MODEL VERIFICATION

The values of $\alpha\eta$ and $\alpha_p\beta$ were calculated separately for coarser and finer particles from monodimensional particle filtration experimental results and were used in a modification of O'Melia's model for filtration of bidimensional particle suspensions to calculate the improvement of removal efficiency of finer particles.

Although the experimental curves of the bidimensional particles in suspension could not be fitted exactly to the theoretical curves, the introduction of an additional factor, $\gamma(= 0.7)$ demonstrated the improvement of finer particle removal efficiency in the presence of coarser particles (Figure 7).

CONCLUSIONS AND PRACTICAL APPLICATIONS

Although this study was performed for a simple case of bidimensional particles in suspension, the experimental observations and the theoretical formulations could be extended to suspensions of particles in a wide range of sizes. The improvement in removal efficiency during the contact flocculation-filtration process can be explained qualitatively and modeled mathematically in the same approach.

NOTATION

d_c = diameter of filter grain
d_p (or d) = diameter of particle
f = porosity
l = depth
N = number of particle collectors
n = number concentration of suspended particles
n_1' = number concentration of finer particles in the presence of coarser particles
t = filtration time
V_o = filtration rate

Greek Letters

α = particle-to-filter grain attachment coefficient
α_p = particle-to-particle attachment coefficient
β = fraction of retained particles that act as particle collectors
γ = constant
η = contact efficiency of a filter grain
η_p = contact efficiency of a particle collector
η_r = removal efficiency of a single collector
η_{r1}^* = removal efficiency of finer particles in the presence of coarser particles when they are in combination in the suspension

Subscripts

1 = finer particles
2 = coarser particles

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Measuring Adsorption Rates from an Aqueous Solution

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Adsorption kinetics of organic solutes in the aqueous phase has been the subject of considerable attention in recent years. Generally, the purpose of such experiments is to determine pore diffusion coefficients for designing industrial equipment to be used in pollution control. Laboratory apparatus is usually a stirred constant-volume tank; and when determining pore diffusion coefficients from concentration-time data, it is necessary to consider the effects of external diffusion resistance as well as possible deviations from the concept of ideal mixing. Below we report briefly on results with three different designs of experimental apparatus.

The differential equations, the initial and the boundary conditions for the constant-volume adsorption rate problem, have been given by Komiyama and Smith (1974). Because the isotherms determined for the systems investigated below are nonlinear, a numerical solution was required. We prefer to go into details of our numerical solution in a later paper in connection with a larger volume of experimental results. This note is concerned primarily with the choice of proper equipment. The numerical procedure permitted a comparison of calculated and experimental adsorption uptake curves $\gamma(t)$.

$$\gamma(t) = \frac{c\,(t) - c_0}{c_\infty - c_0} \tag{1}$$

Diffusion coefficients were varied to obtain a minimum standard deviation between calculated and experimental uptakes.

$$\frac{\sum\limits_{1}^{n} (\gamma_{\text{exp}} - \gamma_{\text{cal}})^2}{n - 1} = \text{min!} \tag{2}$$

We have measured adsorption kinetics for an aqueous solution

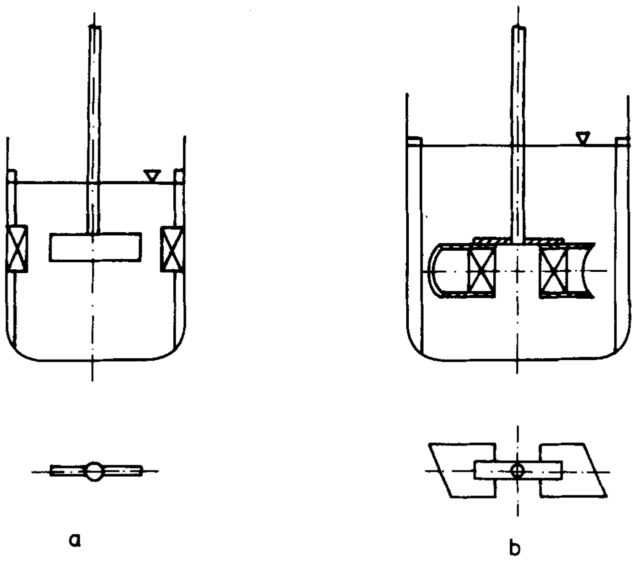

Figure 1. Adsorption vessels. (a) Design of Komiyama and Smith (1974). (b) Propeller mixer with adsorbent in blade tips.

