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NUMERICAL AND SEMI-ANALYTICAL SOLUTION FOR ACTIVATED CARBON COLUMN WITH NONLINEAR BOUNDARY CONDITION*

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ABSTRACT

Carbon adsorption processes are widely used in environmental remediation for removal of organics. The governing equations describing the chemical concentration profile in a fixed bed carbon column system and their analytical and numerical solutions are established if the boundary conditions are linear. However, solution is far more difficult of these governing equations with even one nonlinear boundary condition, which arises from the equilibrium condition between the concentration in the bulk liquid and at the carbon surface. This article investigates a numerical method and a semi-analytical method using orthogonal collocation techniques for the solution of the activated carbon model with nonlinear boundary condition. The proposed approaches use a simple linear iterative method with the Runge-Kutta method to obtain numerical and semi-analytical solution of the activated carbon column model. The close agreement between the experimental data and the solutions given by the two methods suggests that either of the two new approaches would be an acceptable solution technique. However, the semi-analytical solution is considered to be more precise and needs fewer assumptions.

INTRODUCTION

The process of adsorption on granular activated carbon has been widely used to separate inorganic and organic contaminants from water and wastewater. Design

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of full scale activated carbon systems usually has been based on information obtained from pilot plant tests. A key problem in the design of fixed bed adsorbers is the prediction of how the effluent concentration will change with time, in other words, what will be the shape of the "breakthrough curve" of the effluent. Development of mathematical models describing the process can help improve the design of full scale systems and reduce the number of pilot scale tests, resulting in considerable saving of time and money. For adsorption on a single carbon particle, the homogeneous surface diffusion model (HSDM) has been used successfully to describe the dynamics of the adsorption process for various inorganic and organic compounds. The HSDM model seems particularly suitable for simulating adsorption processes on granular activated carbon in a batch reactor.

Several models have been developed and solved for packed column bed reactors which have linear boundary and initial conditions. However, for the activated carbon system, the equilibrium condition between the concentration in the bulk liquid and at the carbon surface is often observed to be a nonlinear equation. Little information is available on methods to solve the governing equations for an adsorption process with nonlinear boundary conditions.

The purpose of this study is to derive and develop a numerical and a semi-analytical approach for solving the nonlinear adsorption model for a packed bed carbon adsorption column.

BACKGROUND

For flow through a packed bed reactor, the equations describing mass and heat transfer have been widely applied in chemical engineering. The government equations describing the chemical concentration in a fixed bed system were given by Deisler and Wilhelm [1]:

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial z^2} - V_z \frac{\partial C}{\partial z} - \frac{\varepsilon}{1-\varepsilon} \frac{\partial \bar{q}}{\partial t} \tag{1}$$

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) \tag{2}$$

where,

C = solute concentration in bulk fluid, ML^{-3},
t = physical time, T,
D_L = column dispersion coefficient, L^2T^{-1},
z = distance in flow direction, L,
V_z = average pore velocity, LT^{-1},
ε = bed porosity,
$\bar{q}$ = volume averaged solute concentration in particles, MM^{-1},
$q(r,z,t)$ = internal concentration in particles, MM^1,

D_s = diffusivity within particle, L^2T^{-1}, and
r = radial distance from center of spherical particle, L.

Part of the initial and boundary conditions are:

$$C(0,t) = C_0 \tag{3}$$

$$C(\infty,t) = 0 \tag{4}$$

$$C(z,0) = 0 \tag{5}$$

$$q_s = KC_s \tag{6}$$

Where q_s is the surface concentration (MM^{-1}) and is the same as q(r,z,t) for r = $d_p/2$, C_s is the bulk fluid concentration (ML^{-3}) at the surface, K is a constant, and d_p is the particle diameter.

Equating the rate of change of the volume-averaged solute concentration $\bar{q}$ with the mass transfer rate through the film leads to:

$$\frac{\partial \bar{q}}{\partial t} = \frac{3K_f}{d_p/2}\left(C - \frac{q_3}{K}\right) \tag{7}$$

Analytical solution of equations (1) and (2) depends on the boundary condition shown in equation (7), which is the linking equation between equations (1) and (2). It is possible to solve the equations when q_s is a linear function of C_s, but the more general nonlinear boundary condition $q_s = KC_s^n$ is much more difficult to solve. By definition the average activated carbon load, $\bar{q}$, in the particles is given by:

$$\bar{q}(z,t) = \frac{3}{(d_p/2)^3}\int_0^{d_p/2} q(r,z,t)r^2 dr \tag{8}$$

Rosen derived q(r,z,t) in terms of the surface concentration $q_s(z,t)$ by applying Duhamel's theorem and showed [2]:

