Dynamic studies of binary adsorption system in fixed beds

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Dynamic studies of binary adsorption system in fixed beds

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Abstract

In this study, a generalized, comprehensive and feasible mathematical model was developed for the description of the adsorption of multicomponent system in a fixed bed containing solid adsorbent. It took into cognizance of all the factors considered negligible in the literature, which included intraparticle, interparticle and interphase diffusional resistances, conditions of non-equilibrium and non-linear binary adsorption of butan-2-ol and 2-methylbutan-2-ol onto activated carbon. The resulting 4N hyperbolic and parabolic differential equations were numerically solved using orthogonal collocation on finite element method. Excellent agreements were achieved between the experimental data and the simulated results of breakthrough times and concentrations of the solutes in fixed beds of 0.41, 0.82 and 1.23 m. Equally, the observed chromatographic tops of the less strongly adsorbed component (butan-2-ol) and the effects of adsorber length on times of breakthrough of the components and height of peaks were precisely simulated. The results of this study are of beneficial use in the design and analysis of fixed beds employed for the treatment of multicomponent aqueous wastewater effluents from industry.

Keywords: adsorption; fixed bed, adsorbent, diffusional resistance, orthogonal collocation on finite element.
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>ARD</td>
<td>Average relative deviation</td>
</tr>
<tr>
<td>EABS</td>
<td>Sum of the absolute errors</td>
</tr>
<tr>
<td>ERRSQ</td>
<td>Sum of the squares of the errors</td>
</tr>
<tr>
<td>HYBRID</td>
<td>Composite fractional error function</td>
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<tr>
<td>MAE</td>
<td>Mean absolute error</td>
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<tr>
<td>MAPE</td>
<td>Mean absolute percentage error</td>
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<tr>
<td>MPE</td>
<td>Mean percentage error</td>
</tr>
<tr>
<td>MPSD</td>
<td>Marquardt’s percent standard deviation</td>
</tr>
<tr>
<td>OCFEM</td>
<td>Orthogonal collocation on finite element method</td>
</tr>
<tr>
<td>RMSE</td>
<td>Root mean square error</td>
</tr>
<tr>
<td>SPE</td>
<td>Standard prediction error</td>
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</table>

### List of symbols

- $\bar{c}_c$: Mean value of experimental breakthrough data (kg/m$^3$)
- $\bar{c}_i$: Dimensionless concentration of solute $i$ in fluid phase of the column
- $c_i$: Concentration of solute $i$ in fluid phase of the column (kg/m$^3$)
- $e_{i,c}$: Experimental breakthrough concentrations of solute for run $i$ (kg/m$^3$)
- $(c_i)_0$: Inlet concentration of solute $i$ in the column (kg/m$^3$)
- $e_{i,p}$: Simulated (or predicted) breakthrough concentrations of solute for run $i$ (kg/m$^3$)
- $s_i$: Amount of solute $i$ adsorbed per unit volume of the particle (kg/m$^3$) at equilibrium with a liquid phase concentration, $X_i$, in a solution containing $N$ solutes
- $C_i$: Constant in Eq. (1) (dimensionless)
- $D_{Li}$: Axial diffusivity for component $i$ in the fluid phase (m$^2$/s)
- $D_{pi}$: Diffusivity for component $i$, in the fluid phase within the pore of an adsorbent (m$^2$/s)
- $D_a$: Diffusion coefficient for the diffusion of component $i$ through the solid phase of an adsorbent (m$^2$/s)
- $k_f$: Freundlich isotherm constant ( (kg/m$^3$)$^{1-n}$)
- $K_f$: Film mass transfer coefficient of solute $i$ (m/s)
- $n$: degree of heterogeneity (dimensionless)
- $N$: Number of solutes in solution (dimensionless)
- $N_e$: Number of experimental runs (dimensionless)
- $Pe_i$: Peclet number of component $i$ (dimensionless)
- $q_i$: Concentration of solute $i$ in the solid (or adsorbed) phase (kg/m$^3$)
- $(q_i)_b$: Concentration of solute $i$ in the solid (or adsorbed) phase (kg/m$^3$)
- $Q_i$: Dimensionless concentration of solute $i$ in the solid (or adsorbed) phase
- $r$: Radial distance in particle, i.e., radius of the adsorbent pellet as measured from center of pellet (m)
- $R$: External radius of the adsorbent (m)
- $R^2$: Coefficient of determination (or regression coefficient) (dimensionless)
- $Sh_i$: Sherwood number of component $i$ (dimensionless)
- $t$: Time from start of sorption process (h)
$U_f$  Linear velocity in the positive direction of $z$ (m/s)

$X_i$  Concentration of solute $i$ in pore fluid phase (kg/m$^3$)

$\bar{X}_i$  Dimensionless concentration of solute $i$ in pore fluid phase

$z$  Axial distance in column (m)

$z_T$  Length of column (m)

$Z$  Dimensionless axial distance

**Greek letters**

$\alpha$  Geometry of the adsorbent (dimensionless)

$\varepsilon_b$  Void fraction in the bed, i.e., volume of voids per unit volume of bed (dimensionless)

$\varepsilon_p$  Void fraction in particles, i.e., volume of pores in the pellet per unit volume of pellet (dimensionless)

$\sigma$  Dimensionless radius

$\tau$  Dimensionless time
1 Introduction

Adsorption process is regarded as a seepage process whereby a fluid passes through a material bed, which has the capability to change its concentration. It takes place when a fluid or solute (called adsorbate) aggregates on a solid or more rarely a liquid (called adsorbent) surface, with the formation of an atomic or molecular film (adsorbate). Hence, adsorption process comprises three phases: the fluid phase, the adsorbed phase and the adsorbent phase. It is a highly significant unit operation employed in industry for the separation of solutes from a fluid stream onto the surface of a solid adsorbent. It is especially significant in advanced wastewater treatment processes.

The adsorption of mono- and multicomponent systems onto porous adsorbents in fixed bed is commonly employed for the separation and purification of mixtures of liquids (i.e., adsorbates). The monocomponent adsorption from a diluent onto activated carbon has been mathematically modelled efficaciously (Aribike and Olafadehan 2008). However, literature is competitively scanty on the mathematical model development for the adsorption of binary or multicomponent system in a fixed bed, which has to be considered industrially, using the highly non-linear adsorption isotherm. A comprehensive review of works on homogeneous liquid phase-solid diffusion and pore diffusion models for multicomponent liquid phase adsorption in fixed beds has been presented by Olafadehan (2000). None of these models accounted for intraparticle and interparticle diffusional resistances, non-equilibrium conditions, non-linear equilibrium relationship and interphase film resistance. However, the design and analysis of multicomponent adsorption systems require these factors to be considered in a flow system. Equally, to design an adsorber, it is required to determine the time for which the fixed bed can be exposed to the fluid before breakthrough of an undesirable component occurs. The time to breakthrough is determined by the equilibrium adsorption isotherm, the axial diffusional and the external and internal diffusional resistances. Hence, the objective of this study is to develop a comprehensive and feasible mathematical model that can be used to describe multicomponent liquid phase adsorption in fixed beds taking cognizance of the factors considered negligible in the literature and proffer numerical solution to the resulting partial differential equations using orthogonal collocation on finite element method (OCFEM). The efficacy of the numerical technique employed in this study was demonstrated by comparing the experimental breakthrough concentrations of butan-2-ol and 2-methylbutan-2-ol in fixed beds with the simulated results and inferences drawn. The modeling and numerical approaches of this study will be of immense benefits in the design and analysis of fixed beds employed for the treatment of multicomponent aqueous wastewater effluents from industry.

