A generalized volumetric dispersion model for a class of two-phase separation/reaction: finite difference solutions

Chairat Siripatana\textsuperscript{1,2}, Hathaikarn Thongpan\textsuperscript{1} and Arwut Promraksa\textsuperscript{1}
\textsuperscript{1}School of Engineering and Resources, Walailak University, 80161, Nakhon Si Thammarat Thailand
\textsuperscript{2}Biomass and Oil-Palm Excellence Center, Walailak University, 80161, Nakhon Si Thammarat Thailand

E-mail: schairat61@gmail.com

Abstract. This article explores a volumetric approach in formulating differential equations for a class of engineering flow problems involving component transfer within or between two phases. In contrast to conventional formulation which is based on linear velocities, this work proposed a slightly different approach based on volumetric flow-rate which is essentially constant in many industrial processes. In effect, many multi-dimensional flow problems found industrially can be simplified into multi-component or multi-phase but one-dimensional flow problems. The formulation is largely generic, covering counter-current, concurrent or batch, fixed and fluidized bed arrangement. It was also intended to use for start-up, shut-down, control and steady state simulation. Since many realistic and industrial operation are dynamic with variable velocity and porosity in relation to position, analytical solutions are rare and limited to only very simple cases. Thus we also provide a numerical solution using Crank-Nicolson finite difference scheme. This solution is inherently stable as tested against a few cases published in the literature. However, it is anticipated that, for unconfined flow or non-constant flow-rate, traditional formulation should be applied.

1. Introduction

Although dispersion models are notorious for complexity it has been proven very useful in describing various dispersive phenomena occurs frequently in chemical and environmental engineering fields [1-11]. However, applying dispersion models in unit operations such as adsorption column, ion-exchange resin, counter-current extractors, continuous anaerobic digestion such as upflow anaerobic sludge blanket (UASB), industrial flow reactors, or even the spread of contaminants along the water passages can be overkill particularly when the cross-sectional area of the columns/passages or/and column porosity vary with linear position. In most cases researchers choose to simplify the problems by assuming well-mixed (infinitely dispersive) or plug-flow (no axial dispersion) formulation otherwise they have to resort specialists who can deal with the mathematical complexity numerically.

The purpose of this article is to tackle mathematical problems for a class of engineering problems where two- or three-dimensional flow problems can be simplified with little loss of model usefulness by treating them as one-dimensional flow problems. Here a volumetric approach in formulating differential equations will be explored for a class of flow problems involving mass transfer and reactions in chemical and environmental engineering. The resulting model will be applicable for dispersive counter-current, co-current, moving-bed, packed-bed or batch modes where the flow passage is not uniform (so do the fluid/solid velocities) and column porosity varies with position.

2. Model development
Although the derivation in this article covers many common cases in industrial unit operations, we will illustrate the analysis for only counter-current configuration (CC) as shown in Figure 1. However, the resulting models (referred as volumetric dispersion model, VDM) for other frequent cases will be also summarized.

Figure 1. Differential volume analysis a) traditional formulation b) volumetric dispersive formulation

2.1 Traditional Dispersion Formulation (TDF) (sometimes referred “backmixing models”)
Conventionally, as elaborated in the monumental work of Mecklenburg and Hartland [15], dispersive mass transport models are formulated based on linear displacement ($z$) and velocity as depicted in Figure 1a. Here $x, y, u_x, u_y, S_x, S_y, D_x, D_y$ are solute concentration, the linear velocity, cross-sectional area, and dispersion coefficients, of dispersed (x-phase) and continuous phase (y-phase) at a certain position respectively. $x^*, y^*$ are the concentration which is in equilibrium with the opposite phase at a specific position. $k_x, k_y$ are the mass transfer coefficient based on x- and y-phase respectively. The following mass balances can written for x-phase.

\[
\text{inflow into } dV_x - \text{outflow from } dV_x + \text{mass transfer into } dV_x = \text{accumulation in } dV_x
\]

\[
u_x S_x - S_x D_x \frac{\partial x}{\partial z} - (1+dz \left( \frac{\partial}{\partial z} \right) (u_x S_x - S_x D_x \frac{\partial x}{\partial z})) + k_x dA(y-y^*) = dV_x \frac{\partial x}{\partial t}
\]

In general $u_x$ and $S_x$ change with $z$, thus we have

\[
u_x S_x dz \frac{\partial x}{\partial z} + S_x D_x \frac{\partial x}{\partial z} + dz \frac{\partial x}{\partial z} \frac{\partial (S_x D_x)}{\partial z} + k_x dA(y-y^*) = dV_x \frac{\partial x}{\partial t}
\]

However, if $u_x$ and $S_x$ can be assumed constant, independent of $z$, we have

\[
u_x S_x dz \frac{\partial x}{\partial z} + k_x dA(y-y^*) = dV_x \frac{\partial x}{\partial t}
\]

Equation (2) is more generic than (3) albeit introduces two extra derivative terms while Equation (3) is much simpler but too restrictive for many practical problems where both $u_x$ and $S_x$ vary with $z$. Certainly we can insist to use Equation (2) to represent non-uniform flow problems but it would be better to start with simpler balance equations that would reduce the complexity in finding solutions considerably. This should be done without significantly compromising model generality.

