Simulated Binary Isothermal Adsorption on Activated Carbon in Periodic Countercurrent Column Operation

ROLAND KLAUS
RICHARD C. AIKEN
and
DAVID W. T. RIPPIN

Technisch-Chemisches Laboratorium
E.T.H.-Zentrum
8092 Zurich
Switzerland

Simulation studies are presented of single- and two-component adsorption in periodic, countercurrent, multicolumn systems. It is demonstrated that long adsorption profiles are likely to occur in the adsorption of organic contaminants from wastewater onto activated carbon, thus favoring the use of multicolumn rather than single-column systems. For two-component adsorption in a multicolumn system, it is shown that more switching periods are needed than in the single-column case before the profiles stabilize, that the stabilized profiles can differ substantially from those found in a single-column system, and that their shape is strongly influenced by the relative concentrations of the components in the feed.

SCOPE

The adsorption of contaminants from fluid streams onto activated carbon is becoming an increasingly important separation method. The use of a single column often gives relatively poor carbon utilization so that, in practice, two or more columns are normally used in series.

Although many studies have appeared in the literature on the modeling and simulation of single-column operation, very little has been reported on periodic countercurrent systems. Continuous countercurrent systems have been modeled for film and film plus pore resistance with linear and irreversible isotherms (Kasten and Amundson, 1952; Neretnieks, 1974*a*, *b*, and *c*). Svedberg (1976) reports results for the simulation of periodic countercurrent operation with film plus pore diffusion and a linear isotherm.

When more than one component is adsorbed, the shape of the concentration profiles in the adsorber will change radically, giving peaks and plateaus which result from interactions between the adsorbed solutes and cannot be modeled by the assumption of linear or irreversible isotherms.

The purpose of the work described here was to simulate multicomponent adsorption on activated carbon in multicolumn periodic operation, since this is the case most commonly found in practice.

CONCLUSIONS AND SIGNIFICANCE

It is demonstrated from approximate calculations that for conditions similar to those commonly found in practice, the adsorption profile is so long that the use of a single-column system is likely to be uneconomic. Multicolumn periodic operation is, thus, the natural choice for carbon adsorption systems.

Results for single-component adsorption with film and pore diffusion in a two-column system show that for the conditions examined, the concentration profiles in a two-column system stabilize rapidly. There is little change in profile shape after the first switch, although there are indications that at lower feed concentrations, the transient phase would be longer.

For the two-component system that is simulated with film resistance, the concentration profiles take much longer to stabilize and can change profoundly with changes in the relative concentration of the components in the feed. The simulations show that as a result of the displacement phenomenon occurring in a multicomponent adsorption, the relative concentrations of components in the two columns can differ widely from the concentration in the feed.

As specifications on the content of processing and processed fluid streams become more stringent, more advanced treatment methods must emerge. Adsorption of impurities onto activated carbon has proved to be a viable step in the treatment of potable and domestic wastewaters; its application in the preparation of industrial processing and effluent waters has also shown great promise, although success depends strongly on the particular local requirements (Lawson and Fisher, 1973).

Correspondence concerning this paper should be addressed to David W. T. Rippin. Richard C. Aiken is at the University of Utah, Salt Lake City, Utah 84112.

Impurities are adsorbed from the fluid stream passing through a carbon bed in an unsteady state process which continues until the desired level of impurities in the emerging fluid stream can no longer be maintained. Some or all of the carbon must then be regenerated. This regeneration is normally carried out by high temperature treatment which is expensive both in terms of the fuel costs required for heating and the loss of carbon incurred. It is therefore important to ensure that the carbon is utilized as efficiently as possible before regeneration.

The effect on process performance of alternative contacting systems and operating conditions could be studied by suitable modeling of the adsorption process. Although complete representation is precluded by the complexity of the mixtures which must generally be treated, simplified models, most often for one component adsorbed onto carbon particles in a single fixed bed, have qualitatively elucidated certain aspects of performance. Major difficulties in deriving a more complete theoretical description are the identification of and necessary data acquisition for the many pertinent components and their incorporation in a realistic model that can be solved.

More can be done, however, in modeling alternative contacting systems used for carbon adsorption in industry and in demonstrating the new features which arise from consideration of the simultaneous adsorption of more than one component in such systems. In this paper, numerical studies are presented to illustrate aspects of one- and two-component adsorption in a sequence of fixed beds which, at discrete intervals, are moved countercurrent to the fluid flow (periodic countercurrent adsorption).

PERIODIC COUNTERCURRENT ADSORPTION

The *periodic* countercurrent arrangement has long been used in industry as a series of discrete bed stages, and the use of a single pulsed bed has also been described (Perry and Chilton, 1973; Winkler and Kaempf, 1972). In these applications, a spent section of carbon is removed from the end where the fluid enters and replaced by fresh carbon at the other end. For the pulsed bed, typical discharges at each replacement of carbon are 5 to 10% of the carbon, while serial beds each commonly contain 25 to 50% of the total amount of carbon (that is, two to four beds). The limit of an infinite number of infinitesimal pulses or, equivalently, an infinite number of infinitesimal beds in series is the continuous countercurrent mode.

Although there may be serious difficulties in implementing the continuous countercurrent adsorber (Westermark, 1975), it nevertheless provides a convenient theoretical upper limit to the attainable separation. Analytical solutions are available for single-component adsorption for a linear isotherm with film resistance (Kasten and Amundson, 1952) and with film plus pore resistance (Neretnieks, 1974*a*) and for an irreversible isotherm with film plus pore resistance (Neretnieks, 1974*b*). Neretnieks (1974*c*) also compares the performance of the continuous countercurrent operation with single-column periodic operation for linear and irreversible isotherms with film plus pore resistance.

