Chapter 5

Solution of Nonlinear Diffusion Models

The numerical computing of the fluid flow models, involving nonlinear isotherm, particle diffusion and molecular diffusion, becomes crucial for the analysis, because it is almost impossible to solve these type of complex mathematical models, analytically. Research in this area has, however, been neglected, and in the existing literature, there are many discrepancies as to how different parameters influence the process of wash liquor and flow through porous particles. A more systematic way of studying the washing process is therefore required.

Two advanced models involving diffusion-dispersion phenomenon, which occurs during the washing of fibers along with mass transfer from fibers to bulk fluid and vice versa, are presented in this chapter. The approach of cubic B-spline collocation method (CSCM) is proposed. The effect of different parameters on the exit solute concentration profile during the washing process, is depicted graphically.
5.1 Introduction

During the washing process, the solute occupying the irregular void spaces of the packed bed is removed by the introduction of a less concentrated solvent. The phenomenon of diffusion and dispersion dominates the process. The solute present inside the pores of the fibers diffuses out when it comes in contact with the bulk fluid. Due to the adherence of solute on the fibrous surface, mass transfer also takes place from external fiber surface to the bulk fluid. The mechanism of intrafiber diffusion, longitudinal dispersion and mass transfer plays a predominant role in the solute removal from inter and intra particle voids. For the purpose of mathematical analysis, following basic assumptions are made for the washing process.

- The system is isothermal (constant temperature during a run) in nature.
- The packed bed comprises of macroscopically uniform cylindrical size particles. The particles are packed randomly in the bed.
- Fiber diameter and the length are very small as compared to the axial distance of bed.
- Film mass transfer is used to describe the interfacial mass transfer between the bulk-fluid and the particle phase.
- Dispersion in the fluid is described by the axial dispersion coefficient, and it is independent of the axial distance and the fluid concentration.
- The movement of solutes inside the lumen of the fibers can be described by the Fick’s diffusion phenomena.
• The diffusivity and the dispersion coefficient do not depend on the thickness of the bed and concentration of solutes.

• Adsorption equilibrium between the interfiber and the intrafiber solute concentrations is assumed to be nonlinear (Langmuir).

There are several diffusion models describing the washing operation, available in literature, listed in Chapter 2, using above assumption fully or partially for describing the washing behavior. In this chapter these assumption are used to describe the flow pattern for bulk fluid phase and particle phase.

5.2 1-D Nonlinear Diffusion Model

The equations (1.4)-(1.7), as given in the Chapter 1, are consider, with nonlinear isotherm as given under:

\[
D_L \frac{\partial^2 C}{\partial X^2} = U \frac{\partial C}{\partial X} + \frac{\partial C}{\partial T} + \mu C_F \frac{\partial N}{\partial T}.
\]  
(5.1)

In equation (5.1), \(N(X, T)\) and \(C(X, T)\) are taken to be related by Langmuir adsorption isotherm:

\[
N(X, T) = \frac{A_0 C(X, T)}{1 + B_0 C(X, T)}.
\]  
(5.2)

where \(A_0\) and \(B_0\) are the functions of Kappa number. The Kappa number is used to determine the amount of residual lignin in wood pulp by a standardized analysis method.
Langmuir adsorption isotherm is widely used to study in heat and mass transfer problems. The detailed description is available elsewhere [84].

**Initial condition**

Initially, it is assumed that the bulk fluid concentration is equal to the inlet solute concentration, *i.e.*, 

\[ C(x, 0) = C_0, \quad \text{for all } X. \quad (5.3) \]

**Boundary conditions**

At the inlet, it is assumed that there is no loss of solute from the bed through the plane at which the displacing fluid is introduced, *i.e.*, 

\[ UC - D_L \frac{\partial C}{\partial X} = UC_s, \quad \text{at } X = 0. \quad (5.4) \]

where \( C_s \) is solute concentration in wash liquor. In this work, the value of \( C_s \) is considered unit.