2.2 Volumetric Dispersion Formulation (VDF)
In searching for simpler approach, we noticed that this class of problems is normally uniform in term of flow rate rather than in term of linear velocities in both phases. Thus we started formulating the balance equation based on constant flow rates instead of velocities. Referring to Figure 1b, we have

For x-phase:
inflow into \( dV_x \) - outflow from \( dV_x \) + mass transfer into \( dV_x \) = accumulation in \( dV_x \)

\[
Q_x - \hat{D}_x \frac{\partial x}{\partial V_x} (1 + dV_x \frac{\partial}{\partial V_x}) (Q_x - \hat{D}_x \frac{\partial x}{\partial V_x}) + k_x dA(y - y^*) = dV_x \frac{\partial x}{\partial t}
\]  

(4)

For y-phase:

inflow into \( dV_y \) - outflow from \( dV_y \) + mass transfer in \( dV_y \) = accumulation in \( dV_y \)

\[
(1 + dV_y \frac{\partial}{\partial V_y}) (Q_y + \hat{D}_y \frac{\partial y}{\partial V_y}) - Q_y - \hat{D}_y \frac{\partial y}{\partial V_y} - k_y dA(y - y^*) = dV_y \frac{\partial y}{\partial t}
\]  

(5)

Here \( V_x, V_y, Q_x, Q_y, \hat{D}_x, \hat{D}_y \) are accumulative volume, volumetric flow rates and volumetric dispersion coefficients of x- and y-phases respectively. Accumulative volume relative to the left-end is referred as \( V = V_x + V_y \), and total volume as \( \mathcal{V} \). Notice that the mass transfer terms can be replaced by different rate relations, equilibrium isotherm or some expression of reaction rates. This is not restrictive although in this article we consider only mass transfer cases exclusively without reaction.

Assuming constant \( Q \) independent of \( V \), we have

\[
-Q_x dV_x \frac{\partial x}{\partial V_x} + Q_x dV_x \frac{\partial}{\partial V_x} \left( \frac{\hat{D}_x}{Q_x} \frac{\partial x}{\partial V_x} \right) + k_x dA(y - y^*) = dV_x \frac{\partial x}{\partial t}
\]  

(6)

For y-phase, assuming constant \( Q_y \) independent of \( V_y \), we have

\[
Q_y dV_y \frac{\partial y}{\partial V_y} + Q_y dV_y \frac{\partial}{\partial V_y} \left( \frac{\hat{D}_y}{Q_y} \frac{\partial y}{\partial V_y} \right) - k_y dA(y - y^*) = dV_y \frac{\partial y}{\partial t}
\]  

(7)

It is more convenient to write Equations (6) and (7) in term of \( \frac{\partial V}{\partial t} \) rather than \( \frac{\partial V_x}{\partial t} \) and \( \frac{\partial V_y}{\partial t} \). Noting that \( dV_x = (1 - \epsilon) dV \) and \( dV_y = \epsilon dV \), where \( \epsilon \equiv dV / (dV_x + dV_y) = dV_y / dV \) is column porosity at a specific position. After some algebraic manipulation, we have.

\[
-Q_x \frac{\partial x}{\partial V_x} + Q_x \frac{\partial}{\partial V_x} \left( \frac{\hat{D}_x}{Q_x} \frac{\partial x}{\partial V_x} \right) + k_x a(y - y^*) = \frac{\partial x}{\partial t}
\]  

(8)

\[
Q_y \frac{\partial y}{\partial V_y} + Q_y \frac{\partial}{\partial V_y} \left( \frac{\hat{D}_y}{Q_y} \frac{\partial y}{\partial V_y} \right) - k_y a(y - y^*) = \frac{\partial y}{\partial t}
\]  

(9)

Here \( a = dA / dV \) is mass transfer area per unit volume, and \( k_y a(y - y^*) = -k_x a(x - x^*) \).

Equation (6-9) have the level of complexity as that of (3) without the being too restrictive as its counterparts. Equation (8) and (9) can be normalized using the following dimensionless groups:

\[
\tau_x \equiv \mathcal{V} / Q_x, \tau_y \equiv \mathcal{V} / Q_y, \theta = t / \tau_x, \kappa = \tau_y / \tau_x, \theta_e = \mathcal{V} / Q_x \hat{D}_x, \theta_\mathcal{E} = \mathcal{V} / Q_y \hat{D}_y, T_y = k_y a \tau_y, Z = V / \mathcal{V} \].

