Design of Cyclic Fixed-Bed Adsorption Processes

Part II: Regeneration and Cyclic Operation

Regeneration of polymeric adsorbents saturated with phenol in a fixed bed is modeled by an "equilibrium model" and a "reaction front model." These models were previously tested over CSTR experiments.

A package for the design of cyclic fixed-bed adsorbers was then prepared by linking the reaction front model for regeneration with a pore-diffusion model for saturation described in Part I (Costa and Rodrigues, 1985) and a model for washing. Predicted and experimental results were compared in a cyclic run.

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SCOPE

Although cyclic fixed-bed adsorption processes are usually carried out in three steps—saturation, regeneration, and washing—only in a few papers is the regeneration of adsorbents (specially activated carbon) studied.

Regeneration of polymeric adsorbents can be achieved by using organic solvents, bases or acids, steam, supercritical fluids, or microwave action. In this work our goals were:

1. To develop a model for the regeneration of fixed beds of polymeric adsorbent (Duolite ES861, Duolite Int.) saturated with phenol by using sodium hydroxide as regenerant.
2. To link this model with models for saturation (Part I, Costa and Rodrigues, 1985) and washing in order to prepare a package for the design of cyclic adsorption processes in fixed beds.
3. To test the robustness of the package and to perform cyclic runs in order to assess the predictive capability of the model.

CONCLUSIONS AND SIGNIFICANCE

Modeling of the regeneration of fixed-bed adsorbers filled with a polymeric adsorbent saturated with phenol was performed in the case where sodium hydroxide is used as regenerant. Previous understanding of the regeneration mechanisms was gained by carrying out simple dynamic experiments in a continuous stirred tank reactor (CSTR), leading to the development of an equilibrium model and a reaction front model.

The equilibrium model for fixed-bed regeneration can only be used to get a qualitative picture of the system behavior. The model which should be used for design includes a reaction front model for the adsorbent particles and axial dispersion in the fluid phase. The particle equations were discretized by using global orthogonal collocation with $N = 6$ interior points. The final system of $N + 3$ partial differential equations was solved by using PDECOL; the bed was divided into ten subintervals over the axial coordinate and third-order interpolating functions were used.

A package for the design of cyclic processes was then constructed by linking models for saturation, regeneration, and washing. The robustness of the package was tested in a number of different situations (e.g., various models for particle diffusion: homogeneous, pore-diffusion, parallel, and series for micro-macropore adsorbents). A cyclic run was carried out in order to test the predictive capability of the package. A good agreement between model and experiment was found.

This package is now ready to be applied to other cyclic processes and can be extended to the simulation of pressure swing adsorption.

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INTRODUCTION

Although cyclic adsorption processes involve generally three steps—saturation, regeneration, and washing—most studies deal with the saturation step. Only a few are dedicated to the other steps, especially when chemical regeneration is concerned (Sutlnko and Himmelstein, 1983).

In this work we analyze the regeneration of a polymeric adsorbent (Duolite ES861, Diaprosim, France) saturated with phenol in order to develop a model for the regeneration of a fixed-bed adsorber and then be able to construct a package for the design of cyclic adsorption processes.

The regeneration of polymeric adsorbents can be achieved by using organic solvents (e.g., methanol), bases or acids, steam, supercritical fluids, or microwave action. In the case of phenol-saturated adsorbents we can use either methanol or sodium hydroxide.

In the present investigation sodium hydroxide was used as regenerant. An increase in pH enhances the formation of phenate species which is not retained by the support. In fact the reaction taking place is

$$C_6H_5OH + OH^- \rightleftharpoons C_6H_5O^- + H_2O \tag{1}$$

with $K_{eq}(20°C) = c^2/(c^1c^3) = 1.3 \times 10^4$ L/mol and c^1, c^2, c^3 the molar concentrations of phenol, phenate, and hydroxide, respectively.

The influence of pH on the adsorption equilibrium isotherm already determined (Costa and Rodrigues, 1985) for the system phenol-water/Duolite ES861 can be expressed by

$$q^1 = \frac{K_L Q \rho_a c_T}{1 + K_{eq} 10^{pH-14} + 10^3 M K_L c_T} \tag{2}$$

where q^1 is the molar concentration of phenol in the adsorbent (mol/L), c_T is the molar concentration of phenol plus phenate in the fluid phase (mol/L), M is the molecular weight of phenol, and ρ_a is an apparent density of the resin (g dry/L).

For the system under consideration at 20°C, $K_L = 4.3 \times 10^{-3}$ L/mg, $Q = 63.6$ mg/g dry; so for $c_T = 2 \times 10^{-3}$ mol/L one gets $q^1 = 16.2 \times 10^{-2}$ at pH = 7, $q^1 = 9.5 \times 10^{-2}$ at pH = 10, and $q^1 = 2.0 \times 10^{-2}$ at pH = 11. This shows that hydroxide concentrations around 1M should be used in the regeneration step.

In order to understand how regeneration proceeds we carried out simple experiments in a CSTR adsorber of Carberry type (Costa and Rodrigues, 1983, 1984). Qualitative agreement was reported by using an equilibrium model and reasonable quantitative agreement was obtained by considering a reaction front model at the adsorbent particle level.

These models will then be considered for the understanding of regeneration of fixed-bed adsorbers.

MODELING REGENERATION OF FIXED-BED ADSORBERS

Equilibrium Model with Axial Dispersion

Let us first consider an equilibrium model for the regeneration of a fixed bed adsorber initially saturated with phenol at concentration c_o^1 in the fluid phase. The model equations are:

Conservation Equations

Phenol (species 1)

$$\frac{1}{Pe}\frac{\partial^2 c^1}{\partial z^2} = \frac{\partial c^1}{\partial z} + \frac{\partial c^1}{\partial t} + \tau \frac{1-\epsilon}{\epsilon}\frac{\partial \bar{q}^1}{\partial t} + \frac{1}{U}$$

(molar flow of phenol disappeared by reaction) (3a)

Phenate (species 2)

$$\frac{1}{Pe}\frac{\partial^2 c^2}{\partial z^2} = \frac{\partial c^2}{\partial z} + \tau\frac{\partial c^2}{\partial t} + \tau \frac{1-\epsilon}{\epsilon}\frac{\partial \bar{q}^2}{\partial t} - \frac{1}{U}$$

(molar flow of phenol disappeared by reaction) (3b)

Hydroxide (species 3)

$$\frac{1}{Pe}\frac{\partial^2 c^3}{\partial z^2} = \frac{\partial c^3}{\partial z} + \tau\frac{\partial c^3}{\partial t} + \tau \frac{1-\epsilon}{\epsilon}\frac{\partial \bar{q}^3}{\partial t} + \frac{1}{U}$$

(molar flow of phenol disappeared by reaction) (3c)

Equilibrium Relationships

$$K_{eq} = \frac{c^2}{c^1c^3} \text{(reaction)} \tag{4a}$$

$$q^1 = \frac{K_L Q \rho_a c^1}{1 + K_L M 10^3 c^1} \text{(adsorption)} \tag{4b}$$

Boundary and Initial Conditions

$$z = 0 \quad c^1 = c_e^1;\ c^2 = c_e^2;\ c^3 = c_e^3 \tag{5a}$$

$$z = 1 \quad \frac{\partial c^1}{\partial z} = \frac{\partial c^2}{\partial z} = \frac{\partial c^3}{\partial z} = 0 \tag{5b}$$

$$t = 0 \quad c^1 = c_0^1;\ c^2 = c_0^2;\ c^3 = c_0^3 \tag{6}$$

In the above equations Pe is the Peclet number, z is the axial coordinate (normalized by L, fixed-bed length), τ is the space time, ϵ the bed porosity, t the current time, U the flowrate, and $\bar{q}^i$ (i = 1, 2, 3) are the average solute concentrations in the adsorbent particles defined as: $\bar{q}^1 = \epsilon_p c^1 + q^1$, $\bar{q}^i = \epsilon_p c^i$ (i = 2,3), where ϵ_p is the internal porosity of the particles.