At the outlet to avoid unacceptable conclusions that the fluid will pass through the maximum or minimum in the interior of the bed, the concentration gradient is taken to be zero, *i.e.*, 

\[ \frac{\partial C}{\partial X} = 0, \quad \text{at } X = L. \quad (5.5) \]

The boundary conditions (5.4) and (5.5) make this problem a case of mixed boundary conditions.
Dimensionless nonlinear diffusion model

Before discretization, the model equations (5.1)-(5.5) are converted into dimensionless form to make them amenable for the mathematical treatment. Following dimensionless parameters are used:

\[
\begin{align*}
n &= \frac{N - N_s}{N_0 - N_s}; \quad c &= \frac{C - C_s}{C_0 - C_s}; \quad x &= \frac{X}{L}; \quad t &= \frac{UT}{L}; \quad Pe = \frac{UL}{D_L}.
\end{align*}
\]

By using above dimensionless parameters in the model equations (5.1)-(5.5), following dimensionless equations are obtained:

**Diffusion model**

\[
\frac{1}{Pe} \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial x} + \left(1 + \frac{\mu A_0 C_F}{[1 + B_0\{c(C_0 - C_s) + C_s\}]^2}\right) \frac{\partial c}{\partial t}, \quad \text{in } \Omega \equiv (0,1), \quad (5.6)
\]

**Initial condition**

\[
c(x,0) = 1, \quad \text{for all } x, \quad (5.7)
\]

**Boundary conditions**

\[
Pec - \frac{\partial c}{\partial x} = 0, \quad \text{at } x = 0, \quad (5.8)
\]

\[
\frac{\partial c}{\partial x} = 0, \quad \text{at } x = 1. \quad (5.9)
\]
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Discretized form of model

This dimensionless form of the model is discretized using the solution methodology given in section 3.6., i.e., symbolic solution by CSCM.

\[
\sum_{i=1}^{N} \frac{d\delta_{k+i-1}(t)}{dt} B_k(u) = \left( \frac{1}{Pe h_i^2} \sum_{i=1}^{N} \delta_{k+i-1}(t) B'_k(u) \right) - \frac{1}{h_i} \sum_{i=1}^{N} \delta_{k+i-1}(t) B''_k(u) \\
\times \left( \frac{\left[ 1 + B_0 \left\{ \left( \sum_{i=1}^{N} \delta_{k+i-1}(t) B_k(u) \right) (C_0 - C_s) + C_s \right\} \right]^2}{1 + B_0 \left\{ \left( \sum_{i=1}^{N} \delta_{k+i-1}(t) B_k(u) \right) (C_0 - C_s) + C_s \right\}^2 + \mu A_0 C_F} \right),
\]

(5.10)

with initial condition

\[
\sum_{i=1}^{N} \delta_{k+i-1}(t) B_k(u) = 1, \quad \text{at } t = 0,
\]

(5.11)

and boundary conditions

\[
P_e \sum_{i=1}^{N} \delta_{k+i-1}(t) B_k(u) - \frac{1}{h_i} \sum_{i=1}^{N} \delta_{k+i-1}(t) B'_k(u) = 0, \quad \text{at } u = 0,
\]

(5.12)

\[
\frac{1}{h_i} \sum_{i=1}^{N} \delta_{k+i-1}(t) B'_k(u) = 0, \quad \text{at } u = 1.
\]

(5.13)

The set of equations (5.10)-(5.13) can be used to predict the concentration of the solute in the packed bed at any location and at any time. Of particular interest is the exit solute concentration \(c_e\), which is calculated at \(u = 1\), i.e., at the last node point of the interested domain. The zeros of the modified Chebyshev polynomial (explanation is
given in Section 3.5, i.e., selection of collocation points) are taken as collocation points per subinterval.

The above system of equation (5.10)-(5.13) can be arranged in the form of a tridiagonal system of differential algebraic equations (DAEs), which is stiff in nature. The DAEs are solved using MATLAB code with ode15s system solver.

5.3 Outcomes of 1-D Nonlinear Diffusion Model

The effect of three parameters, viz: axial dispersion coefficient, interstitial velocity and cake thickness is examined on the washing process. The overall effect of these parameters on exit solute concentration ($c_e$) is clubbed in form of Peclet number ($Pe = U_L/D_L$). For the numerical simulation of nonlinear model represented by equation (5.10)-(5.13), the experimental data of Grahs [40] is used.

5.3.1 Effect of different parameters on $c_e$

The effect of Peclet number, axial dispersion coefficient, interstitial velocity and cake thickness on exit solute concentration is plotted graphically and discussed below:

Effect of Peclet number ($Pe$)

The exit solute concentration profiles for wide range of $Pe$ are shown in Figures 5.1, 5.2 and 5.3. Solution profile for small range of $Pe$ is elongated and takes a large time to converge to zero. It indicates that indefinitely large time is consumed to remove the impurities adsorbed on the fiber surface. For medium range of $Pe$, the solution profile
converges to zero in comparatively lesser time. For large $Pe$, the axial dispersion is very less, thereby mass transfer increases, which causes fast removal of impurities from the packed bed.

