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Purification of Phenolic Wastewater by Parametric Pumping: Nonmixed Dead Volume Equilibrium Model

A new process for purification of phenolic wastewaters by parametric pumping is presented.

An equilibrium (linear) model for nonmixed dead volumes thermal direct mode parametric pumping is developed and the influence of bottom and top dead volume magnitudes on transient separation is analyzed.

Analytical solutions for batch, continuous and semicontinuous operations are presented.

Experimental data on the system phenol/water-Duolite ES861 include equilibrium isotherms at 20°C and 60°C and parapump runs for the cases mentioned above.

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SCOPE

Adsorption is often used as secondary or polishing treatment of phenolic wastewaters.

Recently macrorecticular polymeric resins have been used instead of activated carbon as adsorbent. This is due to easier regeneration and better mechanical resistance although their cost is higher.

However, this operation involves various steps: saturation, regeneration, washing, etc. It can be interesting to use parametric pumping as a purification and/or solute recovery technique instead of classic cyclic operation. Advantages of parametric pumping are: continuous operation, use of low potential thermal energy as regenerant (avoiding regenerant/solute separation) and production of clean water and a concentrated phenol solution, simultaneously.

Modelling of parametric pumping processes has interested many authors; equilibrium (linear and nonlinear) and nonequilibrium models, using continuous and staged approaches have been published.

It is important to notice that in a parapump device, what happens outside the column (reservoirs, dead volumes, feed and drawing points) should be taken into account since it defines the boundary conditions of the column. Two main ideas have been used; everything is well mixed or no mixing at all, outside the column. It has been shown that in the latter case a better transient separation can be obtained.

In a real system dead volumes and sometimes part of the reservoirs can be considered as nonmixed. In this paper a non-

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mixed dead volume model is developed in order to study the influence of dead volumes on transient separation and to compare it with mixed dead volume models (Chen and Hill, 1971).

The experimental system—phenol/water-Duolite ES-681—was chosen because equilibrium isotherms at 20°C and 60°C were very different; these temperatures were used as cold and hot temperatures in parametric pumping runs.

The choice of the mode of operation (batch, continuous and semicontinuous) is also discussed in terms of phenolic wastewater treatment. Start-up and adsorbent efficiency in parapumps are also considered.

CONCLUSIONS AND SIGNIFICANCE

Outer volumes in parametric pumps (reservoirs, dead volumes) often include mixed and nonmixed regions. The model developed in this paper takes into account the nonmixing in dead volumes. Chen and Hill (1971) derived a model that considers the existence of mixed dead volumes, concluding that separation decreases when the top dead volume increases. On the contrary, our model which is closer to reality, tells us that there is a minimum top dead volume above which we get better transient separation than in the mixed case, and also increasing this dead volume increases transient separation.

Analytical solutions for the nonmixed dead volume model were developed.

In the treatment of phenolic wastewaters it is important to get most of the water fed as a low phenol content product. With this condition in mind and looking at the possibilities of operation of a parapump we concluded that the semicontinuous operation is the more suitable for this case giving a free-phenol bottom product with a flowrate approaching the feed flowrate and at the same time a very concentrated top product.

For such a parapump and looking at the start-up operation, it has been concluded that this can be accomplished by equilibrating the adsorbent with the solution in order to obtain a start-up concentration that allows immediate operation; concerning the adsorbent efficiency, it is also concluded that the volume of adsorbent needed is less than the calculated volume, the former volume being closely related to the cold halfcycle penetration distance, L_2.

Finally comparing the performance of our system (phenol/water-Duolite ES-681; 20 and 60°C) with those published we see that it is by far the best since the value of b (equilibrium constant change parameter) is much higher for a pair of operating temperatures within the range of practical interest.

Adsorption operations are used as a secondary or polishing step in the treatment of phenolic industrial effluents. When macroreticular polymeric adsorbents are used, the regeneration step is usually carried out with an organic solvent (methanol) or sodium hydroxide solutions; then, the recovery (recycling) of phenols is made in a subsequent separation (concentration) step (Fox, 1978 and 1979).

The idea of reducing all those steps to one step, thus avoiding cyclic operation plus separation (concentration), suggested the possibility of using a parametric pumping technique.

Parametric pumping is a separation technique, first introduced by Wilhelm and coworkers (1966), based on the influence of certain intensive thermodynamic variables (temperature, pressure, chemical potential, etc) on the equilibrium adsorption isotherm, together with a periodic change in the field flow. Two modes of operation are possible: the direct mode where the cyclic pulsations of the thermodynamic variable are imposed through the "wall" of the column and the recuperative mode where they are imposed at the "ends" of the column, thus being "carried" by the fluid.

In our system, both modes are possible when using thermal energy (temperature) as separation source; however only the recuperative mode can be applied when using pH (chemical potential).

In the following only the thermal direct mode parametric pumping will be considered in order to separate and concentrate phenol from water.

Many authors have worked on the modelling of these processes.

Pigford et al. (1969) treated the case of instantaneous equilibrium and linear isotherm; this model was further generalized by Aris (1969). Chen and coworkers (1971, 1972 and 1973) further developed Pigford's model, presenting the solution for closed (batch) and open (continuous and semicontinuous) parametric pumps considering the existence of well mixed dead volumes out of the column. Thomson and Bowen (1972) considered also the case of batch separation with nonmixed top reservoir, concluding that in this case, nonmixing produces a better transient separation.

The case of nonlinear isotherms has been extensively treated by Camero and Sweed (1976) and the nonequilibrium case by Foo and Rice (1975 and 1977).

A staged model approach has been recently published by Grevillot and Tondeur (1976 and 1977); both linear and nonlinear cases are considered and the analogy between parametric pumping and distillation is stressed.

Two reviews on this subject have been published by Wankat (1974) and Rice (1976).

THEORETICAL BACKGROUND

In order to introduce some concepts and equations needed for model development, let us consider a thermal direct mode parametric pump which is a cyclic operation device with a hot upwards halfcycle and a cold downwards halfcycle. In this section we will follow the papers of Pigford (1969), Aris (1969) and Chen (1971), using almost the same nomenclature.

We assume instantaneous and linear local equilibrium, plug flow, instantaneous heating and cooling and flow reversal in phase with temperature change.

The material balance over a differential volume element of an adsorption column is

$$V\frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} + \frac{1-\epsilon}{\epsilon}\frac{\partial q}{\partial t} = 0 \qquad (1)$$

where C is the concentration of solute in the fluid phase (mass of solute/volume of fluid), q is the solute concentration in the solid phase (mass of solute/volume of solid), V is the intersticial velocity of fluid, ϵ the porosity, t and z the time and space variables, respectively.

If the equilibrium isotherm is linear

$$q = K(T)C \qquad (2)$$

where $K(T)$ is a function of the local temperature (T).

The system of Eqs. 1 and 2 can be solved by the method of characteristics.

Let us define the equilibrium constant change parameter as

$$b = \frac{\xi(T_2) - \xi(T_1)}{2 + \xi(T_1) + \xi(T_2)} \tag{3}$$

and

$$u_i = \frac{2\,v_i}{2 + \xi(T_1) + \xi(T_2)} \quad (i = 1, 2) \tag{4}$$

where $\xi(T) = (1 - \epsilon)/\epsilon\, K(T)$ is a capacity parameter temperature dependent, v_i is the intersticial velocity and subscripts 1 and 2 refer to upwards and downwards respectively.

The slopes of the characteristics are then:

$$\text{Upwards Hot Halfcycle } \left(\frac{\partial z}{\partial t}\right)_C = \frac{u_1}{1 - b} \tag{5}$$

$$\text{Downwards Cold Halfcycle } \left(\frac{\partial z}{\partial t}\right)_C = -\frac{u_2}{1 + b} \tag{6}$$

We also have

$$C[1 - b\,\mathrm{Sq}(\omega t)] = \text{Constant} \tag{7}$$

where Sq( ) is a square wave function and ω is the frequency of temperature change assuming instantaneous heating, cooling and flow reversal. (Later we will establish the relationship between this frequency and real cycle time.)

Equation 7 means that concentrations are constant along the characteristics and that

$$\frac{C_1(1 - b)}{C_2(1 + b)} = 1 \tag{8}$$

which enables us to know what happens to a concentration in the column when the temperature is changed.

From Eqs. 5 and 6 we can calculate the penetration distances for each new concentration entering the column

$$L_i = \frac{u_i}{1 - b\,\mathrm{Sq}(wt)} \cdot \frac{\pi}{\omega} \quad (i = 1, 2) \tag{9}$$

where π/ω is the halfcycle time.

According to the relative magnitudes of L_1, L_2 and H (column height), Chen and Hill (1971) introduced the concept of the three possible regions of operation of a direct mode parametric pump.

Another useful concept, first introduced by Aris (1969) and extended by Chen and Hill (1971) is the number of cycles necessary to attain a constant pattern of characteristics emerging from the column. [See Chen and Hill (1971), Figure 4.]

For instance in region 1 we need $p_1 + 1$ cycles, where

$$p_1 = \frac{H - L_2}{L_1 - L_2} - q_1 \tag{10}$$

with $0 \leqslant q_1 < 1$.

DEAD VOLUME MODELS

Thomson (1972) concluded that, when the concentration profiles emerged from the column are kept in the reservoirs, a better transient separation is obtained if the outer concentrations in the reservoirs are considered as products, although the steady state separation is not affected.