There are very few reports in the literature of the theoretical examination of the serial bed arrangement. Svedberg (1976) compares it numerically with continuous countercurrent operation for linear isotherms with film plus pore diffusion. His formulation also includes axial dispersion, but results are presented only for cases for which the latter is negligible. The ideal performance is quite closely approached with only one or a few divisions of the bed. Fornwalt and Hutchins (1966) and Erskine and Schuliger (1971) suggest a simplified graphical procedure to assess the effectiveness of multiple beds; Chen et al. (1972) used a tanks-in-series model with linear mass transfer driving force.

ADSORPTION EQUATIONS

The mathematical model is the standard one for isothermal adsorption onto spherical carbon particles with film and pore resistances (see, for example, Lee and Weber, 1969). It is assumed that, to a first approximation, longitudinal diffusion in the fluid phase can be neglected so that for plug flow in the external voids

$$v\frac{\partial c}{\partial x} + \epsilon\frac{\partial c}{\partial t} + \frac{\partial w}{\partial t} = 0 \qquad (1)$$

The driving force for transport from the bulk fluid to the particle surface is given by the concentration difference across the (assumed) fluid film surrounding each particle so that the rate of transfer to the particle surface is

$$\frac{\partial w}{\partial t} = kA\,(c - c^*) = \frac{AD_f}{\delta}\,(c - c^*) \qquad (2)$$

where c^* is the value of c_p, the fluid concentration in the particle, at the particle surface $r = r_o$.

The driving force for transport from the surface into the particle is given by the concentration gradient in the particle at the surface, so that the rate of transport is

$$\frac{\partial w}{\partial t} = (\beta\cdot A)\,D_p\frac{\partial c_p}{\partial r}\bigg|_{r=r_o} \qquad (3)$$

Since there is no accumulation at the surface from (2) and (3)

$$\frac{\partial c_p}{\partial r}\bigg|_{r=r_o} = \frac{D_f}{\delta\beta D_p}\,(c - c^*) \qquad (4)$$

This couples (1) to the equation describing diffusion within the particle:

$$\frac{\partial c_p}{\partial t} = D_p\left(\frac{\partial^2 c_p}{\partial r^2} + \frac{2}{r}\frac{\partial c_p}{\partial r}\right) - \left\{\frac{1}{(1-\epsilon)\beta}\right\}\frac{\partial w_p}{\partial t} \qquad (5)$$

It is assumed that equilibrium between fluid and solid within a pore is established instantaneously so that the solid concentration is a function only of the local liquid concentration:

$$\frac{\partial w_p}{\partial t} = \left(\frac{dw_p}{dc_p}\right)\left(\frac{\partial c_p}{\partial t}\right)$$

Thus (5) becomes

$$\frac{\partial c_p}{\partial t} = \frac{D_p}{\left\{1 + \dfrac{1}{(1-\epsilon)\beta}\left(\dfrac{dw_p}{dc_p}\right)\right\}}\left(\frac{\partial^2 c_p}{\partial r^2} + \frac{2}{r}\frac{\partial c_p}{\partial r}\right) \qquad (6)$$

(dw_p/dc_p) is the local slope of the isotherm. The initial conditions must be specified on c and w as functions of x and on c_p and w_p as functions of r and x along with the boundary condition on c at the bed entrance as a function of time.

For single-component adsorption, when the only resistance to mass transfer considered is that of the external fluid film, only Equations (1) and (2) have to be solved. If the fluid concentration at the particle surface c^* is assumed to be in equilibrium with the adsorbed substance when the latter is uniformly adsorbed on the particle, then c^* can be obtained from the isotherm relationship.

For multicomponent adsorption, considering only the film resistance to mass transfer, equations identical to (1) and (2) have to be solved for each component, and c^* for each component can be a function of all c^*, c, and w. Therefore, the whole set of equations has to be solved simultaneously.

In the special case of binary adsorption, using the modified Langmuir isotherm (see Table 3)

$$c_1^* = \frac{1}{b_1} \cdot \frac{w_1}{\left[\overline{w}_1 - \left(\frac{\overline{w}_1}{\overline{w}_2}\right) w_2 - w_1\right]}$$

$$c_2^* = \frac{1}{b_2} \cdot \frac{w_2}{\left[\overline{w}_2 - \left(\frac{\overline{w}_2}{\overline{w}_1}\right) w_1 - w_2\right]} \tag{7}$$

Therefore

$$c_i^* = f_i(w_1, w_2) \qquad i = 1, 2$$

Thus the liquid concentrations at the surface can, in this case, be expressed independently of one another as explicit functions of the average solid concentrations.

NUMERICAL SOLUTION

The above model for one-component adsorption in a single fixed-bed with film and pore resistance was solved numerically by the method of characteristics on the hyperbolic external void equations combined with an explicit central finite-difference formulation on the parabolic particle equations. A considerable amount of testing of the resulting program on a CDC-6500 computer enabled empirical criteria to be found for acceptable step size choice in t, x, and r (Klaus, 1974). Further, it was found that iteration on the local assumed value of (dw_p/dc_p) was not required, so that (6) becomes linear in c_p. For these reasons, the explicit formulation did not require excessive computation.

A check on the accuracy of the numerical procedure for integrating the particle equations was made by calculating the change with time in the concentration at the particle surface when it is exposed to a step change in external concentration in an infinite bath. The results were compared with those of an independent calculation using a collocation method (Liapis and Rippin, 1976). Step sizes chosen by the empirical criteria referred to above produced results agreeing closely with those of the collocation method, except at very short times. The step change in external concentration is likely to produce the sharpest gradients and hence the most severe test of the integration procedure, corresponding to the conditions near the fluid inlet at the start-up of a column of clean adsorbent.

The model used for the simulation of the simultaneous adsorption of two components considers film resistance only and was solved numerically by the method of characteristics using a modified Euler method for integration along the characteristics. The same method was also used for the single-component model when film resistance only was considered.

The numerical procedure for the single-column case can easily be adapted to the multicolumn problem. After a column switch, the initial conditions must be adjusted for the start of the new operating period. That part of the profile is deleted which corresponds to the saturated column that has been removed. The profile of the remaining columns is shifted, and the profile corresponding to the newly regenerated column is added at the other end. In our examples it is assumed that all adsorbed material is removed during regeneration, but, if desired, any profile could be specified in the regenerated column.

