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Theory of Adsorption by Activated Carbon. IV. High-Speed Modeling of Continuous Flow Columns

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Abstract

An algorithm is developed for integrating the differential equations modeling the operation of a continuous flow activated carbon column. This algorithm is more than an order of magnitude faster in computation than the direct numerical integration of the differential equations, and appears to be just as accurate. Computer memory requirements are small. Results are presented showing the dependence of the breakthrough curves on the parameters of the Langmuir adsorption isotherm, flow rate, influent concentrations, mass transfer rate parameter, and other quantities appearing in the model. The theory is extended to the case of several solutes competing for adsorption sites.

INTRODUCTION

Activated carbon is widely used as a readily available, reasonably priced, regenerable adsorbent for trace organics in water (*1*). The carbon can be used in powdered form, later filtering it out, or it may be used in continuous flow packed or expanded columns. When breakthrough of solute becomes unacceptably high, the column is removed from service and the carbon regenerated thermally. This is somewhat expensive and always results in a loss of carbon, so it is desirable to operate the column in such a way as to obtain maximum saturation of the carbon with solutes before breakthrough exceeds the maximum permitted level. This, in turn, dictates a low hydraulic loading rate, which means large columns and correspondingly large capital expense.

In order to optimize the trade-offs in designing for any given situation, it is necessary to have a means of modeling the performance of such columns mathematically.

A number of such models have been used; these are reviewed in one of our earlier papers (*2*). Two books which have quite clear discussions of the modeling of such columns are by Keinath and Wanielista (*3*) and by Weber (*4*).

In these columns a number of processes are going on simultaneously. These include bulk flow of free liquid along the length of the column, axial dispersion of free liquid along the length of the column, diffusion of solute in the free liquid through the boundary layers surrounding the carbon particles to the mouths of the pores in the activated carbon, diffusion of solute into the intrapore liquid, and adsorption and desorption of solute on the adsorption sites within the pores. We showed earlier how a lumped parameter model could be used to approximate this process quite well, and noted the great computational burden of any more exact treatment (*2, 5*). We also used this lumped parameter approach to examine the effects of equalization tanks on time-dependent influent feed rates and concentrations (*6*).

A practical problem occurs in the numerical integration of the set of nonlinear differential equations which arise if one uses a reasonably realistic (and therefore nonlinear) adsorption isotherm for the carbon. The time constants associated with local diffusion and with the rate of equilibration of adsorption–desorption are relatively short, which dictates the use of relatively small values of the time increment Δt in the numerical integration of the system of equations. However, the duration of a run which saturates a carbon column to the point of breakthough may be many hours. This means very long computer runs. We noted this difficulty in an earlier paper and attempted to circumvent it, but the algorithm, while permitting use of a markedly increased Δt as compared to the direct approach, was sufficiently complex that no improvement in efficiency of computation resulted (*2*). Running time was not significantly decreased, and computer memory requirements were markedly larger.

Some recent work we have been doing on solvent sublation suggested a modification to the usual material balance approach used to construct mathematical models for activated carbon column operation. This permits us to use substantially larger values of Δt, and does not change the memory requirement significantly. There follows a derivation of the equations of the model, its extension to columns removing several solutes, and some representative results. We note that this approach should also be applicable to the modeling of ion exchange and macroreticular resin column operation.

ANALYSIS

We consider a packed column of height h and radius r, and partition it into N slabs of equal thickness $\triangle h$, as shown in Fig. 1. We focus our attention on a 1-cm^3 volume in the ith slab, which we allow to rise at the speed of the water rising in the column. This volume element contains $1 - \varepsilon$ cm^3 of carbon and ε cm^3 of mobile water, with a macroscopic interfacial area (neglecting pores) of S cm^3. We assume that