Grevillot (1977) showed that the steady state separation increases if gradients are kept in the reservoirs in the case of finite equilibrium staged parapump.

In a real system, two types of outer volumes can be considered: mixed volumes, such as reservoirs or part of them and nonmixed volumes such as dead volumes.

On the other hand there are situations where a parapump can be operated almost all the time in a transient way. That is the case if we wish to eliminate some solute (most of the feed must be recovered as a free-solute bottom product, e.g., elimination and recovery of phenol from water). In that case it is interesting to study the effect of nonmixed dead volumes in transient separation.

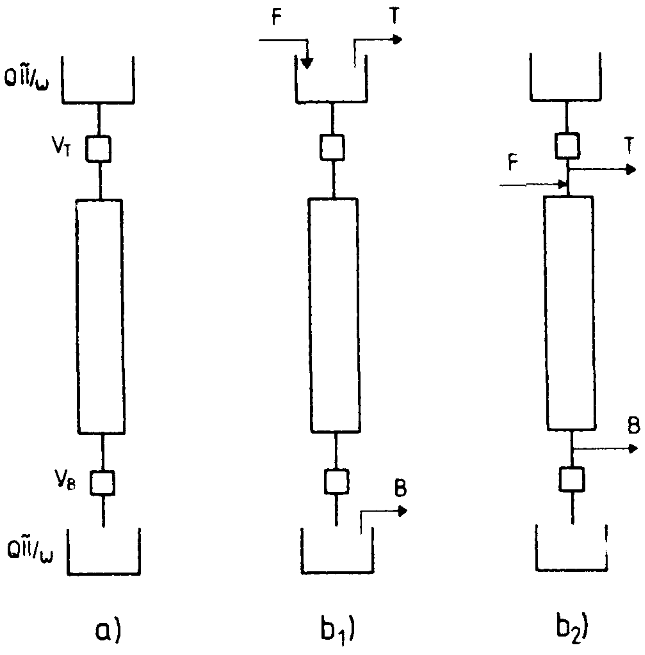

Figure 1. a) Batch parapump: V_T and V_B are top and bottom dead volumes; b) open parapump: *F*-feed; *T*-top product; *B*-bottom product (1—our arrangement; 2—Chen's arrangement).

For the case of instantaneous equilibrium and linear isotherm, Chen and coworkers (1971, 1972 and 1973) derived the analytical solutions for closed (total reflux) and open (partial reflux) parapumps. They considered mixed dead volumes, located at the bottoms of the reservoirs (probably because they used piston type pumps to percolate the fluid into the column); in their model, the feed and products with drawing points were located between the dead volumes and the column.

In our apparatus, described later, the whole volume of the reservoirs is percolated, the feed and product withdrawing points being located in the reservoirs, which represents a different dead volumes relative position (Figure 1). The system of difference equations to be solved, contains two types of equations: the so-called "internal equations" obtained from the application of the method of characteristics (which gives what comes out of the column) and the "external equations" obtained from external macroscopic material balances (boundary conditions of the internal equations) which relate what comes out to what goes into the column. The solutions of that system give the solute concentrations in products (open parapumps)/reservoirs (closed parapumps).

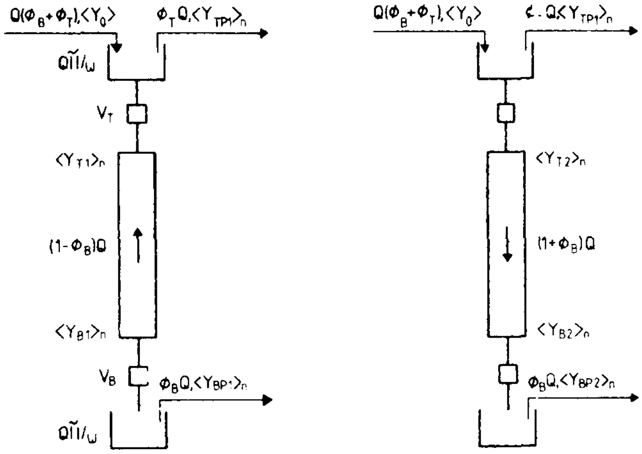

Figure 2. Continuous top feed parametric pump. Feed, products and column flowrates. (See experimental part of this work for the cycle description.)

For the arrangement considered we will first present a mixed dead volume model and then a nonmixed dead volume model.

In the following we consider as initial condition, a column saturated, at the hot temperature, with a solution having the feed composition, which fills also the bottom reservoir and dead volumes. The first halfcycle is always hot and upwards and the parapump is operated in region 1.

It is convenient at this point to define some variables. We call $Q\pi/\omega$ the top reservoir volume after upwards percolation, first feeding and first product drawing (Figure 2); Q is a ficticious flowrate used just to maintain Chen's notation (for batch operation it has a physical meaning: flowrate at which the reservoirs are emptied); V_T and V_S are the top and bottom dead volumes; ϕ_T and ϕ_B are the fractions of $Q\pi/\omega$ that are withdrawn as top and bottom products; $\langle Y_{T1}\rangle_n$, $\langle Y_{T2}\rangle_n$, $\langle Y_{B1}\rangle_n$, and $\langle Y_{B2}\rangle_n$ are the average normalized (by the initial concentration $\langle Y_o\rangle$) concentrations emerging and entering the column during cycle n, at the top and bottom, respectively. For the case of open parapumps the feed volume is $Q(\phi_T + \phi_B)\pi/\omega$ and the top and bottom product volumes are $\phi_T Q\pi/\omega$ and $\phi_B Q\pi/\omega$, their normalized concentrations being $\langle Y_{TP1}\rangle_n$ and $\langle Y_{PB2}\rangle_n$, respectively.

Mixed Dead Volume Model

For this case the internal equations are those obtained by Chen and Hill (1971), Eqs. 4 and 5 in their paper; their solution for the batch parapump also holds.

The external equations are obtained from the material balances around the top and bottom reservoirs.

After rearrangements the system of internal plus external equations takes the following form, for open parapumps (continuous and semicontinuous):

$$a_1\langle Y_{BP2}\rangle_n - a_2\langle Y_{BP2}\rangle_{n-1} = 0, n \geqslant 1 \tag{11}$$

$$d_1\langle Y_{TP1}\rangle_n - d_2\langle Y_{TP1}\rangle_{n-1} = e, n \leqslant p_1 + 1 \tag{12}$$

$$d_1\langle Y_{TP1}\rangle_n - d_2\langle Y_{TP1}\rangle_{n-1} = f\beta^\mu + g, n \geqslant p_1 + 1 \tag{13}$$

whose solution is

$$\langle Y_{BP2}\rangle_n = \alpha\beta^n, n \geqslant 1 \tag{14}$$

$$\langle Y_{TP1}\rangle_n = \phi\delta^n + \eta, n \leqslant p_1 + 1 \tag{15}$$

$$\langle Y_{TP1}\rangle_n = \nu\delta^n + \lambda\beta^\mu + \gamma, n \geqslant p_1 + 1 \tag{16}$$

where

$$\beta = a_2/a_1;\ \alpha = 1$$

$$\delta = d_2/d_1;\ \eta = e/(d_1 - d_2);\ \phi = (1-\eta)/\delta$$

$$\lambda = f/(d_1 - d_2/\beta);\ \gamma = 1 + \phi_B/\phi_T;$$

$$\nu = (\langle Y_{TP1}\rangle_{p_1+1} - \lambda - \gamma)/\delta^{p_1+1}$$

It should be noticed that γ is the steady state solution and $\langle Y_{TP1}\rangle_{p_1+1}$ is obtained from Eq. 15.

Table A1 (see appendix) summarizes the solutions for continuous and semicontinuous top feed parapumps.

Nonmixed Dead Volume Model

Internal Equations. Let us now consider the case of nonmixed dead volumes. We assume that the bottom dead volume is such that only one concentration goes out of column bottom during downflow halfcycle. This implies that

$$\frac{V_B}{D_1} \leqslant 1 - \frac{L_2}{L_1} \tag{17}$$

where D_1 is the volume of fluid percolated during the upflow halfcycle.

Let us analyse the effect of the nonmixed bottom dead volume on the constant pattern of characteristics. Figure 3 shows that two situations may occur according to the magnitude of the bottom dead volume. The dashed lines represent the characteristics originated by nonmixing in the bottom dead volume.

In the first case (Figure 3a) the bottom dead volume is such that the dashed characteristic comes out before point D. This condition is represented by

$$\frac{V_B}{D_1} \leqslant (1 - q_1)\left(1 - \frac{L_2}{L_1}\right) \tag{18}$$

The second case (Figure 3b) occurs when

$$(1 - q_1)\left(1 - \frac{L_2}{L_1}\right) < \frac{V_B}{D_1} \leqslant 1 - \frac{L_2}{L_1} \tag{19}$$

We assume that the top dead volume is such that no portion of fluid is there "memorized" twice during upflow. This condition gives

$$\frac{V_T}{D_1} \leqslant 1 - \frac{L_2}{L_1} \tag{20}$$

Thus, depending on the magnitude of the top dead volume, one, two or three concentrations can be memorized. The limits for this depend also on the magnitude of the bottom dead volume, and so on the conditions expressed by Eqs. 18 and 19.