2 Development of model equations for multicomponent adsorption system in fixed bed

2.1 Equilibrium relationships

Generally, the adsorption equilibria of organic solutes in aqueous streams can be determined using Eq. (1) (Fritz and Schlünder 1974):

\[
\frac{c_{ij}}{C_i} = \frac{a_{ij}X_i^{b_{ij}}}{\sum_{j=1}^{N} a_{ij}X_j^{b_{ij}}} = q_i^* (X_1, X_2, \ldots \ldots \ldots, X_N)
\]  

(1)

Some famous adsorption isotherms are well represented in Eq. (1) as special cases. For example, when \( b_{ij} = b_j = C_i = 1 \), it results in the Langmuir isotherm, given by:

\[
\frac{c_{ij}}{1 + \sum_{j=1}^{N} a_{ij}X_j} = q_i^* (X_1, X_2, \ldots \ldots \ldots, X_N) \]

(2)
which was utilized for the description of two-solute adsorption isotherms (Fritz and Schluender 1974; Cooney and Strusi 1972; Butler and Ockrent 1930; Ockrent 1932; Weber and Morris 1964). For solute 1 in a binary system, Eq. (1) simplifies to the relationship of Jäger and Erdös (1959):

\[ c_{1i} = \frac{a_{10}X_{1b0}}{C_1 + a_{11}X_{1b1} + a_{12}X_{1b2}} \quad (3) \]

For a monocomponent adsorption system, Eq. (1) reduces to (with one of the subscripts 1 dropped):

\[ c_s = \frac{a_0X_{b0}}{C + a_1X^{b_1}} \quad (4) \]

Eq. (4) then becomes the correlation given by Radke and Prausnitz (1972), if \( b_1 = b_0 - 1 \) and \( C = 1 \).

\[ c_s = \frac{a_0X_{b0}}{1 + a_1X^{b_1-1}} \quad (5) \]

When \( C = 1 \), Eq. (4) reduces to the well-known Freundlich isotherm, given by:

\[ c_s = k_fX^n \quad (6) \]

where \( a_0/a_1 = k_f \) (the Freundlich isotherm constant) and the degree of heterogeneity, \( n = b_0 - b_1 \). For \( b_0 = b_1 = C = 1 \), one obtains the Langmuir isotherm:

\[ c_s = \frac{a_0X}{1 + a_1X} \quad (7) \]

In the present study, forms of Eq. (1) are taken to express the equilibrium isotherms of \( N \) (= 2) adsorbed liquid solutes of butan-2-ol and t-amylalcohol (2-methylbutan-2-ol) onto activated carbon.

2.2 The mathematical models

2.2.1 Macro-pore model

The mathematical model presented in this study describes the adsorption of solutes from a flowing stream onto a fixed bed of solid adsorbent particles. The diffusional effects considered in the model include intraparticle diffusion, surface film diffusion and axial dispersion. The essential assumptions used in the development of the model are constant dispersion coefficients and diffusion, constant bed and particle porosities, negligible radial gradients in the bed, dilute solutions and that the adsorbent particles are spherical, have uniform size and homogeneous structure.

A material balance, when applied to the adsorbate carried by the flowing fluid stream (the macro system), is given by Eq. (8) (Olafadehan 2000; Olafadehan and Susu 2004a; 2004b; 2005; Olafadehan 2019):

\[ \frac{\partial c_i}{\partial t} = D_L \frac{\partial^2 c_i}{\partial z^2} - U_f \frac{\partial c_i}{\partial z} - \left( \frac{1 - \varepsilon_b}{\varepsilon_b} \right) \left( \frac{3}{R} \right) K_h(c_i - X_i) \bigg|_{r=R} \quad (8) \]

Eq. (8) is subject to the initial conditions given by the following expressions:

(i) \[ c_i = 0 \quad t \leq 0, \quad z_T \geq z \geq 0 \quad (9) \]

and the boundary conditions given in Eqs. (10) and (11):

(ii) \[ U_f \left( c_{i0}(t) - U_f c_i |_{z=0} + D_L \frac{\partial c_i}{\partial z} |_{z=0} = 0 \quad t > 0 \quad (10) \]

(iii) \[ \frac{\partial c_i}{\partial z} |_{z=z_T} = 0 \quad t > 0 \quad (11) \]
The complicated transport mechanisms of the adsorbates in the adsorbent are often made simpler by assuming that the transport is governed either by the diffusion of the species in the pore fluid, described as a normal diffusion in a fluid or by diffusion in the solid or on the pore surfaces. In this study, the last two mechanistic diffusion in the solid and on the pore surfaces are behandle as one owing to the similar nature of their mathematical descriptions. All the transport mechanisms are taken to be one dimensional and in the particles that have an axis of symmetry. In all cases, it is assumed that local equilibrium exists between solid and fluid phases at each point in the pore since the process of adsorption onto the surface is rarely rate-determining.

2.2.2 Pore diffusion model

In this case, the adsorption rates are controlled by the mass transfer in the particles pores. It is assumed initially that the diffusional flux of each component depends on its concentration gradient alone or in other words, that the off-diagonal terms of the diffusivity matrix may be neglected. This assumption is generally valid for dilute multicomponent solution (Burchard and Toor 1962; Toor and Arnold 1962; Shuck and Toor 1963). The adsorption rates are then described by Eq. (12):

$$\varepsilon_p \frac{\partial X_i}{\partial t} + \frac{\partial c_{si}}{\partial t} = \varepsilon_p \frac{1}{r^a} \frac{\partial}{\partial r} \left( r^a D_{pi} \frac{\partial X_i}{\partial r} \right)$$

which can be used to represent the geometry of the adsorbent in the form of slab, cylinder or sphere by setting $\alpha = 0, 1$ or 2 respectively. It is understood that in the case of the slab and the cylinder, the particles are of infinite extent or alternatively one must artificially assume that the ends of a finite cylinder or edges of a finite slab are sealed to keep the problem one-dimensional. Using the equilibrium relationships in Eq. (1), Eq. (12) was transformed to give:

$$\varepsilon_p \frac{\partial X_i}{\partial t} + \sum_{j=1}^{n} \left( \frac{\partial q_{i}^{*}}{\partial X_j} \right) \frac{\partial X_j}{\partial t} = \varepsilon_p \frac{1}{r^a} \frac{\partial}{\partial r} \left( r^a D_{pi} \frac{\partial X_i}{\partial r} \right)$$

2.2.3 Surface and solid diffusion

The mathematical model describing the surface and solid transport within the adsorbent particle is given by:

$$\varepsilon_p \frac{\partial X_i}{\partial t} + \frac{\partial c_{si}}{\partial t} = \frac{1}{r^a} \frac{\partial}{\partial r} \left( r^a D_{si} \frac{\partial c_{si}}{\partial r} \right)$$

The introduction of the equilibrium relationships given by Eq. (1) into Eq. (14) results in Eq. (15):

$$\varepsilon_p \frac{\partial X_i}{\partial t} + \sum_{j=1}^{n} \left( \frac{\partial q_{i}^{*}}{\partial X_j} \right) \frac{\partial X_j}{\partial t} = \frac{1}{r^a} \frac{\partial}{\partial r} \left( r^a D_{si} \sum_{j=1}^{n} \left( \frac{\partial q_{i}^{*}}{\partial X_j} \right) \frac{\partial X_j}{\partial r} \right)$$

For the use of the surface diffusivity, $D_{si}$, in Eq. (15), its dependence on the surface concentration of the components ought to be expressed in terms of the pore fluid concentrations through the use of the equilibrium relationships.

2.2.4 Combined pore and surface diffusion

Since the two transport processes of pore and surface diffusion are not perpendicular, the combined rate of diffusion is the addition of the right-side quantities of Eqs. (13) and (15) given thus:

$$\varepsilon_p \frac{\partial X_i}{\partial t} + \sum_{j=1}^{n} \left( \frac{\partial q_{i}^{*}}{\partial X_j} \right) \frac{\partial X_j}{\partial t} = \frac{1}{r^a} \frac{\partial}{\partial r} \left( r^a \varepsilon_p D_{pi} \frac{\partial X_i}{\partial r} + D_{si} \sum_{j=1}^{n} \left( \frac{\partial q_{i}^{*}}{\partial X_j} \right) \frac{\partial X_j}{\partial r} \right)$$
subject to the initial conditions, given by:

\[ X_i = q_i(r) \]
\[ c_n = q_n'[q_1(r), q_2(r), \ldots, q_n(r)] \quad 0 \leq r \leq R \]  

Eqs. (13), (15) and (16) are subject to the boundary conditions at \( r=R \):

\[ \varepsilon_p D_{pi} \frac{\partial X_i}{\partial r} \bigg|_{r=R} = K_i [c_i(t) - X_i(r, t)] \]  

\[ D_u \left[ \sum_{j=1}^{n} \left( \frac{\partial q_i^*}{\partial X_j} \right) \left( \frac{\partial X_j}{\partial r} \right) \right] \bigg|_{r=R} = K_i [c_i(t) - X_i(r, t)] \]  

\[ \varepsilon_p D_{pi} \frac{\partial X_i}{\partial r} + D_u \left[ \sum_{j=1}^{n} \left( \frac{\partial q_i^*}{\partial X_j} \right) \left( \frac{\partial X_j}{\partial r} \right) \right] \bigg|_{r=R} = K_i [c_i(t) - X_i(r, t)] \]  