$$\varepsilon \frac{dc_i}{dt} = -Sk(c_i - c_i^{\mathrm{eq}}) \tag{1}$$

where c_i = solute concentration in the rising element of water, mol/cm^3

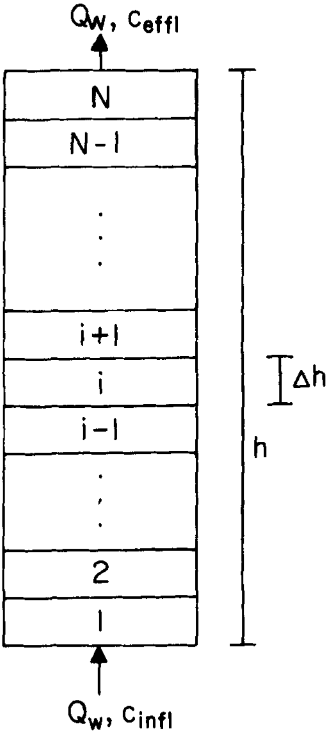

FIG. 1. The partitioning of the column.

k = mass transfer rate coefficient describing the movement of solute from the mobile water into the carbon, cm/s

c_i^{eq} = solute concentration in the water which would be in equilibrium with the carbon in this slab

We assume for definiteness a Langmuir isotherm for the adsorption of the solute on the carbon. (A Freundlich isotherm or any other would work just as well.)

$$\Gamma_i = \frac{\Gamma_{\mathrm{max}}}{1 + c_{1/2}/c_i^{\mathrm{eq}}} \tag{2}$$

where Γ_i = moles of solute adsorbed per $(1 - \varepsilon)$ cm^3 of carbon (bulk volume = 1 cm^3) when it is in equilibrium with solution having a solute concentration c_i^{eq}

and Γ_{max} and $c_{1/2}$ are Langmuir parameters characteristic of the solute, carbon, and temperature.

Rearranging Eq. (1) yields

$$\frac{dc_i}{dt} + \frac{Skc_i}{\varepsilon} = \frac{Skc_i^{\mathrm{eq}}}{\varepsilon} \tag{3}$$

If we assume that Γ_i changes by a negligible fraction as our element of water rises through slab i, c_i^{eq} can be treated as a constant over the time interval required for this element of water to traverse slab i. This permits integration of Eq. (3), yielding

$$c_i(t) = c(0)\exp\left(-\frac{Skt}{\varepsilon}\right) + c_i^{\mathrm{eq}}\left[1 - \exp\left(-\frac{Skt}{\varepsilon}\right)\right] \tag{4}$$

Now the time τ required for our element of liquid to move up across one slab is given by

$$\tau = A\,\Delta h\varepsilon/Q_w \tag{5}$$

where $A = \pi r^2$

Q_w = influent volumetric flow rate, cm^3/s

So the concentration of solute in the solution leaving slab i, c_i, is given by

$$c_i^l = c_{i-1}^l e^{-\alpha} + c_i^{\mathrm{eq}}[1 - e^{-\alpha}] \tag{6}$$

where

$$\alpha = SkA\triangle h/Q_w \tag{7}$$

The rate at which solute is being gained by the carbon in slab i is then given by

$$A\triangle h\frac{d\Gamma_i}{dt} = Q_w(c_{i-1} - c_i) \tag{8}$$

where we are neglecting the small amounts of solute accumulating in slab i as the solute concentration in the liquid phase in the slab gradually increases.

We solve Eq. (2) for c_i^{eq},

$$c_i^{\text{eq}} = \frac{\Gamma_i c_{1/2}}{\Gamma_{\text{max}} - \Gamma_i} \tag{9}$$

Substituting Eq. (9) into Eq. (7) then yields (we drop superscript l's)

$$c_i = c_{i-1}e^{-\alpha} + \frac{\Gamma_i c_{1/2}}{\Gamma_{\text{max}} - \Gamma_i}(1 - e^{-\alpha}) \tag{10}$$

and Eq. (8) becomes

$$\frac{d\Gamma_i}{dt} = \frac{Q_w}{A\triangle h}(c_{i-1} - c_i) \tag{11}$$

When $i = 1$, Eqs. (10) and (11) must be modified; the results are

$$c_1 = c_{\text{infl}}e^{-\alpha} + \frac{\Gamma_1 c_{1/2}}{\Gamma_{\text{max}} - \Gamma_1}(1 - e^{-\alpha}) \tag{12}$$

and

$$\frac{d\Gamma_1}{dt} = \frac{Q_w}{A\triangle h}(c_{\text{infl}} - c_1) \tag{13}$$

where c_{infl} is the influent solute concentration, moles/cm^3.