PROFILE LENGTH

With a long adsorption profile, breakthrough occurs when much of the bed is unsaturated and carbon utilization is poor. If a single column is used, the volume of carbon required and the frequency of replacement can then make the overall process uneconomic. In such circumstances, a multicolumn system may significantly increase the efficiency of carbon utilization (Fornwalt and Hutchins, 1966).

Long profiles can result from the equilibrium or rate characteristics as well as from operating parameters. For a single component with a linear or unfavorable isotherm in a single column, the profile will lengthen indefinitely until breakthrough; as the isotherm becomes more favorable, this effect becomes less important and the profile length will approach that given by the constant pattern assumption. However, the constant pattern profile may itself be long when the rate of adsorption is small in relation to the throughput rate as, for example, with small film or pore mass transfer csoefficients. This means that for a given fluid composition, the profile lengthens as the particle size and flow rate increase. In multicomponent adsorption, the component profiles will continue to separate from one another with increasing distance; thus no overall constant pattern will be attained, although the concentration fronts for the individual components may approach constant pattern profiles.

For a single component with a favorable isotherm, the bed length required to reach the constant pattern profile may also be significant so that the sharpened constant pattern may not be attained before the end of the bed.

For the case of a fully established constant pattern, analytical expressions are available for the concentration profile with external film diffusion and both Langmuir and Freundlich isotherms. These results have been supplemented by graphs showing the additional effects of various types of particle diffusion in terms of a dimensionless variable (NT) (Fleck, Kirwan and Hall, 1973). The length of the profile L_p between specified concentration limits can be deduced from the value of (NT) by the expression

$$L_p = \frac{(NT)v}{kA} \tag{8}$$

The effect of pore diffusion within the particle either alone or in series with the external fluid film resistance can be approximated by using an expression for an equivalent fluid film resistance analogous to that given by Glückauf (1955):

$$k_pA = \frac{15\, D_p \cdot (1 - \epsilon)}{r_o^2} \tag{9}$$

The term $(1 - \epsilon)$ arises because the solid concentration is defined relative to the column rather than the particle volume. For a Langmuir isotherm, the dimensionless distance (NT) between the dimensionless fluid phase concentrations $\phi_1 = c^1/c_0$ and $\phi_2 = c^2/c_0$ is given by

$$(NT) = \frac{R \ln \dfrac{1 - \phi_1}{1 - \phi_2} - \ln \dfrac{\phi_1}{\phi_2}}{1 - R} \tag{10}$$

where the Langmuir isotherm $w = w_0bc/(1 + bc)$ is characterized by the parameter $R = 1/(1 + bc_0)$ (Michaels, 1952). Results for mixed resistance diffusion kinetics are given by Fleck, Kirwan, and Hall (1973).

For the examples discussed later with the data given in Tables 1 and 3, approximate estimates may be made of the length of the constant pattern profile for single-component adsorption between the dimensionless concentrations $\phi_1 = 0.05$ and $\phi_2 = 0.95$:

Phenol (Langmuir isotherm, film resistance only, feed concentration 0.01 mole/m^3, $r_o = 4.10^{-3}$m)	2.4 m
Phenol (Langmuir isotherm, film resistance only, feed concentration 0.001 mole/m^3, $r_o = 4.10^{-3}$m)	16.19 m
Dodecyl benzene sulfonate (DBS) (Langmuir isotherm, film resistance only, feed concentration 0.01 mole/m^3, $r_o = 4.10^{-3}$)	1.5 m
Acetic acid (Freundlich isotherm, film and pore resistance, feed concentration 1 mole/m^3, $r_o = 1.24 \cdot 10^{-3}$m	0.63 m

Estimates of the bed length required to attain the constant pattern profile for single-component adsorption with a Langmuir isotherm may be made from the results of Garg and Ruthven (1975). These show that for single-component adsorption of DBS with a feed concentration of 0.01 mole/m^3, the profile is fully developed in a bed length of approximately 1 m. Development of the profile for phenol with the same feed concentration requires approximately 5 m, but with a lower concentration of 0.001 mole/m^3 more than 20 m will be required. Thus, from these results the length of bed required to develop the stable form of the constant pattern profile for single-component adsorption will be of the same order of magnitude as the length of the fully developed constant pattern profile itself.

The length of a profile also depends on definition. The profile length at breakthrough may be increased several times by increasing separation requirements an order of magnitude.

From Equation (10), if $\phi_1 = 1 - \phi_2$ then

$$(NT) = \frac{1+R}{1-R} \ln \frac{\phi_2}{\phi_1}$$

Thus, with a Langmuir isotherm, the relative lengths of the fully developed, single-component constant pattern profiles for $\phi_1 = 0.05$ ($\phi_2 = 0.95$), $\phi_1 = 0.01$, and $\phi_1 = 0.0001$ will be 1:1.6:3. The effective profile length thus increases with increasingly high removal specifications, as for example on expected carcinogens in potable water.

The quantitative estimates made above indicate that for normal operating conditions the concentration profile can be one or several meters in length. High utilization of carbon will only be achieved either by using a single column which is long relative to the length of the concentration profile or by using a series of columns of which only the most highly saturated is removed. The first alternative is hardly practical, particularly when one considers the further lengthening effects on the profile arising from more stringent specifications for the removal of impurities, and the consideration of pore diffusion and multicomponent effects. Thus, the system of periodic countercurrent columns will be the natural choice for the removal of impurities from wastewater by treatment with activated carbon.