The system of partial differential equations, Eqs. 3a–6 can be reduced to a system of two parabolic PDE's after elimination of c^2, $\bar{q}^i$(i = 1,2,3), i.e.,

TABLE I. EXPERIMENTAL CONDITIONS FOR REGENERATION OF A FIXED BED OF DUOLITE ES861 SATURATED WITH PHENOL

Run	Operation	$c_o^1 \times 10^4$ mol/L	c_e^1 mol/L	c_o^3 mol/L	c_e^3 mol/L	U mL/min	Pe*
1	Regeneration	9.7	0	10^{-8}	1.080	109.7	25.3
2	Regeneration	9.7	0	10^{-8}	1.035	56.6	35.7
	Washing	$\simeq 0$	0	1.035	10^{-8}	53.9	36.0
3	Regeneration	8.7	0	10^{-8}	0.0082	122.8	22.0
4	Regeneration	8.8	0	10^{-8}	1.07	17.4	70.0

* Calculated from tracer experiments, Part I (Costa and Rodrigues, 1985).

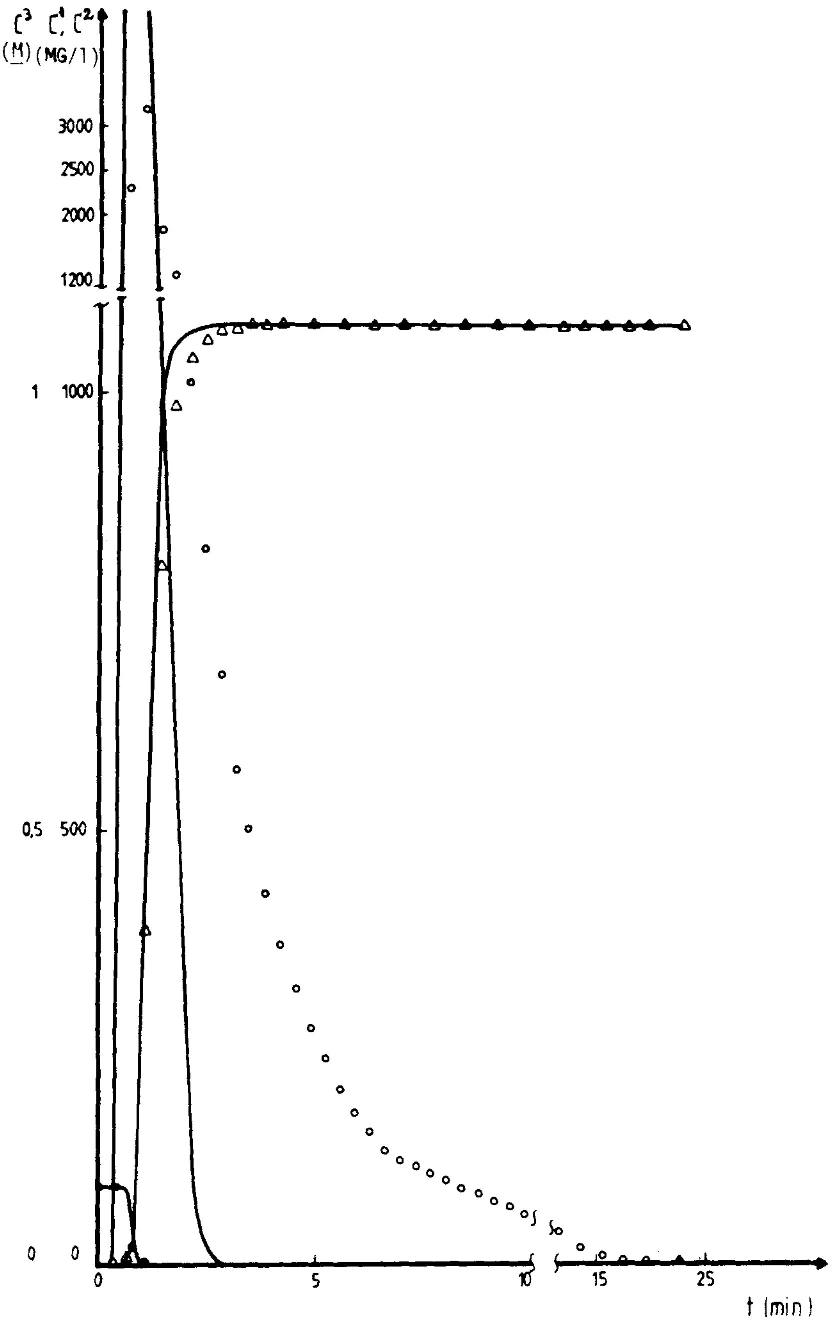

Figure 1. Regeneration of a saturated fixed bed, run 1. Experimental concentration histories for phenol (●), phenate (○), and hydroxide (△) species; simulation with the equilibrium model (—).

$$[B(1+A)+C]\frac{\partial c^1}{\partial t} = \frac{1}{Pe}(1+A)\frac{\partial^2 c^1}{\partial z^2} - (1+A)\frac{\partial c^1}{\partial z} + \frac{2A}{Pec^3}\frac{\partial c^1}{\partial z}\frac{\partial c^3}{\partial z} \qquad (7a)$$

$$\frac{\partial c^3}{\partial t} = \frac{1}{BPe}\frac{\partial^2 c^3}{\partial z^2} + \frac{A}{BPe}\frac{\partial^2 c^1}{\partial z^2} - \frac{1}{B}\frac{\partial c^3}{\partial z} - \frac{A}{B}\frac{\partial c^1}{\partial z} + \frac{2A}{BPec^3}\frac{\partial c^1}{\partial z}\frac{\partial c^3}{\partial z} - A\frac{\partial c^1}{\partial t} \qquad (7b)$$

where

$$A = \frac{K_{eq}c^3}{1+K_{eq}c^1}; \quad B = \tau\left(1 + \frac{1-\epsilon}{\epsilon}\right) \text{ and}$$
$$C = \tau\frac{1-\epsilon}{\epsilon}\frac{K_L Q \rho_a}{(1+K_L M 10^3 c^1)^2} \qquad (8)$$

This system of parabolic PDE's was integrated using the PDECOL package (Madsen and Sincovec, 1979) with ten equally spaced subintervals and third-order base functions (Costa and Rodrigues, 1985).