If the bottom dead volume obeys the condition 18 we have:

—only one concentration memorized ($\langle Y_{B1}\rangle_{n-p_1}$) if

$$0 < \frac{V_T}{D_1} \leqslant (1 - q_1)\left(1 - \frac{L_2}{L_1}\right) - \frac{V_B}{D_1} \tag{21}$$

—two concentrations memorized ($\langle Y_{B1}\rangle_{n-p_1}$ and $\langle Y_{B1}\rangle_{n-p_1-1}$ $(1-b)/(1+b)$) if

$$(1 - q_1)\left(1 - \frac{L_2}{L_1}\right) - \frac{V_B}{D_1} < \frac{V_T}{D_1} \leqslant (1 - q_1)\left(1 - \frac{L_2}{L_1}\right) \tag{22}$$

—three concentrations memorized ($\langle Y_{B1}\rangle_{n-p_1}$, $\langle Y_{B1}\rangle_{n-p_1-1}$ $(1-b)/(1+b)$ and $\langle Y_{B1}\rangle_{n-p_1-1}$) if

$$(1 - q_1)\left(1 - \frac{L_2}{L_1}\right) < \frac{V_T}{D_1} \leqslant 1 - \frac{L_2}{L_1} \tag{23}$$

A similar procedure can be applied to the second case, that is, when the bottom dead volume obeys the condition 19.

The construction of internal equations proceeds as in the case of the mixed dead volume model (Chen, 1971).

The same bottom internal equation applies if condition 17 is valid.

To construct the top internal equation we are going to consider separately all the concentrations coming out of the column ($\langle Y_{T1}\rangle_n$) and those staying in the top dead volume ($\langle Y_{T1}^1\rangle_n$).

As an example Figure 4 represents the top concentrations arrangement when condition 18 is verified and two concentrations are memorized in the top dead volume (condition 22); as we have said the top internal equations are constructed considering weighted contributions of the concentrations coming out, the weights being obtained by considering the fraction of the total halfcycle time during which each concentration comes out of the column.

From Figure 4, we can then write

$$\begin{aligned}\langle Y_{T1}\rangle_n = {} & \left(1 - \frac{V_T}{D_2}\right)\frac{L_2}{L_1}\frac{1+b}{1-b}\langle Y_{T2}\rangle_{n-1} \\ & + \left[\frac{L_2}{L_1}\frac{V_T}{D_2} + \frac{1-b}{1+b}\left(\frac{V_B}{D_1} - (1-q_1)\left(1 - \frac{L_2}{L_1}\right)\right)\right]\langle Y_{B1}\rangle_{n-p_1-2} \\ & + \frac{1-b}{1+b}\left[(1-q_1)\left(1 - \frac{L_2}{L_1}\right) - \frac{V_B}{D_1}\right]\langle Y_{B1}\rangle_{n-p_1-1}\frac{1+b}{1-b} \\ & + q_1\left(1 - \frac{L_2}{L_1}\right)\langle Y_{B1}\rangle_{n-p_1-1} + \frac{V_B}{D_1}\langle Y_{B1}\rangle_{n-p_1-1}\frac{1-b}{1+b} \\ & + \left[(1-q_1)\left(1 - \frac{L_2}{L_1}\right) - \frac{V_B}{D_1}\right]\langle Y_{B1}\rangle_{n-p_1}\end{aligned} \tag{24}$$

$$\begin{aligned}\langle Y_{T1}^1\rangle_n = {} & \left[(1-q_1)\left(1 - \frac{L_2}{L_1}\right) - \frac{V_B}{D_1}\right]\langle Y_{B1}\rangle_{n-p_1} \\ & + \left[\frac{V_T}{D_1} - (1-q_1)\left(1 - \frac{L_2}{L_1}\right) + \frac{V_B}{D_1}\right]\langle Y_{B1}\rangle_{n-p_1-1}\frac{1-b}{1+b}\end{aligned} \tag{25}$$

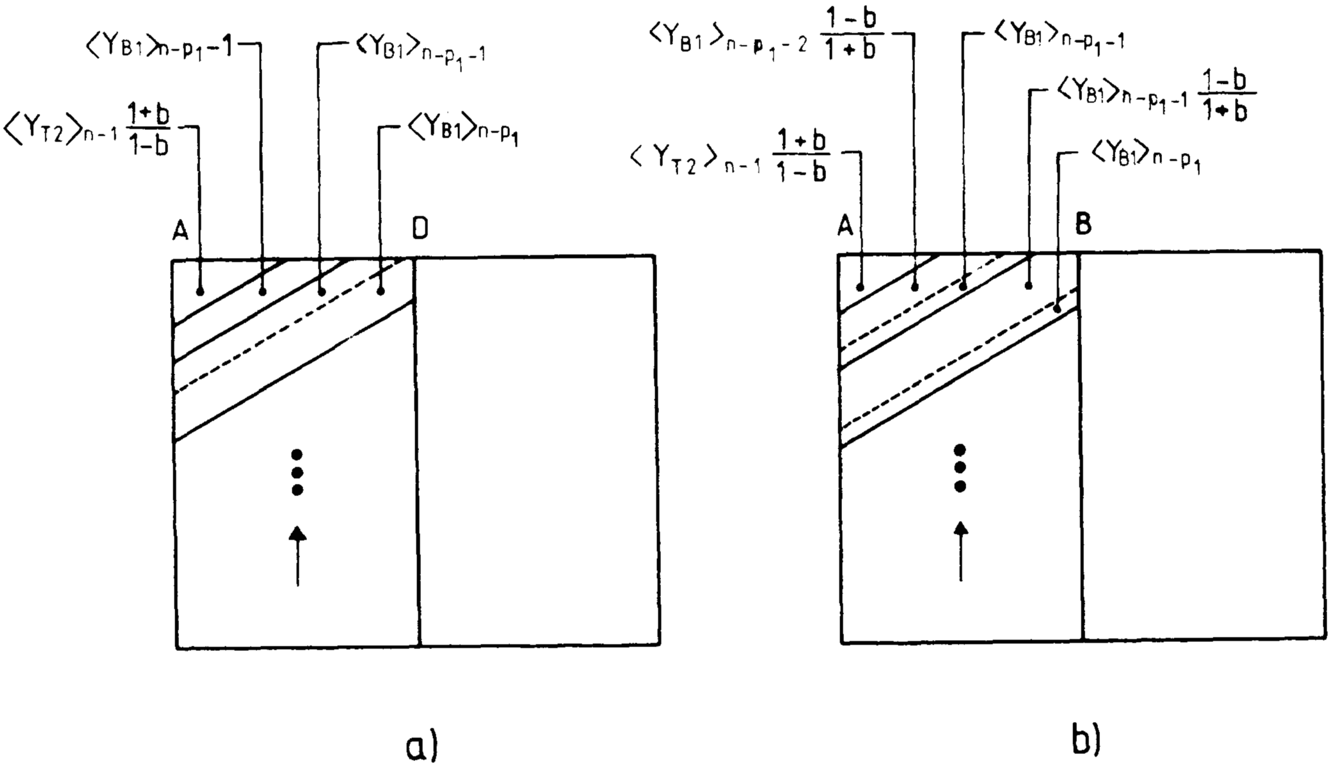

Figure 3. Influence of the bottom dead volume on constant pattern of characteristics (cycle *n*) (characteristics due to top dead volume are not shown).

For each case described we can construct equations such as (Eqs. 24 and 25).

More general equations can be written, which are valid for conditions 18 and 20 and also for conditions 19 and 20.

Thus, if condition 18 is verified

$$\langle Y_{T1}\rangle_n = \left(1 - \frac{V_T}{D_2}\right)\frac{L_2}{L_1}\frac{1+b}{1-b}\langle Y_{T2}\rangle_{n-1} + Z_1\langle Y_{B1}\rangle_{n-p_1-2} + Z_2\langle Y_{B1}\rangle_{n-p_1-1} + Z_3\langle Y_{B1}\rangle_{n-p_1} \quad (26)$$

$$\langle Y_{T1}^1\rangle_n = Z_1\langle Y_{B1}\rangle_{n-p_1-1} + Z_4\langle Y_{B1}\rangle_{n-p_1} \quad (27)$$

and for condition 19

$$\langle Y_{T1}\rangle_n = \left(1 - \frac{V_T}{D_2}\right)\frac{L_2}{L_1}\frac{1+b}{1-b}\langle Y_{T2}\rangle_{n-1} + W_1\langle Y_{B1}\rangle_{n-p_1-3} + W_2\langle Y_{B1}\rangle_{n-p_1-2} + W_3\langle Y_{B2}\rangle_{n-p_1-1} \quad (28)$$

$$\langle Y_{T1}^1\rangle_n = W_1\langle Y_{B1}\rangle_{n-p_1-2} + W_4\langle Y_{B1}\rangle_{n-p_1-1} \quad (29)$$

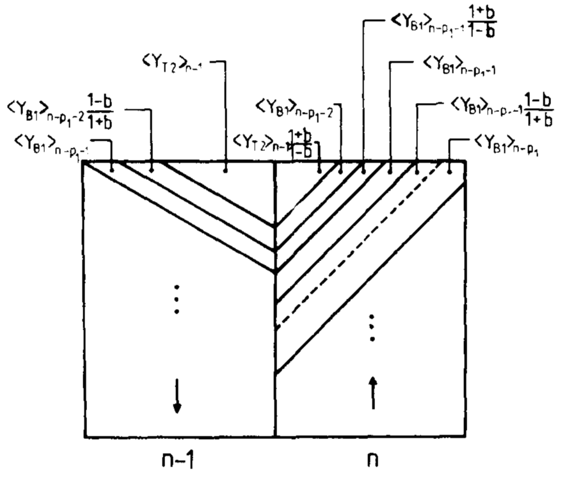

Figure 4. Influence of the top dead volume on constant pattern of characteristics.