$$q(r,z,t) = 2D_s \sum_{n=1}^{\infty}\left[(-1)^{n+1}\sigma_n \frac{\sin(\sigma r)}{r}\int_0^t q_s(z,\lambda)\exp\left[-D_s\sigma_n(t-\lambda)\right]d\lambda\right] \tag{9}$$

where,

$$\sigma_n = 2n\pi/d_p^2.$$

Rasmuson and Neretnieks substituted equation (9) into (8), took the derivative of $\bar{q}$ with respect to time, and introduced the expression for $\partial\bar{q}/\partial t$ into equation (1) [3]. They also substituted equation (7) into equation (1). Then, the Laplace transform with respect to time was taken for the two substituted equations and variable $q_s(z,s)$ was eliminated. The inverse Laplace transform was taken and

finally partial differential equations describing the packed column reactors with a linear boundary condition were solved. The result is:

$$\frac{c(z,t)}{c_o} = \frac{1}{2} + \frac{2}{\pi}\int_0^\infty \exp\left(\frac{v_z}{2D_L} - z\,\frac{\sqrt{\sqrt{x'(\lambda)^2 + y'(\lambda)^2} - x'(\lambda)}}{2}\right) * \sin\left(\sigma\lambda^2 t - z\,\frac{\sqrt{\sqrt{x'(\lambda)^2 + y'(\lambda)^2} - x'(\lambda)}}{2}\right) d\lambda, \tag{10}$$

with,

$$x'(\lambda) = \frac{v_z^2}{4D_L^2} + \frac{\gamma}{mD_L} H_1,$$

$$y'(\lambda) = \frac{\sigma\lambda^2}{D_L} + \frac{\gamma}{mD_L} H_2,$$

$$H_1(\lambda,\nu) = \frac{H_{D_1} + \nu(H_{D_1}^2 + H_{D_2}^2)}{(1 + \nu H_{D_1})^2 + (\nu H_{D_2})^2},$$

$$H_2(\lambda,\nu) = \frac{H_{D_2}}{(1 + \nu H_{D_1})^2 + (\nu H_{D_2})^2},$$

$$H_{D_1}(\lambda) = \lambda\left(\frac{\sinh 2\lambda + \sin 2\lambda}{\cosh 2\lambda - \cos 2\lambda}\right) - 1,$$

$$H_{D_2}(\lambda) = \lambda\left(\frac{\sinh 2\lambda + \sin 2\lambda}{\cosh 2\lambda - \cos 2\lambda}\right),$$

$$\gamma = \frac{12 D_s K}{d_p^2},$$

$$\nu = \gamma R_f,$$

$$R_f = \frac{d_p}{6K_f},$$

$$\sigma = \frac{8D_s}{d_p^2},$$

$$m = \frac{\varepsilon}{1 - \varepsilon}, \text{ and}$$

λ = variable of integration.

Raghavan and Ruthven applied the orthogonal collocation method to solve the same problem with linear boundary conditions which Rasmuson and Neretnieks solved analytically [4]. They reported close agreement between results from the numerical and analytical methods. Accordingly, the orthogonal collocation method is suitable to solve the equations describing the packed column bed reaction process.

Kim, et al. described the models for the dichloramine-activated carbon reaction [5]; these consist of a pore model that is a nonlinear partial differential equation, a batch reactor model, and a model for the reaction in the packed bed. However, the equations they used for boundary conditions are all linear. They used the orthogonal collocation method to convert partial differential equations to ordinary differential equations and the predictor-corrector method was used to solve them. The quasi-linearization technique was used to determine the necessary constants from batch reactor data. Their method did not involve any nonlinear boundary conditions.

In this article we propose to solve the activated carbon packed bed model with the nonlinear equilibrium condition ($q_s = KC_s^n$) using a different numerical technique and compare the results with those obtained by a semi-analytical method we propose to develop. For the numerical solution the two linear partial differential governing equations (1) and (2) can be converted to a system of ordinary differential equations by using the orthogonal collocation method. The system of ordinary differential equations is then solved by the Runge-Kutta method with other linear or nonlinear equations from the boundary conditions. For the semi-analytical solution, the convective-dispersive equation for the column bed reaction can be solved using an analytical approach, the partial differential diffusion equations can be converted to ordinary differential equations which can be solved by using Runge-Kutta method and nonlinear boundary condition will link the analytical and numerical approaches. Due to the nonlinear equation from the boundary condition, the solution must be iterative at each time interval. We consider the case of the finite length reactor in contrast to the semi-infinite length reactor assumed by many previous investigators.