**Effect of axial dispersion coefficient ($D_L$)**

The effect of axial dispersion coefficient on exit solute concentration is shown in Figure 5.4, for initial solute concentration $0.0773 \, kg/m^3$, cake thickness $0.5 \, m$ and bed porosity $0.986$. Axial dispersion is basically a convective mixing process that arises due to the velocity profiles in the individual particle pores and because of the complex branching and intertwining of flow paths in a porous medium. With the increase in the axial dispersion coefficient, $Pe$ decreases, as a result more back mixing occurs, leading to less removal of the black liquor solids from the solute. Figure 5.4 indicates that for large values of the $Pe$, the breakthrough curve becomes broaden as a result less time is evolved in the recovery of black liquor solids and hence better washing efficiency can be achieved. For effective washing operations higher $Pe$ is preferred.

**Effect of interstitial velocity ($U$)**

The Figure 5.5 shows that the interstitial velocity effects on exit solute concentration for cake thickness $0.5 \, m$ and bed porosity $0.986$. It happens that with the increase in the interstitial velocity, the axial dispersion increases and the particle porosity decreases. Thereby, the consistency of the fibers increases. The small flow rates results in better removal of black liquor solids whereas high flow rates results in poor washing operations as more time is consumed to remove the black liquor solids. Overall, not much significant change on concentration profiles is apparent for high flow rates.
**Effect of cake thickness ($L$)**

The consequent change in the concentration profiles due to the change in the cake thickness is shown in Figure 5.6, for axial dispersion coefficient $5.2 \times 10^{-4} \, m^2/s$, interstitial velocity $2.1 \times 10^{-2} \, m/s$ and bed porosity 0.986. It is clear that as $L$ increases from 0.04 m the breakthrough time decreases. The lab scale data indicates that as $L$ increases from 0.5 m the concentration profiles start overlapping each other. Trinh *et al.* [97] has also found that increase in cake thickness is beneficial for washing efficiency but with in certain limits of consistency.

From the above observations, it is clear that the technique of cubic B-spline collocation method is giving highly accurate results, even for very small as well as large Peclet numbers in case of nonlinear equation. For efficient washing operation $D_L$ and $U$ should be kept small, but $L$ should be kept sufficiently large. These variations should be done within reasonable range to get optimum results.

### 5.3.2 Computational cost and convergence of method

In Table 5.1, the computational cost of CSCM is found by calculating the total time elapsed (in seconds) for execution of MATLAB program for evaluation of $c_e$ at different Peclet numbers ($Pe$). In the same table, by taking results at $n = 150$ as the exact solution and based on that the order of convergence is found to be at least two using cubic spline collocation method.
5.4 2-D Nonlinear Diffusion Model

A 2-D nonlinear diffusion model links models for two phases (particle and bulk fluid), which are used to describe the diffusion-dispersion phenomenon that occurs during the removal of solutes along with mass transfer from the particles to bulk fluid and vice versa.

To discretize the model equations, the technique of cubic spline collocation method (CSCM), utilizing the uniform grid over the entire domain of the independent variable, is used. The differential equations for different phases are presented below.

**Model for particle phase**

The accumulation of solute on the fiber surface is best represented by particle diffusion model. The boundary conditions describing the solute exchange between the fiber surface and the bulk fluid are dependent of mass transfer rates. It is assumed that the intrafiber diffusion is described by Fick’s law. The rate of solute transport from the fiber surface, located at an axial distance \( X \), is equal to the external film resistance mass transfer coefficient times the difference in intrapore solute concentration and bulk fluid concentration at ‘\( X \)’. Hence, finite liquid phase mass transfer resistance exists.

The intrafiber diffusion equation can be written as:

\[
D_F \left( \frac{\partial^2 Q}{\partial r^2} + \frac{1}{r} \frac{\partial Q}{\partial r} \right) - \frac{\partial Q}{\partial T} - C_F \left( \frac{1 - \omega}{\omega} \right) \frac{\partial N}{\partial T} = 0, \quad (5.14)
\]

where \( \omega Q + C_F(1 - \omega)N = \omega W \). The \( W \) is local intrafiber solute concentration at any radial distance \( r \). It is also assumed that local equilibrium prevails in the individual intrafiber pores.
Adsorption isotherm

It is assumed that the adsorption rate of solutes is of second order in the forward direction where as the desorption rate of solutes is of first order in the opposite direction, therefore:

\[
\frac{\partial N}{\partial T} = k_1 \frac{Q(N_i - N)}{C_F} - k_2 N, \quad (5.15)
\]

where \(k_1\) and \(k_2\) are adsorption and desorption rate constants. It reduces to Langmuir adsorption isotherm at equilibrium.