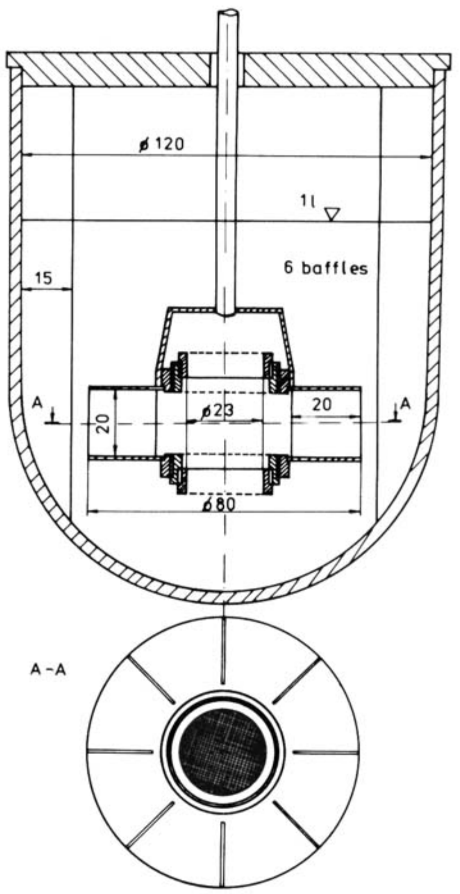

Figure 2. Adsorption tank with submerged centrifugal pump.

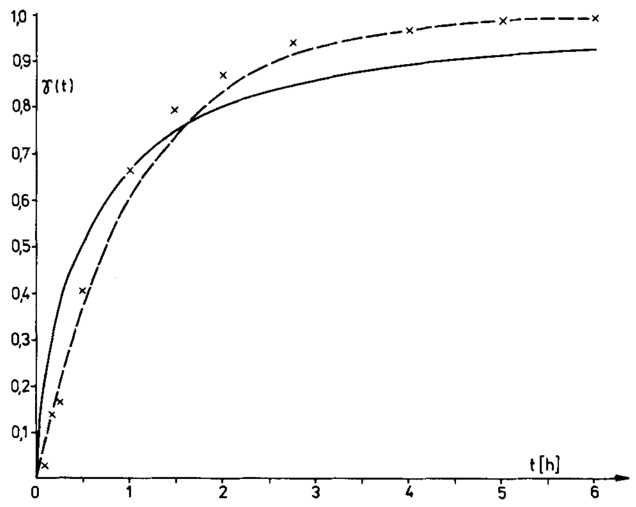

Figure 3. Kinetic evaluation of *p*NT-Y 29 data at 20°C in vessel (Figure 1a). c_o = 0.451, c_∞ = 0.0351, q_o = 0.108. —— nonlinear internal diffusion model; – – linear external diffusion model; x x experimental points.

of *p*-nitrotoluene on the polymeric adsorbent Y 29, a product comparable to XAD-4, supplied by the VEB Chemical Works at Bitterfeld-Wolfen, GDR, and for aqueous phenol solutions on Hydraffin 71, an activated carbon produced by the Lurgi Corporation, West Germany. Adsorption uptake in all cases was measured at 20°C. At the start of an experiment the adsorbent, loaded to q_0 at $c_{\infty,p}$ in the previous run, is lowered into a solution of higher concentration c_0, and liquid samples are withdrawn until equilibrium is established at q_∞, c_∞. Samples were analyzed with a UV spectrometer "Specord" manufactured by VEB Carl Zeiss, Jena, GDR. Sample withdrawal was more frequent in the initial phase of the experiment than toward the end to achieve a suitable distribution of measured concentrations. Sample size was 2 mL at higher concentrations and up to 5 mL at lower concentrations, with about one dozen samples being removed during a 24-hr period, but the system was treated as being at constant volume in evaluating results.

A commonly used equipment design was proposed in this journal several years ago by Komiyama and Smith (1974). Their adsorber is described in detail in Figure 1 of the paper cited, and shown *schematically in* Figure 1a of this paper. Baskets, which hold the adsorbent particles, are mounted circumferentially at the vessel wall; the impeller is intended to minimize external mass transfer resistance. We used this setup to measure uptake rates for *p*-nitrotoluene on Y 29. Radeke et al. (1983) have shown that the best-fit equilibrium isotherm for *p*-nitrotoluene/Y 29 is a Langmuir equation:

$$q_{\text{equ}} = 11.32\, c/(1 + 7.97\, c) \tag{3}$$

Typical uptake data are shown in Figure 3. The experimental points rise more slowly from the origin than the best-fit internal diffusion curve but require considerably less time to reach uptakes above 0.8. This is typical of rate control by external diffusional resistance. Indeed, the experimental points agree much better with a curve calculated according to the simple equation

$$\gamma(t) = 1 - \exp[-\, k_{f}a\, (1 + 1/\phi)\, t] \tag{4}$$

with

$$\phi = V_{fl}/V_s\, (\epsilon_p + K) \tag{5}$$

$$K = \rho(q_\infty - q_0)/(c_\infty - c_{\infty,p}) \tag{5a}$$

which is the solution of the external diffusion model using a linear equilibrium relation. (We saw no purpose in writing a nonlinear external diffusion computational program, which one would expect to give even better agreement with experimental data.) We thus confirm results recently published by Muraki et al. (1982), who investigated the adsorption uptake of several aqueous organic solutions in Figure 1a type of equipment and also found significant laminar boundary-layer resistance. It should be noted that the external mass transfer coefficients determined in such experiments are of little practical importance, since they are valid only for the particular equipment involved and may not be applied to column performance.