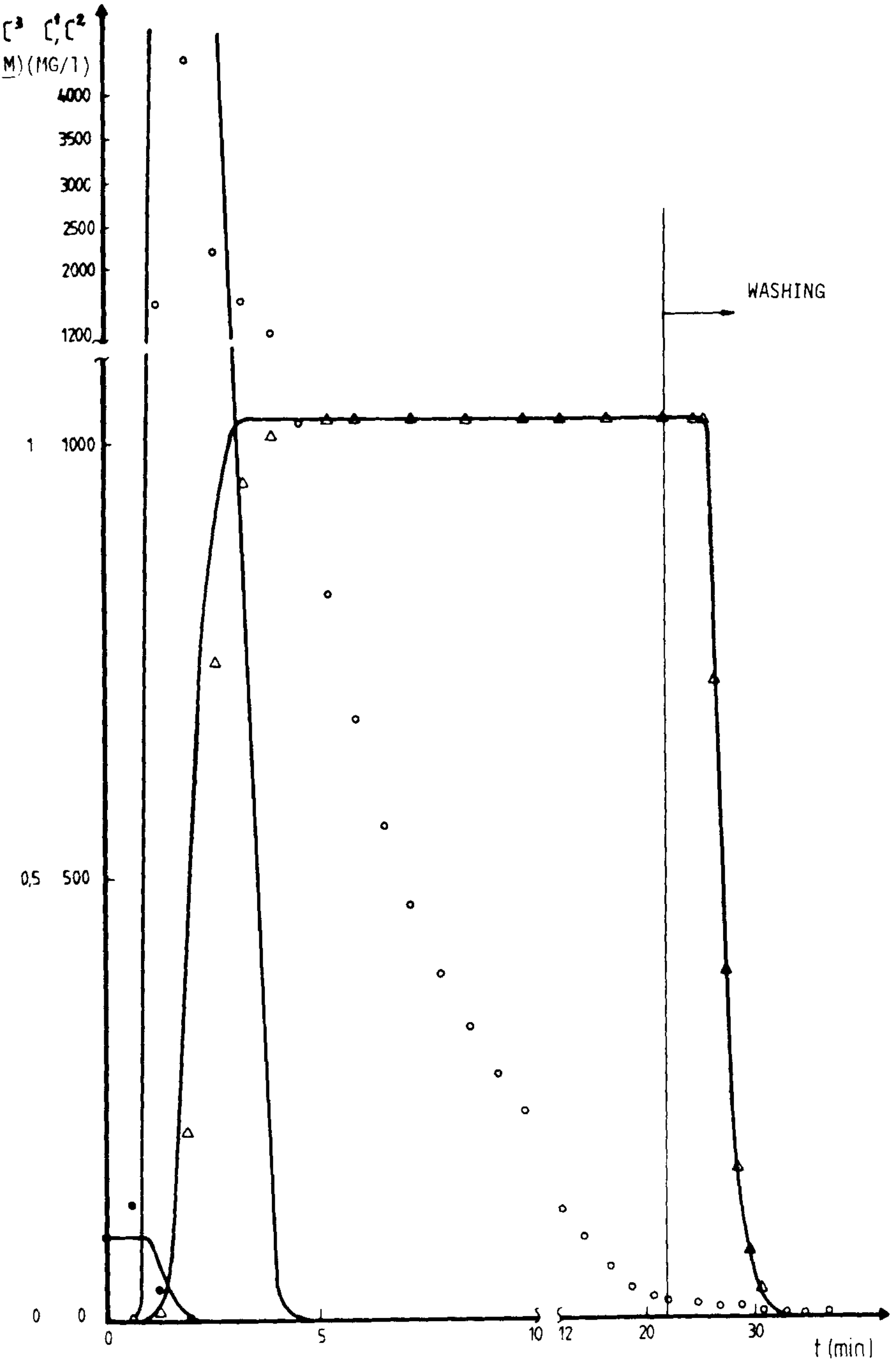

Figure 2. Regeneration of a saturated fixed bed, run 2. Experimental concentration histories for phenol (●), phenate (○), and hydroxide (△) species; simulation with the equilibrium model (—).

Comparison with Experimental Results

We carried out four runs in the equipment described in Part 1; the experimental conditions are summarized in Table 1 of the present paper.

Two operating parameters were changed: flowrate and input concentration of hydroxide species. Figures 1–4 show the comparison between results predicted by the equilibrium model and experimental response curves of the fixed bed for the various species in four separate runs.

Let us first analyze the results for runs 1, 2 and 4 where the flowrate has been changed. Here phenol output concentration is well described, whereas the predicted output phenate concentration shows higher and narrower peaks than the experimental ones; this was expected as the model does not account for intraparticle diffusion. The predicted curves for hydroxide species fit the experimental ones better for high flowrates. This behavior can be justified as we have an excess of this species and simultaneously an equilibrium model; for high flowrates experimental hydroxide

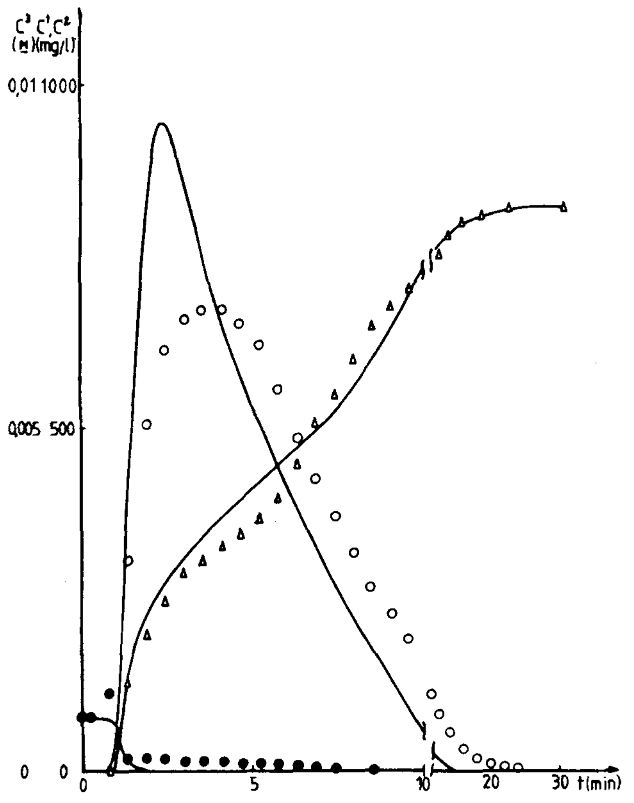

Figure 3. Regeneration of a saturated fixed bed, run 3. Experimental concentration histories for phenol (●), phenate (○) and hydroxide (△) species; simulation with the equilibrium model (—).

curves approach the response of a diffusional plug-flow fixed bed.