Owing to the symmetry of the adsorbent particles, the boundary condition at \( r=0 \) is given by:

\[ \frac{\partial X_i}{\partial r} \bigg|_{r=0} = \sum_{j=1}^{n} \left( \frac{\partial q_i^*}{\partial X_j} \right) \left( \frac{\partial X_i}{\partial r} \right) \bigg|_{r=0} = 0 \]  

For non-dilute mixtures with unalike components, \( D_{pi} \neq 0 \) for \( i \neq j \). Eqs. (13), (15), (16) and (17)-(20) become:

\[ \varepsilon_p \frac{\partial X_i}{\partial t} + \sum_{j=1}^{n} \left( \frac{\partial q_i^*}{\partial X_j} \right) \left( \frac{\partial X_j}{\partial t} \right) = \varepsilon_p \frac{1}{r^a} \sum_{j=1}^{n} \frac{\partial}{\partial r} \left( r^a D_{pi} \frac{\partial X_j}{\partial r} \right) \]  

\[ \varepsilon_p \frac{\partial X_i}{\partial t} + \sum_{j=1}^{n} \left( \frac{\partial q_i^*}{\partial X_j} \right) \left( \frac{\partial X_j}{\partial t} \right) = \varepsilon_p \frac{1}{r^a} \sum_{j=1}^{n} \frac{\partial}{\partial r} \left( r^a D_{pi} \frac{\partial X_j}{\partial r} \right) \]  

\[ \varepsilon_p \frac{\partial X_i}{\partial t} + \sum_{j=1}^{n} \left( \frac{\partial q_i^*}{\partial X_j} \right) \left( \frac{\partial X_j}{\partial t} \right) = \varepsilon_p \frac{1}{r^a} \sum_{j=1}^{n} \frac{\partial}{\partial r} \left( r^a D_{pi} \frac{\partial X_j}{\partial r} \right) \]  

\[ \varepsilon_p \sum_{j=1}^{n} \left( D_{pi} \right)_{ij} \frac{\partial X_j}{\partial r} \bigg|_{r=R} = K_i [c_i(t) - X_i(R, t)] \]  

\[ \sum_{j=1}^{n} \left( D_{ij} \right) \left[ \sum_{k=1}^{n} \left( \frac{\partial q_i^*}{\partial X_k} \right) \left( \frac{\partial X_k}{\partial r} \right) \right] \bigg|_{r=R} = K_i [c_i(t) - X_i(R, t)] \]  

\[ \varepsilon_p \sum_{j=1}^{n} \left( D_{pi} \right)_{ij} \frac{\partial X_j}{\partial r} \bigg|_{r=R} + \sum_{j=1}^{n} \left( D_{ij} \right) \left[ \sum_{k=1}^{n} \left( \frac{\partial q_i^*}{\partial X_k} \right) \left( \frac{\partial X_k}{\partial r} \right) \right] \bigg|_{r=R} = K_i [c_i(t) - X_i(R, t)] \]  

Eqs (17) and (21) remain unchanged. However, in this study, only the case where \( \left( D_{pi} \right)_{ij} = 0 \) for \( i \neq j \) was considered since the binary adsorption system of butan-2-ol and 2-methylbutan-2-ol investigated is rather dilute. This implies that each liquid species diffuses independently of the others.

3 Method of numerical solution for spherical particles

The present work investigates principally the binary adsorption of butan-2-ol (CH₃CH(OH)CH₂CH₃) and tert-amylalcohol (2-methylbutan-2-ol, ((CH₃)₂C(OH)CH₂CH₃) (from
an aqueous waste streams) in activated porous carbon spheres, considering the fluid phase and the pore diffusion models. Before applying the method of orthogonal collocation on finite element, a new set of dimensionless variables is defined thus:

\[ Z = \frac{z}{z_e}, \quad \sigma = \frac{r^2}{R^2}, \quad \tau = \frac{tU_f}{L}, \quad \bar{c}_i = \frac{c_i}{(c_i)_0}, \quad \bar{X}_i = \frac{X_i}{(c_i)_0}, \quad Q^* = \frac{q^*}{(c_i)_0}, \quad P\varepsilon_i = \frac{LU_f}{D_{li}}, \quad Sh_i = \frac{2RK}{\varepsilon_p D_{pi}} \]

In the fluid phase enveloping the spherical particles in a packed column, in dimensionless form, the mass balance for a binary system in the fluid phase, where only the axial diffusion and film resistance effects are considered, is given by:

\[
\frac{\partial \bar{c}_i}{\partial \tau} + \frac{1}{Pe_i} \frac{\partial^2 \bar{c}_i}{\partial Z^2} = -\psi_i(\bar{c}_i - \bar{X}_i)_{i=1,2} \quad (i=1,2) \tag{28}
\]

where

\[
\psi_i = \begin{pmatrix} \left(1 - \frac{e_b}{e_b} \right) \left(3 \frac{K_b L}{R} \right) \frac{U_f}{U_f} & \left(1 - \frac{e_b}{e_b} \right) \left(3 \frac{K_b L}{R} \right) \frac{U_f}{U_f} \end{pmatrix} \tag{29}
\]

Eq. (28) is subject to the transformation of the initial and boundary conditions, given thus:

(i) \[ \bar{c}_i(0, \tau) = 0 \quad (i=1,2); \quad \tau \leq 0, \quad 1 \geq Z \geq 0 \tag{30} \]

(ii) \[ \bar{c}_i(0, \tau) = 1 + \frac{1}{Pe_i} \left( \frac{\partial \bar{c}_i}{\partial Z} \right)_{Z=0} \quad (i=1,2); \quad \tau > 0 \tag{31} \]

(iii) \[ \left. \frac{\partial \bar{c}_i}{\partial Z} \right|_{Z=1} = 0 \quad (i=1,2); \quad \tau > 0 \tag{32} \]

For spherical pellets, Eq. (13) for pore diffusion, with no chemical reaction, can be written for components 1 and 2, in dimensionless form, as given in Eqs. (33) and (34) respectively thus:

\[
\begin{bmatrix} \varepsilon_p + (q_1)_0 \frac{\partial Q^*_{11}}{\partial \bar{X}_1} \frac{\partial \bar{X}_1}{\partial \tau} + (q_1)_0 \frac{\partial Q^*_{11}}{\partial \bar{X}_1} \frac{\partial \bar{X}_1}{\partial \tau} = \frac{4 \varepsilon_p D_{p1} L}{R^2 U_f} \left( \sigma \frac{\partial^2 \bar{X}_1}{\partial \sigma^2} + \frac{3}{2} \frac{\partial \bar{X}_1}{\partial \sigma} \right) \\
\left( q_2 \right)_0 \frac{\partial Q^*_{22}}{\partial \bar{X}_1} \frac{\partial \bar{X}_1}{\partial \tau} + (q_2)_0 \frac{\partial Q^*_{22}}{\partial \bar{X}_1} \frac{\partial \bar{X}_1}{\partial \tau} = \frac{4 \varepsilon_p D_{p2} L}{R^2 U_f} \left( \sigma \frac{\partial^2 \bar{X}_2}{\partial \sigma^2} + \frac{3}{2} \frac{\partial \bar{X}_2}{\partial \sigma} \right)
\end{bmatrix} \tag{33, 34}
\]

In matrix-vector form, Eqs. (33) and (34) become:

\[
\begin{bmatrix} \Phi_1 & \Phi_2 & \bar{X}_1 \Phi_3 & \Phi_3 \\
\Phi_4 & \Phi_5 & \bar{X}_2 \Phi_6 & \Phi_6 \end{bmatrix} = 0 \tag{35}
\]

The solution to Equation (35) is:

\[
\begin{align*}
\dot{X}_1 &= \frac{\partial \bar{X}_1}{\partial \tau} = \frac{\Phi_3 \Phi_5 - \Phi_2 \Phi_6}{\Phi_1 \Phi_5 - \Phi_2 \Phi_4} \\
\dot{X}_2 &= \frac{\partial \bar{X}_2}{\partial \tau} = \frac{\Phi_6 \Phi_5 - \Phi_2 \Phi_4}{\Phi_1 \Phi_5 - \Phi_2 \Phi_4}
\end{align*} \tag{36, 37}
\]

where the expressions for \( \Phi_i, i=1-6 \), are given thus:

\[
\begin{align*}
\Phi_1 &= \varepsilon_p + \frac{(q_1)_0 \partial Q^*_{11}}{\partial \bar{X}_1} \\
\Phi_2 &= (q_1)_0 \frac{\partial Q^*_{11}}{\partial \bar{X}_1} \\
\Phi_3 &= \frac{4 \varepsilon_p D_{p1} L}{R^2 U_f} \left( \sigma \frac{\partial^2 \bar{X}_1}{\partial \sigma^2} + \frac{3}{2} \frac{\partial \bar{X}_1}{\partial \sigma} \right)
\end{align*} \tag{38, 39, 40}
\]
\[
\Phi_4 = \frac{(q_x)_0 \partial Q^*}{(c_2)_0 \partial x_i}
\]

\[
\Phi_5 = \varepsilon_p \frac{(q_x)_0 \partial Q^*}{(c_2)_0 \partial x_2}
\]

\[
\Phi_6 = \frac{4 \varepsilon_p D_{pq} L}{R^2 U_f} \left( \frac{\partial^2 x_2 + 3 \partial x_2}{2 \partial \sigma} \right)
\]