BED SWITCHING CRITERIA AND PROFILE STABILIZATION

When several beds are to be used in series to treat a fluid producing a long profile, then the criterion must be developed for when to remove the spent bed at the upstream fluid end and to introduce a fresh bed at the other end. For a single component, the obvious criterion is to switch as soon as the exit concentration is no longer acceptable, either as an instantaneous value or on a time averaged basis. If input flows and compositions are relatively steady, the instrumentation required for exit concentration measurement may be dispensed with and the beds switched at regular intervals determined from experience. When the time for a switch is near, the effluent may be monitored for premature breakthrough. A safety time factor is commonly incorporated to make this unlikely. Regular exit concentration monitoring is necessary when irregular fluctuations occur, and, if the analysis is time consuming, the fluid leaving the penultimate bed may be monitored, the last bed then providing a reserve capacity to ensure that unacceptable material is not released.

Klaus (1974) has shown that for the limiting case of a linear isotherm and for a linear driving force, a specified maximum instantaneous output concentration requires approximately the same time between switches after the first switch. A stable shape for the fluid concentration profile at the switching time is also quickly established. This profile stabilization after a few cycles has also been found by Svedberg (1976) for a linear isotherm. The reason for the stabilization of an inherently unstable profile is that the switch eliminates the tails of the profile, both front and rear. If the switching criterion is based on instantaneous outlet concentration, then, just before switching, the fluid concentration profile over the total length of the adsorbent varies between the feed concentration and the outlet concentration specified for switching. The profile shape will stabilize between these fixed concentration limits. It will will be demonstrated that for single-component adsorption with a favorable isotherm, the profile also stabilizes at the first switch, but this is not the case for multicomponent adsorption.

SINGLE-COMPONENT ADSORPTION

The above model for adsorption with film and pore resistance was solved numerically for the adsorption of acetic acid onto activated carbon using data of Heil (1971), as summarized in Table 1. The film mass transfer coefficients are based on the correlation of Wilke and Hougen (1945) with the modification given in Perry and Chilton (1973). The resulting fluid and solid adsorption concentration profiles are shown in Figures 1 and 2 for film resistance only and for film plus pore resistance. Also given is a profile for which the effect of pore resistance is approximately represented by an equivalent fluid film resistance in series with the external fluid film resistance.

In the two-column system, when the concentration in the effluent fluid reaches the limit of acceptability, column switching takes place. The upstream column which is the more highly saturated is removed. The downstream column is moved up or switched to take its place, and a column of freshly regenerated carbon is added to become the new downstream column. After the first switch, the new upstream column will already be partly saturated; thus the time to the second switch will be less than the time from start-up to the first switch, since in the latter case both columns initially contained fresh carbon. In a single-column system the whole of the carbon would be replaced when the exit fluid concentration reached the limit of acceptability.

For all three models considered in the example of Table 1, the concentration profile just prior to the first switch, which also corresponds to single-column operation, is essentially identical with that found just prior to the second and subsequent switches. Thus one would expect the time interval between successive switches after the first to be constant Table 2 confirms that this is the case. The time to the first switch would, of course, be equal to the period of the operating cycle of a single-column system. For the two-column system, the unused carbon capacity in the column

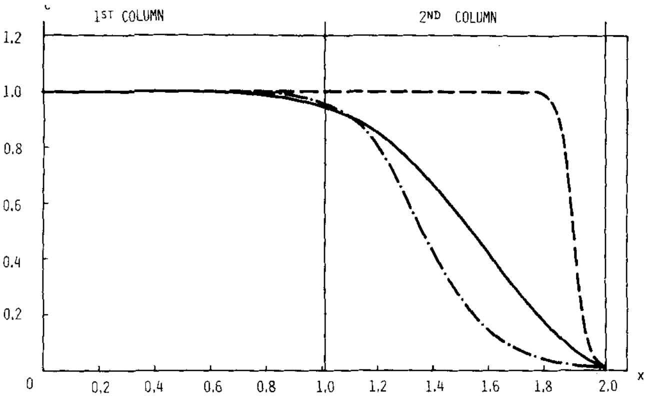

Fig. 1. Fluid concentration profiles of acetic acid for operating conditions of Table 1
——— film and pore resistance in series
—·—·— film and equivalent pore resistance in series
- - - - - film resistance only
profiles at switching times

Table 1. Data Used for Acetic Acid Adsorption Simulations

Carbon	Type	Hydraffin B 10
	d_p	1.24×10^{-3} m
	ρ	0.53×10^{3} kg/m^3
	β	0.79
Isotherm for acetic acid		$w = 72.345\, c^{0.4}$ mole/m^3 (bed)
Diffusion coefficients	D_f	0.92×10^{-9} m^2/s
	D_p	0.9×10^{-9} m^2/s
Column	ϵ	0.5
	v	2.2×10^{-3} m/s
column length 1.01 m		2 columns in series
	A	2.419×10^{3} m^2/m^3
input concentration acetic acid		1.0 mole/m^3
Film mass transfer coefficient giving kA values		
for film resistance only		0.0712 s^{-1}
for equivalent resistance with film and pore diffusional resistance in series		0.0139 s^{-1}

Table 2. Switching Times for Acetic Acid Adsorption

	Hours elapsed between switches		
Switch number	Film pore	Film	Film pore lumped
1	14.1	17.3	12.5
2	9.5	9.4	9.4
3	9.5	9.4	9.3
4	9.5	9.3	9.3
5		9.4	9.4
6		9.4	9.3

removed is less than 0.3%, whereas with the single-column system, if we assume film plus pore resistance, about 25% of the carbon capacity is unused.

In the two-column system the times between successive switches for the different models is almost the same. This is because the carbon capacity of the column removed is almost completely saturated for all the models considered.

For the calculation with film resistance alone and with the addition of pore resistance lumped as an equivalent film satisfactory results were obtained with a length increment of 0.025 m and a time increment of 360 s. The increments correspond for the case of film resistance alone to a dimensionless distance increment $kA\,\Delta x/v = 0.81$ and a dimensionless time increment $kAc_0\Delta t/w_\infty = 0.35$. The central processor time required on a CDC-6500 was approximately 25 to 40 s/switching interval computed. For the full pore diffusion model it was found necessary to use ten increments across the adsorbent particle and a time increment ten times smaller than in the film resistance calculation. Computing time required per switch was ten to fifteen times greater than in the film resistance case.