Thus, we obtain

\[
\kappa \left( \frac{\partial (1 / \theta_e)}{\partial Z} - 1 \right) \frac{\partial x}{\partial Z} + k_x a \theta e \left( \frac{\partial^2 x}{\partial Z^2} + \frac{T_y}{1 - \epsilon} \right) \theta_e = \frac{\partial x}{\partial \theta}
\]  

(10)

BCs: At \( Z = 0 \):
\[ x_a = x - (\kappa / \theta_e) (\partial x / \partial Z) \] and at \( Z = 1 \):
\[ x_m = x \] or \( \partial x / \partial Z = 0 \)

\[
\frac{\partial (1 / \theta_e)}{\partial Z} + 1 \frac{\partial y}{\partial Z} + \frac{\partial^2 y}{\partial Z^2} \theta_e \theta e (y - y^*) = \frac{\partial y}{\partial \theta}
\]  

(11)

BCs: At \( Z = 0 \):
\[ y_m = y \] or \( \partial y / \partial Z = 0 \) and at \( Z = 1 \):
\[ y_m = y + (1 / \theta_e) (\partial y / \partial Z) \]

Similarly, it can be shown that, if y-phase flows through the column in the direction as portrayed in Figure 1b, the following equations are applied for x-phase for other important cases.

For fixed-bed adsorption and desorption (FB) where solid (x-phase) is not moving \((\kappa = 0, 1 / \theta_e \rightarrow \infty)\), equation (10) becomes

\[
\frac{T_y}{1 - \epsilon} (y - y^*) = \frac{\partial x}{\partial \theta}
\]  

(12)

For moving bed without in- and out-flow in x-phase \((\kappa = 0, 1 / \theta_e \neq 0)\), Equation (10) becomes.

\[
\kappa \left[ \frac{\partial (1 / \theta_e)}{\partial Z} \right] \frac{\partial x}{\partial Z} + \kappa \frac{\partial^2 x}{\partial Z^2} + \frac{T_y}{1 - \epsilon} \theta_e (y - y^*) = \frac{\partial x}{\partial \theta} \text{ where } \kappa \neq 0
\]  

(13)

It seems that, since \( \kappa = 0 \), then Equation (13) would reduce to the same form of (12). However, we observe that \( \kappa / \theta_e = [\mathcal{V} / \hat{D}_x] / (\mathcal{V} Q_x) \) which is non-zero. Thus if we denote \( \kappa / \theta_e \) as \( 1 / \theta_{e'} \).
Table 1 summarized the similarity and differences of these two models. The boundary and initial conditions are to \( \text{Pe} \) and \( S \) or \( \text{Pe} \) are constant, practically \( \kappa = \tau \) \( (16) \) are functions of \( \theta \) \( (15) \) and at \( \theta \) \( (18) \) \( (19) \) and at \( \theta \) \( (17) \) \( \partial \) and \( \partial \) are constant, practically \( x \) \( x \) and \( u \) \( u \) are varied with \( \theta \). Approximations (Figure 2.) for \( x \) derivatives. These are applied for \( y \) derivatives in a similar way.

**Remarks**
This comparison only valid when we assume constant \( u_x, u_y, S_x, S_y \) and \( Q_x, Q_y \) can be varied with \( Z \) and \( \theta \) This comparison only valid when we assume constant \( Q_x, Q_y \) and \( \kappa, \tau_x, \tau_y \) can be varied with \( Z \) and \( \theta \).

### 3. Solution methods: implicit finite difference

A large class of two-phase separation or reaction can be described by system of partial differential equation of the following form.

\[
a_x \frac{\partial^2 x}{\partial Z^2} + a_y \frac{\partial^2 y}{\partial Z^2} + b_x \frac{\partial x}{\partial Z} + b_y \frac{\partial y}{\partial Z} + c_x = \frac{\partial x}{\partial \theta} + O(\Delta x^2) \tag{16}
\]

\[
a_y \frac{\partial^2 y}{\partial Z^2} + b_x \frac{\partial^2 x}{\partial Z^2} + b_y \frac{\partial x}{\partial Z} + c_y = \frac{\partial y}{\partial \theta} + O(\Delta x^2) \tag{17}
\]

Here, \( a_x, b_x, c_x, a_y, b_y, c_y \) are functions of \( Z \). The boundary and initial conditions are to be given for specific cases. For simplicity, clarity and stability, we choose the Crank-Nicolson implicit finite difference method to obtain numerical solutions by replacing the following discrete approximations (Figure 2.) for \( x \) derivatives. These are applied for \( y \) derivatives in the a similar way.