We designed a second type of equipment (Figure 1b). The baskets containing the adsorbent are inserted into the tips of the hollow propeller blades, and the aqueous solution is pumped through the baskets when the propeller is rotated. The half-life of

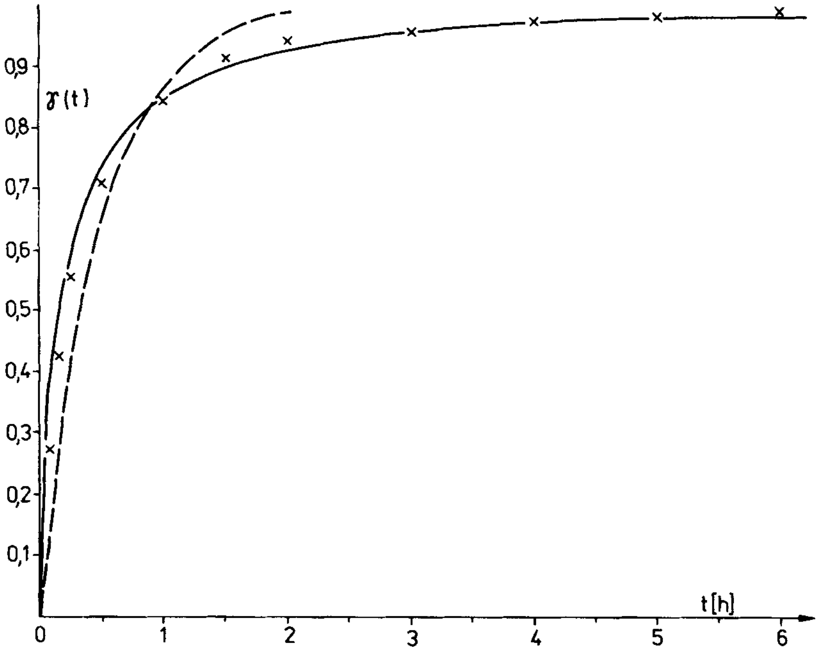

Figure 4. Kinetic evaluation of pNT-Y 29 data at 20°C in vessel (Figure 1b). $c_o = 0.356$, $c_\infty = 0.0340$, $q_o = 0.104$. —— nonlinear internal diffusion model; – – linear external diffusion model; x x experimental points.

the process being studied varied from system to system from 10 min to 2 hr. The rate of pumping was designed to displace the vessel volume, equal to 0.5 L, within 38 s at an impeller speed of 300 rpm, ensuring an adequate approximation of ideal mixing. Using the same system as above, the experimental uptake curve was measured, as shown in Figure 4.

Significantly better agreement is now found with the nonlinear internal diffusion model than with the external diffusion equation, particularly at uptakes above 0.8, although residual laminar boundary-layer effects may still be present in the steep initial portion of the curve. The standard deviation between measured values and those calculated with the nonlinear internal diffusion model has been reduced from 0.123 (Figure 3) to 0.052 (Figure 4). Thus, a change in the rate-limiting mechanism has been achieved by redesigning the experimental adsorber. The best-fit diffusion coefficient is $3.5 \cdot 10^{-13}$ ($m^2 \cdot s^{-1}$) based on a particle radius of 0.34 mm.

In preparing for uptake measurements on activated carbons, it was necessary to take into account the observations of previous investigators. Peel and Benedek (1980) have demonstrated that the adsorption uptake on activated carbons is characterized by a rapid initial phase followed by a prolonged slow adsorption period lasting up to 4 weeks. Many authors have supported this contention, for example, Famularo et al. (1980) and Van Vliet and Weber (1981). In the latter paper it is concluded that the prolonged adsorption equilibria attained after 8 days is not representative of breakthrough column capacity for carbons characterized by a bidisperse pore distribution. In this journal, Peel et al. (1981) proposed a branched pore kinetic model to account for two-stage adsorption in activated carbons. Thus, it seemed desirable to prolong uptake experiments over a period of 2 weeks, whereas 24 h was sufficient in the amberlite runs. Since a larger total sample volume would be withdrawn, a larger vessel volume was deemed advantageous and a submerged pump with a higher capacity than the one in the vessel in Figure 1b became necessary. We installed the equipment shown in Figure 2, which is similar to apparatus previously described by baskets by Voss (1975) and Ladendorf (1971). Here, the adsorbent baskets are inserted in the suction lines of a submerged centrifugal pump. The time required to displace one vessel volume is reduced to 5.4 s at 300 rpm, although the tank volume has been enlarged to 1 L. (At stirrer speeds above 500 rpm incipient vortex formation was observed despite the relatively large baffles.)