Run 3 (Figure 3) was performed using a low input concentration of hydroxide (≃0.01 M). As can be seen, the hydroxide concentration history presents a quasiplateau which is reasonably predicted by the model; as in the other cases, the phenate curve is poorly predicted from a quantitative point of view.

In run 2 (Figure 2) we stopped the regeneration before completion; then we started washing. This can be done in practice and is certainly of economic interest since regeneration continues without spending fresh regenerant.

An Improved Approach: The Reaction Front Model

In order to improve the predictive capability of the model let us consider a reaction front model for the adsorbent particle. The main assumptions of the model are:

1. The reaction between phenol and hydroxide is instantaneous and irreversible. This hypothesis should be true if there is an excess of hydroxide which leads to a negligible equilibrium phenol concentration. Also acid-base reactions are usually very fast.
2. Phenol is quiescent inside the particles; this is supported by the fact that in CSTR experiments there is no phenol in the outlet stream.
3. Hydroxide can diffuse inside the particles.
4. Film mass transfer resistance is negligible considering the calculated values for N_f in the saturation step (Part I).
5. Velocity of hydroxide species through the fixed bed is higher than that of phenol species.
6. Phenate produced in the bed porosity is negligible compared with that produced by reaction inside the particles (e.g., for $c_0^1 = 1.06 \times 10^{-3}$ mol/L that quantity is about 1.2% of the total phenate produced).

The model equations are then:

Conservation Equations for the Fluid Phase

Phenate (species 2)

$$\frac{1}{Pe}\frac{\partial^2 c^2}{\partial z^2} = \frac{\partial c^2}{\partial z} + \tau\left\{1 + \frac{1-\epsilon}{\epsilon}\epsilon_{\mathrm{p}}\left[1 - \left(\frac{R_f}{R_o}\right)^3\right]\right\}\frac{\partial c^2}{\partial t} + 3\epsilon_p\tau\frac{1-\epsilon}{\epsilon}D_p^3\frac{R_f^2}{R_o^3(R_o - R_f)}\left(\frac{\epsilon_p c^2}{q_o^1} - 1\right)\frac{\partial c_p^3}{\partial R^+}\bigg|_{R^+=0} \quad (9)$$

Hydroxide (species 3)

$$\frac{1}{Pe}\frac{\partial^2 c^3}{\partial z^2} = \frac{\partial c^3}{\partial z} + \frac{\partial c^3}{\partial t} + 3\epsilon_p\tau\frac{1-\epsilon}{\epsilon}D_p^3\frac{1}{R_o(R_o - R_f)}\frac{\partial c_p^3}{\partial R^+}\bigg|_{R^+=0} \quad (10)$$

Conservation Equation for the Adsorbent Particle

$$\frac{\partial c_p^3}{\partial t} = \frac{D_p^3}{R_o - R_f}\left[\frac{2}{R_f + R^+(R_o - R_f)}\frac{\partial c_p^3}{\partial R^+} + \frac{1}{R_o - R_f}\frac{\partial^2 c_p^3}{\partial R^{+2}}\right] \quad (11)$$

Mass Conservation for the Reaction Front

$$\frac{\partial R_f}{\partial t} = -\frac{\epsilon_p D_p^3}{R_o - R_f}\frac{1}{q_o^1}\frac{\partial c_p^3}{\partial R^+}\bigg|_{R^+=0} \quad (12)$$

Boundary Conditions

$$z = 0 \quad c^2 = c_e^2;\ c^3 = c_e^3 \quad (13a)$$

$$z = 1 \quad \frac{\partial c^2}{\partial z} = \frac{\partial c^3}{\partial z} = 0 \quad (13b)$$

$$R^+ = 0 \quad c_p^3 = 0 \left(\text{if } R_f = 0 \quad \text{then } \frac{\partial c_p^3}{\partial R^+} = 0\right) \quad (14a)$$

$$R^+ = 1 \quad c_p^3 = c^3 \quad (14b)$$

Initial Conditions

$$t = 0 \quad c^2 = c_o^2;\ c^3 = c_o^3 \quad (15a)$$

$$q_o^1 = \epsilon_p c_o^1 + \frac{K_L Q \rho_a c_o^1}{1 + K_L M 10^3 c_o^1} \quad (15b)$$

$$c_p^3 = c_o^3;\ R_f = R_o \quad (15c)$$

In the above equations $R^+ = (R - R_f)/(R_o - R_f)$ is a variable change made in order to transform the moving boundary into a fixed one, where R_o is the particle radius, R the radial coordinate, and R_f the radial position of the moving reaction front. Also in the above equations, c_p^3 is the hydroxide molar concentration inside the particles, and D_p^3 is the effective diffusivity in pores for hydroxide species.

We have then a system of four PDE's in two spatial dimensions in which the dependent variables are: $c^2 = C^2(z,t)$, $c^3 = c^3(z,t)$, $c_p^3 = c_p^3\,(R^+,z,t)$ and $R_f = R_f(z,t)$.

We used global collocation for discretization of the radial coordinate with $N = 6$ interior points (Costa and Rodrigues, 1985); for Eq. 11 we get,

$$\frac{\partial c_{pj}^3}{\partial t} = D_p^3\left[\frac{2}{(R - R_f)\{R_f + (R - R_f)R_j^+\}}\left(\sum_{i=1}^{N} A_{ji}c_{pi}^3 + A_{j,N+1}c^3\right) + \frac{1}{(R - R_f)^2}\left(\sum_{i=1}^{N} B_{ji}c_{pi}^3 + B_{j,N+1}c^3\right)\right] \quad j = 1, 2, \ldots, N \quad (16)$$

We also need to know the quantities

$$\frac{\partial c_p^3}{\partial R^+}\bigg|_{R^+=0} = \sum_{i=1}^{N} A_{oi}c_{pi}^3 + A_{o,N+1}c^3 \quad (17)$$