EQUATION DEVELOPMENT

For activated carbon packed bed column reactors, if we consider diffusion within a particle, and convection and dispersion between particles, then the process is also represented by equations (1) and (2). The boundary and initial conditions are:

$$\left(-D_L \frac{\partial C}{\partial z} + V_z C\right)_{z=0} = V_z C \tag{11}$$

$$\left.\frac{\partial C}{\partial z}\right|_{z=L} = 0 \tag{12}$$

$$C = 0 \quad at\ t = 0, \quad 0 < z < L \tag{13}$$

The boundary condition at the center of the carbon particle is:

$$\left.\frac{\partial q(r,z,t)}{\partial r}\right|_{r=0} = 0 \tag{14}$$

Since the continuity of flux at the solid-liquid interface has to be satisfied, we have:

$$D_s \rho_p \left.\frac{\partial q}{\partial r}\right|_{r=d_p/2} = K_f(C - C_s) \tag{15}$$

where ρ_p is apparent particle density, ML^{-3}, and K_f is a kinetic parameter which represents the liquid film mass transfer coefficient, LT^{-1}.

The instantaneous equilibrium between liquid and solid phase concentrations at the solid-liquid interface is usually expressed by:

$$q_s = KC_s^n \tag{16}$$

where K and n are the Freundlich isotherm parameters. Also:

$$q(r,0) = 0 \tag{17}$$

In order to simplify these equations, five groups of dimensionless parameters are defined below:

$$C^* = \frac{C}{C_o}, \quad q^* = \frac{q}{q_o}, \quad T = \frac{4D_s t}{d_p^2}, \quad R = \frac{2r}{d_p}, \quad \xi = \frac{z}{L_b}$$

where q_o is in equilibrium with C_o, and L_b is the column length. After applying these dimensionless parameters, equations (1) and (2) can be rewritten in non-dimensional form as:

$$\frac{\partial C^*}{\partial t} = \frac{D_L}{L_b^2}\frac{\partial^2 C^*}{\partial \xi^2} - \frac{V_z}{L_b}\frac{\partial C^*}{\partial \xi} - \rho_p \frac{1-\varepsilon}{\varepsilon}\frac{q_0}{C_0}\frac{\partial \bar{q}^*}{\partial t} \tag{18}$$

$$\frac{\partial q^*}{\partial T} = \frac{1}{R^2}\frac{\partial}{\partial R}\left[R^2 \frac{\partial q^*}{\partial R}\right] \tag{19}$$

equations (8), (11), (12), (14), (15), and (16), can be reduced to:

$$\bar{q}^* = 3\int_0^1 q^*(R,\xi,T)R^2 dR \tag{20}$$

$$\frac{D_L}{L_b V_z}\frac{\partial c*}{\partial \xi}\Big|_{\xi=0.0} = (C_0^* - C*) \tag{21}$$

$$\frac{\partial C^*}{\partial \xi}\Big|_{\xi=1.0} = 0.0 \tag{22}$$

$$\frac{\partial q*}{\partial R}\Big|_{R=0} = 0 \tag{23}$$

$$\frac{\rho_p D_s}{d_p/2}\frac{q_o}{C_o}\frac{\partial q*(R,\xi,T)}{\partial R}\Big|_{R=1.0} = K_f(C* - C_s^*) \tag{24}$$

$$q_s^* = C_s^{*n} \tag{25}$$

Then equation (25) is substituted into equation (24) to obtain:

$$\frac{\partial q*(R,\xi,T)}{\partial R}\Big|_{R=1.0} = B_{io}\left(C^* - q_s^{*n}\right) \tag{26}$$

where B_{io} is the Biot number defined as

$$B_{io} = \frac{k_f C_o (d_p/2)}{\rho_p D_s q_o}.$$

Both sides of equation (18) are multiplied by $(4D_s)/d_p^2$ and become:

$$\frac{\partial C^*}{\partial T} = \alpha\frac{\partial^2 C^*}{\partial \xi^2} - \beta\frac{\partial C^*}{\partial \xi} - \gamma\frac{\partial \bar{q}*}{\partial T} \tag{27}$$

where,

$$\alpha = \frac{d_{p_2} D_z}{4L_b s D_s}, \qquad \beta = \frac{d_p^2 V_z}{4L_b D_s}, \qquad \gamma = \rho_p\frac{1-\varepsilon}{\varepsilon}\frac{q_0}{C_0}$$

NUMERICAL SOLUTION

The set of equations from (19) to (27) defines a nonlinear boundary value problem involving diffusion within a particle and convection-dispersion in a packed column bed.