Appendix Table A2 shows the expressions for Z_1, Z_2, Z_3, Z_4, W_1, W_2, W_3 and W_4.

Solutions. The solution of the system of internal plus external equations leads to two difference equations of the same form as Eqs. 11 and 12 or Eq. 13. Using the same nomenclature, we summarize in Tables A3, 4, 5 (see appendix) the solutions for three cases of open pumps: continuous, semicontinuous and a special case of semicontinuous, where we consider that we feed all the time (see experimental part).

For the top equations of batch systems we obtain

$$n \leqslant p_1 + 1 \qquad \langle Y_{TR1}\rangle_n - \langle Y_{TR1}\rangle_{n-1} = e \quad (30)$$

$$n \geqslant p_1 + 1 \qquad \langle Y_{TR1}\rangle_n - \langle Y_{TR1}\rangle_{n-1} = f\beta^{\mu} \quad (31)$$

The solution for Eq. 30 is of the form

$$\langle Y_{TR1}\rangle_n = 1 + (n-1)e \quad (32)$$

and for Eq. 31

$$\langle Y_{TR1}\rangle_n = \langle Y_{TR1}\rangle_{p_1+1} + f \cdot h \quad (33)$$

Table A6 (see appendix) presents the values of e, f, μ and h for the cases considered.

The results for region 2 are published elsewhere (Costa, 1979).

With little effort, the more general case of partially mixed reservoirs can be treated using the methodology presented above, if we assume that the remaining mixed reservoir volume is enough to fill at least the adjacent dead volume.

SIMULATION RESULTS

Figures 5a, b and c show the influence of the top and bottom dead volume magnitudes on the gap between top reservoir concentrations for the case of mixed (2) and nonmixed (1) dead volumes, in a batch parapump in region 1. As it can be seen this gap increases with the ratio between top and bottom dead volumes.

Figure 6 shows the same situation, but now for a continuous top feed parapump in region 1.

In these figures, the top reservoir curve for the nonmixed case

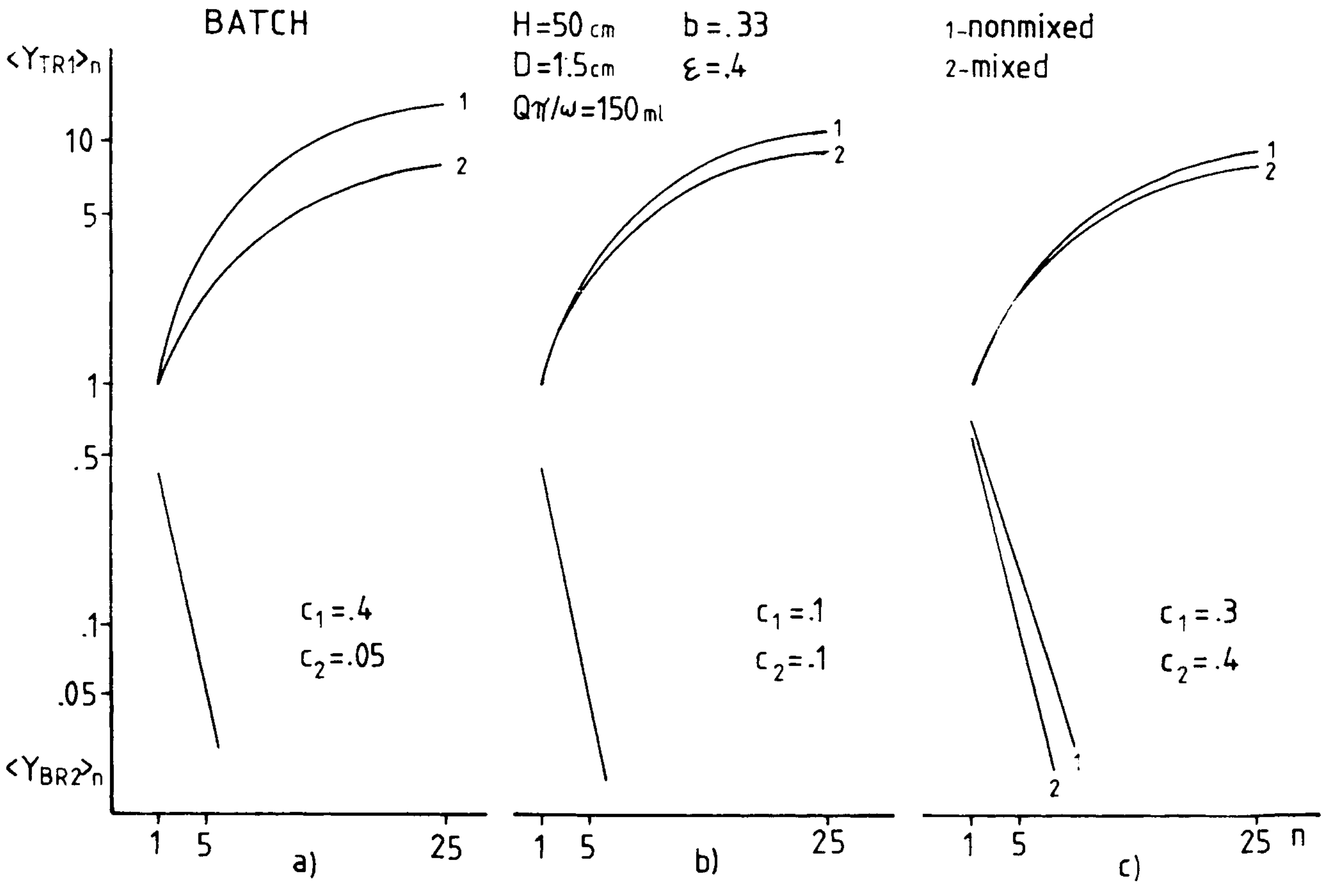

Figure 5. Influence of the top and bottom dead volumes on top reservoir concentration (batch parapump).

is always above the mixed one, which means that nonmixing improves transient separation. Nevertheless this is not the general case, as it can be shown that the inverse situation may also occur.

The curves plotted in Figure 7a represent the boundary between those situations described for a batch parapump operated in region 1, meaning that for each bottom dead volume (c_2) magnitude there is a minimum top dead volume (c_1) above which the nonmixed case gives better transient separation. For fixed values of H, D and ϵ, Figure 7 also shows that for a fixed value of c_2 the minimum value of c_1 decreases when $Q\pi/\omega$ increases and b decreases.

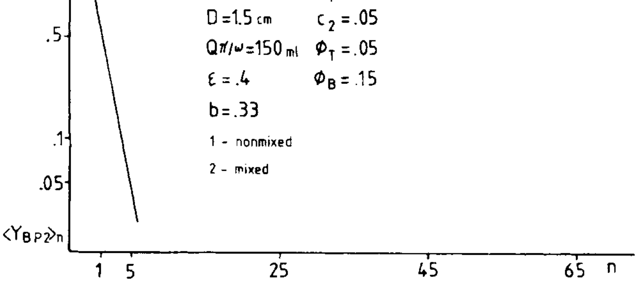

Figure 6. Influence of the top and bottom dead volumes in top product concentration (continuous parapump).

Taking into account Eq. 9 one can say that this limit value decreases when the penetration distances ($Q\pi/\omega \sim L_1, L_2$) and the ratio L_2/L_1 increases.

The same can be said, in general, for open top feed pumps operated in region 1.

Let us compare now the nonmixed dead volume model with the mixed dead volume model (Chen, 1971); in the latter increasing the bottom dead volume top concentration increases, the opposite being true for the top dead volume. For the nonmixed dead volume model this is no longer valid since then small bottom dead volume and large top dead volume improve transient separation.

Let's take first Chen's results. For a parapump operating in region 1, cycle after cycle, we have the top effluents more and more concentrated. When we consider a cycle i, the top dead volume contains the average concentration corresponding to cycle $i - 1$, thus inferior to that of cycle i. As the top reservoir concentration in cycle i, is the result of two contributions: top dead volume and effluent from the column, it is clear that when we increase top dead volume we increase the volume of the less concentrated contribution, thus diminishing average concentration.

For the nonmixed dead volume model, Figure 8 (Grevillot, 1978), which is a sketch of experimental results, shows that increasing the top dead volume the average concentrations in the top reservoirs and dead volume increase at the same time.

From a practical point of view this conclusion is also important as dead volumes are always present in parametric pumps, and usually can be considered nonmixed. It can be said that for each parapump (hot upwards and operated in region 1) there is a minimum top dead volume that should be maintained in order to get an improved transient separation.