\[
\frac{\partial x}{\partial Z} \approx \frac{x_j^i - x_{j-1}^i}{2 \Delta Z} + O(\Delta x^2) \tag{18}
\]

\[
\frac{\partial^2 x}{\partial Z^2} \approx \frac{x_{j+1}^i - 2x_j^i + x_{j-1}^i}{\Delta Z^2} + O(\Delta x^2) \tag{19}
\]
Although in general \( a_x, b_x, c_x, a_y, b_y, c_y \) are functions of \( Z \) as well as \( \theta \), for simplicity we will limit the finite difference solutions only for the cases that they are time independent.

| Types                      | Terms | Values               |
|----------------------------|-------|----------------------|
| All flow arrangements      | \( a_x \) | \( \partial (1/\hat{P}_e) / \partial Z + 1 \) |
|                            | \( b_y \) | \( 1/\hat{P}_e \) |
|                            | \( c_y \) | \( (T_y / \epsilon) (y - y^* ) \) |
|                            | \( b_x \) | \( 1/\hat{P}_e \) |
|                            | \( c_x \) | \( (T_y / (1 - \epsilon) (y - y^* ) \) |
| Counter-current (CC)       | \( a_x \) | \( \kappa [\partial (1/\hat{P}_e) / \partial Z - 1] \) |
| Moving bed (MB)            | \( a_x \) | \( \partial (1/\hat{P}_e) / \partial Z \) |
| Fixed bed (FB)             | \( a_x \) | 0 |
| Batch or co-current (BCC)  | \( a_x \) | \( \partial (1/\hat{P}_e) / \partial Z + 1 \) |

**Figure 2.** Volumetric channel discretization for the finite difference method.

\[
\frac{\partial x}{\partial \theta} = \frac{x^{i+1} - x^i}{\Delta \theta} + O(\Delta x^2) \tag{20}
\]

Here \( i \) and \( j \) are position and time index respectively. \( \Delta Z = 1/(n+1) \). And \( \Delta \theta \) is chosen to be sufficiently small to ensure stable output. The numerical solution for Equation (16) and (17) can be written in the following matrix forms.

\[ A_{x} x = C_{x}, \quad A_{y} y = C_{y} \tag{21} \]

Thus

\[ x = A_{x}^{-1} C_{x} \quad \text{and} \quad y = A_{y}^{-1} C_{y} \tag{22} \]

For \( k \in [x, y] \)

\[
A_{k} = \begin{bmatrix}
F_{k} & G_{k} & M_{k,1} & N_{k,1} & O_{k,1} & 0_{k,1} \\
M_{k,2} & N_{k,2} & O_{k,2} & 0_{k,2} & \ddots & \ddots \\
M_{k,n-2} & N_{k,n-2} & O_{k,n-2} & 0_{k,n-2} & \ddots & \ddots \\
M_{k,n-1} & N_{k,n-1} & O_{k,n-1} & 0_{k,n-1} & H_{k} & I_{k}
\end{bmatrix}
\]

For \( y \)-phase, from BCs we have \( Z = 0, \rightarrow y_{-1} = y_{1} \) and \( Z = 1, \rightarrow y_{n+1} = y_{0} \); \( y_{n+1} = 2 \hat{P}_e \Delta Z \). All flow arrangements have same forms of \( F_y, G_y, H_y, I_y, C_{y,0}, C_{y}, \); that is \( F_y = N_y, \quad G_y = M_y, \quad H_y, \quad I_y, \quad C_{y,0}, \quad C_{y} \); \( \Delta Z = 1/(n+1) \). And \( \Delta \theta \) is chosen to be sufficiently small to ensure stable output. The numerical solution for Equation (16) and (17) can be written in the following matrix forms.
in Table 3. The simulation procedure can be summarized schematically as in Figure 3. An illustrative results shown in this article will based on a moving-bed (MB) column depicted in Figure 4 (a section of vertical cone). The results will be compared with the simulation results from the volumetrically equivalent uniform column and that from the inverted column of the same shape.