The system of Eqs. (10)–(13) can then be integrated forward in time by use of a number of algorithms; we used the same predictor-corrector which we used previously. Note that the time increment Δt is limited only by Eqs. (11) and (13); the much more severe constraint on Δt which would be imposed by Eq. (1) if it were included in the numerical integration scheme has been eliminated by integrating it separately and using the resulting algebraic Eqs. (10) and (12).

This approach can also be extended to deal with more than one solute. We outline the procedure for doing this, with a few changes in notation.

Let Γ_{ji} = concentration of the *j*th solute in the carbon, *i*th slab, moles/cm^3
c_{ji} = concentration of the *j*th solute in the liquid phase, *i*th slab, moles/cm^3

We assume that our adsorption isotherms are generalized Langmuir isotherms, given by Eq. (14).

$$\Gamma_j = \frac{K_j c_j}{1 + \sum_n^M b_n c_n}, \qquad j = 1, 2, \ldots, M \tag{14}$$

where K_j and the b_n are constants. Solution of this system of equations for the c's then yields

$$c_j^{\text{eq}} = \Gamma_j \Big/ \left[K_j\left(1 - \sum_n^M \frac{b_n \Gamma_n}{K_n}\right)\right], \qquad j = 1, 2, \ldots, M \tag{15}$$

Equations (15) were obtained by solving Eqs. (14) for the c_j's for the cases $M = 2$ and 3, guessing on the basis of these results that Eqs. (15) are the general solution to Eqs. (14) for arbitrary M, and verifying that substitution of Eqs. (15) into Eqs. (14) leads to an identity.

For the *j*th solute in the *i*th slab, the analog to Eq. (3) is

$$\frac{dc_{ji}}{dt} + \frac{Sk_j}{\varepsilon} c_{ji} = \frac{Sk_j}{\varepsilon} c_{ji}^{\text{eq}} \tag{16}$$

which has the solution

$$c_{ji}(t) = c_{ji}(0) \exp\left(-\frac{Sk_j t}{\varepsilon}\right) + c_{ji}^{\text{eq}}\left[1 - \exp\left(-\frac{Sk_j t}{\varepsilon}\right)\right] \tag{17}$$

Here k_j is the mass transfer rate coefficient of the jth solute. As before, we calculate the concentrations of the solutes leaving slab i; the reasoning is identical to that leading to Eq. (6).

$$c_{ji} - c_{ji-1} \exp(-\alpha_j) + c_{ji}^{eq}[1 - exp(-\alpha_j)] \qquad (18)$$

where

$$\alpha_j = Sk_jA\triangle h/Q_w \qquad (19)$$

and

$$c_{ji}^{eq} = \Gamma_{ji}/[K_j(1 - \sum_n^M b_n\Gamma_{ni}/k_n)] \qquad (20)$$

from Eq. (15).

We next determine the rate at which solute j is being gained by the carbon in slab i; it is given by

$$\frac{d\Gamma_{ji}}{dt} = \frac{Q_w}{A\triangle h}(c_{ji-1} - c_{ji}) \qquad (21)$$

If $i = 1$ in Eq. (18) or Eq. (20), c_{ji-1} is replaced by $c_{j\text{infl}}$. Equations (18) and (21) are then integrated forward in time with the help of Eqs. (19) and (20). Again we note that the short time constants associated with Eq. (16) have been eliminated from the numerical integration scheme by virtue of the use of Eq. (18), so that much larger values of $\triangle t$ can be used than would otherwise be possible.

It is possible to examine the effects of time-dependent influent flow rates and solute concentrations simply by making Q_w and c_{infl} the desired functions of time. Our analysis presumes that the changes in these quantities during the time interval $\tau = A\triangle h\varepsilon/Q_w$ are relatively small.

We have left axial dispersion out of this model because our previous work indicated that it was impossible to distinguish the effects of axial dispersion from the effects of the mass transfer rate coefficient k (*2*). Rather than have to deal with this ambiguity, we decided to drop the axial dispersion terms and thereby have one less adjustable parameter to assign.