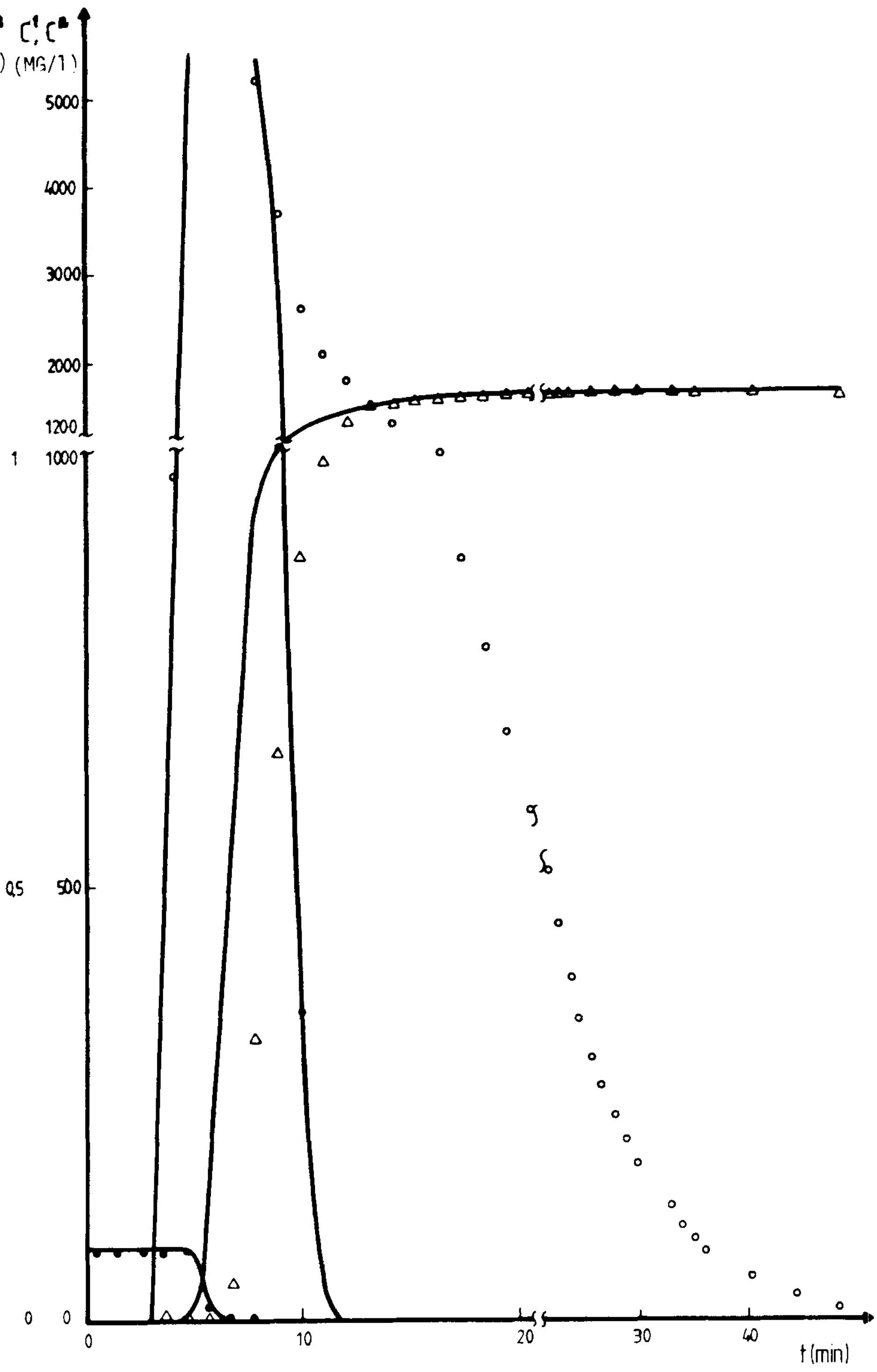

Figure 4. Regeneration of a saturated fixed bed, run 4. Experimental concentration histories for phenol (●), phenate (○) and hydroxide (△) species; simulation with the equilibrium model (—).

$$\frac{\partial c_p^3}{\partial R^+}\Big|_{R^+=1} = \sum_{i=1}^{N} A_{N+1,i}c_{pi}^3 + A_{N+1,N+1}c^3 \qquad (18)$$

where A and B are collocation matrices for first and second derivatives (Villadsen and Michelsen, 1978). We finally get a system of $N + 3$ partial differential equations in one spatial dimension which is integrated by using PDECOL (Madsen and Sincovec, 1979) with ten equally spaced subintervals and third-order interpolators for the axial coordinate (Part I).

The values of D_p^3 used in subsequent simulations were estimated in the CSTR experiments (Costa and Rodrigues, 1984); we got $D_p^3 = 5.7 \times 10^{-10}\,m^2s^{-1}$ and $D_p^3 = 1.1 \times 10^{-9}\,m^2s^{-1}$ for hydroxide feed concentrations around 1 and 0.01 mol/L, respectively.

Figures 5–8 show the comparison between predicted and ex-

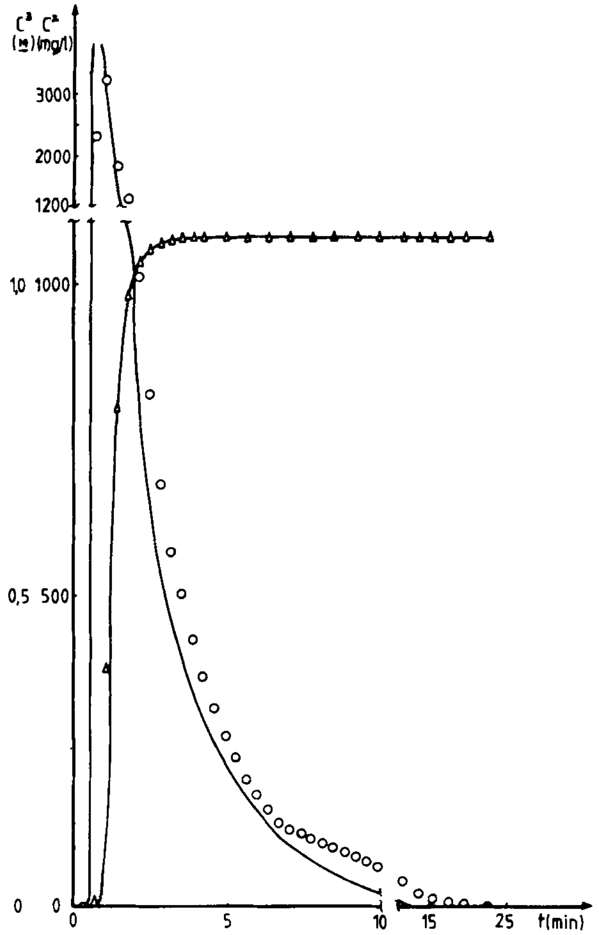

Figure 5. Simulation of run 1 (○ phenate; △ hydroxide) with the reaction front model (—).

perimental histories of concentration, i.e., fixed-bed outlet concentration for phenate and hydroxide species as a function of time.

A good agreement between experimental and model results is observed except for run 3. One should take into account that in this experiment hydroxide concentration is low ($\simeq 0.01$) and of the same order of magnitude as phenol concentration, e.g., there is no excess of hydroxide. Then the assumption of irreversible reaction can be questionable. As far as phenol is present in the bed, hydroxide is consumed, and indeed this species only leaves the bed when phenate concentration starts decreasing.

On the other hand, the reaction front model cannot predict with accuracy the phenate peak with regard to its height and time of appearance; this can probably be due to the assumption of no diffusional limitations for phenate species.