| Type       | Terms                                                                 |
|------------|----------------------------------------------------------------------|
| CC         | BCs: \( Z=0 \rightarrow x_n = \rho_{x,0}(x_n - x_0) + x_1 \), \( \rho_{x,0} = 2 \text{Pe}_{x,0} \Delta Z \) and \( Z=1 \rightarrow x_{n+1} = x_{n-1} \) |
|            | \( F_z = N_{x,0} - \rho_{x,0}M_{z,0} \), \( G_z = O_{x,0} + M_{z,0} \), \( H_z = M_{x,0} + O_{x,0} \), \( I_z = N_{x,0} \) |
|            | \( C_{x,0} = \rho_{x,0}P_{x,0}x_0 \Delta Z - \rho_{x,0}M_{z,0}x_0 \sqrt{1 + (Q_{z,0} - \rho_{x,0}P_{x,0})x_0 + (R_{z,0} + P_{x,0})x_0^2 - Y_{z,0}} \) |
|            | \( C_{x,n} = (P_{x,n} + R_{z,n})x_0x_j^2 - O_{x,n}x_0 \sqrt{1 + (Q_{z,0} - \rho_{x,0}P_{x,0})x_0 + (R_{z,0} + P_{x,0})x_0^2 - Y_{z,0}} \) |
| BCC        | BCs: \( Z=0 \rightarrow x_n = x_1 \) and \( Z=1 \rightarrow x_{n+1} = \rho_{x,0}(x_n - x_0) + x_1 \), \( \rho_{x,0} = 2 \text{Pe}_{x,0} \Delta Z \) |
|            | \( F_z = N_{x,0} \), \( G_z = M_{x,0} + O_{x,0} \), \( H_z = M_{x,0} + O_{x,0} \), \( I_z = N_{x,0} - \rho_{x,0}O_{x,0} \) |
|            | \( C_{x,0} = O_{x,0}x_0^2 + (P_{x,0} + R_{z,0})x_0 - Y_{z,0} \), \( C_{x,n} = (P_{x,n} + R_{z,n})x_0x_j^2 - O_{x,n}x_0 \sqrt{1 + (Q_{z,0} - \rho_{x,0}P_{x,0})x_0 + (R_{z,0} + P_{x,0})x_0^2 - Y_{z,0}} \) |
| MB/ FB     | \( x_{n+1} = x_n, x_0 = x_n - 1 \) \( F_z = N_{x,0}, G_z = M_{x,0} + O_{x,0}, H_z = M_{x,0} + O_{x,0}, I_z = N_{x,0} \) |
|            | \( C_{x,0} = O_{x,0}x_0^2 + (P_{x,0} + R_{z,0})x_0 - Y_{z,0} \), \( C_{x,n} = (P_{x,n} + R_{z,n})x_0x_j^2 - O_{x,n}x_0 \sqrt{1 + (Q_{z,0} - \rho_{x,0}P_{x,0})x_0 + (R_{z,0} + P_{x,0})x_0^2 - Y_{z,0}} \) |

**Figure 3.** Solution algorithm for simulating concentration profile inside a column based on Equations (10-16)

**Figure 4.** A moving bed with no in-out-flow, having variable (as a function of \( Z \)) cross-sections \( S, \epsilon, T_y, \text{Pe}_x \), and \( \text{Pe}_y \)

4. Verification with the work of Rittirut et al. [13,14]

Rittirut et al [13,14] developed a counter-current diffusion-dispersion model for industrial extraction of fruit juices based on a specific case similar to current volumetric formulation. They verified the numerical solutions of the model by comparing them with the well-established/analytical solutions for steady-state counter-current configuration provided by Mecklenburgh and Hartland [15]. To use their results as a specific case for comparison, we did the following steps.

Firstly, we mapped our models with their models to relate all parameters. Essentially, we found that their model is a special case of the current models which include more popular flow arrangement including counter-current, co-current/batch, fixed and moving bed. One of their inherently-limited assumption, unfortunately, is that the extraction draft \( \alpha \): the ratio of the flow rate of continuous
such that over the flow rate of dispersed phase ($Q_s$) determined the porosity ($\epsilon$) such that 
$$\alpha = Q_s/Q_L = V_s/V_L = \alpha_s = \epsilon/(1-\epsilon).$$
This assumption implies that 
$$\kappa = (\alpha_s/Q_s)/(\alpha_s/Q_s) = 1,$$
$$\tau = \tau_c = \tau_x$$
and 
$$\theta = \theta_c = \theta_x = \theta(1-\epsilon).$$
Although this assumption may be not serious for their experimental cases, it severely restricted the utility of their formulation for more general counter-current flow configuration. This restriction is largely removed in the current VDF formulation however. That is to say the formulation in this article allows the independence between the hold-up (as indicated by $\epsilon$) in the column and the corresponding flow ratio (as indicated by $\alpha$).