The transformation of the initial and boundary conditions in terms of the dimensionless variables yields:

(i) \( \bar{X}_i = 0 \quad (i=1,2); \quad \tau \leq 0, \quad 1 \geq \sigma \geq 0 \) \hspace{1cm} (44)

(ii) \( \frac{4}{Sh_i} \left( \frac{\partial \bar{X}_i}{\partial \sigma} \right)_{\sigma=1} = \left( \bar{c}_i - \bar{X}_i \right)_{\sigma=1} \quad (i=1,2); \quad 0 \leq Z \leq 1, \quad \tau > 0 \) \hspace{1cm} (45)

(iii) \( \frac{\partial \bar{X}_i}{\partial \sigma} = 0 \quad (i=1,2); \quad 0 \leq Z \leq 1, \quad \tau > 0 \) \hspace{1cm} (46)

Eqs. (28), (36) and (37) represent a set of four coupled, stiff, non-linear hyperbolic and parabolic partial differential equations respectively, which cannot be solved analytically but must be integrated numerically by any known method, which is stiffly stable. The set of four coupled, non-linear hyperbolic and parabolic partial differential equations are integrated numerically by the method of orthogonal collocation on finite element.

3.1 Orthogonal collocation on finite element method

The orthogonal collocation on finite element method (OCFEM) is a useful method for problems whose solution has steep gradients. Equally, the method can be applied to time-dependent problems and there is a combination of ordinary differential equations (ODEs) and algebraic equations (AEs) in achieving solution with the method. The method of orthogonal collocation on finite elements can be used for small times to better advantage than orthogonal collocation since the solution is steep and a global polynomial (in orthogonal collocation) requires many terms to approximate the solution. The arrangement of the collocation points is shown in Fig. 1.

![Fig. 1 Collocation points for OCFEM](image)

The orthogonal collocation on finite elements is a discretization approach, which combines the method of weighted residual with finite element method (Carey and Finlayson 1975; Finlayson 1980). The OCFEM is derived by dividing both axial and radial domains, \((0<Z<1, \, 0<\sigma<1)\), into a number of finite elements (in this study, of equal length) as shown in Fig. 2 and orthogonal collocation method (OCM) is applied within each element. The orthogonal collocation on finite elements...
element divides the domain $[0, 1]$ into finite elements and sets the residual to zero at the collocation points interior to the elements.

![Diagram of orthogonal collocation on finite elements](image)

**Fig. 2** Illustration of orthogonal collocation on finite elements

Each distributed variable, $u(x, t)$ is approximated by a low order (e.g., cubic) polynomial in each element, of the form:

$$u(x, t) = \alpha_0(t) + \alpha_1(t)x + \alpha_2(t)x^2 + \alpha_3(t)x^3$$  \hspace{1cm} (47)

which can be expressed as a linear combination of Lagrange polynomials. For instance, consider one finite element with four collocation points, $x_1, x_2, x_3$ and $x_4$, the Lagrange polynomial, $L_i(x_j)$ is given by:

$$L_i(x) = \prod_{j \neq i} \frac{x - x_j}{x_i - x_j}, \hspace{1cm} i, j = 1, \ldots, 4$$  \hspace{1cm} (48)

These polynomials have the property that:

$$L_i(x_j) = 1 \hspace{1cm} \text{if} \hspace{1cm} i = j$$

$$L_i(x_j) = 0 \hspace{1cm} \text{if} \hspace{1cm} i \neq j$$  \hspace{1cm} (49)

Eq. (47) in terms of Lagrange polynomial is written as:

$$u(x, t) = \sum_{j=1}^{4} \beta_j(t)L_i(x)$$  \hspace{1cm} (50)

Note that by the virtue of Eq. (49), we have:

$$u(x_i, t) = \beta_i(t)$$

Thus, $\beta_i(t)$ has a physical meaning as the value of distributed variable $u(x, t)$ at $x = x_i$. This is a special advantage of Eq. (50) over the usual expression, Eq. (47), since it is difficult to attach any physical importance to the coefficient $\alpha_i(t)$ appearing in Eq. (47).

Each finite element is normalized and the two ends of the element are chosen to be $x_1 = 0$ and $x_4 = 1$. Both $x_2$ and $x_3$ are chosen to be roots of shifted orthogonal polynomials because only this will lead to better approximation (Finlayson 1980). It can be seen that four unknowns such as $\beta_i, (i = 1, \ldots, 4)$ are introduced in each finite element. Thus, four equations are needed to be
able to solve the problem. Two equations are derived by enforcing the partial differential equation (PDE) at the interior collocation points $x_2$ and $x_3$.

It is mandatory that the trial function and its first derivative be continuous at the nodal or boundaries of element. The trial function is expressed in terms of Lagrange interpolation polynomial. The collocation points are the zeros of shifted Legendre and Chebyshev polynomials in the axial and radial domains respectively.

### 3.2 Application of orthogonal collocation on finite elements method

The numerical technique adopted for the solution of the developed models for the fluid and pore-fluid phases (Eqs. (28), (36) and (37)) is based on the method of lines with collocation technique coupled with an integrator for stiff ordinary differential equations. The two spatial coordinates (i.e., the column axis and particle radius) are then discretized using orthogonal collocation on finite element, also called orthogonal spline collocation (Villadsen and Michelsen 1978). The choice is required by the presence of very steep concentration profiles, both inside the spherical adsorbent and the column axis. As already observed, the stiff partial differential equations, which constitute the fixed bed adsorption model, are approximated through a semi-discrete system of differential algebraic equations (DAEs) through suitable piecewise polynomial approximation.

The OCFEM was applied by defining a new set of dimensionless variables for the axial position in the column and particle radius, with values lying between 0 and 1 i.e., $0 \leq Z \leq 1$ and $0 \leq \sigma \leq 1$. Both the axial and radial domains are divided into small number of elements and orthogonal collocation is applied within each element. The domains $Z$ and $\sigma$ are divided into a time independent spatial net constituted by $n_eA$ and $n_eR$ elements respectively in the interval $[0, 1]$. In this technique, the residual function is set orthogonal to the weight function. The choice of the weight function depends upon the type of orthogonal polynomial chosen. In OCFEM, the whole domain of interest such as $0 \leq Z \leq 1$ is divided into sub-domains called elements by placing the dividing points at $Z_p$ where $p = 1, 2, 3, \ldots, n_eA$ with $Z_1 = 0$ and $Z_{n_eA} = 1$. Within each element, a new variable, $u = \left(\frac{Z - Z_p}{h_{eA}}\right)$, is introduced such that $Z$ changes from $Z_p$ to $Z_{p+1}$. The collocations equations are obtained in terms of the solutions at the collocation points by applying orthogonal collocation directly on $u$. The trial functions and its first derivative are assumed to be continuous at the node points. The trial function is usually expressed in terms of Lagrangian interpolation polynomial.