\[
N = \frac{k_2 N_i Q}{k_1 C_F + k_2 Q}, \quad (5.16)
\]

Model for bulk fluid phase

The fluid phase is represented by one dimensional axial dispersion model related to the intrapore solute concentration at the fiber surface at an axial distance \(X\). It is assumed that there is no loss of solute from the bed through the plane at which the displacing fluid is introduced. The difference of inlet solute concentration and concentration gradient at the inlet, multiplied by the ratio of axial dispersion coefficient to the interstitial velocity is equal to the concentration of weak wash liquor.

The concentration of the solute in bulk fluid phase can be described as follows:

\[
U \frac{\partial C}{\partial X} + \frac{\partial C}{\partial T} + D_F \gamma \left(1 - \epsilon \frac{\partial Q}{\partial r} \right)_{r=R} = D_L \frac{\partial^2 C}{\partial X^2}, \quad (5.17)
\]
where $\gamma = 1, 2, 3$ depending upon the particle geometry. Because of the geometry of solutes of the packed bed is cylindrical in nature, therefore $\gamma = 2$ in this case.

To correlate intrapore solute concentration and the bulk fluid concentration, it is necessary to define a relation between these two in terms of axial distance.

\[
Q = \frac{2}{R^2} \int_{0}^{R} Q(r, X, T) r \, dr.
\]  

(5.18)

The equation (5.18) serves as the link between particle phase and bulk fluid phase. Neretnieks [67], and Raghvan and Ruthven [78] have related the particle phase and bulk fluid phase by defining the condition at particle boundary. Therefore, equation (5.18) reduces to:

\[
Q = \frac{2k_f \omega}{KR} (C - Q_{r=R}).
\]  

(5.19)

The equation (5.19) reduces the mathematical complexities which simplifies the model.

**Boundary conditions**

The rate of change of pore liquid concentration with respect to radial position inside the particle is assumed to be zero at the center of the particle, i.e., at $r = 0$:

\[
\frac{\partial Q}{\partial r} = 0.
\]  

(5.20)
Similarly, the rate of change of concentration with respect to radial position at the boundary of the particle is assumed to be controlled by film resistance mass transfer coefficient, i.e., at \( r = R \):

\[
-D_F \left( \frac{\partial Q}{\partial r} \right) = \frac{k_f \omega}{K} (Q|_{r=R} - C').
\]  

(5.21)

In the axial direction, at the inlet of the bed, i.e., at \( X = 0 \), it is assumed that no solute from the bed is lost through the plane at which the displacing fluid is introduced, therefore,

\[
UC - D_L \frac{\partial C}{\partial X} = 0,
\]  

(5.22)

Similarly, at the outlet of the bed in axial direction, i.e., at \( X = L \), the concentration gradient is assumed to be zero, i.e.,

\[
\frac{\partial C}{\partial X} = 0.
\]  

(5.23)

**Initial conditions**

At \( T = 0 \), the concentrations are assumed equal to their initial value, i.e.,

\[
C = C_0; \quad Q = Q_0; \quad N = N_0.
\]  

(5.24)
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5.5 Solution Strategy

The mathematical equations (5.14), (5.16), (5.17) and from (5.20) to (5.24) are expressed in the dimensionless form, to make them amenable for better mathematical treatment.

\[ c = \frac{C}{C_0}; \quad q = \frac{Q}{C_0}; \quad n = \frac{N}{N_0}; \quad C_1 = \frac{C_0}{C_F}; \quad N_1 = \frac{N_0}{C_1}; \]

\[ Pe = \frac{UL}{D_L}; \quad Bi = \frac{k_f \omega R}{KD_F}; \quad k = \frac{k_1}{k_2}; \quad t = \frac{T D_F}{R^2}; \]

\[ \xi = \frac{X}{L}; \quad \eta = \frac{r}{R}; \quad \theta = \frac{2(1 - \epsilon)}{\epsilon}; \quad \psi = \frac{R^2 U}{L D_F}. \]

Models get converted into following dimensionless form:

**Model for particle phase**

\[ \frac{\partial^2 q}{\partial \eta^2} + \frac{1}{\eta} \frac{\partial q}{\partial \eta} = \frac{\partial q}{\partial t} + N_1 \left( 1 - \frac{\omega}{\omega} \right) \frac{\partial n}{\partial t}, \quad (5.25) \]

with boundary conditions

\[ \frac{\partial q}{\partial \eta} = 0, \quad \text{at} \ \eta = 0, \quad (5.26) \]

\[ \frac{\partial q}{\partial \eta} = -Bi(q - c), \quad \text{at} \ \eta = 1. \quad (5.27) \]