From their work, the following intermediate differential equations were obtained after direct substituting $Q_s, Q_x$ for $S, L$ (the notations used in Rittitur et al as equivalent to $Q_s, Q_x$).

$$-\frac{\partial x}{\partial Z} + \frac{1}{\partial x} \frac{dA}{\partial Z} (x-x^*) = -\frac{\partial x}{\partial Z} + \frac{1}{\partial x} \frac{dA}{\partial Z} (1-\epsilon) = \frac{\partial x}{\partial 0_x} = \frac{\partial x}{\partial 0_x}$$

Similarly for continuous phase,

$$\frac{\partial y}{\partial Z} + \frac{1}{\partial x} \frac{dA}{\partial Z} (x-x^*) = \frac{\partial y}{\partial Z} + \frac{1}{\partial x} \frac{dA}{\partial Z} (1-\epsilon) = \frac{\partial y}{\partial 0_x} = \frac{\partial y}{\partial 0_x}$$

Matching Equation (23) and (24) to (10) and (11), assuming equilibrium constant ($m$) as unity, and noting that $k_a(y-x^*) = -k_a(x-x^*)$, we have

$$P = \tilde{U}_x, \alpha = R = \tilde{U}_x, \kappa = 1, \alpha = Q_s/Q_x = V_s/V_x = \alpha_s = \epsilon/(1-\epsilon), T_s = T_s/(1-\epsilon).$$

**Table 4. Parameters’ values used for stability test and verification as compared to those of Rittitur et al [13,14] and Mecklenburgh and Hartland [15].**

| Parameters | Values |
|------------|--------|
| $\alpha = Q_s/Q_x = \alpha_s = \epsilon/(1-\epsilon)$ | 0.5 | 0.5 | 0.5 | 1.0 | 1.5 | 1.5 | 1.5 | 1.5 | 2.0 |
| $P = \tilde{U}_x$ | 2.0 | 5.0 | 20 | 100 | 10 | 20 | 20 | 100 | 100 |
| $R = \tilde{U}_x/\alpha$ | 0.1 | 5.0 | 20 | 100 | 20 | 0.01 | 1.0 | 20 | 100 | 100 |
| $T_s = T_s/(1-\epsilon)$ | 0.01 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 20 |

For counter-current extraction, the numerical solutions for this work give identical solutions as their works for all cases given in their articles. The steady-state solutions in their results (and thus our results) agreed well (within 1% relative error) with the well-established solution given by Mecklenburgh and Hartland [15]. Since the formulation of Rittitur et al [13,14] is simply a special case of the current formulation, the current VDF is verified only partially. However, to verify the simulation results for unsteady state cases thoroughly, we need much more elaborate effort since only few solutions for (only) plug-flow cases are available. This is not treated in this article.

**5. Illustrative simulation: Batch and Moving-bed (MB) adsorption**

In order to illustrate the applicability of VDM, we will consider a special case of a MB/FB adsorption as depicted in Figure 4. It should be noted that a FB adsorber is a special case of MB which has $\kappa = 0$ and $\tilde{U}_x \to \infty$ or the bed is completely at rest. This means $a = b_c = 0$. This flow (MB) configuration covers many unit operations including: fluidized-bed adsorbers, fluidized-dryers, fluidized-bed reactors, ion-exchange column, packed-bed reactor, up-flow anaerobic sludge blanket (UASB) reactors etc.

*5.1 Batch direct yellow ARLE dye adsorption*

Suppose we want to adsorb ARLE dye onto coconut palm shell-based activated carbon (CPS-AC) in a moving-bed adsorber depicted in Figure 4. The illustration presented here is based on the equilibrium sorption isotherm of CPS-AC versus the ARLE dye given by Módenes et al. [16]. In their papers, the best isotherm representation was the famous Langmuir equation of the following form.

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} = \frac{101.56 \times 0.044 C_e}{1 + 0.044 C_e}$$

where $C_e$ (mg dm$^{-3}$) the concentration of ARLE dye at equilibrium, $q_e$ (mg g$^{-1}$) the amount of
dye adsorbed onto CPS-AC at equilibrium, \( Q_* \approx 101.56 \) (mg g\(^{-1}\)) the maximum capacity of the absorbent and \( b=0.044 \) (dm\(^3\) mg\(^{-1}\)) a Langmuir parameter. Given the density of water-saturated CPS-AC as approximately equal to that of water (1,000 g dm\(^{-3}\)), equation (25) can be translated as follows. That is \( y^* = C_* \), and \( x^* = 1000q_* \). If we define \( x(t=0) = 0 \) and \( x_w \) as the maximum absorbent capacity in mg dm\(^{-3}\). Thus we have,

\[
x^* = 1000q_* = \frac{1000Q_0}{1+b} + \frac{x_w b y_*}{1+b} = \frac{4468 y_*}{1+0.044 y_*} \quad \text{or} \quad y^* = \frac{x^*}{4468-0.044 x^*} = \frac{x}{b(x_w-x)} \quad (26)
\]

Then we can obtain the numerical solution from the following PDEs and their respective boundary conditions.