For the sake of convenience, we take the direction of velocity in the column as opposite to that of the z coordinate. Using that convention, the equations (27), (21), and (22) can be rewritten as:

$$\frac{\partial C^*}{\partial T} = \alpha\frac{\partial^2 C^*}{\partial \xi^2} + \beta\frac{\partial C^*}{\partial \xi} - \gamma\frac{\partial \bar{q}*}{\partial T} \tag{28}$$

$$\frac{D_L}{L_b V_z}\frac{\partial C^*}{\partial \xi}\Big|_{\xi=1.0} = (C_0^* - C^*) \tag{21a}$$

$$\frac{\partial C^*}{\partial \xi}\Big|_{\xi=0.0} = 0.0 \tag{22a}$$

By taking M collocation points along the bed (see Figure 1) in equation (28) and N collocation points along the particle radius in equation (19), one can write a system of ordinary differential equations [6]. The details are presented in the Appendix.

$$\frac{dC_i^*}{dT} = \left(\alpha \sum_{j=1}^{M} B_{ij} + \beta \sum_{j=1}^{M} A_{ij} - Z_2\left(\alpha B_{i,m+1} + \beta A_{i,m+1}\right) \sum_{j=1}^{M} A_{m+1,j}\right) C_j^*$$
$$+ Z_1\left(\alpha B_{i,m+1} + \beta A_{i,m+1}\right) - 3\gamma \left[\sum_{j=1}^{N+1} W_j \frac{\partial q_{ij}^*}{\partial t} + W_{N+1}\frac{\partial q_{si}^*}{\partial t}\right] \tag{29}$$

$$\frac{dq_{Li}^*}{dT} = \sum_{j=1}^{N+1} B_{Lj} q_j^* \tag{30}$$

$$\sum_{j=1}^{N+1} A_{n+1,j} q_{ij}^* = B_{oi}\left(C_i^* - q_{si}^{*\frac{1}{n}}\right) \tag{31}$$

Equations (29), (30), and (31) can be integrated numerically and solved simultaneously by suing techniques such as the Runge-Kutta method, the Euler method, or the predictor corrector method. In this article, the Runge-Kutta method is employed. Because equation (31) is nonlinear, a linear iterative method will be used to solve these equations. The calculation starts from initial time with time step H which can be specified beforehand. In every time interval, the following steps and calculations would be involved:

Step 1 = Assume q_{si}^*.
Step 2 = Calculate $q^*_{1i}, q^*_{2i}, \ldots, q^*_{Ni}$ from equation (30).
Step 3 = Substitute the values of $q^*_{1i}, q^*_{2i}, \ldots, q^*_{Ni}, q_{si}^*$ into equation (29), and obtain C^*_i.
Step 4 = Substitute the values of $q^*_{1i}, q^*_{2i}, \ldots, q^*_{NI}, q_{si}^*$ into equation (31) and obtain C^*_i.
Step 5 = Compare C^*_i obtained from equation (29) with those from equation (31), if the sum of square of difference between the two sets of C^*_i is less than the criterion, then stop; otherwise, calculate the new values of q^*_{si} from two sets of values of C^*_i and return to step 2 to iterate until the true values are obtained.