In many practical problems, it is impossible to determine the exact solution to the governing differential equations. The exact solution defined in this context is an explicit expression for the solution, in terms of known functions, which exactly satisfies the governing differential equations and boundary conditions. The Lagrange interpolation polynomials are algebraically simple and easy for implementation on a computer. They provide a systematic procedure for constructing trial functions and for evaluating their derivatives at collocation points. Hence, the Lagrange formulation is used in this work as it was used in finite elements method (Zienkiewicz 1977; Bathe and Wilson 1976). Two dimensional linear transformations of the trial functions taken in terms of Lagrangian interpolation formula were used (Michelsen and Villadsen 1978; Arora et al. 2005). The value of concentration, $c$, at any point $(u_A, u_R, \tau)$ can be defined as the sum of the element of the tensor product $L_A(u_A) \otimes L_R(u_R) \otimes \hat{c}^* (\tau)$ so that:

$$
\hat{c}^* (\sigma, Z) = \sum_{jA=1}^{n_eA} \sum_{jR=1}^{n_eR} l_{jA}(u) l_{jR}(v) \hat{c}^* (jA, jR)
$$

$$
u = \frac{(Z - Z_{jA})}{h_{eA}}
$$
\( v = \frac{(\sigma - \sigma_{ir})}{h_R} \) (54)

Here, \( \bar{c}^{*R} (jA, jR) \) is the value of \( \bar{c}^* \) at the collocation points, \( u_{jA} \) and \( v_{jR} \) in both \( i_A \) and \( i_R \) elements. The collocation points, \( u_{jA} \), are the zeroes of the \((ncA-1)^{th}\) degree shifted Legendre polynomial on \( 0 \leq u \leq 1 \). Similar definitions apply in the \( \sigma(v) \) direction, though the collocation points \( v_{jR} \) are the zeroes of the \((ncR-1)^{th}\) degree shifted Chebyshev polynomial on \( 0 \leq v \leq 1 \). The element sizes are \( h_{ia} = z_{ia} - z_{ia} \), \( h_{ir} = \sigma_{ir+1} - \sigma_{ir} \) where \( z_{ia} \) denotes the \( z \) positions of the element sides, \( u_{jA} \) is a point in element \( i_A \) in the axial domain and \( v_{jR} \) is a point in element \( i_R \) in the radial direction. \( j_A \) and \( j_R \) the collocation points in the axial and radial domains respectively, \( L_A(u_A) \) and \( L_R(v_R) \) represent the value of the interpolating Lagrange polynomial in axial and radial domains respectively.

The first partial derivatives of the concentrations, \( \bar{c} \) and \( \bar{X} \) with respect to \( u_A \), \( u_R \) and \( \tau \) are thus:

\[
\frac{dc^*}{dZ} = \sum_{jA=1}^{ncA} \sum_{jR=1}^{ncR} l_A'(u_A) l_R(u_R) \bar{c}_{iA}^{*R}(j_A, j_R)(\tau)
\]

\[
\frac{d\bar{X}^*}{d\sigma} = \sum_{jA=1}^{ncA} \sum_{jR=1}^{ncR} l_A'(u_A) l_R(u_R) \bar{X}_{iA}^{*R}(j_A, j_R)(\tau)
\]

\[
\frac{dc^*}{d\tau} = \sum_{jA=1}^{ncA} \sum_{jR=1}^{ncR} l_A(u_A) l_R(u_R) \frac{dc_{iA}^{*R}(j_A, j_R)(\tau)}{d\tau}
\]

\[
\frac{d\bar{X}^*}{d\tau} = \sum_{jA=1}^{ncA} \sum_{jR=1}^{ncR} l_A(u_A) l_R(u_R) \frac{d\bar{X}_{iA}^{*R}(j_A, j_R)(\tau)}{d\tau}
\]

while the second derivatives are:

\[
\frac{d^2c^*}{dZ^2} = \sum_{jA=1}^{ncA} \sum_{jR=1}^{ncR} l_A''(u_A) l_R(u_R) \bar{c}_{iA}^{*R}(j_A, j_R)(\tau)
\]

\[
\frac{d^2\bar{X}^*}{d\sigma^2} = \sum_{jA=1}^{ncA} \sum_{jR=1}^{ncR} l_A''(u_A) l_R(u_R) \bar{X}_{iA}^{*R}(j_A, j_R)(\tau)
\]

Therefore, for each element, the first derivative with respect to \( u_A \) at the collocation points can be written as:

\[
\bar{c}^*(u_A, u_R) = \sum_{jA=1}^{ncA} (l_A'(u_A) u_A(j_A)) \bar{c}_{iA}^{*R}(j_A, j_R)(\tau), \quad j_A = 1, 2, \ldots, ncA, \quad j_R = 1, 2, \ldots, ncR
\]

In this study, equal number of elements in both \( Z \) and \( \sigma \) is used, i.e., \( neR = neA = 4 \). In axial domain, the zeros of shifted Legendre polynomial have been taken as collocation point. The zeros of Legendre polynomial are calculated from Eq. (62).

\[
F_{jA}(z) = (z - 0.5)F_{jA+1}(z) - \frac{(jA-1)^2}{4(2jA-1)(2jA-3)}F_{jA+2}(z), \quad jA = 1, 2, \ldots, ncA
\]

where \( F_1(z) = 0 \) and \( F_2(z) = 1 \).

In the radial domain, the zeros of shifted Chebyshev polynomial have been used due to its tendency to keep the error down to a minimum at the corners of a single spherical particle (Fan et al. 1971) since results are required at the corners in radial domain.
The approach adopted numerically involves substituting the approximate solution given by Eq. (52) into the coupled differential equations (28), (36) and (37) relative to each element in both \( Z \) and \( \sigma \) and into all the boundary conditions, given in Eqs. (31) and (32) for the fluid phase model and Eqs. (45) and (46) for the pore-fluid phase model, thereby obtaining the residual function. Then, all the conditions mentioned above are obtained by imposing the vanishing of the residuals at the boundaries and the vanishing of the residuals relative to the coupled differential equations at the selected \((nA−2)\) and \((ncR−2)\) internal collocation points in each \( i_A \) and \( i_R \) elements. Thus, the non-linear hyperbolic and parabolic partial differential equations for the fluid and pore-fluid phases respectively with boundary conditions are reduced to coupled algebraic differential systems, as given in Eqs. (63)–(70).

\[
\frac{d\overline{c}^{\text{IA}}_{1,k}}{d\tau} = \frac{1}{P e_{1}} \frac{1}{h_{eA}} \left( \sum_{s=1}^{N+1} A_{i_A, s} \overline{c}^{\text{IA}}_{1,s} \right) - \frac{1}{h_{eA}} \left( \sum_{s=1}^{N+1} A_{j_A, s} \overline{c}^{\text{IA}}_{1,s} \right) - \psi_{1} \left[ \overline{c}^{\text{IA}}_{1,k} - \overline{X}^{R}_{1,1A}(jA, p) \right] \tag{63}
\]

\[
\frac{d\overline{c}^{\text{IA}}_{2,k}}{d\tau} = \frac{1}{P e_{2}} \frac{1}{h_{eA}} \left( \sum_{s=1}^{N+1} A_{i_A, s} \overline{c}^{\text{IA}}_{2,s} \right) - \frac{1}{h_{eA}} \left( \sum_{s=1}^{N+1} A_{j_A, s} \overline{c}^{\text{IA}}_{2,s} \right) - \psi_{2} \left[ \overline{c}^{\text{IA}}_{2,k} - \overline{X}^{R}_{2,1A}(jA, p) \right] \tag{64}
\]

with \( \psi_{1} \) and \( \psi_{2} \) as already defined in Eq. (29). Eqs. (63) and (64) are subject to the initial conditions given in Eq. (44) as well as the following conditions:

**Continuity condition 1:** \( \overline{c}^{\text{IA}}_{k,N+1} = \overline{c}^{\text{IA}}_{k,1}, \ k = 1, 2 \) \tag{65}

The derivatives are given by:

\[
\frac{1}{h_{eA}} \left( \sum_{s=1}^{N+1} A_{i_A, s} \overline{c}^{\text{IA}}_{k,s} \right) = \frac{1}{h_{eA}} \left( \sum_{s=1}^{N+1} A_{N+1,s} \overline{c}^{\text{IA}}_{k,s} \right), \ k = 1, 2 \tag{66}
\]

**Boundary condition 1:** \( \overline{c}^{\text{IA}}_{k,1} = 1 + \frac{1}{P e_{k}} \frac{1}{h_{eA}} \left( \sum_{s=1}^{N+1} A_{i_A, s} \overline{c}^{\text{IA}}_{1,s} \right), \ k = 1, 2 \tag{67}
\]