EXPERIMENTAL

The experimental set-up is shown in Figure 9. The glass-jacketed column

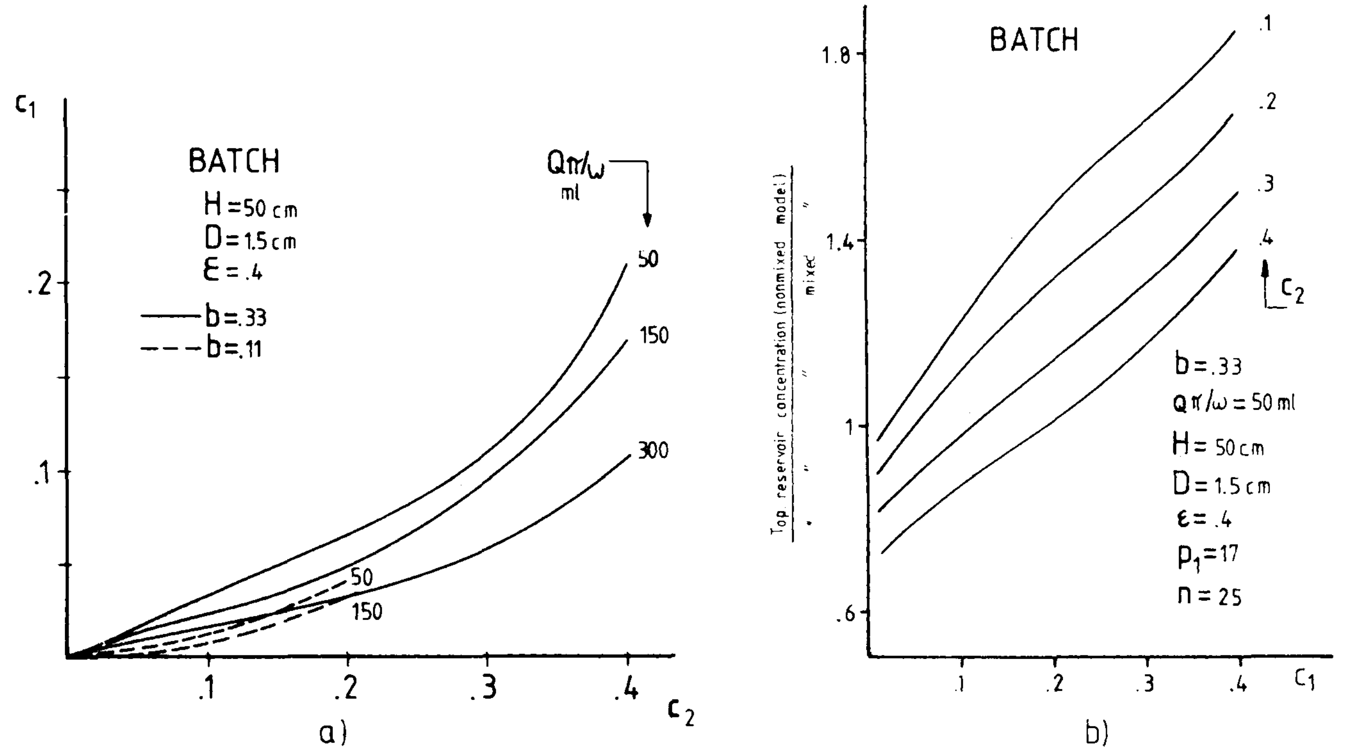

Figure 7. a) Lines representing conditions where both models give the same top reservoir concentration; b) ratio of top reservoir concentrations (nonmixed/mixed) as a function of c_1 and c_2.

is 60 cm long and 1.5 cm internal diameter (Serva-Tecknic). The heating and cooling is ensured by two thermostatic baths (one at 60°C and the other at 20°C) together with three pneumatic three-way valves. Only one peristaltic pump (Desaga) is used to percolate the fluid. Flow inversion is obtained with the help of two electromagnetic valves (Fig. 9b). The control of halfcycle end is made using a photoelectric cell to detect the falling of a float. The problem of column degasing during operation has been solved by means of capillaries placed at the ends of the column which ensure operation under pressure. Magnetic stirrers were used to mix the fluid in the reservoirs. A card programmer commands all operations.

A DUOLITE ES-861 polymeric adsorbent, with an average particle diameter of 0.77 mm, was used.

The equilibrium isotherms have been obtained using the technique described by Rodrigues et al. (1978).

In batch experiments phenol analysis were carried out using FID Chromatography (8 μL samples). In open parapump experiments (continuous and semicontinuous), we used UV spectrophotometry (272 nm) for concentrations greater than 1 mg/L and a colorimetric method described by Rodier (1971), for lower concentrations.

The experimental set-up described by Chen and Hill (1971) needs constant flow product withdrawing pumps in order to ensure the equality of the volumes fed and withdrawn.

This may present some difficulties, and so we used the experimental scheme shown (Figure 9) which is simpler; in this apparatus feed and product withdrawing are carried out simultaneously with column heating and cooling, directly to and from the reservoirs. The use of prepositioned suction tubes also ensures the equality of the volumes fed and withdrawn, thus avoiding the need of a constant flow pump.

A typical cycle is as follows (where the numbers in brackets are the times, in minutes, for the continuous top feed run shown in Figure 12): end of hot halfcycle → feeding(2) → mixing(0.5) → top product drawing(2.5) → feeding(2) → mixing(0.5) → percolation (cold halfcycle)(18.6) → end of cold halfcycle → mixing(0.5) → bottom product drawing(2.5) → percolation (hot halfcycle)(14.2)

Temperature equilibrium time for cooling—7 min
Temperature equilibrium time for heating—5 min

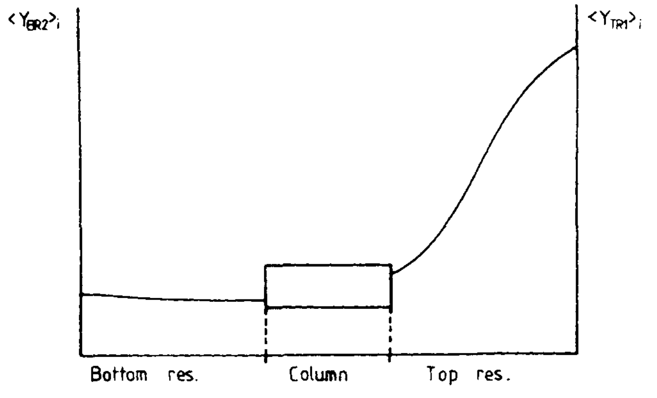

Figure 8. Nonmixed reservoir concentration profiles.

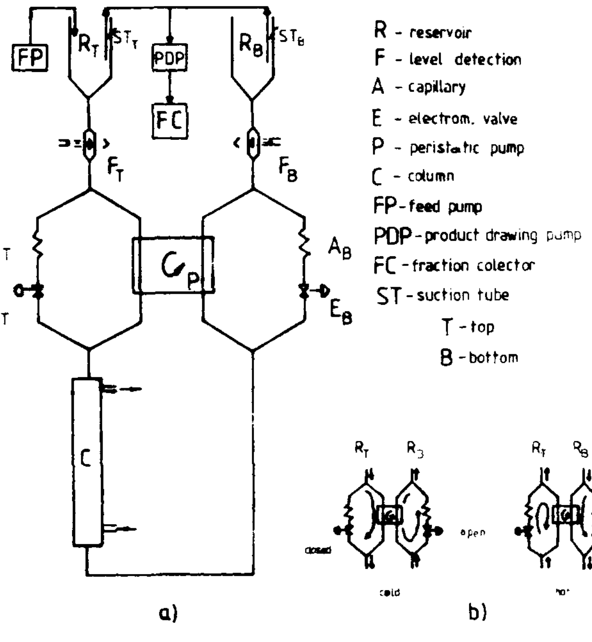

Figure 9. Experimental setup.

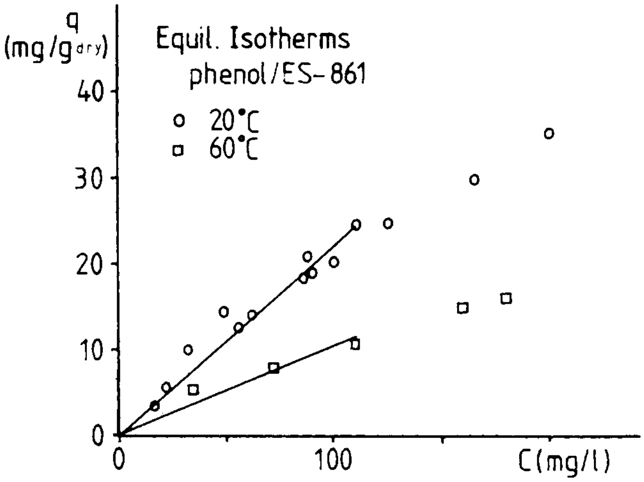

Figure 10. Equilibrium isotherms (20 and 60°C) for the system phenol/water-DUOLITE ES 861.

For a semicontinuous top feed parapump the cycle is as described but without first feeding and mixing.

In this paper we consider also a modified semicontinuous parapump, to which the cycle described is still valid: this modified parapump corresponds to a semicontinuous pump with continuous feed.

We should note that our way of operation is similar to that proposed by Chen and for this reason we kept Chen's terminology (continuous and semicontinuous).

The real cycle time (RCT) is not $2\ \pi/\omega$ but $2\ \pi/\omega$ plus dead times between percolations; in the example given we have: 45.3 min.

Reflux ratios were measured by weighing the collected bottom and top product fractions. For continuous top feed pumps, steady state was assured when overall material balance was verified. The initial conditions for all experiments are those described in the model development.