**Adsorption isotherm**

\[ \frac{\partial n}{\partial t} = \frac{R^2 k_1}{D_F} \left( C_1 q(1 - n) - \frac{n}{k} \right), \quad (5.28) \]
Model for bulk fluid phase

\[
\frac{\partial c}{\partial t} = \frac{\psi}{Pe} \frac{\partial^2 c}{\partial \xi^2} - \psi \frac{\partial c}{\partial \xi} - \theta Bi \left( c - q|_{\eta=1} \right),
\]  

(5.29)

with boundary conditions

\[
c - \frac{1}{Pe} \frac{\partial c}{\partial \xi} = 0, \quad \text{at } \xi = 0,
\]

(5.30)

\[
\frac{\partial c}{\partial \xi} = 0, \quad \text{at } \xi = 1,
\]

(5.31)

and initial conditions

\[
c = q = n = 1, \quad \text{at } t = 0.
\]

(5.32)

5.5.1 Mesh selection

The radial domain \(0 \leq \eta \leq 1\) is divided into \(\alpha\) subdomains by placing the dividing nodes at \(\eta_\alpha, \alpha = 1, 2, \ldots, l + 1\), with \(\eta_1 = 0\) and \(\eta_{l+1} = 1\). Each subdomain is mapped to \([0, 1]\) by using the transformation:

\[
u = \frac{\eta - \eta_\alpha}{\eta_{\alpha+1} - \eta_\alpha} = \frac{\eta - \eta_\alpha}{h_\alpha}, \quad \alpha = 1, 2, \ldots, l + 1,
\]

where \(h_\alpha\) is the width of the \(\alpha^{th}\) subdomain. The zeros \(u_2 = \frac{1}{2} \left(1 - \frac{1}{\sqrt{3}}\right)\) and \(u_3 = \frac{1}{2} \left(1 + \frac{1}{\sqrt{3}}\right)\) of the shifted Legendre polynomial \(P_2(u) = (2u - 1)^2 - 1/3\) are used as collocation points within each subdomain. The end points are taken as \(u_1 = 0\) and \(u_4 = 1\).
Similarly, the axial domain $0 \leq \xi \leq 1$ is divided into $\beta$ subdomains by placing the dividing nodes at $\xi_\beta$, $\beta = 1, 2, \ldots, m+1$, with $\xi_1 = 0$ and $\xi_{m+1} = 1$. Each subdomain is mapped to $[0, 1]$ by using the transformation:

$$v = \frac{\xi - \xi_\beta}{\xi_{\beta+1} - \xi_\beta} = \frac{\xi - \xi_\beta}{h_\beta}, \quad \beta = 1, 2, \ldots, m+1,$$

where $h_\beta$ is the width of the $\beta^{th}$ subdomain. The zeros $v_2 = \frac{1}{2} \left(1 - \frac{1}{\sqrt{2}}\right)$ and $v_3 = \frac{1}{2} \left(1 + \frac{1}{\sqrt{2}}\right)$ of the shifted Chebyshev polynomial $T_2(v) = (2v - 1)^2 - 1$ are used as collocation points within each subdomain. The end points are taken as $v_1 = 0$ and $v_4 = 1$.

### 5.5.2 Discretization of the model

Let $q_\alpha^\beta(u, v, t)$ denote the approximation solution of $q(u, v, t)$ in the element $(\alpha, \beta)$, then this approximation can be expressed in terms of B-spline basis, using solution methodology given in Section 3.6., i.e., symbolic solution by CSCM, as:

$$q_\alpha^\beta(u, v, t) = \sum_{i,j=1}^{4} \lambda_{i+\alpha-1}^{j+\beta-1}(t) B_i^j(u,v). \quad (5.33)$$

Similarly $n(u, v, t)$ can be approximated by:

$$n_\alpha^\beta(u, v, t) = \sum_{i,j=1}^{4} \mu_{i+\alpha-1}^{j+\beta-1}(t) B_i^j(u,v). \quad (5.34)$$
Since there are no boundary conditions for the differential equation (5.34) all points are regarded as interior collocation points.