**Boundary conditions 2:** \( \sum_{s=1}^{N+1} A_{N+1,s} \overline{c}^{\text{IA}}_{k,N+1} = 0, \ k = 1, 2 \tag{68}
\]

For pore diffusion, Eqs. (24), (36) and (37) become:

\[
\frac{d\overline{X}^{R}_{1,1A}(jA, jR)}{d\tau} = \frac{1}{\Delta} \left[ \Phi_{0} \Phi_{7} \left( \frac{4\Phi_{9}}{h_{eR}} \sum_{i=1}^{p} B^*_{j_R,i} \overline{X}^{R}_{1,1A}(jA, i) + \frac{6}{h_{eR}} \sum_{i=1}^{p} A^*_{j_R,i} \overline{X}^{R}_{1,1A}(jA, i) \right) \right] \tag{69}
\]

\[
- \Phi_{0} \Phi_{8} \left( \frac{4\Phi_{9}}{h_{eR}} \sum_{i=1}^{p} B^*_{j_R,i} \overline{X}^{R}_{2,1A}(jA, i) + \frac{6}{h_{eR}} \sum_{i=1}^{p} A^*_{j_R,i} \overline{X}^{R}_{2,1A}(jA, i) \right), \ i = 1, 2, \ldots, ncR = p \tag{70}
\]

\[
\frac{d\overline{X}^{R}_{2,1A}(jA, jR)}{d\tau} = \frac{1}{\Delta} \left[ \Phi_{1} \Phi_{8} \left( \frac{4\Phi_{9}}{h_{eR}} \sum_{i=1}^{p} B^*_{j_R,i} \overline{X}^{R}_{2,1A}(jA, i) + \frac{6}{h_{eR}} \sum_{i=1}^{p} A^*_{j_R,i} \overline{X}^{R}_{2,1A}(jA, i) \right) \right] \tag{71}
\]

\[
- \Phi_{1} \Phi_{7} \left( \frac{4\Phi_{9}}{h_{eR}} \sum_{i=1}^{p} B^*_{j_R,i} \overline{X}^{R}_{1,1A}(jA, i) + \frac{6}{h_{eR}} \sum_{i=1}^{p} A^*_{j_R,i} \overline{X}^{R}_{1,1A}(jA, i) \right), \ i = 1, 2, \ldots, ncR = p \tag{72}
\]

where

\[
\Delta = \Phi_{1} \Phi_{5} - \Phi_{2} \Phi_{4} \tag{73}
\]

\[
\Phi_{7} = \frac{\varepsilon_{p} D_{p} L}{R^2 U_f} \tag{74}
\]

\[
\Phi_{8} = \Phi_{7} D_{p2} / D_{p1} \tag{75}
\]

\[
\Phi_{9} = \nu_{j_R} h_{eR} + \sigma_{j_R} (jA, i) \tag{76}
\]

Eqs. (69) and (70) are subject to the initial conditions given in Eq. (44) as well as the following transformed conditions:
Continuity conditions: \( \overline{X}_{k_A}^{R} (k, p) = \overline{X}_{k_A}^{R} (j, i) , \quad k = 1, 2 \) \tag{75}

The derivatives are given as follows:
\[
\frac{1}{h} \sum_{i=1}^{n} \frac{A_{p,i}^*}{h} \overline{X}_{k_A}^{R} (j, i) = \frac{1}{h} \sum_{i=1}^{n} \frac{A_{i,j}^*}{h} \overline{X}_{k_A}^{R} (j, i) , \quad k = 1, 2 \tag{76}
\]

Boundary conditions 1: \( \sum_{i=1}^{n} A_{p,i}^* \overline{X}_{k_A}^{1} = 0 , \quad k = 1, 2 \) \tag{77}

Boundary conditions 2: \( \frac{4}{Sh} \left( \frac{1}{h} \sum_{i=1}^{n} A_{p,i}^* \overline{X}_{k_A}^{R} (j, i) = \overline{c}_{k_A}^{i} - \overline{X}_{k_A}^{R} , \quad k = 1, 2 \right) \tag{78}
\]

Eqs. (63), (64), (69) and (70) results in a stiff system of \( (4 \times ncA \times ncR \times neA \times ncR) \) coupled differential algebraic equations (DAEs), which is solved using the MATLAB built-in function ode15s, an implicit, multistep scheme suitable for solving stiff differential equations to avoid the problem of instability associated with explicit method. The subroutine uses backward differentiation formula to solve the resulting system of (63), (64), (69) and (70). In addition, an equal length of finite element was used for the solution of these modelling equations.

### 3.3 Convergence criterion

The convergence of the method for steady state is checked by using Eq. (79):
\[
L^* = (\Delta x_p)^2 \| M^{-1} \| C \quad \text{with} \quad 0 < L^* < 1 \tag{79}
\]

where \( M \) is the lumped coefficient matrix and \( C \) is the column matrix of the collocation solutions at any time \( t \). The value of \( \Delta x_p \) should be kept small enough to make \( L^* < 1 \) or more elements should be inserted (Arora et al. 2005). The method converges asymptotically as the number of elements increases.

### 3.4 Analysis of error functions

The bias, \( B \), value between the experimental and simulated pilot plant data was estimated thus (Kumar et al. 2015):
\[
B = \exp \left[ \frac{1}{N_e} \sum_{i=1}^{N_e} \text{In} \left( \frac{\overline{c}_{i,e}}{\overline{c}_{i,p}} \right) \right] \tag{80}
\]

Equally, the following error functions were used to compare the experimental breakthrough concentration of solute with the corresponding simulated (or predicted) values (Yaseen et al. 2019; Bello and Olafadehan 2021; Olafadehan 2021):
\[
R^2 = 1 - \frac{\sum_{i=1}^{N_e} (\overline{c}_{i,e} - \overline{c}_{i,p})^2}{\sum_{i=1}^{N_e} (\overline{c}_{i,p} - \overline{c})^2} \tag{81}
\]
\[
ERSSQ = \sum_{i=1}^{N_e} (\overline{c}_{i,e} - \overline{c}_{i,p})^2 \tag{82}
\]
\[
HYBRID = \sum_{i=1}^{N_e} \left( \frac{\overline{c}_{i,e} - \overline{c}_{i,p}}{\overline{c}_{i,e}} \right)^2 \tag{83}
\]
\[
MPSD = \sum_{i=1}^{N_e} \left( \frac{\overline{c}_{i,e} - \overline{c}_{i,p}}{\overline{c}_{i,e}} \right)^2 \tag{84}
\]
\[ EABS = \sum_{i=1}^{N_e} \left| \tilde{c}_{i,e} - \tilde{c}_{i,p} \right| \]  
(85)

\[ MAE = \frac{1}{N_e} \sum_{i=1}^{N_e} \left| \tilde{c}_{i,e} - \tilde{c}_{i,p} \right| \]  
(86)

\[ ARD = \frac{100}{N_e} \sum_{i=1}^{N_e} \left| \frac{\tilde{c}_{i,e} - \tilde{c}_{i,p}}{\tilde{c}_{i,e}} \right| \]  
(87)

\[ RMSE = \sqrt{\frac{\sum_{i=1}^{N_e} (\tilde{c}_{i,p} - \tilde{c}_{i,e})^2}{N_e}} \]  
(88)

\[ MAPE = \frac{1}{N_e} \sum_{i=1}^{N_e} \left( \frac{\tilde{c}_{i,e} - \tilde{c}_{i,p}}{\tilde{c}_{i,e}} \right) \]  
(89)

\[ MPE = \frac{100}{N_e} \sum_{i=1}^{N_e} \left| \frac{\tilde{c}_{i,e} - \tilde{c}_{i,p}}{\tilde{c}_{i,e}} \right| \]  
(90)

\[ SEP = \left( \frac{RMSE}{\tilde{c}_e} \right) \times 100 \]  
(91)

4 Simulation results and discussion

The computer program for the solution of the model equations developed for the liquid phase binary adsorption system of butan-2-ol and 2-methylbutan-2-ol on activated carbon as the adsorbent was written in MATLAB. The adsorbent material was Filtrasorb 100. The program employed orthogonal collocation on finite element method (OCFEM) with a non-linear ode integrator, ode 15s, in MATLAB environment to integrate the resulting stiff differential algebraic equations. An equal length of finite element was adopted. The asymptotic convergence of the method was found to be of order \( h^2 \).

The equilibrium adsorption isotherms determined for the binary system used in this study have the following form (Balzli 1977):

\[ q_1^* = \frac{1.06X_1^{1.217}}{X_1^{0.812} + 0.626X_2^{0.764}} \]  
(92)

\[ q_2^* = \frac{1.07X_2^{1.254}}{0.045X_1^{0.634} + X_2^{0.906}} \]  
(93)

where butan-2-ol and tert-amylalcohol (2-methylbutan-2-ol) are designated as components 1 and 2 respectively.