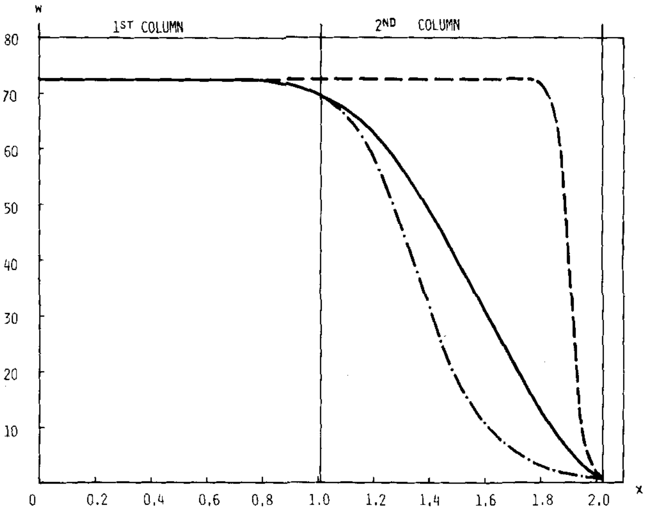

Fig. 2. Solid concentration profiles of acetic acid for operating conditions of Table 1
——— film and pore resistance in series
—·—·— film and equivalent pore resistance in series
- - - - - film resistance only
profiles at switching times

TWO-COMPONENT ADSORPTION

One of the first difficulties encountered in attempting to simulate multicomponent adsorption is acquiring realistic data on the components. For example, very few experimental multicomponent isotherms are available in the literature. The extension of the Langmuir form to multisolutes has been used for some time in theoretical studies (Wilson, 1940) and is used here with the parameters as obtained experimentally by Weber and Morris (1964) for dodecyl benzene sulfonate (DBS) and phenol. These components, originating from detergents, commonly occur in municipal wastewater. Their binary isotherms as constructed from single-component data agree very well with experiment on the two components together. Details on the carbon used were not given, however, so that a number of assumptions were made, as listed in Table 3, which also gives the isotherms and other component and operating data used in the simulations. The diffusion coefficients were each estimated by the structural group method of Wilke and Chang (1955) for dilute solutions; the film mass transfer coefficients are based on the correlation of Wilke and Hougen (1945), with the modification given in Perry and Chilton (1973).

As already pointed out, the binary simulations were carried out assuming only film resistance to mass transfer. Garg and Ruthven (1975) refer to the usefulness of lumped fluid or solid film models to represent adsorption column behavior, which our own studies have confirmed. Gariepy and Zwiebel (1971) and Zwiebel et al. (1972, 1974) present simulated results for the fluid film model for one- and two-component adsorption and desorption in single columns. They show qualitative agreement between simulated and experimental results. Garg and Ruthven (1973) indicate that their simulated results for single-component adsorption and desorption with solid diffusional resistance in the adsorbent particles are qualitatively similar to those of Zwiebel et al. (1972). Ferrell et al. (1976) describe the successful use of an equivalent film resistance model to fit experimental data.

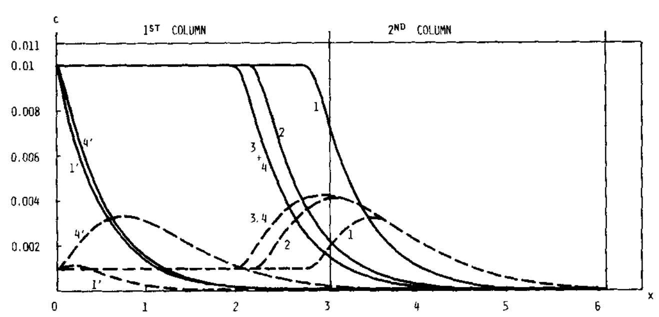

Fig. 3. Fluid concentration profiles of DBS and phenol (case A) (binary adsorption, film resistance only)

——— DBS
- - - - - - Phenol
1′: 300 hours after start
1: first switch
2: second switch
3&4: third and following switches
4′: 300 hours after fourth switch

Table 3. Data Used for the DBS-Phenol Adsorption Simulation

Carbon Type Coconut

d_p For cases *A* and *B* 4×10^{-3} m

for case *C* 1.24×10^{-3} m

ρ 0.48×10^3 kg/m³

β 0.55

Isotherm $$w_i = \frac{\overline{w}_i b_i c_i}{1 + \sum_{j=1}^{2} b_j c_j} \qquad i = 1, 2$$

If $i = 1$ denotes dodecyl benzene sulfonate (DBS), $i = 2$ phenol

$\overline{w}_1 = 144$ mole/m³ (bed) $\overline{w}_2 = 180$ mole/m³ (bed)

$b_1 = 4\,200$ m³/mole $b_2 = 110$ m³/mole

Fluid diffusion coefficients D_f

DBS 4.15×10^{-10} m²/s Phenol 9.48×10^{-10} m²/s

Column

ϵ 0.5

v 5.5×10^{-3} m/s

Column length 3.05 m 2 columns in series

A for cases A and B 0.75×10^3 m²/m³

for case C 2.419×10^3 m²/m³

Input concentration DBS 0.01 mole/m³

	Case A	Case B	Case C	
Input concentration phenol	0.001	0.01	0.001	mole/m³

Effective film mass transfer coefficients giving kA values

For cases A and B with film resistance alone

DBS $0.0115\ \mathrm{s}^{-1}$ phenol $0.00194\ \mathrm{s}^{-1}$

For case C effective overall coefficients including film resistance and fluid film approximation to pore diffusion resistance assuming pore diffusivity equal to diffusivity in water