RESULTS AND DISCUSSION

Figure 10 represents equilibrium isotherms; full lines refer to a linear fitting of experimental points (valid over the range 0–100 mg/L) made for model application purposes. Parameter b, Eq. 3, was calculated, its value being 0.35 for an apparent packing density of 0.2 g (dry adsorbent)/mL (packing).

Figure 11 represents experimental points and model results (full line) for a batch parapump; the parameters for simulation are those of the legend. The value of b used, was calculated from the bottom reservoir equation (Chen, 1971) together with the average slope of the straight lines defined by point ($n = 0$, $\langle Y_{BR2} \rangle = 1$) and the experimental points. The value obtained was 0.32. We note that with the coordinate system used (semilog) the bottom reservoir concentration curve should be a straight line passing through point (0, 1).

Figure 12 represents experimental results for two continuous top feed parapumps, one operating in region 1(o) and the other in region 2(Δ). Simulation was carried out using a $b = 0.32$, calculated from the batch experiment. In this case, region 1 parapump, we note that the observed steady state top product concentration, $\langle Y_{TP1} \rangle_\infty \simeq 2.31$, is very near the value that can be calculated with reflux ratios (Eq. 16):

$$\langle Y_{TP1} \rangle_\infty = 1 + \frac{\phi_B}{\phi_T} = 2.25$$

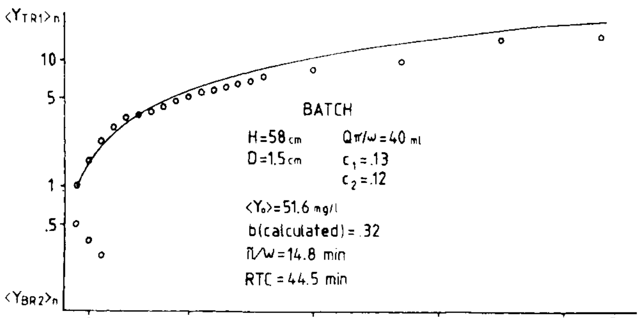

Figure 11. Experimental results and model simulation for a batch parapump (region 1); phenol/water-ES 861 system.

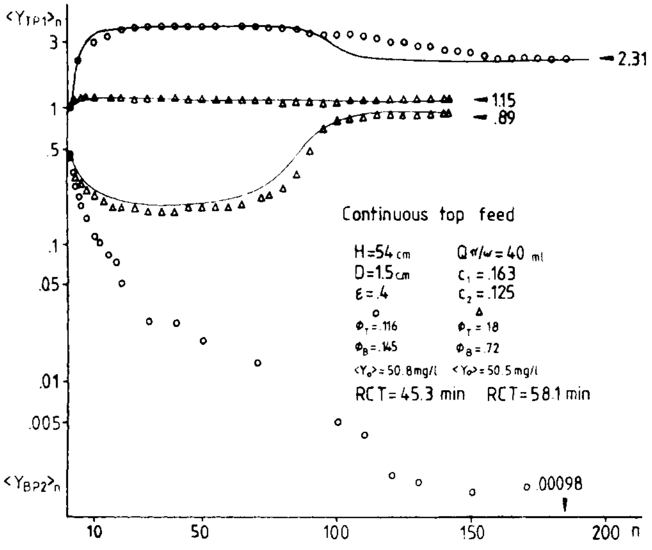

Figure 12. Experimental results and model simulations for continuous parapumps (regions 1 and 2); phenol/water-ES 861 system.

For the region 2 parapump, the experimental values of steady state top and bottom product concentrations are 1.15 and 0.89, respectively; these values agree well with the values calculated with reflux ratios (Chen, 1971): $\langle Y_{TP1} \rangle_\infty = 1.38$ and $\langle Y_{BP2} \rangle_\infty = 0.9$.

Finally, Figure 13 represents experimental and simulation results for a modified semicontinuous top feed parapump. The b value used for simulation was calculated using Eq. 14 and the slope of the straight line that fits bottom product experimental points: $b = 0.377$.

Analysing now globaly the last three figures we can see that top

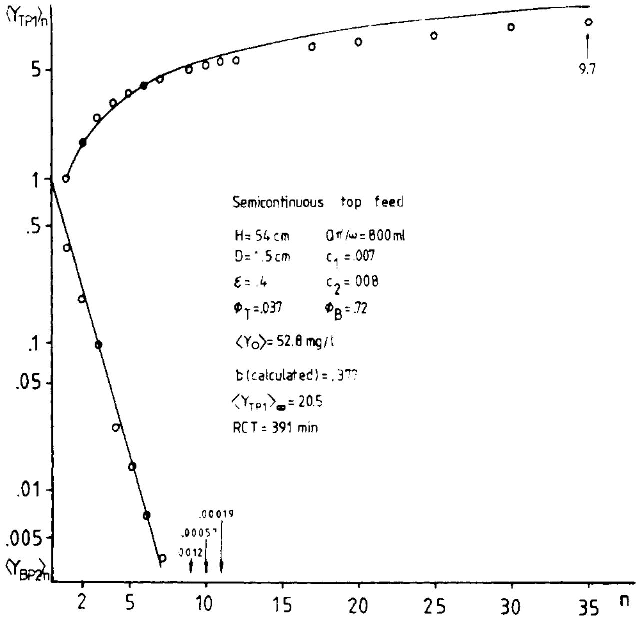

Figure 13. Experimental results and model simulation for a modified semicontinuous parapump (region 1); phenol/water-ES 861 system.

TABLE 1. CALCULATED VALUES OF L_1, L_2 AND ΔL

	b	L_1 (cm)	L_2 (cm)	ΔL (cm)
Batch	0.32	1.74	0.9	0.84
Continuous	0.32	1.49	1.03	0.46
Semicontinuous	0.377	34.8	27.1	7.7

concentrations predicted by the model are higher than those experimentally observed, which can be explained by the existence of some diffusional effects, axial mixing, and other secondary phenomena. For the bottom curve we see that in batch and continuous top feed (region 1) experiments, we do not obtain experimentally a straight line whereas in the semicontinuous case a straight line is obtained. The situation can be explained if we look at the penetration distances used in those experiments (Table 1). As we can see, in the semicontinuous case we worked with a longer net penetration (ΔL) and we obtained very good results for the bottom curve. This means that in other experiments (batch and continuous) bottom entrance disturbances produced some mixing which affected the bottom concentration in the cases of little net penetration. We note also that values of b calculated from bottom curves approach well the value calculated from the isotherms.

In our case (treatment of phenolic wastewaters) most of the water should be obtained as a phenol-free water bottom product. In order to work in region 1, which permits to obtains a very low concentrated bottom product, there are restrictions to be imposed to ϕ_B maximum value. In the case of a top feed pump we obtain:

$$\text{continuous } \phi_b < b$$

$$\text{semicontinuous } \phi_B < \frac{2b}{1-b}$$

and for $0 \leqslant b < 1$, we have always

$$\frac{2b}{1-b} \geqslant b \tag{34}$$

Thus, the semicontinuous parapump can operate at higher values of ϕ_B than the continuous, since for both these open parapumps, Eq. 34 holds for steady state top product concentration. We can say that semicontinuous is better than continuous operation for two main reasons:

- Most of the feed volume is obtained as a very low concentrated bottom product
- A more concentrated top product is obtained

Looking now at Table 2, where some known b parameter values are given, we see that our system is by far the best one, and at the same time uses a temperature difference of only 40°C between two normal industrial working temperatures (20 and 60°C); those temperatures are normally met in cooling water (fed to process-cold, and residual-hot), condensates, etc.

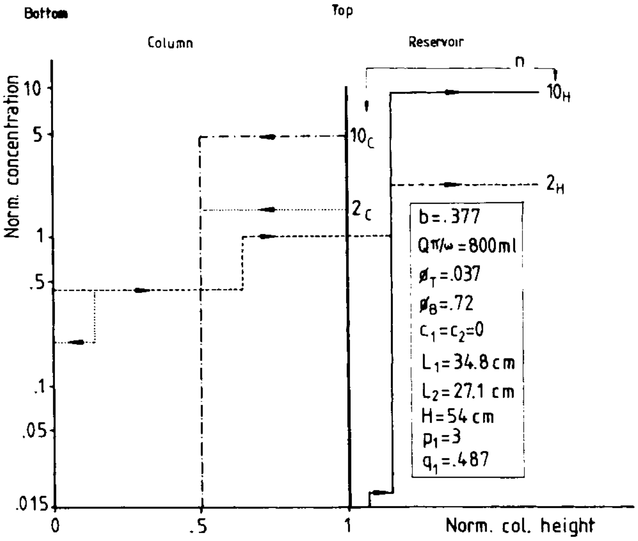

Figure 14. Concentration profiles in the column.

Figure 14 represents the concentration profiles in the column for a semicontinuous (continuous feed) parametric pump without dead volumes; the concentration profiles coming out the column during upflow halfcycle (H-hot) are also represented. It can be seen that after ten cycles the concentrations inside the column are very low (less than 0.0086) for upflow halfcycle and the same can be said for the bottom half-column in downflow halfcycle. Thus for a parapump as described, after some cycles part of the adsorbent is not used effectively in the separation (of course it should be noted that from the equilibrium theory point of view an infinitesimal height of adsorbent is sufficient to achieve separation in certain conditions). So, for a parapump operated in region 1 after a certain number of cycles, the separation effective height of adsorbent is slightly greater than L_2. From this we can conclude that for certain operating conditions and for a certain separation we can use less than the column height filled with adsorbent and at the same time the start up of the parapump can be made equilibrating the adsorbent with solution in order to obtain the desired start-up concentration. In Figure 14, and to start in cycle 10, we will have about 50% of column height filled with resin equilibrated with a solution of concentration 5.