The calculated values of the axial diffusion coefficients, \( D_{l1} \) and \( D_{l2} \), using Liles and Geankoplis (1960) correlations are \( D_{l1} = D_{l2} = 4.0 \times 10^{-6} \) m²/s for butan-2-ol (component 1) and 2-methylbutan-2-ol (tert-amylalcohol), which indicate flat velocity profiles since \( \left( \frac{d_p}{d_p} \right)_{15} > 15 \). In this study, this ratio is 50. The film mass transfer coefficients for component 1, \( K_{f1} \), and component 2, \( K_{f2} \), are obtained using Wilson and Geankoplis (1966) and Mandelbaum and Böhm (1973) correlations as \( K_{f1} = 2.12 \times 10^{-5} \) m/s and \( K_{f2} = 1.68 \times 10^{-5} \) m/s. These correlations are well suited at low Reynolds numbers, \( Re \). In the binary adsorption system of butan-2-ol and 2-methylbutan-2-ol under investigation, \( Re \approx 1.58 \). The other parameter values used in the simulation studies are as follows (except where otherwise stated) : \( D_{p1} = 7.40 \times 10^{-10} \) m²/s,
\[ D_{p2} = 1.303 \times 10^{-9} \text{ m}^2/\text{s}, \quad \epsilon_b = 0.5, \quad \epsilon_p = 0.94, \quad U_f = 2.8 \times 10^{-3} \text{ m/s}, \quad (c_i)_0 = 1.0 \text{ kg/m}^3, \quad (i=1,2), \]
\[ \bar{c}_i(0,Z) = \bar{c}_i(0,Z) = 0, \quad \bar{X}_i(0,\sigma) = \bar{X}_z(0,\sigma) = 0, \quad q_{i0} = q_{i2} = 0 \text{ and } R = 5.0 \times 10^{-4} \text{ m}. \]

The constants in the Fritz and Schluender isotherms for butan-2-ol and 2-methylbutan-2-ol are given in Eqs. (92) and (93) respectively. These parameter values and constants were employed in the experimental work of Balzli (1977) and the simulation results in this study were thus compared with his experimental results.

The Biot number, \( Bi, \)
\[ = \frac{K_i R}{\epsilon_b D_{pi}}, \quad i = 1,2 \]
which represents the ratio of the solid phase mass transfer resistance to the fluid phase mass transfer resistance was found to be 28.6486 and 12.8933 for butan-2-ol and 2-methylbutan-2-ol respectively. The Sherwood number, \( Sh, \) is twice the Biot number. These values of \( Bi \) and \( Sh \) numbers affirm that both resistances are significant and none can be ignored. However, the solid phase mass transfer resistance for butan-2-ol is more than twice that for 2-methylbutan-2-ol.

The numerical solution of the resulting equations using orthogonal collocation method on finite element was obtained for three separate inlet concentrations of butan-2-ol and 2-methylbutan-2-ol in a fixed bed of 0.41 m, as depicted in Figs. 3–5.

**Fig. 3** Experimental and simulated breakthrough curves for simultaneous adsorption of butan-2-ol and 2-methylbutan-2-ol in a 0.41 m fixed bed (\( c_{i0} = c_{i2} = 1.0 \text{ kg/m}^3, \quad D_{pi} = 7.77 \times 10^{-10} \text{ m}^2/\text{s}, \quad D_{p2} = 1.303 \times 10^{-9} \text{ m}^2/\text{s} \))
Fig. 4  Experimental and simulated breakthrough curves for simultaneous adsorption of butan-2-ol and 2-methylbutan-2-ol in a 0.41 m fixed bed ($c_{01} = 1.0 \text{ kg/m}^3$, $c_{02} = 2.0 \text{ kg/m}^3$)

Fig. 5  Experimental and simulated breakthrough curves for simultaneous adsorption of butan-2-ol and 2-methylbutan-2-ol in a 0.41 m fixed bed ($c_{01} = 1.02 \text{ kg/m}^3$, $c_{02} = 2.53 \text{ kg/m}^3$, $D_{p1} = 7.40 \times 10^{-10} \text{ m}^2/\text{s}$, $D_{p2} = 1.303 \times 10^{-9} \text{ m}^2/\text{s}$)
Equally, the numerical solution of the resulting equations was obtained at two other different bed lengths of 0.82 m and 1.23 m, as shown in Figs. 6 and 7, in addition to the already presented simulated results for a bed length of 0.41 m.

**Fig. 6** Experimental and simulated breakthrough curves for adsorption of butan-2-ol in the binary system at different bed lengths ($c_{01} = c_{02} = 1.0 \text{ kg/m}^3$, $K_{f1} = 1.95 \times 10^{-5} \text{ m/s}$, $K_{f2} = 1.68 \times 10^{-5} \text{ m/s}$)

**Fig. 7** Experimental and simulated breakthrough curves for adsorption of 2-methylbutan-2-ol in the binary system at different bed lengths ($c_{01} = c_{02} = 1.0 \text{ kg/m}^3$, $K_{f1} = 1.95 \times 10^{-5} \text{ m/s}$, $K_{f2} = 1.68 \times 10^{-5} \text{ m/s}$)
In Figs. 3–7, the effluent concentration curves are all smooth and somewhat S-shaped (sigmoid) and are characterized by an initial low level of normalized concentration of solutes, which are then followed by a sharp and rather steep ascent to the exhaustion point where \( \tilde{c}_i = \frac{c_i}{(c_0)} \approx 1.0 \). At this point, all the adsorption sites had been occupied. The low normalized concentrations of butan-2-ol and 2-methylbutan-2-ol for appreciable times is due to the fact that during these times, effective adsorption occurs on the adsorbent surface since an enormous quantity of fresh adsorbent micropores is provided to produce a substantial rate of adsorption. After which, most of the activated carbon micro- and transitional pores are filled up with solutes (butan-2-ol and 2-methylbutan-2-ol) thereby resulting in a dramatic decline in adsorption, which is indicated by the sharp rising trend of the normalized concentration profile. Also, the dimensionless exit concentration of the less preferentially adsorbed component, butan-2-ol, is higher than its inlet concentration to the adsorption column for some time, as depicted in Figs. 3–6. This implies competitive multicomponent adsorption behavior on the adsorbent surface between butan-2-ol and 2-methylbutan-2-ol. In the previously adsorption stages, both butan-2-ol and 2-methylbutan-2-ol are adsorbed on the adsorbent (Filtrasorb 400). Afterwards, the non-key component (butan-2-ol) is being replaced owing to the stronger affinity of the key component (2-methylbutan-2-ol) than the former. Thus, butan-2-ol emerges in the effluent as a concentration summit, as shown in Figs. 3–6, even at increasing bed length. However, 2-methylbutan-2-ol is better selectively adsorbed on the adsorbent than butan-2-ol.