RESULTS

A FORTRAN program was written to carry out the solution of Eqs. (10)–(13). A typical run of the sort plotted below required about 28 s of DEC

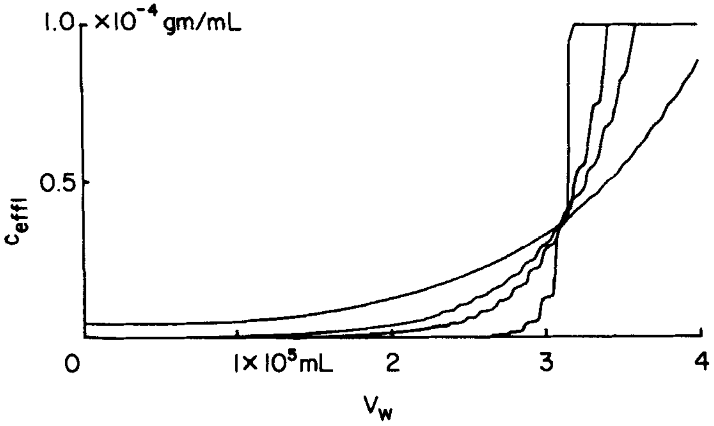

FIG. 2. Breakthrough curve dependence on k, the mass transfer rate parameter, for $N = 30$. In this and the following figures the effluent concentration, c_{effl}, is plotted as a function of the volume of water which has passed through the column, V_w. Here $h = 100$, $r = 1$ cm; $Q_w = 10$ mL/s; $S = 10$ cm^{-1}; $k = 0.01$, 0.02, 0.03, 0.10 cm/s; $\Gamma_{max} = 0.1$ g/cm^3; $c_{1/2} = 10^{-6}$, $c_{infl} = 10^{-4}$ g/cm^3; $\Delta t = 10$ s; $\varepsilon = .25$.

1099 time. This compares quite favorably with the 5 min per run required by our earlier algorithm (*2*).

Figures 2 and 3 show the effect of varying the mass transfer coefficient k on the shapes of the breakthrough curves. We see the expected broadening of the breakthrough and deterioration in column performance as the mass transfer rate coefficient is decreased. In these runs $c_{1/2}$ is very much less than

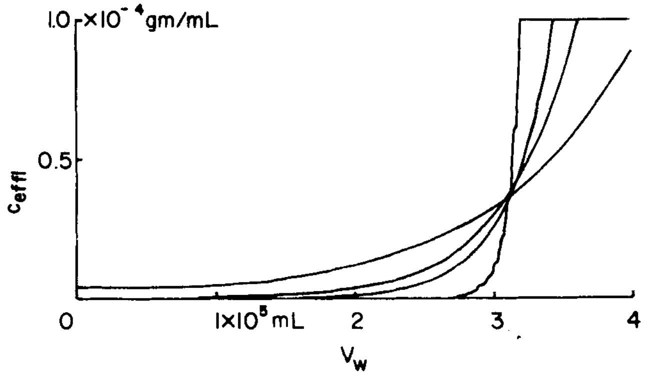

FIG. 3. Breakthrough curve dependence on k for $N = 60$. Here $k = 0.01, 0.02, 0.03, 0.10$ cm/s; other parameters (except N) as in Fig. 2.

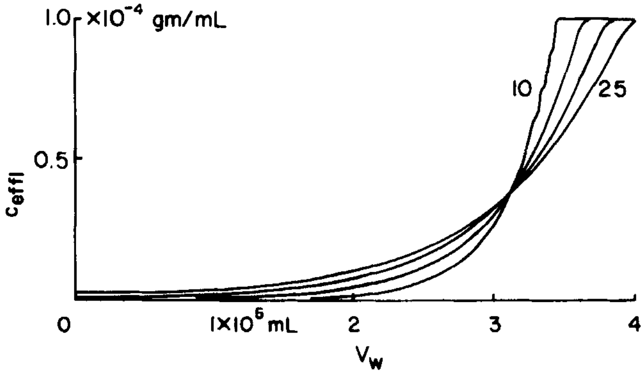

FIG. 4. Breakthrough curve dependence on influent flow rate. $N = 60$; $k = 0.03$ cm/s; $Q_w = 10, 15, 20, 25$ mL/s; other parameters as in Fig. 2.