\[
\left( \frac{\partial (1/Pe)}{\partial Z} \right) + \left. \frac{1}{Pe} \frac{\partial^2 y}{\partial Z^2} \right|_{Z=0} - \frac{k_a y \tau}{\epsilon} x \left( \frac{4468 y}{1+0.044 y} \right) = \frac{\partial y}{\partial \theta} \quad (27)
\]

**BCs:** At \( Z=0 \): \( x_w = x - (\epsilon/Pe)e_{t-0}(\partial x/\partial Z) \) and at \( Z=1 \): \( x_{out} = x \) or \( \partial x/\partial Z = 0 \)

\[
\left( \frac{1}{Pe_t} \frac{\partial^2 y}{\partial Z^2} \right) + \left. \frac{k_a y \tau}{\epsilon} x \left( \frac{4468 y}{1+0.044 y} \right) = \frac{\partial y}{\partial \theta} \quad (28)
\]

**BCs:** At \( Z=0 \): \( x_1 = x_1 \) or \( \partial x/\partial Z = 0 \) and at \( Z=1 \): \( x_{out+1} = x_{out-1} \) or \( \partial x/\partial Z = 0 \)

Mődenes et al. [16] also studied the kinetics of ARLE dye batch adsorption onto CPS-AC (0.177 mm particle size). An experiment was carried out for 96 h at pH 2.0, temperature 30 °C, stirring speed 120 rpm, the initial dye concentration 70 mg dm\(^{-3}\) and used 0.3 g of CPS-AC suspending in 0.125 dm\(^3\) dye solutions. We analysed their data by assuming well-mixed in both solid and liquid phases \( 1/Pe_t \approx 1/Pe = 0 \) of which equation (27) and (28) reduced to the following most simplified form.

\[
\frac{dx}{dt} = k_a \frac{1}{1-\epsilon} \left( y - y^* \right) = \frac{1}{1-\epsilon} \left( \frac{x}{4468-0.044 x} - \frac{4468 y}{1+0.044 y} \right) \quad (29)
\]

\[
\frac{dy}{dt} = k_a \frac{1}{1-\epsilon} \left( y - y^* \right) = \frac{1}{1-\epsilon} \left( \frac{x}{4468-0.044 x} - \frac{4468 y}{1+0.044 y} \right) \quad (30)
\]

**Initial conditions:** \( x(0) = 0 \) an \( y(0) = 70 \) (mg dm\(^{-3}\))

In deriving equations (29) and (30) a few assumptions were made including constant overall mass transfer coefficient \( K_s = k_a \), Langmuir equilibrium isotherm and constant solid-liquid ratio (or external porosity, \( \epsilon \)). This two first-order ODEs were solved numerically using standard methods provided in Scipy: a scientific module for Python programming language. Our task here is to estimate the magnitudes of \( k_a \) and \( \epsilon \) by matching some experimental data from the article to the simulation produced from Equation (29) and (30). As shown in Figure 4, although the model did not fit the data well in the initial period (\( t<10 \) h) due to surface adsorption, \( K_s \) was found to be 5.x10\(^{-3}\) h\(^{-1}\) with \( \epsilon = 0.9945 \) approximately. Figure 5a demonstrates the good fit between experimental data provided by Mődenes et al. [16] and the best estimated profile simulated by Equation (29) and (30). Figure 5b is the sorption isotherm taken from the same source to be used in our demonstration.

5.2 Direct yellow ARLE dye adsorption in moving-bed and fixed-bed adsorbers

Now let us proceed to MB illustrative simulation which based on the column geometry as depicted in Figure 4 given \( r_0, r_s \) and \( L \) as 0.05, 0.1 and 1 m respectively. This provides the total volume of 0.018326 m\(^3\) (or 18.326 dm\(^3\)) which equivalent to the uniform column having \( r \) of 0.076376 m. In the subsequent simulations \( K_s \) of 5.x10\(^{-3}\) h\(^{-1}\) was used exclusively. Firstly we will show how variable \( \epsilon(t) \) affects concentration profile in the absorber (uniform cross-sectional area, \( r = 0.076376 \) m) (Figure 6) and secondly we illustrate how VDM is used for non-uniform column (Figure 7).

It is illustrated that both external porosity and variable column cross-section have strong effects on concentration profiles in both solid and liquid phases. In the examples given, however, we assume that the solid phase is essential fixed \( Pe_t \to \infty \) and the liquid phase disperses such that \( Pe_r = 5 \). Low porosity (thus high density of absorbent) at the liquid inlet tends to make the concentration profile in solid phase flat while variable cross-sectional area causes the profile skew depending on the direction
of increasing (or decreasing) cross-sectional area. Similar trends occur for liquid phase but adsorption time only weakly affects the liquid profile in the simulation ranges.