In an analogous way, the approximate solution of \( c(v, t) \) in the element \((\alpha, \beta)\) can be represented by:

\[
c^\beta(v, t) = \sum_{i=1}^{4} \phi^{j+\beta-1}(t)B_j(v).
\]  \hspace{1cm} (5.35)

Substituting equations (5.33), (5.34) and (5.35) into (5.25), (5.28) and (5.29), respectively, one obtains the following residual equations:

\[
R_q(u, v, t) = 4 \sum_{i,j=1}^{4} \frac{d\lambda^{j+\beta-1}_{i+\alpha-1}(t)}{dt} B^j_i(u, v) - \frac{1}{h_\alpha^2} \sum_{i,j=1}^{4} \lambda^{j+\beta-1}_{i+\alpha-1}(t) \frac{\partial^2 B^j_i(u, v)}{\partial u^2} - \frac{1}{(uh_\alpha + \eta_\alpha)h_\alpha}
\]

\[
\times \sum_{i,j=1}^{4} \lambda^{j+\beta-1}_{i+\alpha-1}(t) \frac{\partial B^j_i(u, v)}{\partial u} + N_1 \left[ \frac{1}{\omega} \sum_{i,j=1}^{4} \frac{d\rho^{j+\beta-1}_{i+\alpha-1}(t)}{dt} B^j_i(u, v) \right].
\]  \hspace{1cm} (5.36)

\[
R_n(u, v, t) = 4 \sum_{i,j=1}^{4} \frac{d\rho^{j+\beta-1}_{i+\alpha-1}(t)}{dt} B^j_i(u, v) + \frac{1}{k} \frac{R^2 k_1}{D_F} \sum_{i,j=1}^{4} \rho^{j+\beta-1}_{i+\alpha-1}(t) B^j_i(u, v)
\]

\[
- \frac{R^2 k_1}{D_F} \left[ C_1 \sum_{i,j=1}^{4} \lambda^{j+\beta-1}_{i+\alpha-1}(t) B^j_i(u, v) \left( 1 - \sum_{i,j=1}^{4} \rho^{j+\beta-1}_{i+\alpha-1}(t) B^j_i(u, v) \right) \right].
\]  \hspace{1cm} (5.37)

\[
R_c(v, t) = \sum_{j=1}^{4} \frac{d\phi^{j+\beta-1}(t)}{dt} B_j(v) - \frac{\psi}{Pe h_\beta^2} \sum_{j=1}^{4} \phi^{j+\beta-1}(t) \frac{\partial^2 B_j(v)}{\partial v^2} - \frac{\psi}{h_\beta} \sum_{j=1}^{4} \phi^{j+\beta-1}(t) \frac{\partial B_j(v)}{\partial v}
\]

\[
+ \theta Bi \left( \sum_{j=1}^{4} \phi^{j+\beta-1}(t) B_j(v) - \sum_{i,j=1}^{4} \rho^{j+\beta-1}_{i+\alpha-1}(t) B^j_i(u, v) \right). \hspace{1cm} (5.38)
\]
The residuals $R_q$, $R_n$ and $R_c$ are set to zero at the appropriate interior collocation points. For the solution $q(u, v, t)$, the collocation points situated at $\eta = 0$ and $\eta = 1$ are regarded as boundary collocation points. Likewise for $c(v, t)$, the collocation points situated at $\xi = 0$ and $\xi = 1$ are boundary collocation points. After discretizing the boundary conditions (5.26), (5.27), (5.30) and (5.31), for $j = 1, 2, 3, 4; \beta = 1, 2, \ldots, m$, following equations are obtained:

$$\lambda^{j+\beta-1}_i(t) = \lambda^{j+\beta-1}_{i+3}(t), \quad (5.39)$$

$$\frac{\lambda^{j+\beta-1}_{i+3}(t)}{2} - \frac{\lambda^{j+\beta-1}_{i+1}(t)}{2} = -h_{\alpha}Bi \left( \frac{\lambda^{j+\beta-1}_{i+1}(t)}{6} + \frac{2\lambda^{j+\beta-1}_{i+2}(t)}{3} + \frac{\lambda^{j+\beta-1}_{i+3}(t)}{6} - \phi^{j+\beta-1}(t) \right), \quad (5.40)$$

$$\phi^1(t) + 4\phi^2(t) + \phi^3(t) - \frac{1}{Pe h_{\beta}} (3\phi^3(t) - 3\phi^1(t)), \quad (5.41)$$

$$\phi^{m+1}(t) = \phi^{m+3}(t), \quad (5.42)$$

and initial condition (5.34) yields:

$$\lambda^{j+\beta-1}_{i+\alpha-1}(0) = 1; \quad \phi^{j+\beta-1}(0) = 1; \quad \rho^{j+\beta-1}_{i+\alpha-1}(0) = 1. \quad (5.43)$$