MODELING WASHING OF FIXED BED ADSORBERS

Modeling of the washing step was made on the basis of a plug-diffusional model for the hydrodynamics of the fluid phase and diffusion of hydroxide in the pores of the adsorbent. Model equations are:

Mass Balance for Hydroxide in the Fluid Phase

$$\frac{1}{Pe}\frac{\partial^2 x^3}{\partial z^2} = \frac{\partial x^3}{\partial z} + \frac{\partial x^3}{\partial \theta} + \frac{1-\epsilon}{\epsilon}\epsilon_p \frac{\partial \bar{x}_p^3}{\partial \theta} \tag{19}$$

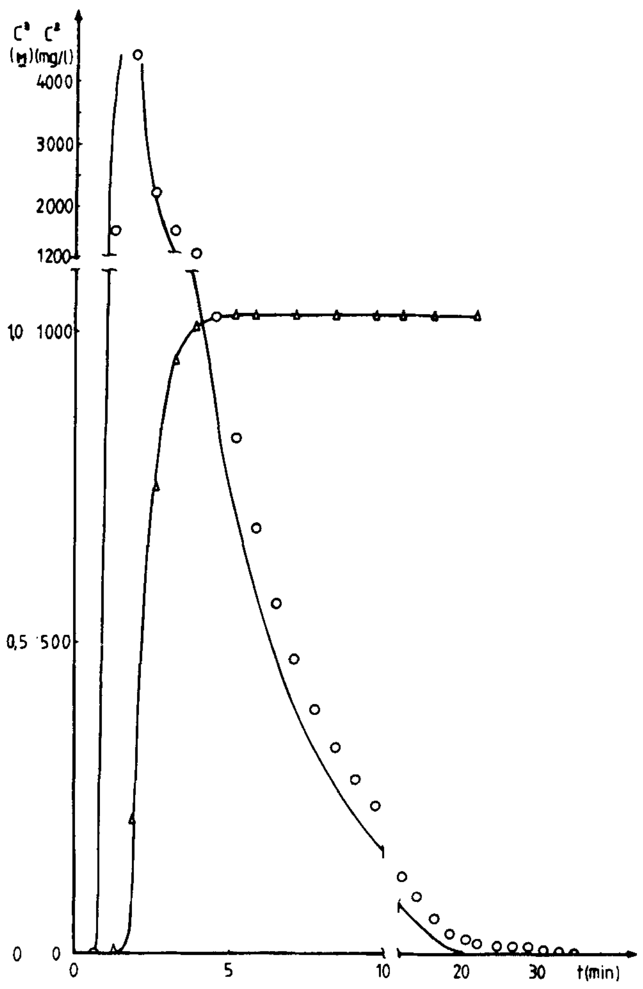

Figure 6. Simulation of run 2 (○ phenate; △ hydroxide) with the reaction front model (—).

Mass Balance for Hydroxide Inside the Particles

$$\frac{\partial x_p^3}{\partial \theta} = N_D\left(\frac{\partial^2 x_p^3}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial x_p^3}{\partial \rho}\right) \tag{20}$$

Average Concentration of Hydroxide in the Adsorbent

$$\frac{\partial \bar{x}_p^3}{\partial \theta} = 3N_D \left.\frac{\partial x_p^3}{\partial \rho}\right|_{\rho=1} \tag{21}$$

Boundary Conditions

$$z = 0 \quad x^3 = x_e^3 \tag{22a}$$

$$z = 1 \quad \frac{\partial x^3}{\partial z} = 0 \tag{22b}$$

$$\rho = 0 \quad \frac{\partial x_p^3}{\partial \rho} = 0 \tag{22c}$$

$$\rho = 1 \quad x_p^3 = x^3 \tag{22d}$$

Initial Conditions

$$\theta = 0 \quad x^3 = x_p^3 = 1 \tag{22e}$$

In the above equations x^3 and x_p^3 are reduced (by the initial hydroxide concentration) concentrations for hydroxide in interparticular and intraparticular fluid, respectively; $\theta = t/\tau$ is the time reduced by the space time; ρ is the reduced radial coordinate for

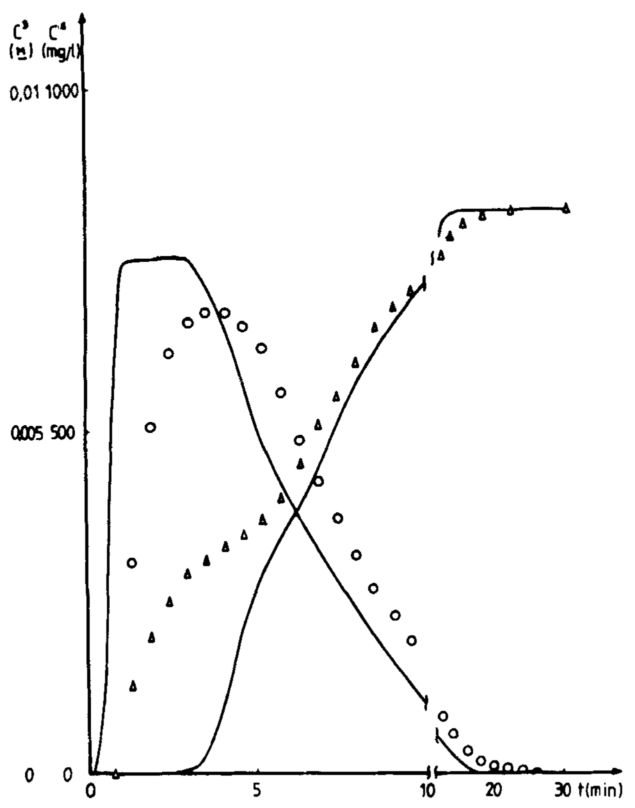

Figure 7. Simulation of run 3 (○ phenate; △ hydroxide) with the reaction front model (—).

the particle ($\rho = R/R_o$), and $N_D = D_p^3\tau/R_o^2$ is the number of pore diffusion units.

This linear system of PDE's can be solved using Laplace transform methods with numerical inversion. Alternatively we can use as before global collocation in N interior points for the particle equation leading to

$$\frac{\partial x_{pj}^3}{\partial \theta} = \sum_{i=1}^{N} C_{ji}x_{pi}^3 + C_{j,N+1}x^3 \qquad j = 1, 2, \ldots, N \tag{23}$$

with $C_{ji} = N_D(6A_{ji} + 4u_jB_{ji})$, where $u = \rho^2$. For this case we also used $N = 6$ and PDECOL for solving the remaining PDE's.

Two runs were carried out whose conditions are shown in Table 2. The model results are compared with experimental ones in Figure 9. We also plotted in that figure the model prediction if the hydroxide diffusion coefficient in the pores D_p^3 was considered to be infinite (equilibrium model).

CYCLIC OPERATION

Cyclic fixed-bed operations have been dealt with by a number of researchers. In ion-exchange processes saturation is stopped when the effluent concentration reaches a given value; then regeneration is carried out either in cocurrent or countercurrent flow and is also stopped at a given value on the basis of economic considerations. Both saturation and regeneration are not complete. The mentioned cycle is then repeated; cyclic steady state is established when the histories of concentration are identical from cycle to cycle. Usually four to six cycles are needed to reach the cyclic regime.

Simple methods have been developed for the design of cyclic ion-exchange processes (Dodds and Tondeur, 1972a,b, 1974); Klein (1981) presents an interesting review of such methods.