The breakthrough concentration, \( c_b \), of a component represents the maximum concentration that can be discarded and is often taken as \( 0.01 \leq c_b/c_0 \leq 0.05 \). The breakthrough (or allowable) concentration is determined by the process specifications (i.e., how the process is to be operated). For example, if a pollutant is being removed, the breakthrough concentration, \( c_b \), will be the government regulation for what the treatment plant can discharge to the environment without causing harmful effects to human being and watercourses. However, for a commercial product, where the column is removing color and odor, the breakthrough concentration is determined by the specification for product quality. In Fig. 3, the breakthrough point, \( (c_b, t_b) \) for butan-2-ol and 2-methylbutan-2-ol corresponds to \((0.02, 0.50 \text{ h})\) and \((0.02, 1.10 \text{ h})\) respectively under the specified pilot plant conditions in a 0.41 m adsorber. Keeping the allowable dimensionless exit concentration of components 1 and 2 at 0.02, the breakthrough times of butan-2-ol are obtained as 0.54 h and 0.76 h in Figs. 4 and 5 respectively. Equally in these figures, the predicted breakthrough times of 0.69 h and 0.81 h are obtained for 2-methylbutan-2-ol under the specified conditions in a 0.41 m adsorber. In Fig. 6, the breakthrough point, \( (c_b, t_b) \) for butan-2-ol corresponds to \((0.02, 0.64 \text{ h})\), \((0.02, 2.03 \text{ h})\) and \((0.02, 4.2 \text{ h})\) at bed lengths of 0.41 m, 0.82 m and 1.23 m respectively under the specified pilot plant conditions. The breakthrough times of 2-methylbutan-2-ol are obtained as 1.05 h, 2.89 h and 5.47 h at bed lengths of 0.41, 0.82 and 1.23 m respectively, as depicted in Fig. 7. Hence, the simulated results presented in Figs. 3–7 reveal that 2-methylbutan-2-ol elutes the bed at longer times than butan-2-ol since the former has stronger affinity than the latter and thus emerges in the effluent only after a long time. From Figs. 6 and 7, the breakthrough curves for butan-2-ol and 2-methylbutan-2-ol are delayed in the 0.82 m and 1.23 m adsorber when compared with the simulated results for these components in a 0.41 m adsorber. Therefore, in Figs. 6 and 7, it can be deduced that the length of bed affects the zenith of the wave fronts obtained for the non-key component as well as the breakthrough times of the solutes (i.e., the longer the bed, the greater the breakthrough times). The peak heights increase on doubling and tripling the bed length: the longer the bed, the greater the total amount of the non-key component (butan-2-ol) displaced. Equally, as peak increases, the breakthrough time increases. The separation between the wave fronts for the components increases in the longer beds, as presented in Figs. 6 and 7.
In Fig. 3, the bias values for \( \bar{c}_1 \) and \( \bar{c}_2 \) are estimated to be 0.996011 and 0.989171 respectively. In Fig. 4, these values are computed to be 0.997170 and 0.997320 respectively while in Fig. 5, they are obtained as 0.994019 and 0.998541 respectively for \( \bar{c}_1 \) and \( \bar{c}_2 \). The bias values obtained indicate that the errors between the experimental and simulated dimensionless exit concentrations of components 1 and 2 are normally distributed in Figs. Figs. 3–5. Moreover, in Fig. 3, the values of the coefficient of determination, \( R^2 \), for \( \bar{c}_1 \) and \( \bar{c}_2 \) are calculated to be 0.999946 and 0.999843 respectively. In Fig. 4, \( R^2 \) values for \( \bar{c}_1 \) and \( \bar{c}_2 \) are calculated to be 0.999807 and 0.999925 respectively while in Fig. 5, these values are 0.999397 and 0.999929 respectively. The error functions of \( ERRSQ, HYBRID, MPSD, EABS, MAE, ARD, RMSE, MAPE, MPE \) and \( SEP \) are computed as (7.0758 \times 10^{-5}, 8.4944 \times 10^{-5}, 0.000712, 0.019968, 0.002496, 0.600734\%, 0.002974, -0.004040, 0.592828\% and 0.394757\%) and (2.4649 \times 10^{-4}, 3.6934 \times 10^{-4}, 0.001444, 0.035982, 0.004498, 1.097747\%, 0.005551, -0.010977, 1.080052\% and 0.907602\%) for components 1 and 2 respectively in Fig. 3. The \( ERRSQ, HYBRID, MPSD, EABS, MAE, ARD, RMSE, MAPE, MPE \) and \( SEP \) values are computed as (2.8850 \times 10^{-4}, 2.8831 \times 10^{-4}, 3.3928 \times 10^{-4}, 0.046024, 0.003835, 0.464684\%, 0.004903, -0.002848, 0.462837\% and 0.571892\%) and (1.1680 \times 10^{-4}, 1.8435 \times 10^{-4}, 7.8399 \times 10^{-4}, 0.032311, 0.002485, 0.579054\%, 0.002997, -0.003671, 0.579266\% and 0.448258\%) for components 1 and 2 respectively in Fig. 4. In Fig. 5, the \( ERRSQ, HYBRID, MPSD, EABS, MAE, ARD, RMSE, MAPE, MPE \) and \( SEP \) values are computed as (5.7746 \times 10^{-4}, 5.6059 \times 10^{-4}, 5.4621 \times 10^{-4}, 0.060551, 0.006055, 0.602642, 0.007599, -0.006026, 0.597242\% and 0.871653\%) and (8.0758 \times 10^{-5}, 9.3184 \times 10^{-5}, 1.0802 \times 10^{-4}, 0.012578, 0.001258, 0.146552\%, 0.002842, -0.001466, 0.145480\% and 0.431577\%) for components 1 and 2 respectively. Hence, as revealed in Figs. 3–5, excellent agreements are achieved between the experimental and simulated dimensionless exit concentrations of butan-2-ol and 2-methylbutan-2-ol in a fixed bed of 0.41 m since \( B \approx 1.0, \ R^2 \approx 1.0 \) and very low values of error functions used in this study were obtained.

Table 1 shows the computed values of bias (\( B \)), regression coefficient, \( R^2 \), and error functions when the simulated breakthrough concentrations of the solutes were compared with their experimental values at different bed lengths.

**Table 1** Values of bias, regression coefficient and error functions with respect to comparison of the experimental breakthrough concentration with simulated results

<table>
<thead>
<tr>
<th>Functions</th>
<th>Error in simulated ( \bar{c}_1 )</th>
<th>Error in simulated ( \bar{c}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( L = 0.41 \text{ m} )</td>
<td>( L = 0.82 \text{ m} )</td>
</tr>
<tr>
<td>( B )</td>
<td>1.011405</td>
<td>0.994609</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.999612</td>
<td>0.999938</td>
</tr>
<tr>
<td>( ERRSQ )</td>
<td>5.1510 \times 10^{-4}</td>
<td>1.4244 \times 10^{-4}</td>
</tr>
<tr>
<td>( HYBRID )</td>
<td>0.001926</td>
<td>1.4915 \times 10^{-4}</td>
</tr>
<tr>
<td>( MPSD )</td>
<td>0.007991</td>
<td>7.3525 \times 10^{-4}</td>
</tr>
<tr>
<td>( EABS )</td>
<td>0.035769</td>
<td>0.025207</td>
</tr>
<tr>
<td>( MAE )</td>
<td>0.003974</td>
<td>0.002521</td>
</tr>
<tr>
<td>( ARD )</td>
<td>1.205944%</td>
<td>0.544238%</td>
</tr>
<tr>
<td>( RMSE )</td>
<td>0.007565</td>
<td>0.003774</td>
</tr>
<tr>
<td>( MAPE )</td>
<td>0.010870</td>
<td>-0.005442</td>
</tr>
<tr>
<td>( MPE )</td>
<td>1.302799%</td>
<td>0.537027%</td>
</tr>
</tbody>
</table>
In Table 1, the computed bias values for the simulated $\bar{c}_1$ and $\bar{c}_2$, when compared with the experimental results, are approximately 1.0, the values of the coefficient of determination, $R^2$, are close to unity and the error function values ($ERRSQ$, $HYBRID$, $MPSD$, $EABS$, $MAE$, $ARD$, $RMSE$, $MAPE$, $MPE$ and $SEP$) are very low. These values are indicative of excellent agreements being achieved between the experimental and simulated dimensionless exit concentrations of butan-2-ol and 2-methylbutan-2-ol in fixed beds of 0.41, 0.82 and 1.23 m, which are also obvious in Figs. 6 and 7.

5 Conclusion

A generalized, comprehensive and feasible mathematical model was presented in this study for the description of multicomponent adsorption in a fixed bed containing solid adsorbent. It accounted for intraparticle, interparticle and interphase diffusional resistances, conditions of non-equilibrium and non-linear binary adsorption of butan-2-ol and 2-methylbutan-2-ol onto activated carbon. The necessary numerical solution method of orthogonal collocation on finite element of the resulting equations was presented. Detailed statistical analyses were used to show that excellent agreements were achieved between the experimental data and the simulated results of breakthrough times and concentrations of the solutes in fixed beds of 0.41, 0.82 and 1.23 m. Equally, the observed chromatographic peaks of the less strongly adsorbed component and the effects of length of adsorber on breakthrough times and height of peak were accurately simulated. The results of this study are most useful in the design and analysis of fixed beds employed for the treatment of multicomponent aqueous wastewater effluents from industry.

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Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Declarations

Ethical Approval

This declaration is not applicable.

Authors’ contributions

Conceptualization: Olaosebikan Abidoye Olafadehan; Methodology: Kehinde Olawale Amoo and Ayo Joshua Adesina; Formal analysis and investigation: Olaosebikan Abidoye Olafadehan, Kehinde Olawale Amoo, Kamilu Folorunsho Kayode Oyedeko and Ayo Joshua Adesina; Writing – original draft preparation: Kehinde Olawale Amoo, and Ayo Joshua Adesina, Writing – review and editing: Olaosebikan Abidoye Olafadehan, Kehinde Olawale Amoo, Kamilu Folorunsho Kayode Oyedeko and Ayo Joshua Adesina; Resources: Olaosebikan Abidoye Olafadehan and Ayo Joshua Adesina; Supervision: Olaosebikan Abidoye Olafadehan and Kamilu Folorunsho Kayode Oyedeko
Availability of data and materials

All the data reported in this work can be made available upon request.

References