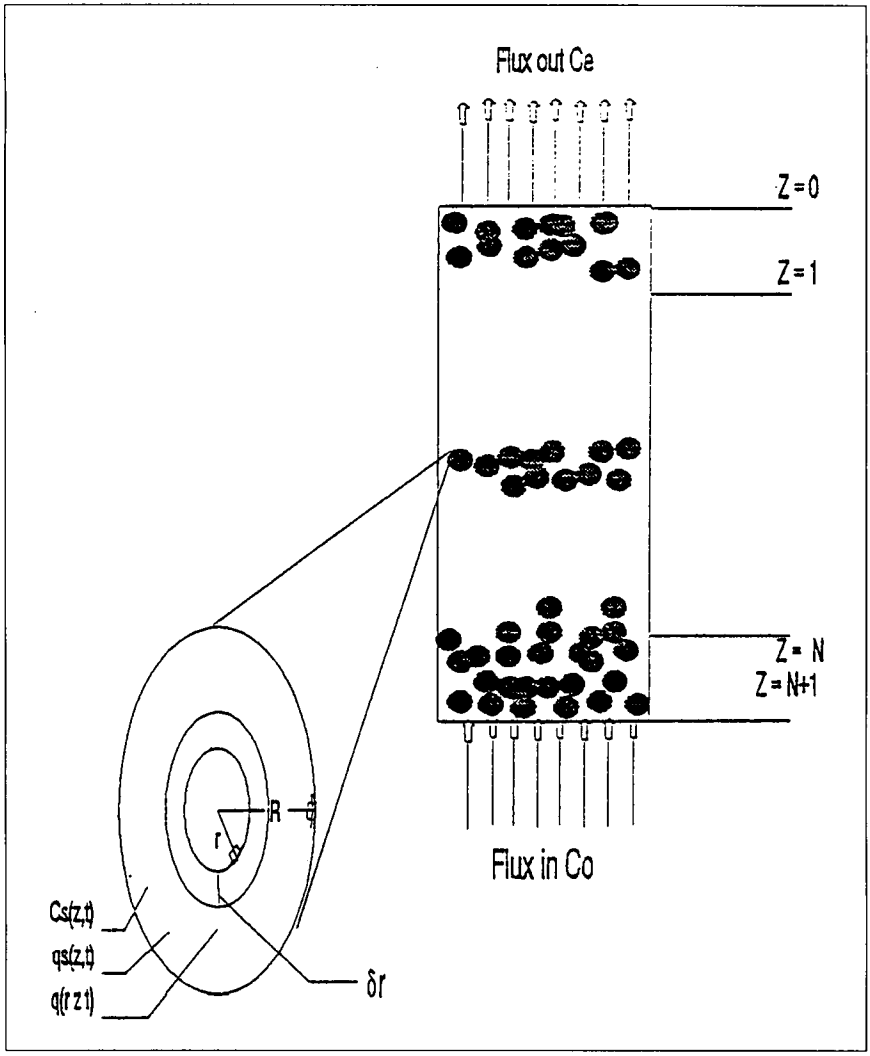

Figure 1. Collocation points in a packed bed.

Step 6 = Calculate effluent concentration at $\xi = 0$, which is of major interest, by determining the coefficient d_i [7].

$$\overline{d} = \overline{Q}^{-1}\overline{C}* \tag{32}$$

where,

$$\bar{d} = \left[d_1, d_2, \ldots, d_{m+1}\right]^T, \quad \bar{C}* = \left[C_1^*, C_2^*, \ldots, C_{m+1}^*\right]^T$$

$$\bar{Q} = \sum_{j=1}^{m+1} \xi_j^{2i-2} \tag{33}$$

$$C_0^* = d_1 = \sum_{i=1}^{m+1} [Q^{-1}]_{1i} C_i^* \tag{34}$$

SEMI-ANALYTICAL METHOD

A new approach using a semi-analytical method to solve the model is proposed in this research. The semi-analytical approach consists of an analytical method for the convection-dispersion equation (equation (27)) in the column bed and a numerical method for the diffusion equation in the particle (equation (19)). For the packed bed column, convection-dispersion equation (27) with the boundary conditions (21) and (22) was solved by van Genuchten, who reported [8]:

$$C^*(z,t) = C_0 A(z,t) + B(z,t) \tag{35}$$

where,

$$A(z,t) = 0.5\,\mathrm{erfc}(g_1) + g_2 \exp(-g_1^2) - 0.5\, g_3\, \mathrm{erfc}(g_4), \text{ and}$$

$$B(z,t) = -\gamma \frac{\partial \bar{q}^*}{\partial t}\left[t + g_5 erfc(g_1) - g_6 \exp(-g_1^2) + g_7 erfc(g_4)\right]$$

where,

$$g_1 = \frac{(z - vt)}{2(D_L t)^{1/2}}$$

$$g_2 = \left(\frac{v^2 t}{\pi D_L}\right)^{1/2}$$

$$g_3 = \left(1 + \frac{vz}{D_L} + \frac{v^2 t}{D_L}\right) \exp\left(\frac{vz}{D_L}\right)$$

$$g_4 = \frac{z + vt}{2(D_L t)^{1/2}}$$

$$g_5 = \frac{1}{2v}\left(z - vt + \frac{D_L}{v}\right)$$

$$g_6 = \left(\frac{t}{4}\pi D_L\right)^{1/2}\left(z + vt + \frac{2D_L}{v}\right)$$

$$g_7 = \left[\frac{t}{2} - \frac{D_L}{2v^2} + \frac{(z - vt)^2}{4D_L} \right] \exp\left(\frac{vz}{D_L} \right)$$

The term $\partial\bar{q}^*/\partial t$ is a function of $q^*_1(t)$, $q^*_2(t)$, . . . , $q^*_s(t)$, which can be obtained from activated carbon diffusion equation (19) with the boundary conditions (24) and (25). Equation (19) can be converted to ordinary differential equations by using the orthogonal collocation method, for N collocation points:

$$\frac{dq_i^*}{dt} = \sum_{j=1}^{N+1} B_{ij} q_j^* \qquad i = 1, 2, 3, \ldots, N \tag{36}$$

The boundary condition (26) can be written as

$$\sum_{j=1}^{N+1} A_{N+1,j}\, q_j^* = B_{oi}(C^* - q_s^{*\frac{1}{n}}) . \tag{37}$$

Equation (20) becomes

$$\bar{q}^* = 3(w_1 q_1^* + w_2 q_2^* + \ldots + w_{N+1} q_s^*) . \tag{38}$$

Taking the derivative of equation (38) with respect to time,

$$\frac{\partial\bar{q}^*}{\partial t} = 3\left(w_1 \frac{dq_1^*}{dt} + w_2 \frac{dq_2^*}{dt} + \ldots + w_{N+1} \frac{dq_s^*}{dt} \right) . \tag{39}$$

The procedures for calculating concentration C* is as follows:

Step 1 = Assume q_s^*.