DBS $0.00723\ \mathrm{s}^{-1}$ phenol $0.0159\ \mathrm{s}^{-1}$

Table 4. Switching Times for DBS-Phenol Systems

	Hours elapsed between switches		
Switch number	Case A	Case B	Case C
1	2 380	1 456	2 080
2	1 716	1 006	1 728
3	1 752	1 008	1 720
4	1 768	1 008	1 720
5	1 772	1 008	
6	1 772	1 008	
All additional	1 772	1 008	
[See figures	3, 4	5, 6	7, 8]

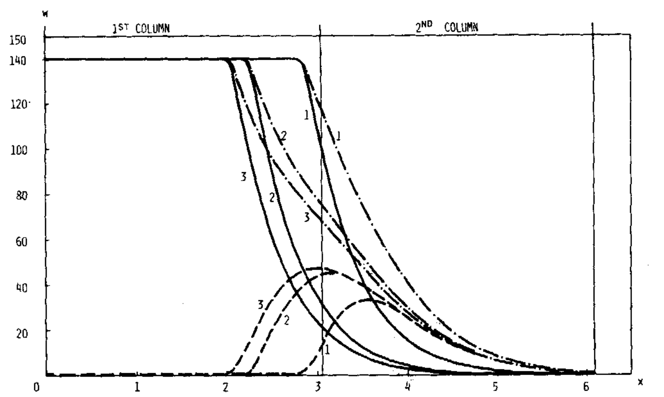

Fig. 4. Solid concentration profiles of DBS and Phenol (case A) (binary adsorption, film resistance only)

——— DBS
- - - - - - Phenol
—·—·—·— DBS and Phenol
1: first switch
2: second switch
3: third and following switches

Our Figures 1 and 2 and Table 2 show that although there are differences between the concentration profiles predicted in the one component case by the pore resistance and the equivalent pore resistance models, nevertheless the factors of economic significance in the multicolumn case, namely, the time between column switches and the degree of saturation of the column removed, are surprisingly insensitive to the assumed transport mechanism. Thus it seems reasonable to expect that simulation studies with a film or equivalent film resistance model will give some initial insight into the behavior of multicomponent, multicolumn systems.

Of the many possible effluent specifications for a binary system, a 99% total molar reduction was chosen. Other choices for this, as well as for the influent concentrations, could give a very different profile behavior. The results of the simulation of case A for a one- and two-column system are shown in Figure 3 for the fluid concentration and in Figure 4 for the solid concentration profile; switching times are given in Table 4. If a single column is used, about 40% of the carbon is not utilized at breakthrough, whereas if the column is split into two columns, only about 0.5% of the carbon content of the column removed at the first switch is not utilized. After stabilization of the profile in the two-column system, about 10% of the carbon in the column removed at each switch will not be utilized. All the carbon is removed about every 3 544 hr during the periodic countercurrent operation, compared with every 2 380 hr for a single column.

Figures 5 and 6 show the results of case B giving the effects of different feed concentrations of the same materials on the profiles in the column. Under these conditions, about 33% of the carbon would not be utilized if only a single column were used. With two columns, 5% of the carbon in the column removed at the first switch would not be used, but after the profile had stabilized, about 8% of the carbon removed would not be utilized. The whole of the carbon would be removed for regeneration every 2 016 hr, compared with every 1 456 hr if only a single column were used.

In the two-column case, after starting with fresh carbon in both columns, the concentration profile just prior to switching changed for the first two or three switches before stabilizing. The aggregate profiles and those for the individual components after stabilization were markedly different from those at the first switch. In contrast to the behavior for two-component adsorption, the results from studies of single-component adsorption, including those described earlier for acetic acid and runs made for the individual components, phenol and DBS, used in the two-

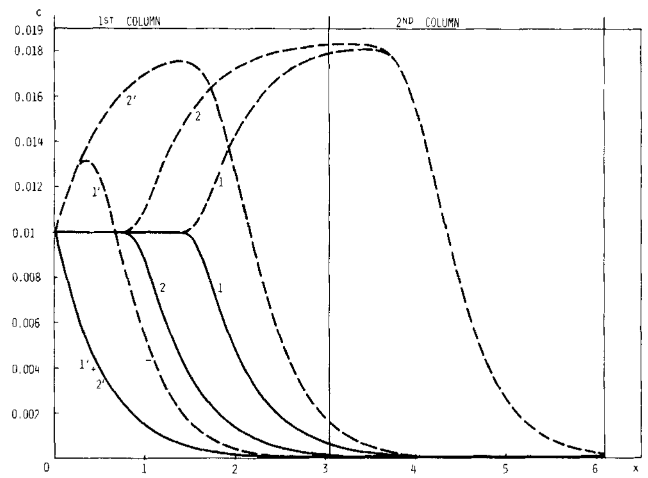

Fig. 5. Fluid concentration profiles of DBS and Phenol (case B) (binary adsorption, film resistance only)

——— DBS
- - - - - - Phenol
1': 300 hours after start
1: first switch
2: second and following switches
2': 300 hours after second switch

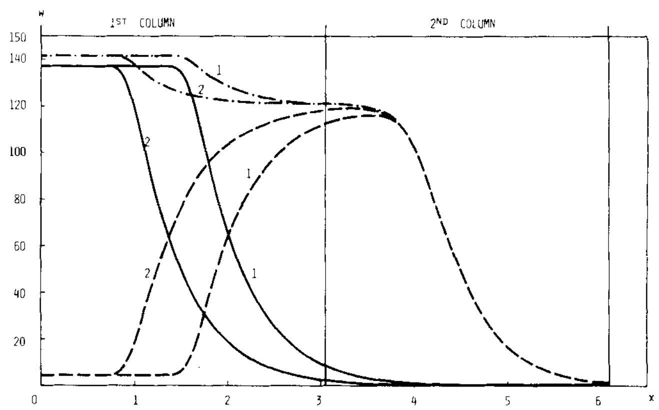

Fig. 6. Solid concentration profiles of DBS and Phenol (case B) (binary adsorption, film resistance only)

——— DBS
- - - - - - Phenol
–·–·–·– DBS and Phenol
1: first switch
2: third and following switches