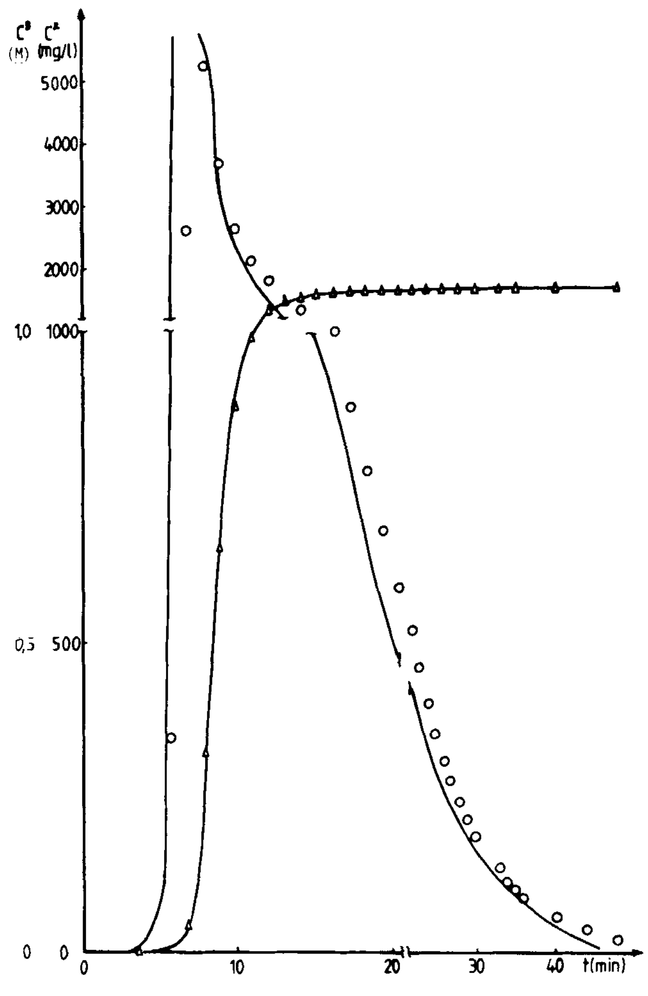

Figure 8. Simulation of run 4 (○ phenate; △ hydroxide) with the reaction front model (—).

Some authors worked out the prevision of cyclic regime with mathematical models. Using the Rosen model for gas adsorption Bunke and Gelbin (1975, 1978) and Gelbin and Bunke (1979) numerically studied the influence of various parameters. Results were recently presented (Gelbin et al., 1983) for the system n-heptane-hydrogene/zeolite NaX at 300°C.

In this work the cyclic operation of a fixed bed of polymeric adsorbent has three steps: saturation, regeneration and washing. Using the models developed for each step and using model parameters determined by independent experiments we were able to prepare a package for the calculation of cyclic fixed bed adsorbers. The capability of the model was tested by running a cyclic experiment whose conditions are summarized in Table 3.

TABLE 2. EXPERIMENTAL CONDITIONS USED IN FIXED-BED WASHING

Run	c_o^3 mol/L	c_e^3 mol/L	U mL/min	Pe*	N_D
1	0.0082	10^{-8}	122.7	22.7	0.487
2	1.07	10^{-8}	17.4	68.7	1.859

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* Calculated from tracer experiments, Part I (Costa and Rodrigues, 1985).

TABLE 3. EXPERIMENTAL CONDITIONS AND PARAMETERS USED IN CYCLIC OPERATION OF FIXED-BED ADSORBER

Cycle No.	Step	U mL/min	Breakpoint conc × 10^5 mol/L	Leakage %	N_f	N_D	Pe	ξ
1	Saturation	96.2	7.12 (phenol)	1.3	46.8	0.427	25.3	89.8
	Regeneration	96.8	8.62 (phenate)	—	—	0.314	25.3	—
	Washing	96.8	0	—	—	0.314	25.3	—
2	Saturation	98.3	8.19 (phenol)	1.6	45.8	0.418	25.0	89.8
	Regeneration	98.0	8.62 (phenate)	—	—	0.310	25.0	—
	Washing	100.0	0	—	—	0.304	24.7	—
3	Saturation	100.7	9.04 (phenol)	1.5	45.4	0.408	24.7	89.7
	Regeneration	98.0	8.62 (phenate)	—	—	0.310	25.0	—
	Washing	98.0	0	—	—	0.310	25.0	—
Avg. Conditions	Saturation	98.4	8.09 (phenol)	1.5	45.8	0.418	25.0	89.8
	Regeneration	97.4	8.62 (phenate)	—	—	0.312	25.0	—
	Washing	98.4	0	—	—	0.309	25.0	—

Fixed bed: Length L = 40 cm; diameter d = 2.18 cm; porosity ϵ = 0.536; particle diameter d_p = 0.06 cm.
Saturation $c_e^1 = 1.03 \times 10^{-3}$ mol/L; regeneration c_e^3 = 0.965 mol/L.
T = 20°C.

We started with a completely regenerated bed. The end of each step was set on a time basis: 36 min for saturation, 16 min for regeneration, and 6 min for washing. This criterion is more easily implemented than a criterion on a concentration basis. The final time for saturation was set in order to get an average outlet phenol concentration of the order of 2% of feed concentration. The breakpoint concentrations presented in Table 3 are defined as the outlet concentrations when a given step is stopped; they refer to phenol and phenate species at the ends of saturation and regeneration steps, respectively.

The leakage was defined as the ratio between the mass of phenol which leaves the bed during saturation and the mass of phenol introduced in the bed during the same time. We observe that the leakage increases smoothly from cycle to cycle due to the small increase in the flowrate. Experimental results and model predictions are shown in Figure 10. One can notice a good agreement between theory and experiments.

We should point out some details used in the algorithm for the cyclic regime.

Since saturation and regeneration are not complete, the initial condition for these steps is not that of a uniformly saturated or regenerated bed. We now have bed axial profiles as well as particle radial concentration profiles. We replaced the radial particle profiles by an average concentration calculated by Gaussian