CONCLUSIONS

The nonmixed dead volume model tells us that for each bottom dead volume magnitude there is a minimum top dead volume that should be maintained in order to get an improved transient separation, relatively to the mixed case where inexistence of the top dead volume gives a better separation.

We attempted with this work to apply the parametric pumping technique to the purification of phenolic wastewaters. We have experimentally shown that we can obtain with this technique a treated effluent with only some ppb of phenol which is an improvement when compared with classic adsorption methods

TABLE 2. SOME b PARAMETERS FROM LITERATURE

System	T_{Hot} (°C)	T_{Cold} (°C)	b	b^*	References
n-heptane/toluene-silica gel	70	4	—	0.125	Pigford (1969) and Wilhelm (1968)
n-heptane/toluene-silica gel	70	15	—	0.083	Pigford (1969) and Wilhelm (1968)
NaCl-Biorad AG11A8	55	5	0.173**	—	Sweed (1971)
n-heptane/toluene-silica gel	70	4	—	0.22	Chen (1972, 1973 and 1974)
n-heptane/toluene-silica gel	60	25	—	0.15	Chen (1974)
$AgNO_3$ sorption on DUOLITE C265	60	4	—	0.065	Grevillot (1978)
$AgNO_3$ sorption on DUOLITE C265	60	20	—	0.047	Grevillot (1978)
Phenol/water-DUOLITE ES-861	60	20	0.35	0.32 or 0.377	Present Paper

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b = calculated from equilibrium data

b^* = calculated from parapump experiments

** = calculated assuming an apparent resin density of 0.2 g dry/mL bed and a bed porosity of 0.4

(leakage of the order of ppm); also chemical regenerants are not used which is economic.

ACKNOWLEDGMENT

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NOTATIONS

b = equilibrium constant change parameter
C = concentration in the fluid phase
C_1 = concentration in the fluid phase (hot halfcycle)
C_2 = concentration in the fluid phase (cold halfcycle)
c_1 = dimensionless top dead volume ($V_T/Q\pi/\omega$)
c_2 = dimensionless bottom dead volume ($V_B/Q\pi/\omega$)
D = column diameter
D_1 = volume percolated upwards per cycle
D_2 = volume percolated downwards per cycle
H = column height
$K(T)$ = isotherm constant
L_i = penetration distances (i = 1-upwards; i = 2-downwards)
n = number of cycles
p_1 = parameter defined in Eq. 16
Q = ficticious flowrate (in batch systems is the flowrate at which reservoirs are emptied)
$Q\pi/\omega$ = reservoir volume
q = concentration in the solid phase
q_1 = parameter defined in Eq. 16
RCT = real cycle time
T = absolute temperature
T_1 = hot absolute temperature
T_2 = cold absolute temperature
t = time
u_i = parameter defined in Eq. 4
V = intersticial fluid velocity
v_i = intersticial fluid velocity (i = 1-upwards; i = 2-downwards)
V_T = top dead volume
V_B = bottom dead volume
Y = dimensionless fluid phase concentration
z = spatial coordinate

Greek letters

ϵ = porosity
$\xi(T)$ = capacity temperature dependent parameter
ω = frequency of temperature change
ϕ_T = fraction of reservoir volume obtained as top product
ϕ_B = fraction of reservoir volume obtained as bottom product
ΔL = net penetration distance
π/ω = halfcycle time

Subscripts

B = bottom
$B1$ = bottom, upflow
$B2$ = bottom, downflow
$BP2$ = bottom product, downflow
$T1$ = top, upflow
$T2$ = top, downflow
$TP1$ = top product, upflow
$TP2$ = top product, downflow
0 = initial

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APPENDIX

TABLE A-1. SOLUTIONS FOR THE MIXED, DEAD-VOLUME MODEL EQUATIONS

	a) Bottom Equations [Eqs. 11 and 14]		
	a_1		a_2
Continuous and Semicontinuous	$\frac{1+\phi_B+c_2}{1+\phi_B}$		$\frac{c_2}{1+\phi_B}+\frac{1-b}{1+b}$
	b) Top Equations ($n \leqslant p_1 + 1$) [Eqs. 12 and 15]		
	d_1	d_2	e
Continuous	$\frac{(1-\phi_B+c_1)(1+\phi_T)}{(1-\phi_B)^2}$	$\frac{1}{1-\phi_B}\left(1-\phi_T+\frac{c_1(1+\phi_T)}{1-\phi_B}\right)$	$2\frac{\phi_T+\phi_B}{1-\phi_B}+1$ $-\frac{1-b}{1+b}\frac{1+\phi_B}{1-\phi_B}$
Semicontinuous	$1+c_1$	$1-\phi_T+c_1$	$1+\phi_T+\phi_B-\frac{1-b}{1+b}(1+\phi_B)$
	c) Top Equations ($n \geqslant p_1 + 1$) [Eqs. 13 and 16]		
	μ	f	g
Continuous	$n-p_1-1$	$\left(1-\frac{L_2}{L_1}\right)\left[1-q_1+\frac{q_1}{\beta}\right]$	$2\frac{\phi_T+\phi_B}{1-\phi_B}$
Semicontinuous	$n-p_1-1$	$\left(1-\frac{L_2}{L_1}\right)\left[1-q_1+\frac{q_1}{\beta}\right]$	$\phi_T+\phi_B$

TABLE A-3. SOLUTION FOR THE BOTTOM EQUATIONS EQS. 11 AND 14

	a_1	a_2
Batch	$1/(1-c_2)$	$c_2/(1-c_2)+\frac{1-b}{1+b}$
Continuous	$(1+\phi_B)/(1+\phi_B-c_2)$	$c_2/(1+\phi_B-c_2)+\frac{1-b}{1+b}$
Semi-continuous	idem	idem
Semi-continuous (Continuous Feed)	idem	idem

TABLE A-2. EXPRESSIONS FOR Z_1, Z_2, Z_3, Z_4, W_1, W_2, W_3 AND W_4

$$\begin{aligned}
Z_1 = {} & \frac{1-b}{1+b}\left(\frac{V_T}{D_1}+\frac{V_B}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right) * \left[H\left(\frac{V_T}{D_1}+\frac{V_B}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right)-H\left(\frac{V_T}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right)\right] \\
& + \left(\frac{V_B}{D_1}\frac{1-b}{1+b}+\frac{V_T}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right) * \left[H\left(\frac{V_T}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right)-H\left(\frac{V_T}{D_1}-\left(1-\frac{L_2}{L_1}\right)\right)\right]
\end{aligned}$$

$$\begin{aligned}
Z_2 = {} & \left(q_1\left(1-\frac{L_2}{L_1}\right)+\frac{V_B}{D_1}\frac{1-b}{1+b}\right) * \left[1-H\left(\frac{V_T}{D_1}-\left(1-\frac{L_2}{L_1}\right)\right)\right]+\frac{V_T}{D_1} * \left[1-H\left(\frac{V_T}{D_1}+\frac{V_B}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right)\right] \\
& + \left((1-q_1)\left(1-\frac{L_2}{L_1}\right)-\frac{V_B}{D_1}\right) * \left[H\left(\frac{V_T}{D_1}+\frac{V_B}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right)-H\left(\frac{V_T}{D_1}-\left(1-\frac{L_2}{L_1}\right)\right)\right]
\end{aligned}$$

$$Z_3 = \left((1-q_1)\left(1-\frac{L_2}{L_1}\right)-\frac{V_B}{D_1}\right) * \left[1-H\left(\frac{V_T}{D_1}-\left(1-\frac{L_2}{L_1}\right)\right)\right]$$

$$Z_4 = \frac{V_T}{D_1}\left[1-H\left(\frac{V_T}{D_1}+\frac{V_B}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right)\right]+\left((1-q_1)\left(1-\frac{L_2}{L_1}\right)-\frac{V_B}{D_1}\right) * \left[H\left(\frac{V_T}{D_1}+\frac{V_B}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right)-H\left(\frac{V_T}{D_1}-(1-\frac{L_2}{L_1})\right)\right]$$

$$W_1 = \frac{1-b}{1+b}\left(\frac{V_T}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)-\left(1-\frac{L_2}{L_1}\right)+\frac{V_B}{D_1}\right) * \left[H\left(\frac{V_T}{D_1}-\left(1-\frac{L_2}{L_1}\right)+(1-q_1)\left(1-\frac{L_2}{L_1}\right)-\frac{V_B}{D_1}\right)-H\left(\frac{V_T}{D_1}-\left(1-\frac{L_2}{L_1}\right)\right)\right]$$