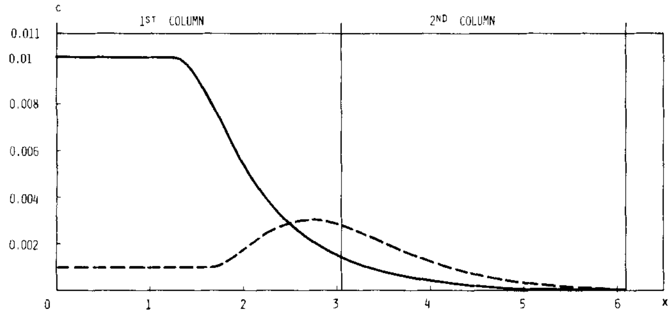

Fig. 7. Fluid concentration profiles of DBS and Phenol (Case C) (binary adsorption, film and equivalent pore resistance in series, 4th switch)

——— DBS
- - - - - - Phenol

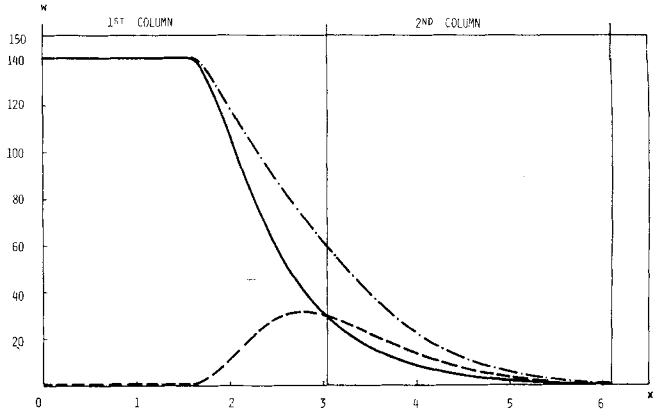

Fig. 8. Solid concentration profiles of DBS and Phenol (case C) (binary adsorption, film and equivalent pore resistance in series, 4th switch)

——— DBS
- - - - - - Phenol
–·–·–·– DBS and Phenol

component studies, showed stabilization at the profile obtained just prior to the first switch or with very little deviation from this. In single-component simulations for DBS and phenol with inlet concentrations of 0.01 mole/m^3 and for acetic acid, the profiles at the second and subsequent switches are virtually indistinguishable from those at the first switch. For phenol with a concentration of 0.001 mole/m^3, stabilization is slower but is essentially complete by the third switch when the relative concentration difference from the profile at the first switch is less than 10%.

As in the single-component case, an approximate indication of the effect of diffusional resistance within the particle can be obtained by postulating an equivalent fluid film resistance in series with the resistance of the external fluid. The simulation of the two-column system of case A was repeated using this approximation but with a smaller particle size and the assumption, in default of experimental data, that the pore diffusivities of the components were equal to their diffusivities in water (case C). The resulting overall film mass transfer coefficients were lower than those used in case A and resulted in flatter concentration profiles and a lower maximum value for the phenol concentrations (Figures 7 and 8). However, the time between switches and the degree of saturation of the carbon in the column removed were similar to those observed for case A.

The computing time required between switches for the two-component, two-column case was approximately seven to ten times that needed for the single-component simulation with film diffusion alone or about two thirds of that needed for the single component combined film and pore diffusion model.

The occurrence of peaks or plateaus in the concentration profiles of the less strongly adsorbed components is a characteristic feature of multicomponent adsorption. This phenomenon is clearly illustrated in the concentration profiles for phenol in Figures 3 to 8. In the two-column system, between successive switches, a peak in the phenol concentration profile moves through the columns from the inlet. One effect of the two-column switching procedure, in comparison with the single-column procedure, is to enlarge the area under the phenol profile and to push this profile, as well as that of the DBS, further back into the first column. The mean concentration of phenol in the column removed is much greater than the concentration which would be in equilibrium with the feed (fourteen times as great in case A and twenty-three times as great in case B).

In the second column, the ratio of the mean concentration of phenol to that of DBS is very much greater than in the feed (in case A 150 and in case B 50 times the ratio in the feed). This chromatographic effect might be used in a suitably designed multicolumn adsorption system to separate, concentrate, and recover valuable components in high yield.

ACKNOWLEDGMENT

The authors are grateful to Markus Balzli for helpful discussions during the course of this work.

NOTATION

A = outer particle surface area per volume of column, m^2/m^3
b = parameter in Langmuir isotherm, m^3/mole
c = bulk fluid concentration in the column (a function of x and t), mole/m^3
c_o = concentration in the fluid at the input to the column, mole/m^3
c_p = local concentration in the pore liquid of the particles (a function of r and t), mole/m^3
c^* = hypothetical concentration in the fluid at the outer surface of the particle, mole/m^3
c^1 = lower concentration of the constant pattern profile (by definition), mole/m^3
c^2 = upper concentration of the constant pattern profile (by definition), mole/m^3
D_f = free fluid diffusion coefficient, m^2/s
D_p = effective pore diffusion coefficient (relative to r and outer particle surface fraction open to pores), m^2/s
f = functional relation of some variables
k = external film mass transfer coefficient, D_f/δ, m/s
k_p = equivalent film coefficient for pore resistance, Equation (9), m/s
L_p = length of the profile in the column, m
(NT) = dimensionless distance, see Equation (10)
R = parameter characterizing the Langmuir isotherm
r = radial distance in the spherical particle, m
r_o = radius of the spherical particle, m
t = time, s
v = superficial fluid velocity, m/s
w = average concentration adsorbed in the particle (relative to column volume), mole/m^3
$\bar{w}$ = parameter in modified two component Langmuir isotherm, mole/m^3
w_o = parameter in single component Langmuir isotherm, mole/m^3
w_p = local concentration adsorbed in the particle, mole/m^3
w_∞ = concentration adsorbed in the particle in equilibrium with input liquid concentration
x = direction of flow along the column axis, m

Greek Letters

β = pore volume fraction of the particles
δ = hypothetical film thickness of the fluid film surrounding the particle, m
ϵ = void fraction of the packed column
ρ = bulk density of a particle, kg/m^3
ϕ_1, ϕ_2 = dimensionless concentration, see Equation (10)

Subscript

$i = 1, 2, \ldots n$ = component

LITERATURE CITED

Chen, J. W., R. L. Cunningham, and J. A. Buege, "Computer Simulation of Plant-Scale Multicolumn Adsorption Processes under Periodic Counter-Current Operation," *Ind. Eng. Chem. Process Design Develop.*, **11**, 430 (1972).