Step 2 = Using Runge-Kutta method, solve equation (36) and get q_1^*, q_2^*, . . . , q_N^*.

Step 3 = Substitute q_1^*, q_2^*, . . . , q_N^* and q_s^* into equation (37) and obtain concentration C*.

Step 4 = Substitute equation (36), that is dq_1^*/dt, dq_2^*/dt, . . . , dq_N^*/dt dq_s^*/dt, into equation (39) to calculate $\partial\bar{q}^*/\partial t$ and substitute $(\gamma\partial\bar{q}^*/\partial t)$ into equation (35) to obtain concentration C*.

Step 5 = Compare C* obtained from equation (37) with that from equation (35). If the difference between the two values of C* is less than the criterion, then stop; otherwise calculate the new value of q_s^* from two values of C* and return to step 2 to iterate until the true value is obtained.

CALIBRATION OF THE NUMERICAL AND SEMI-ANALYTICAL SOLUTIONS

The packed bed activated carbon adsorption model was solved using the numerical technique and the semi-analytic method developed in this study. The model was calibrated using experimental data. The packed bed column experiment was conducted by Boudreau [9]. In this experiment, 459 grams (1000 ml) of 4 x 12 mesh Darci lignite granular activated carbon was placed in a 2-inch diameter x 36-inch long glass column. A synthetic waste having the same characteristics of an agricultural waste produced by a multinational chemical industry was used in this research. This aqueous waste was diluted to obtain a 2000 ppm initial total organic carbon (TOC) and was passed through the column at a rate of about 2.8 ml/min. The total volume of the effluent was monitored every hour and the TOC of the samples was analyzed by a TOC analyzer.

The values of the film and surface diffusion coefficients for this waste were reported earlier by us [10]. These coefficients and other experimental parameters for this column adsorption study are presented in Table 1.

The breakthrough curve for the above experiment was predicted by solving the activated carbon packed bed model using the numerical technique and the semi-analytic method described above. The predicted breakthrough curves and the experimental data are presented in Figure 2. The close agreement in the predicted and experimental data supports the accuracy of the techniques.

Table 1. Values of Constants and Parameters

Parameter	Value
D_s	$2.376*10^{-7}$ cm^2/sec
K_f	$6.563*10^{-5}$ cm/sec
K	$8.85*10^{-5}$
n	0.63993
D_z	0.20–0.8 cm^2/sec
Vz	0.1644–0.5482 cm/sec
L_b	49.338 cm
ρ_p	459000 mg/l
C_0	2000.0 mg/l
ε	0.5
d_p	0.26 cm

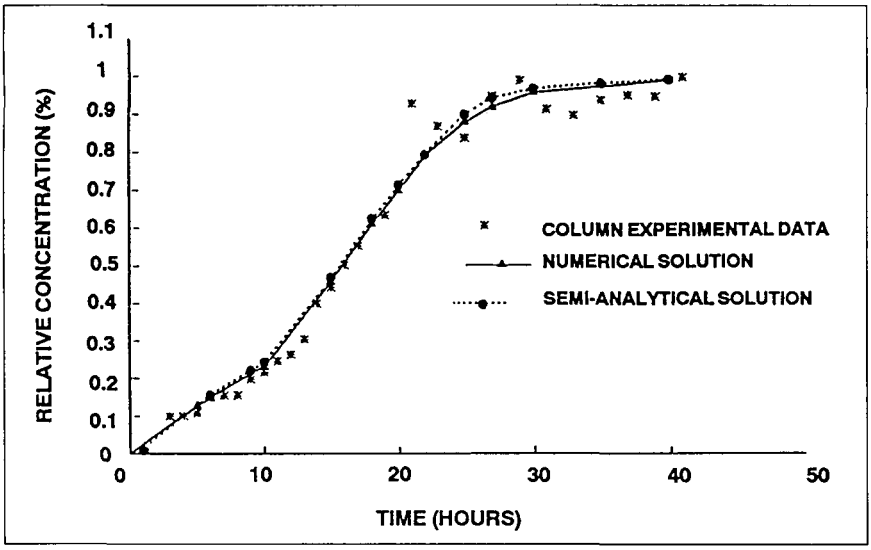

Figure 2. Comparison of results from numerical and semi-analytical solution with column experimental data.

DISCUSSION AND CONCLUSIONS

In this study, the partial differential equations were converted to ordinary differential equations using the orthogonal collocation method. Then the Runge-Kutta method and an iteration procedure were employed to solve the ordinary differential equations.