$$\begin{aligned}
W_2 = {} & \frac{1-b}{1+b}\left(\frac{V_B}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right) * \left[1-H\left(\frac{V_T}{D_1}-\left(1-\frac{L_2}{L_1}\right)\right)\right]+\frac{1-b}{1+b}\frac{V_T}{D_1}\left[1-H\left(\frac{V_T}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right)\right] \\
& + \frac{1-b}{1+b}(1-q_1)\left(1-\frac{L_2}{L_1}\right) * \left[H\left(\frac{V_T}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right)-H\left(\frac{V_T}{D_1}-\left(1-\frac{L_2}{L_1}\right)\right)\right] \\
& + \left(\frac{V_T}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right) * \left[H\left(\frac{V_T}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right)-H\left(\frac{V_T}{D_1}-\left(\left(1-\frac{L_2}{L_1}\right)+(1-q_1)\left(1-\frac{L_2}{L_1}\right)-\frac{V_B}{D_1}\right)\right)\right] \\
& + \left(\left(1-\frac{L_2}{L_1}\right)-\frac{V_B}{D_1}\right) * \left[H\left(\frac{V_T}{D_1}-\left(\left(1-\frac{L_2}{L_1}\right)+(1-q_1)\left(1-\frac{L_2}{L_1}\right)-\frac{V_B}{D_1}\right)\right)-H\left(\frac{V_T}{D_1}-\left(1-\frac{L_2}{L_1}\right)\right)\right]
\end{aligned}$$

$$W_3 = \left(\frac{1-b}{1+b}(1-q_1)\left(1-\frac{L_2}{L_1}\right)+\left(1-\frac{L_2}{L_1}\right)-\frac{V_B}{D_1}\right) * \left[1-H\left(\frac{V_T}{D_1}-\left(1-\frac{L_2}{L_1}\right)\right)\right]$$

$$\begin{aligned}
W_4 = {} & \frac{1-b}{1+b}\frac{V_T}{D_1}\left[1-H\left(\frac{V_T}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right)\right]+\frac{1-b}{1+b}(1-q_1)\left(1-\frac{L_2}{L_1}\right) * \left[H\left(\frac{V_T}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right)-H\left(\frac{V_T}{D_1}-\left(1-\frac{L_2}{L_1}\right)\right)\right] \\
& + \left(\frac{V_T}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right) * \left[H\left(\frac{V_T}{D_1}-(1-q_1)\left(1-\frac{L_2}{L_1}\right)\right)-H\left(\frac{V_T}{D_1}-\left(\left(1-\frac{L_2}{L_1}\right)+(1-q_1)\left(1-\frac{L_2}{L_1}\right)-\frac{V_B}{D_1}\right)\right)\right] \\
& + \left(\left(1-\frac{L_2}{L_1}\right)-\frac{V_B}{D_1}\right) * \left[H\left(\frac{V_T}{D_1}-\left(\left(1-\frac{L_2}{L_1}\right)+(1-q_1)\left(1-\frac{L_2}{L_1}\right)-\frac{V_B}{D_1}\right)\right)-H\left(\frac{V_T}{D_1}-\left(1-\frac{L_2}{L_1}\right)\right)\right]
\end{aligned}$$

Note: $H(x)$ represents the Heaviside function, defined as:

$$H(x) = \begin{cases} 0, & x < 0 \\ 1, & x \geqslant 0 \end{cases}$$

TABLE A-4. SOLUTIONS FOR THE TOP EQUATIONS ($n \leqslant p_1 + 1$) EQS. 12 AND 15

a) CONDITION 18 VERIFIED

d_1	d_2	e
Continuous $\frac{1+\phi_T}{1-\phi_B}$	$\frac{c_1(1-\phi_T)}{(1+\phi_B)(1-\phi_B)} + \frac{1-\phi_T}{1+\phi_B} \cdot \frac{1+\phi_B-c_1}{1-\phi_B}$	$\frac{\phi_T+\phi_B}{1-\phi_B} + \frac{c_1(\phi_T+\phi_B)}{(1-\phi_B)(1+\phi_B)}$ $+ \frac{\phi_B+\phi_T}{1+\phi_B} \frac{1+\phi_B-c_1}{1-\phi_B}$ $+ Z_1 + Z_2 + Z_3 - \frac{c_1}{1-\phi_B}(Z_1 + Z_4)$
Semicontinuous 1	$\frac{c_1(1-\phi_T)}{1+\phi_B} + (1+\phi_B-c_1)\frac{1-\phi_T}{1+\phi_B}$	$\frac{c_1(\phi_T+\phi_B)}{1+\phi_B}$ $+ (1+\phi_B-c_1)\frac{\phi_T+\phi_B}{1+\phi_B}$ $+ Z_1 + Z_2 + Z_3 - c_1(Z_1 + Z_4)$
Semicontinuous (Cont. Feed) $1+\frac{\phi_T+\phi_B}{2}$	$\frac{c_1\left(1+\frac{\phi_B-\phi_T}{2}\right)}{1+\phi_B}$ $+ (1+\phi_B-c_1)\frac{1+\frac{\phi_B-\phi_T}{2}}{1+\phi_B}$	$\frac{c_1\frac{\phi_B+\phi_T}{2}}{1+\phi_B} + \frac{\phi_T+\phi_B}{2}$ $+ (1+\phi_B-c_1)\frac{\frac{\phi_T+\phi_B}{2}}{1+\phi_B}$ $+ Z_1 + Z_2 + Z_3 - c_1(Z_1 + Z_4)$

b) CONDITION (19) VERIFIED

d_1	d_2	e
Continuous $\frac{1+\phi_T}{1-\phi_B}$	$\frac{c_1(1-\phi_T)}{(1+\phi_B)(1-\phi_B)} + \frac{1-\phi_T}{1+\phi_B} \frac{1+\phi_B-c_1}{1-\phi_B}$	$\frac{\phi_T+\phi_B}{1-\phi_B} + \frac{c_1(\phi_T+\phi_B)}{(1-\phi_B)(1+\phi_B)}$ $+ \frac{\phi_T+\phi_B}{1+\phi_B} \frac{1+\phi_B-c_1}{1-\phi_B}$ $+ W_1 + W_2 + W_3 - \frac{c_1}{1-\phi_B}(W_1 + W_4)$
Semicontinuous 1	$\frac{c_1(1-\phi_T)}{1+\phi_B} + (1+\phi_B-c_1)\frac{1-\phi_T}{1+\phi_B}$	$\frac{c_1(\phi_T+\phi_B)}{1+\phi_B}$ $+ (1+\phi_B-c_1)\frac{\phi_T+\phi_B}{1+\phi_B}$ $+ W_1 + W_2 + W_3 - c_1(W_1 + W_4)$
Semicontinuous (Cont. Feed) $1+\frac{\phi_T+\phi_B}{2}$	$\frac{c_1\left(1+\frac{\phi_B-\phi_T}{2}\right)}{1+\phi_B}$ $+ (1+\phi_B-c_1)\frac{1+\frac{\phi_T-\phi_B}{2}}{1+\phi_B}$	$\frac{c_1\frac{\phi_B+\phi_T}{2}}{1+\phi_B} + \frac{\phi_T+\phi_B}{2}$ $+ (1+\phi_B-c_1)\frac{\frac{\phi_T+\phi_B}{2}}{1+\phi_B}$ $+ W_1 + W_2 + W_3 - c_1(W_1 + W_4)$

TABLE A-5. SOLUTIONS FOR THE TOP EQUATIONS ($n > p_1 + 1$) EQS. 13 AND 16

a) CONDITION 18 VERIFIED

μ	f	g
Continuous $n - p_1 - 3$	$Z_1 + \beta Z_2 + \beta^2 Z_3 - \frac{c_1}{1 - \phi_B}(Z_1\beta + \beta^2 Z_4)$	$2\frac{\phi_T + \phi_B}{1 - \phi_B}$
Semicontinuous $n - p_1 - 3$	$Z_1 + \beta(Z_2 - c_1 Z_1) + \beta^2(Z_3 - c_1 Z_4)$	$\phi_T + \phi_B$
Semicontinuous (Cont. Feed) $n - p_1 - 3$	$Z_1 + \beta(Z_2 - c_1 Z_1) + \beta^2(Z_3 - c_1 Z_4)$	$\phi_T + \phi_B$

b) CONDITION 19 VERIFIED

μ	f	g
Continuous $n - p_1 - 4$	$W_1 + \beta W_2 + \beta^2 W_3 - \frac{c_1}{1 - \phi_B}(\beta W_1 + \beta^2 W_4)$	$2\frac{\phi_T + \phi_B}{1 - \phi_B}$
Semicontinuous $n - p_1 - 4$	$W_1 + \beta(W_2 - c_1 W_1) + \beta^2(W_3 - c_1 W_4)$	$\phi_T + \phi_B$
Semicontinuous (Cont. Feed) $n - p_1 - 4$	$W_1 + \beta(W_2 - c_1 W_1) + \beta^2(W_3 - c_1 W_4)$	$\phi_T + \phi_B$

TABLE A-6. SOLUTION FOR TOP EQUATION IN BATCH SYSTEMS

$n \leqslant p_1 + 1$	$n \geqslant p_1 + 1$		
e	μ	f	h
Batch Condition 18 $Z_1 + Z_2 + Z_3 - c_1(Z_1 + Z_4)$	$n - p_1 - 3$	$Z_1 + \beta(Z_2 - c_1 Z_1) + \beta^2(Z_3 - c_1 Z_4)$	$\frac{1 - \beta^{n-p_1-1}}{\beta(1 - \beta)}$
Batch Condition 19 $W_1 + W_2 + W_3 - c_1(W_1 + W_4)$	$n - p_1 - 4$	$W_1 + \beta(W_2 - c_1 W_4) + \beta^2(W_3 - c_1 W_4)$	$\frac{1 - \beta^{n-p_1-1}}{\beta^2(1 - \beta)}$