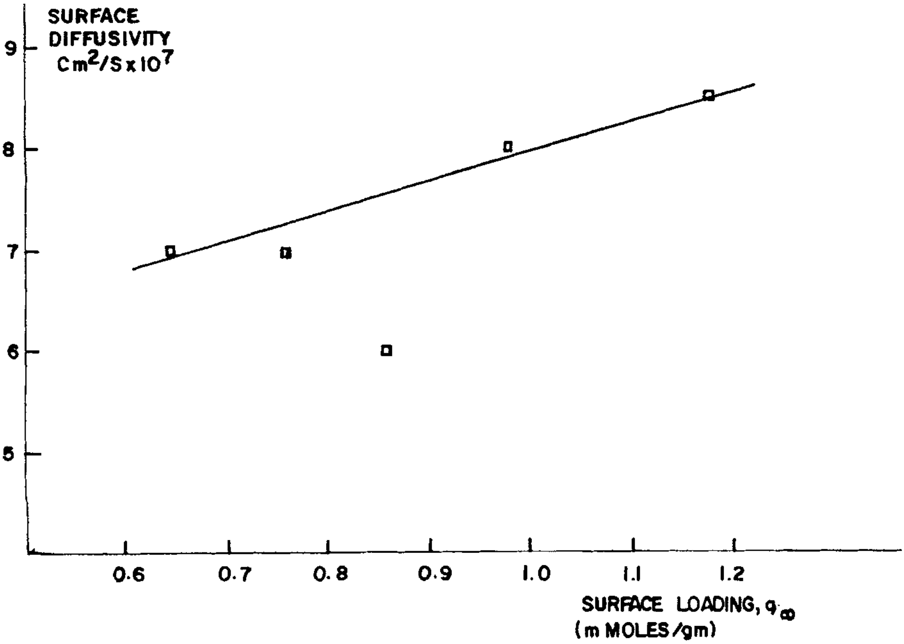

FIG. 8 Effect of surface loading on diffusivity.

creases with surface loading (adsorption), but the exact nature of the relationship is not known clearly (3, 4, 5).

In the present study the surface diffusion coefficient also shows a dependence on surface loading as is evident from the plot shown in Fig. 8.

CONCLUSION

The concentration decay curves obtained during batch kinetic studies on the adsorption of acetic acid on activated carbon were simulated by a combined external film transfer–surface diffusion model. The surface diffusion coefficient shows a dependence on surface loading within the range of feed concentrations studied. The surface diffusion coefficient will find application in the simulation of column breakthrough behavior for this system.

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NOMENCLATURE

A	term defined in Eq. (7)
Bi	Biot number
C	concentration in liquid (mmol/L)
D_0	surface diffusivity (cm^2/s)
K	term defined in Eq. (7)
k_f	external film transfer coefficient (cm/s)
q	concentration in adsorbed phase (mmol/g)
R	particle radius (cm)
r	radial position in adsorbent (cm)
T	temperature (°K)
T_b	boiling point of adsorbate (°K)
t	time (s)
u	Dimensionless liquid concentration
V_f	volume of liquid (L)
W	weight of carbon (g)

Greek Symbols

ρ_S	solid density (g/L)
ρ	dimensionless radial distance
τ	dimensionless time
η	dimensionless solid phase concentration
$\alpha_1, \alpha_2, \alpha_3$	isotherm parameters

Subscripts

0 initial value
S value at solid–liquid interface

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