Figure 5. (a) Fitting Equation (29) and (30) to a batch adsorption data in Módenes et al. [16] from which $K_x$ was estimated as $5 \times 10^{-5}$ h$^{-1}$ (b) Its corresponding sorption isotherm.

Figure 6. Illustrated numerical simulation of a moving-bed adsorption having variable external porosity ($\epsilon$) (a) concentration profile in solid phase (b) concentration profile in liquid phase. ($\overline{Pe}_x = 200$, $\overline{Pe}_y = 5$)

Figure 7. Illustrated numerical simulation of a moving-bed adsorption having variable cross-sectional area (a) concentration profile in solid phase (b) concentration profile in liquid phase. ($\overline{Pe}_x = 200$, $\overline{Pe}_y = 5$)
In the specific cases illustrated here, it seems that, although both variable porosity and cross-section affected strongly the concentration profiles in dispersed phase, the adsorption effectiveness was essentially the same as judged from the concentration profiles in liquid phase. This can be explained that CPS-AC had very high adsorption capacity such that, in the range of our simulated experiments, its unused capacity did not decrease low enough to have a significant effect on the profile of the liquid phase.

Although it is not shown here, we also conducted a similar simulation experiments based on batch adsorption data provided by Yasemin and Zeki [17] and Kujundziski et al [18] and had similar results albeit there were some instability for the simulation cases based on the data from [18] due to very high non-linearity of the corresponding adsorption isotherm.

6. Conclusions

Volumetric dispersion models developed in this work can simplify a class of problems appeared in many continuous and batch mass-transfer operations where the cross-sectional area and porosity are varied with position (thus so too the velocities of dispersed and continuous phases) as long as the flow-rates of both dispersed and continuous phases are essentially constant. This work also suggests that many problems in chemical and environmental engineering can be simplified and extended by using volumetric approaches in model formulation to achieve better models in terms of both simplicity and generality. However, it is anticipated that for unconfined flow where flow rate is not constant TDF should be applied because the constant flow-rate assumption is invalid for VDF.

7. Acknowledgment

The authors would like to thanks Walailak University and Ministry of Science and Technology of Thailand grant for financial support.

8. References

[1] Mohanty S 2000 Rev. Chem. Eng. 16 3 199-248
[2] Pirdashti M, and Kompany R. 2009 Iranian J. Chem. Eng. 6 3 46-56
[3] Rados R, Al-Dahhan M H, and Dudikovic M P 2003 Catalysis Today. 79-80 211-218
[4] Mahdi I H 2009 Al-Khwarizmi Eng. J. 5 4 1-12
[5] Ganaie I A, Arora S, and Kukreja V K 2013 Int. J. of Differential Equations. 2013:ID 875298
[6] Choi J-W, Min J, Lee W-H, and Lee S-B 2000 Biotechnol. and Bioproc. Eng. 5 65-70
[7] Zeng Y, Mu S J, Lou S J, Tartakovsky B, Guiot S R and Wu P 2005 Biochem. Eng. J. 25 113-123
[8] Iliuta I, Bildea S C, Iliuta, M C and Larachi F 2002 Brazilian J. Chem. Eng. 19 1 1-19
[9] Pérez J, Aldana G, Useche M, Rincón N, Bracho N, and Mesa J 2010 Rev. Téc. Ing. Univ. Zulia. 33 3 213-222
[10] Nigam K D P, Iliuta 1, and Larachi F 2001 Chem. Eng. and Processing 41 365-371
[11] Ren T-T, Mu Y, Yu H-Q, Harada H, and Li Y-Y 2008 Chem. Eng. J. 142 182-189
[12] Korsak L 2008 Anaerobic Treatment of Wastewater in a UASB Reactor. Master Thesis, Department of Chemical Engineering and Technology, Royal Institute of Technology, Stockholm, Sweden.
[13] Rittirut W, Thongurai C and Siripatana C 2010 Int. J. of Chem. Reactor Eng. 8 A112. 1-35.
[14] Rittirut W, Thongurai C and Siripatana C. 2010 Int. J. of Chem. Reactor Eng. 8 A113. 1-30.
[15] Mecklenburgh J C and Hartland S 1975 The Theory of Backmixing: The Design of Continuous Flow Chemical Plant with Backming, John Wiley & Son, London.
[16] Módenes A N, Scheufele F B, Espinoza-Quíñones F R, Carraro de Souza P S, Cripa C R B, dos Santos J, Steffen V, and Kroumov A D 2015 Int. J. Bioautomation, 19 2 187-206
[17] Yasemin B, and Zeki T 2007 J. Environ. Sc. 19 160-166
[18] Kujundziski A P, Markovska L and Meshko V 2015 Zaštita Materijala, 56 2 179-190