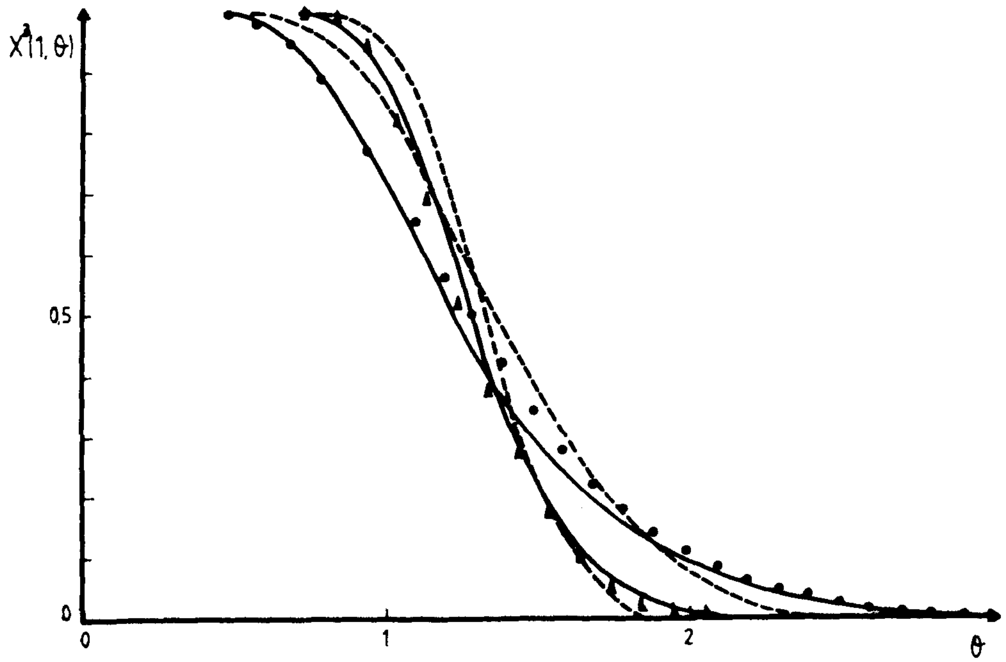

Figure 9. Washing of a regenerated fixed bed: experimental results (● run 1; ▲ run 2) and simulation with equilibrium (- - -) and pore diffusion (—) models.

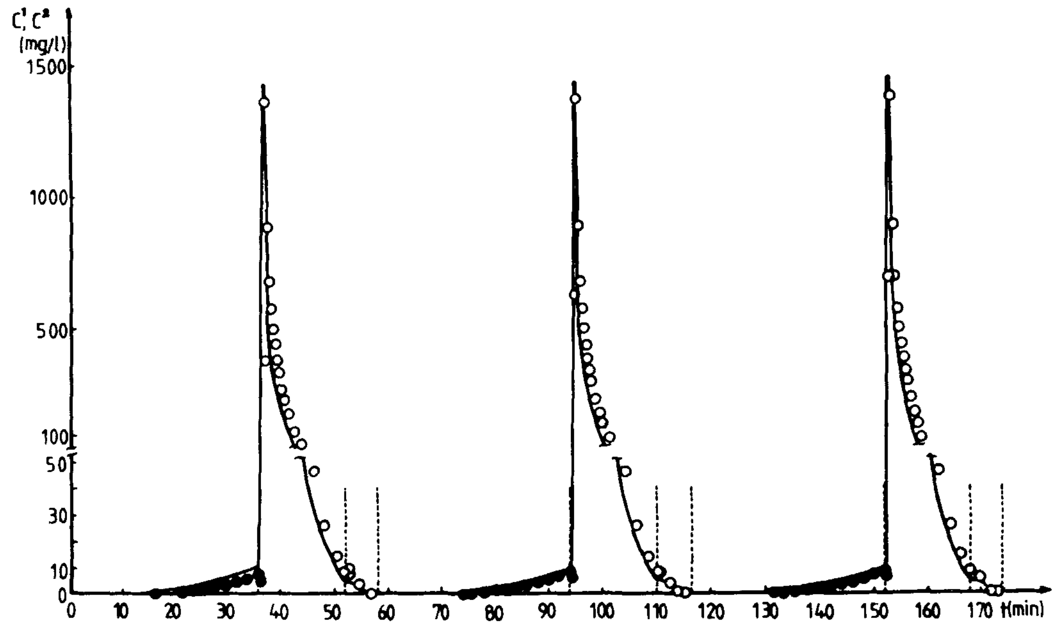

Figure 10. Cyclic operation: experimental and simulated results (● phenol; ○ phenate).

quadrature. As we used PDECOL with the same number of subintervals and the same interpolating functions for simulating all steps, axial profiles are known precisely in the points where they are needed as initial condition for simulating the next step.

When the washing step begins in cyclic operation, phenate is still present in the bed. To solve this problem we used the model described for washing but allowed also for phenate; e.g., we considered also a diffusional plug-flow model with intraparticle pore diffusion for this species. It should be noted that this model does not account for adsorption or reaction. In the simulations we used as effective pore diffusivity for phenate species the same value as determined for phenol (Costa and Rodrigues, 1983).

CONCLUSIONS

A reaction front model for regeneration with hydroxide was developed assuming instantaneous and irreversible reaction between phenol and hydroxide and allowing for hydroxide diffusion inside the adsorbent particles. This model quantitatively represents well the experimental results for high hydroxide concentration (1M). It should be noticed that this work can be extended to regeneration with methanol; in this case, as we have an extraction, the reaction equation is replaced by a distribution law.

Concerning the washing step, we concluded that a diffusional plug-flow model considering intraparticle diffusion of hydroxide represents well the washing of a fixed bed without phenols.

The package developed for the design of cyclic fixed-bed adsorption can be used for optimization of cyclic operation. The optimization procedure will be made over the operating time for each step as well as flowrates. One important point to be considered is the recycle of regeneration effluent as well as of the washing agent.

The robustness of the package has been tested and several options are available for the adsorbent particle model according to its structure. The methodology is being applied to other cyclic processes, namely parametric pumping and pressure swing adsorption.

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NOTATION

A = first derivatives matrix
B = second derivatives matrix
c^i = molar concentration of species i in fluid phase, mol·L^{-3}
c_T = total molar concentration, phenol + phenate, mol·L^{-3}
D_p^3 = effective pore diffusivity for hydroxide species, L^2·T^{-1}
d = fixed bed diameter, L
d_p = particle diameter, L
K_{eq} = acid-base reaction equilibrium constant, L^3·mol^{-1}
K_L = parameter of the adsorption isotherm, L^3·M^{-1}
L = fixed bed length, L
M = molecular weight of phenol, M
N = number of interior collocation points
N_D = number of intraparticle mass transfer units
N_f = number of film mass transfer units
Pe = Peclet number
Q = parameter of the adsorption isotherm, M·M^{-1} (dry resin)
q^1 = molar phenol concentration in the solid phase, mol·L^{-3}
$\bar{q}^i$ = average molar concentration of species i in the solid phase, mol·L^{-3}
R = particle radial coordinate, L
R^+ = modified radial coordinate
R_f = reaction front radial position, L
R_o = particle radius, L
T = temperature, °C
t = time, T

U = volumetric flow rate, $L^3 \cdot T^{-1}$
u = modified radial coordinate
x^3 = normalized hydroxide concentration in fluid phase
$\bar{x}_p^3$ = average normalized hydroxide concentration in the particles
z = normalized axial coordinate

Greek Letters

ϵ = fixed bed external porosity
ϵ_p = particle internal porosity
ξ = capacitance parameter
ρ = normalized radial coordinate
ρ_a = apparent density, M (dry resin)$\cdot L^{-3}$
τ = space time, T
θ = normalized time

Superscripts

$i = 1$ = phenol species
$i = 2$ = phenate species
$i = 3$ = hydroxide species

Subscripts

e = input
p = pore
o = initial

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