Erskine, D. B., and W. G. Schuliger, "Activated Carbon Processes for Liquids," *Chem. Eng. Progr.*, **67**, 41 (1971).

Ferrell, J. K., R. W. Rousseau, and M. R. Branscome, "The Development and Testing of a Mathematical Model for Complex Adsorption Beds," *Ind. Eng. Chem. Process Design Develop.*, **15**, 114 (1976).

Fleck, R. D., D. J. Kirwan, and K. R. Hall, "Mixed Resistance Diffusion Kinetics in Fixed-Bed Adsorption under Constant Pattern Conditions," *Ind. Eng. Chem. Fundamentals,* **12**, 95 (1973).

Fornwalt, H. J., and R. A. Hutchins, "Purifying Liquids with Activated Carbon," *Chem. Eng.* (May, 1966).

Garg, D. R., and D. M. Ruthven, "On Fixed Bed Sorption Behaviour of Gases with Nonlinear Equilibria," *AIChE J.*, **19**, 852 (1973).

——————, "Linear Driving Force Approximations for Diffusion controlled Adsorption in Molecular Sieve Columns," *ibid.*, **21**, 200 (1975).

Gariepy, R. L., and I. Zwiebel, "Adsorption of Binary Mixtures in Fixed Beds," *AIChE Symposium Ser. No. 117,* **67**, 17 (1971).

Glueckauf, R., "Theory of Chromotography," *Trans. Faraday Soc.*, **51**, 1540 (1955).

Heil, G., "Untersuchungen zum Transportmechanismus bei der Adsorption organischer Stoffe aus wässrigen Lösungen an Aktivkohle," Dissertation, Karlsruhe University (1971).

Kasten, P. R., and N. R. Amundson, "Analytical Solution for Simple Systems in Moving Bed Adsorbers," *Ind. Eng. Chem.*, **44**, 1704 (1952).

Klaus, R., "Computermodelle zur Aktivkohleadsorption in Festbettkolonnen bei der Abwasserreinigung," Diplomarbeit Technisch-Chemisches Labor, Eidgenössische Technische Hochschule Zürich (June, 1974).

Lawson, C. L., and S. A. Fisher, "Limitations of Activated Carbon Adsorption for Upgrading Petrochemical Effluents," *AIChE Symposium Ser. No. 136,* **70**, 577 (1973).

Lee, R. G., and T. W. Weber, "Isothermal Adsorption in Fixed Beds," *Can. J. Chem. Eng.*, **41**, 54 (1969).

Liapis, A., and D. W. T. Rippin, "A General Model for the Simulation of Multi-Component Adsorption from a Finite Bath," *Chem. Eng. Sci.*, **32**, 619 (1977).

Michaels, A. A., "Simplified Method of Interpreting Kinetic Data in Fixed-Bed Ion Exchange," *Ind. Eng. Chem.*, **44**, 1922 (1952).

Neretnieks, I., "A Mathematical Model for Continuous Counter-Current Adsorption," *The Swedish Paper Journal,* **77**, 407 (1974*a*).

————, "Adsorption of Components having a Saturation Isotherm," *Chem. Ing. Techn.*, **46**, 781 (1974*b*).

————, "A Simplified Theoretical Comparison of Periodic Counter-Current Adsorption," report DECHEMA, Frankfurt/M., (Oct., 1974*c*).

Perry and Chilton, *Chemical Engineers' Handbook,* 5 ed., pp. 16-20, McGraw-Hill, New York (1973).

Svedberg, G., "Numerical Solution of Multicolumn Adsorption Processes under Periodic Counter-Current Operation," *Chem. Eng. Sci.*, **31**, 345 (1976).

Weber, W. J., and J. C. Morris, "Adsorption in Heterogeneous Aqueous Systems," *J. Am. Water Works' Assn.*, **56**, 447 (1964).

Westermark, M., "Purification of Municipal Wastewater by Adsorption on Granular Activated Carbon," Doctoral thesis, Dept. of Chemical Engineering, Royal Institute of Technology, Stockholm, Sweden (1975).

Wilke, C. R., and Pin Chang, "Correlation of Diffusion Coefficients in Dilute Solutions," *AIChE J.*, **1**, 264 (1955).

Wilke, C. R., and O. W. Hougen, "Mass Transfer in the Flow of Gases through Granular Solids Extended to Low Modified Reynolds Numbers," *Trans. Am. Inst. Chem. Engrs.*, **41**, 445 (1945).

Wilson, J. N., "A Theory of Chromatography," *J. Am. Chem. Soc.*, **62**, 1583 (1940).

Winkler, H. E., and H. J. Kaempf, "Adsorption—Ein physikalisches Verfahren zur Reinigung von Industrieabwässern," *Wasser, Luft und Betrieb,* **16**, (June, 1972).

Zwiebel, I., R. L. Gariepy, and J. J. Schnitzer, "Fixed Bed Desorption Behaviour of Gases with Nonlinear Equilibria Part I Dilute, One Component, Isothermal Systems," *AIChE J.*, **18**, 1139 (1972).

Zwiebel, I., C. M. Kralik, and J. J. Schnitzer, "Fixed Bed Desorption Behaviour of Gases with Nonlinear Equilibria Part II Dilute, Multicomponent, Isothermal Systems," *ibid.*, **20**, 915 (1974).

Manuscript received July 28, 1976; revision received May 4, and accepted May 12, 1977.