Because equation (31) is nonlinear, q_{si}^* cannot be expressed in terms of q_{ij}^* and C^*. As a result, one cannot eliminate the unknown values of q_{si}^*, so the routine method would make the calculation complex and tedious.

By assuming the values of q_{si}^*, the nonlinear algebraic equations are reduced to linear equations which can be solved very easily and they converge quickly. For numerical solution, q_s^* needs to be assumed at a number of points along the carbon bed and the accuracy of the solution increases with an increase of the value of N. However, for the semi-analytical approach, only one q_s^* needs to be assumed at the outlet point at any time, that is q_s^* at $z = L_b$ and $t = t$.

The semi-analytical approach can be used to obtain the values of any points in the z-direction and at any time. The approach utilized Runge-Kutta integration to get the value of term $(\gamma \partial \bar{q}^*/\partial t)$, and it is easy for the engineer to use.

In the semi-analytical approach, the orthogonal collocation method was only applied to convert the partial differential diffusion equation into ordinary differential equations. An analytical approach was used to solve the convective

dispersion equation. Therefore, the result is more accurate than that from the numerical method.

APPENDIX

By taking M collocation points along the bed (Figure 1), equation (28) is reduced to an ordinary differential equation:

$$\frac{dC_i^*}{dT} = \alpha \sum_{j=1}^{M+1} B_{ij}C_j + \beta \sum_{j=1}^{M+1} A_{ij}C_i - \gamma \frac{d\bar{q}_i^*}{dT} \qquad i = 1, 2, \ldots, M, \tag{1'}$$

where, $\partial^2 C^*/\partial\xi^2$ and $\partial C^*/\partial\xi$ are replaced by collocation matrices ΣB_{ij} and ΣA_{ij}, respectively.

Equation (21*a*) is reduced to

$$\frac{D_z}{L_b V_z} \sum_{j=1}^{M+1} A_{M+1,j}C_j^* = (1.0 - C_{M+1}^*). \tag{2'}$$

In order to separate out C_{M+1},, equation (1′) can be rewritten as

$$\frac{dC_i^*}{dT} = \alpha \sum_{j=1}^{M} B_{ij}C_j^* + \beta \sum_{j=1}^{M} A_{ij}C_j^* + \left(\alpha B_{i,m+1} + \beta A_{i,M+1}\right) C_{M+1}^* - \gamma \frac{\overline{dq_i}}{dT}$$

$$i = 1, 2, \ldots, M \tag{3'}$$

Equation (2′) can be decomposed to the following form:

$$\frac{D_z}{L_b V_z} \sum_{j=1}^{M} A_{m+1,j}C_j^* + \frac{D_z}{L_b V_z} A_{M+1,M+1}C_{M+1}^* = (1.0 - C_{M+1}^*) \tag{4'}$$

$$C_{M+1}^* = Z_1 - Z_2 \sum_{j=1}^{M} A_{M+1,j}C_j^*, \tag{5'}$$

where,

$$Z_1 = \frac{1.0}{1.0 + \dfrac{D_z}{L_b V_z} A_{m+1,M+1}}, \qquad Z_2 = \frac{\dfrac{D_z}{L_b V_z}}{1.0 + \dfrac{D_z}{L_b V_z} A_{M+1,M+1}}. \tag{6'}$$

Substituting equation (5′) into equation (3′) we will get:

$$\frac{dC_i^*}{dT} = \left(\alpha \sum_{j=1}^{M} B_{ij} + \beta \sum_{j=1}^{M} A_{ij} \right) C_j^* + \left(\alpha B_{i,M+1} + \beta A_{i,M+1} \right)$$

$$\times \left(z_1 - z_2 \sum_{j=1}^{M} A_{m+1,j} C_j^* \right) - \gamma \frac{\overline{dq_i^*}}{dT} \qquad (7')$$

Equation (7′) can be rearranged in the following form:

$$\frac{dC_{si}^*}{dT} = \left(\alpha \sum_{j=1}^{M} B_{ij} + \beta \sum_{j=1}^{M} A_{ij} - Z_2 \left(\alpha B_{i,m+1} + \beta A_{i,m+1} \right) \sum_{j=1}^{m} A_{m+1,j} \right) C_j^*$$

$$+ Z_1 \left(\alpha B_{i,M+1} + \beta A_{i,M+1} \right) - \gamma \frac{\overline{dq_i^*}}{dT} \qquad i = 1, 2, \ldots, M. \qquad (8')$$

Equation (8′) includes the term ($r d\bar{q}_i^*/dT$), which depends on the (HSDM).