The above discretization leads to a system of $(m + 3)(2l + 7)$ differential algebraic equations (DAEs) involving $n+2$ unknowns. The resulting system is solved with MATLAB ode15s built in differential equation solver using the initial approximation from equation (5.43).
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5.6 Outcomes of 2-D Diffusion Model

The stiff system of differential algebraic equations (5.36)-(5.43) is solved using MATLAB coding with ode15s by taking two collocation points within each element in the axial and radial domains. The verification of the model is done by using the laboratory data of Arora and Potucek [10], generated on the basis of ten samples collected from the industry. These samples are obtained for varying consistency, concentration of black liquor solids, density of fibers, density of liquor, surface tension and viscosity of black liquor. Range of parameters obtained from the experiments are listed in the Table 5.2. Experimental data of pulp fibres [11] is given in Table 5.3.

5.6.1 Effect of different parameters on $c_e$

The theoretical effects of different parameters such as $D_L$, $L$, $U$, $k_1/k_2$, $\epsilon$, $D_F/R^2$ on the exit solute concentration are discussed. The same are plotted in Figures 5.7, 5.8, 5.9, 5.10, 5.11 and 5.12, respectively, with respect to time and discussed below.

Effect of $D_L$

Peclet number is inversely proportional to axial dispersion coefficient. For the experimental data reported in the present work Peclet number is found in the range of 18 to 26. The numerical results are calculated for exit solute concentration and average solute concentration. From Figure 5.7, it is observed that less time is consumed to remove black liquor solids for large values of $Pe$. Therefore for effective washing, the value of $D_L$ should be small.
**Effect of U**

With an increase in interstitial velocity, viscosity and porosity decreases and axial dispersion coefficient increases simultaneously. In Figure 5.8, interstitial velocity is not showing much effect on the solute concentration, therefore it can be concluded that $U$ does not effect the washing operation drastically.

**Effect of L**

With an increase in cake thickness, diffusion phenomenon occurs very fast, leading to rapid diffusion of solutes from cake lumen. From Figure 5.9, it is clear that $L$ has significant effect on concentration profile.

**Effect of $\epsilon$**

The porous the fiber lumen is, faster will be the permeation rate of black liquor solute. In Figure 5.10, solute concentration curve approaches to zero for higher value of porosity and this implies that efficiency of washing operation increases.

**Effect of $k_1/k_2$**

A higher value of reaction rate constant means detachment rate is very less therefore solute will take more time to move out of fiber pores. This effect is shown in Figure 5.11, where the convergence of solute profiles to the steady state condition is elongated.

**Effect of $D_F/R^2$**

As the value of $\psi$ decreases the distribution ratio $D_F/R^2$ increases, as illustrated in Figure 5.12, which results in an increase in the retention time of solute. Subsequently, concentration profiles take large time to reach the steady state condition.
As above, the effect of parameters like $D_L$, $L$, $U$, $k_1/k_2$, $\epsilon$, $D_F/R^2$ is discussed on the exit solute concentration. Simulation from the model gives that the washing operation is highly sensitive to parameters like $D_L$, $L$, $\epsilon$, $D_F/R^2$, where as $U$ and $k_1/k_2$ have little affects on the washing operation. Finally, by maintaining large $Pe$ and small $D_F/R^2$ during washing operation good results can be achieved.

5.6.2 Comparison of CSCM with OCM and OCFE

The numerical results are compared with the experimental values reported by Arora and Potucek [11], and tabulated in Table 5.4, for different experiments for washing effluent taken at different time intervals for $h_{\alpha} = h_{\beta} = h$. In Figure 5.13, the exit solute concentration profiles for different Biot numbers ($Bi$) are plotted, for same partition points, by the three different numerical techniques OCM, OCFE and CSCM. Clearly, the breakthrough curves of CSCM show that results obtained for different values of $Bi$ are smooth, stable and fast as compared to other methods like OCM and OCFE.

5.6.3 Comparison with respect to computational cost

The computational cost of CSCM is found by calculating the total time elapsed (in seconds) for execution of MATLAB program for evaluation of $c_e$ at different Peclet numbers ($Pe$). For better comparison purpose same number of partitions were used as in [9] through OCFE. Results in Table 5.5, indicate a 10 fold decline in the computational time, thereby establishing that the technique of CSCM is cost effective.
5.6.4 Convergence of method

Due to the nonlinearity, the model is quite complex and consequently its exact solution is not possible. In Table 5.6, numerical results for different values of Peclet numbers with $Bi = 10$ and $\epsilon = 0.968$ are given. For comparison purpose the results obtained at $l = m = 100$ are considered as the exact solution and based on that the order of convergence is found to be at least 2 using cubic spline collocation method. The relative error clearly demonstrates the accuracy of the cubic B-spline collocation method and yields smooth and stable solutions.