c_{infl} (10^{-6} mol/mL as compared to 10^{-4} mol/mL), which, if k is fairly large, causes each slab to become essentially completely saturated before the next slab in the column begins to accumulate solute. This imposes a somewhat stairstep-like response on the breakthrough curves, as seen particularly clearly in Fig. 2. The width of the steps is decreased and the curves smoothed out by increasing the number of slabs into which the column is partitioned, as is seen by comparing the plots in Fig. 2 (30 slabs) with those of Fig. 3 (60 slabs). These oscillations, mathematical artifacts caused by the approximation of a partial differential equation by a finite set of ordinary differential equations, should be ignored.

The effect of increasing the flow rate of the influent on the appearance of

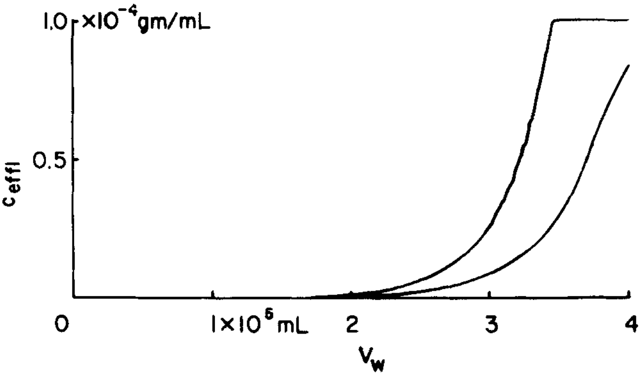

FIG. 5. Breakthrough curve dependence on Δt. $N = 60$, $k = .03$ cm/s; $\Delta t = 10, 20, 30$ (left curve), and 40 sec (right curve). Other parameters as in Fig. 2.

the breakthrough curves is shown in Fig. 4. It is essentially the same as the effect of decreasing k—we see the expected deterioration of column performance as the initial removal efficiency decreases and the breadth of the breakthrough region increases with increasing influent flow rate.

We were particularly interested in the extent to which we could increase Δt (thereby reducing the computer time required for a run) without decreasing the accuracy of the computations. Some representative results are shown in Fig. 5. The plots for $\Delta t = 10, 20$, and 30 s are superimposed, but the plot with $\Delta t = 40$ s is markedly different. The runs shown in the other figures were all made with $\Delta t = 10$ s. We used a value of Δt of 0.1 s in most of the work with our other algorithm (*2*).

The runs plotted in Fig. 6 explore the effects of increasing the value of the Langmuir parameter $c_{1/2}$, the solution concentration of which is in equilibrium with a concentration of adsorbed solute of $\frac{1}{2}\Gamma_{\max}$. Increasing $c_{1/2}$ corresponds to weakening the strength of the binding between the solute molecules and the adsorption sites on the carbon. Increasing $c_{1/2}$ causes a decrease in the volume of solution which can be treated before breakthrough occurs in two ways: (a) the curves are shifted to the left and (b) the transition region is broadened. We also note that the stairstep irregularities which are barely noticeable in the curve for which $c_{1/2} = 10^{-6}$ completely disappear at larger values of $c_{1/2}$. In addition, the very sharp break in the curve for $c_{1/2} = 10^{-6}$ which occurs when the column becomes saturated becomes more and more gradual with increasing $c_{1/2}$.