We investigated adsorption uptake with the aqueous phenol/Hydraffin 71 system in Figure 2 equipment. The adsorption equilibrium curve was best-fitted by a Redlich-Peterson isotherm:

$$q_{\text{equ}} = 524\, c/(1 + 329\, c^{0.78}) \qquad (6)$$

The nonlinear internal diffusion model with a constant diffusion coefficient of $1.5 \cdot 10^{-13}\ m^2 \cdot s^{-1}$ (for a particle radius of 0.75 mm) agrees well with measured uptakes below $\gamma = 0.7$ (Figure 5). At higher uptakes, despite some scatter, the experimental values drop below the calculated curve. This is the opposite of the behavior observed in Figure 3, where laminar boundary-layer resistance was dominating. Due to the excellent agreement at the start of the run, standard deviation for the 6 h shown is only 0.031, but increases steadily with time during a 2-week period, since experimental uptakes remain consistently below those calculated.

Our results appear to confirm the theory that after a rapid initial adsorption phase, the effective diffusion coefficient drops to a lower value in a second uptake stage. Clearly, if one is to make a quan-

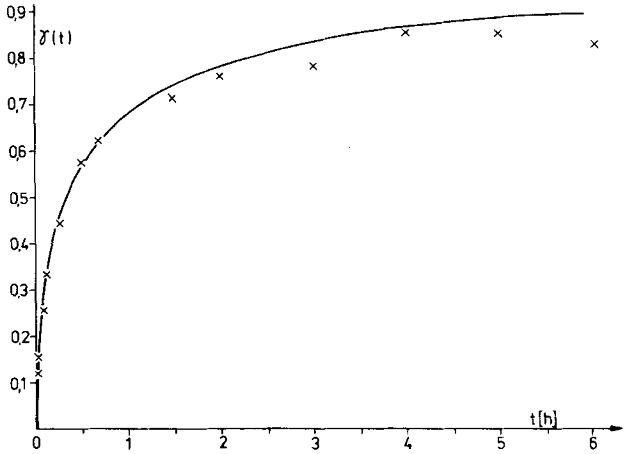

Figure 5. Kinetic evaluation of phenol-Hydraffin 71 data at 20°C in vessel (Figure 2). $c_o = 0.227$, $c_\infty = 0.0473$, $q_o = 0.754$. – – nonlinear internal diffusion model; x x experimental points.

titative study of subtle changes in the diffusion coefficient it is better to eliminate the effects of external mass transfer in improved experimental equipment than to account for external mass transfer in more complicated mathematical descriptions of adsorption uptake.

NOTATION

a = specific surface area for mass transfer, cm^2/cm^3
c = concentration of solute in aqueous soln., mmol/L
c_0 = concentration of solute in aqueous soln. at start of run, mmol/L
c_∞ = concentration of solute in aqueous soln. at end of run, mmol/L
$c_{\infty,p}$ = concentration of solute in aqueous soln. at end of previous run, mmol/L
K = adsorption equilibrium constant for linear isotherm
k_f = external mass transfer coefficient, cm/s
n = number of measurements
q_0 = concentration of adsorbed solute at start of run, mmol/g
q_∞ = concentration of adsorbed solute at end of run, mmol/g
q_{equ} = equilibrium concentration of adsorbed solute, mmol/g
t = time, s
V_{fl} = volume of particle-free liquid in adsorber, cm^3
V_s = total volume of wet particles in adsorber, cm^3

Greek Letters

γ = adsorption uptake, Eq. 1
ϵ_p = porosity of wet particles
ϕ = defined by Eq. 5
ρ = apparent adsorbent density, g/L

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The Hopping Model for Residence Time Distributions of Systems with Splitting and Merging Streams

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The residence time distribution for fluid flow through packed beds has been analyzed by considering a main path through which all the fluid flows and along which are distributed relatively stagnant zones into which some fluid elements enter and are delayed for some time (the delay time) in their passage through the system (Buffham et al., 1970; Buffham and Gibilaro, 1970). This notion leads to a family of simple models for the overall residence time distribution of flow material in terms of parameters that are