5.7 Summary

The nonlinear diffusion models are solved conveniently. Numerical computations are carried out in order to compare the three methods viz: OCM, OCFE and CSCM on the basis of computational costs, efficiency and accuracy. The comparison reveals that CSCM gives the best result with minimum error as the analysis is done under the same numerical experiment. The order of convergence of CSCM is actually found to be higher than 2.
Figure 5.1: Exit concentration $c_e$ for small range of $Pe$ for 1-D diffusion model.
Figure 5.2: Exit concentration $c_e$ for medium range of $Pe$ for 1-D diffusion model.
Figure 5.3: Exit concentration $c_e$ for large range of $Pe$ for 1-D diffusion model.
Figure 5.4: Effect of axial dispersion coefficient $D_L$ for 1-D diffusion model.
**Figure 5.5:** Effect of interstitial velocity $U$ for 1-D diffusion model.
Figure 5.6: Effect of cake thickness $L$ for 1-D diffusion model.
Figure 5.7: Effect of Peclet number $P_e$ for 2-D diffusion model.
Figure 5.8: Effect of interstitial velocity $U$ for 2-D diffusion model.
Figure 5.9: Effect of cake thickness $L$ for 2-D diffusion model.
Figure 5.10: Effect of bed porosity $\epsilon$ for 2-D diffusion model.
Figure 5.11: Effect of reaction rate constant $k_1/k_2$ for 2-D diffusion model.
Figure 5.12: Effect of distribution ratio $D_F/R^2$ for 2-D diffusion model.
Figure 5.13: Exit concentration $c_e$ for different $Bi$ by OCM, OCFE and CSCM for 2-D diffusion model.
### Table 5.1: Elapsed time (in sec.) and rate of convergence of CSCM for 1-D diffusion model.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>n</th>
<th>Elapsed time</th>
<th>Rate of convergence</th>
</tr>
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Table 5.2: Results from the experimental study [10] for 2-D diffusion model.

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<th>Parameter</th>
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<tr>
<td>( C_0 )</td>
<td>((8.3341 - 8.3782) \times 10^0)</td>
<td>kg/m³</td>
</tr>
<tr>
<td>( C_F )</td>
<td>((4.7059 - 6.6176) \times 10^1)</td>
<td>kg/m³</td>
</tr>
<tr>
<td>( N_0 )</td>
<td>((4.3186 - 4.3415) \times 10^{-3})</td>
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</tr>
<tr>
<td>( U )</td>
<td>((1.9321 - 1.9584) \times 10^{-3})</td>
<td>m/s</td>
</tr>
<tr>
<td>( D_F/R^2 )</td>
<td>((2.2700 - 6.9400) \times 10^{-2})</td>
<td>1/s</td>
</tr>
<tr>
<td>( L )</td>
<td>((0.6960 - 1.0531) \times 10^{-1})</td>
<td>m</td>
</tr>
<tr>
<td>( k_1/k_2 )</td>
<td>((2.9389 - 4.1104) \times 10^{-3})</td>
<td>–</td>
</tr>
<tr>
<td>( k_f )</td>
<td>((1.8394 - 1.8415) \times 10^{-6})</td>
<td>m/s</td>
</tr>
<tr>
<td>( \omega )</td>
<td>((8.8400 - 9.1800) \times 10^{-1})</td>
<td>–</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>((9.5500 - 9.6800) \times 10^{-1})</td>
<td>–</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$P_e$</th>
<th>$U \times 10^4$</th>
<th>$\epsilon$</th>
<th>$D_L \times 10^7$</th>
<th>$B \times 10^{12}$</th>
<th>$Re \times 10^3$</th>
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<tr>
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TABLE 5.4: Comparison of experimental and numerical values of $c_e$ for 2-D diffusion model.

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Table 5.5: Elapsed time (in sec.) for $Bi = 0.67$, $\epsilon = 0.968$ for 2-D diffusion model.

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<th>Parameters</th>
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Table 5.6: Rate of convergence of CSCM for $Bi = 10, \epsilon = 0.968$ for 2-D diffusion model.

<table>
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<th>Parameter($Pe$)</th>
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<td>7</td>
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