The effect of increasing the capacity parameter of the activated carbon, $\Gamma_{\max}$, is shown in Fig. 7. This merely results in a shift in the position of the breakthrough to the right, proportional to the increase in $\Gamma_{\max}$, which is what

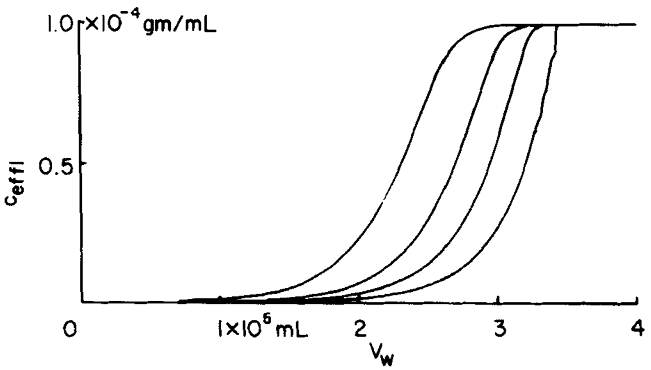

FIG. 6. Breakthrough curve dependence on the Langmuir parameter $c_{1/2}$. $N = 60$; $k = 0.03$ cm/s; $c_{1/2} = 10^{-6}$, 10^{-5}, 2×10^{-5}, and 4×10^{-5} g/cm^3, from right to left. Other parameters as in Fig. 2.

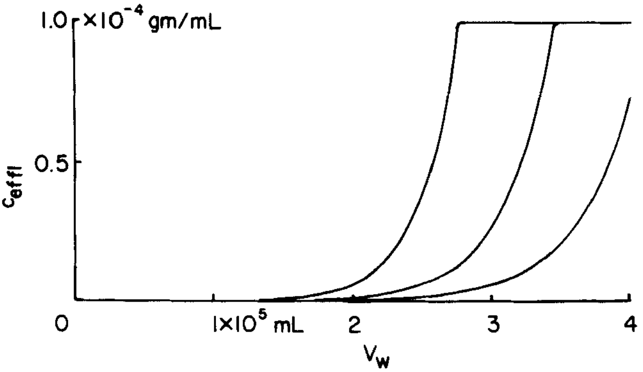

FIG. 7. Breakthrough curve dependence on the Langmuir parameter $\Gamma_{\max}$. $N = 60$; $k = 0.03$ cm/s; $\Gamma_{\max} = 0.12$, 0.10, 0.08 g/cm^3 (from right to left). Other parameters as in Fig. 2.

one would expect. The effects of increasing c_{infl} are shown in Fig. 8. As one anticipates, the volume of effluent at which breakthrough occurs (c_{effl} equal to some specified small fraction of c_{infl}) is inversely proportional to c_{infl}, and the final plateau concentration reached is of course equal to c_{infl}, whatever it may be.

We conclude that the algorithm used here to solve the equations modeling the operation of a continuous flow activated carbon column is more than an order of magnitude faster than those based upon the usual continuity and mass transfer relationships. Computer memory requirements for both

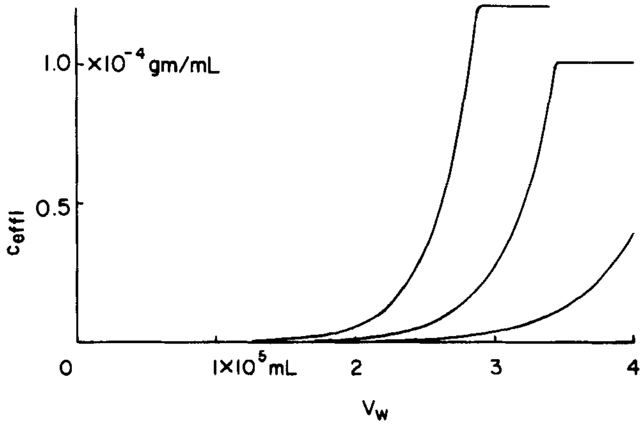

FIG. 8. Breakthrough curve dependence on influent solute concentration. $N = 60$; $k = 0.03$ cm/s; $c_{\text{infl}} = 0.8$, 1.0, and 1.2×10^{-4} g/cm^3 (from right to left). Other parameters as in Fig. 2.

algorithms are relatively small. This new algorithm yields results which are qualitatively in agreement with the dictates of physical intuition, and which are quantitatively in excellent agreement with the results of the slower algorithm. This approach can also be used for solutions containing several solutes which compete for adsorption sites on the carbon. The method, originally developed for solvent sublation modeling, should be very easily adapted to ion exchange and macroreticular resin columns.

Acknowledgment

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