By taking N collocation points along R, equation (19) reduces to ordinary differential equations:

$$\frac{\partial q_i^*}{\partial T} = \sum_{j=1}^{N+1} B_{ij} q_j^* \qquad i = 1, 2, \ldots, N. \qquad (9')$$

Equations (20) and (24) are reduced to:

$$\bar{q}_i^* = 3(w_i q_{i1}^* + w_2 q_{i2}^* + \ldots + w_{N+1} q_{i,N+1}^*) \qquad (10')$$

and

$$\sum_{j=1}^{N+1} A_{N+1,j}\, q_j^* = B_{oi} (C^* - C_s^*), \qquad (11')$$

where ΣB_{ij} and ΣA_{ij} are collocation matrices to replace the Laplacian operator and gradient, respectively.

Taking the derivative of $\bar{q}^*$ with respect to time in equation (10′), we obtain:

$$\frac{\partial \bar{q}_i^*}{\partial T} = 3 \left(w_1 \frac{\partial q_{i1}^*}{\partial T} + W_2 \frac{\partial q_{i2}^*}{\partial T} + \ldots + w_{N+1} \frac{\partial q_{i,N+1}^*}{\partial T} \right). \qquad (12')$$

Substituting equation (12′) into equation (8′), results in:

$$\frac{dC_i}{dT} = \left[\alpha \sum_{j=1}^{M} B_{ij} + \beta \sum_{j=1}^{M} A_{ij} - Z_2 (\alpha B_{i,M+1} + \beta A_{i,M+1}) \sum_{j=1}^{m} A_{M+1,j} \right] C_j^*$$

$$+ Z_a(\alpha B_{i,M+1} + \beta A_{i,M+1}) - 3\gamma\left(\sum_{j=1}^{N} w_j \frac{\partial q^*_{ij}}{\partial T} + w_{N+1}\frac{\partial q^*_{s,N+1}}{\partial T}\right). \tag{13'}$$

Introducing boundary condition equation (11'),

$$\sum_{j=1}^{N+1} A_{N+1,j}\, q^*_{ij} = B_{oi}\left(C^*_i - q^{*^{1/n}}_{si}\right), \tag{14'}$$

and equation (9) becomes

$$\frac{dq^*_{Li}}{dT} = \sum_{j=1}^{N+1} B_{Lj} q^*_{ij} \qquad (i = 1, 2, \ldots, M;\ L = 1, 2, \ldots, N). \tag{15'}$$

If n = 1, equation (14') is reduced to a linear equation, and the q^*_{si} can be expressed in terms of C^*_{bi} and q^*_{ij}. Then, substitute the equation (14') into (13') and (15') and eliminate q^*_{is}. The system of equations (14') and (15') would be expanded into a number of (N+1)M first order ordinary differential equations.

REFERENCES

1. P. F. Deisler, Jr. and R. H. Wilhelm, Diffusion in Beds of Porous Solids Measurement by Frequency Response Techniques, *Industrial Engineering Chemistry, 45*, p. 1219, 1953.
2. J. B. Rosen, Kinetics of a Fixed Bed System for Solid Diffusion into Spherical Particles, *Journal of Chemical Physics, 20*, p. 387, 1952.
3. A. Rasmuson and I. Neretnieks, Exact Solution of a Model for Diffusion in Particles and Longitudinal Dispersion in Particles and Longitudinal Dispersion in Packed Beds, *AIChE Journal, 26*, p. 686, 1980.
4. N. S. Raghavan and D. M. Ruthven, Numerical Simulation of a Fixed-Bed Adsorption Column by the Method of Orthogonal Collocation, *AIChE Journal, 27*:6, p. 922, 1983.
5. B. R. Kim, R. A. Schmitz, V. L. Snoeyink, and G. W. Tauxe, Analysis of Models for Dichloramine Removal by Activated Carbon in Batch and packed Bed Reactors Using Quasi-Linearization and Orthogonal Collocation Methods, *Water Research, 12*, p. 317, 1978.
6. B. A. Finlayson, *Nonlinear Analysis in Chemical Engineering*, McGraw Hill International Book Company, New York, 1980.
7. B. A. Finlayson, *The Method of Weighted Residuals and Variational Principles*, Academic Press, New York, 1972.
8. M. Th. van Genuchten, Analytical Solution for Chemical Transport with Simultaneous Adsorption, Zero-Order Production, and First-Order Decay, *Journal of Hydrology, 49*, pp. 213-233, 1981.
9. R. B. Boudreau, Laboratory and Pilot Evaluation of Aerobic Fixed Film Biotreatment as a Pretreatment Method for Environmental Management of Chemical Plant Wastewater Systems, B. S. thesis, Louisiana State University, Baton Rouge, Louisiana, 1991.

10. D. Roy, G-T. Wang, and D. D. Adrian, A Simplified Solution Technique for Carbon Adsorption Model, submitted to *Water Research* for review, 1992.

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