Adsorption in fixed bed – mathematical modelling

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1. Introduction
The development and application of predictive and simulative mathematical models for designing treatment processes has become an important area in environmental engineering in recent years. Process modelling is an important tool not only for experimental data analysis but also for the process design and optimization. Advanced numerical methods are necessary whenever a more sophisticated mathematical model is to be solved. Often, simplified models, neglecting some of the mass transfer resistances, are used. Obviously, the applicability of these simplified models is limited.

This paper deals with a single component isothermal fixed bed adsorption. Axial dispersion, external mass transfer, intra-particle diffusion and adsorption equilibrium are considered. The corresponding mathematical model is solved applying the finite difference method. Some numerical results have been compared with those published in Hang (2003).

The main goal of this research is to formulate and solve adsorption module that might be incorporated in a model of adsorption - catalytic oxidation gas purification unit. The proposed mathematical model is solved using tools provided by MATLAB.

2. Mathematical model

An adsorber is considered as a fixed bed column with constant void fraction $\varepsilon_2$. The fixed bed is composed of spherical particles of adsorbent with the mean diameter $d_p$. The adsorbent is a porous solid with void fraction $\varepsilon_1$.

![Fig. 2.1 Model of the fixed bed column](image)

For the model investigated let us consider the following assumption:

- single component adsorption,
- plug flow with constant volumetric flow rate through the column,
- no radial concentration gradient in the column,
isothermal process within the column,
• solid particles are spherical, uniform in size,
• constant pore diffusivity,
• constant mass transfer coefficient,
• the kinetics of surface adsorption is fast enough and so it need not be considered in the model.

The heterogeneous model has been used to describe overall process. Accumulation, convection, axial dispersion, and interfacial flux terms are included in the governing equation (1) for the bulk-fluid phase of the column.

$$\frac{\partial C^*}{\partial \tau} = \frac{1}{Pe} \frac{\partial^2 C^*}{\partial \eta^2} - \frac{\partial C^*}{\partial \eta} - \gamma \left( C^* - C^{*}_{p|z=1} \right)$$ \hspace{1cm} (1)

The boundary conditions for the inlet and the outlet of the column, and the initial condition are of the following form

$$\frac{\partial C^*}{\partial \eta} \bigg|_{\eta=0} = Pe \left( C^*_{p|\eta=0} - 1 \right),$$ \hspace{1cm} (2)

$$\frac{\partial C^*}{\partial \eta} \bigg|_{\eta=1} = 0,$$ \hspace{1cm} (3)

$$C^*(\eta,0) = 0.$$ \hspace{1cm} (4)

Accumulation in the pores as well as in the solid phase, and radial diffusion in the particle is described by equation (5).

$$\left( 1 + K \frac{\partial q^*}{\partial C^*_p} \right) \frac{\partial C^*_p}{\partial \tau} = \delta \left( \frac{\partial^2 C^*_p}{\partial \xi^2} + \frac{2}{\xi} \frac{\partial C^*_p}{\partial \xi} \right)$$ \hspace{1cm} (5)

The Langmuir type of adsorption isotherm has been considered in this paper:

$$q^* = \frac{AC^*_p}{1 + (A-1)C^*_p},$$ \hspace{1cm} (6)

where $A$ is

$$A = 1 + bC_f.$$ \hspace{1cm} (7)

Substituting the $\partial q^*/\partial C^*_p$ term in the equation (5) by

$$\frac{\partial q^*}{\partial C^*_p} = \frac{A}{\left[ 1 + (A-1)C^*_p \right]^2},$$ \hspace{1cm} (8)

we obtain the following equation for the particle

$$\left( 1 + \frac{KA}{\left[ 1 + (A-1)C^*_p \right]^2} \right) \frac{\partial C^*_p}{\partial \tau} = \delta \left( \frac{\partial^2 C^*_p}{\partial \xi^2} + \frac{2}{\xi} \frac{\partial C^*_p}{\partial \xi} \right).$$ \hspace{1cm} (9)
The following boundary conditions and the initial condition are considered

\[
\left. \frac{\partial C_p^*}{\partial \xi} \right|_{\xi=0} = 0, \quad (10)
\]

\[
\left. \frac{\partial C_p^*}{\partial \xi} \right|_{\xi=1} = Bi \left( C_p^* - C_p^* \right), \quad (11)
\]

\[
C_p^*(\xi,0) = 0. \quad (12)
\]

Since the equations (1) - (12) are written in dimensionless form let us introduce the following dimensionless variables and parameters

\[
C^* = \frac{C}{C_f}, \quad C_p^* = \frac{C_p}{C_f}, \quad q^* = \frac{q}{q_f}, \quad \eta = \frac{x}{L}, \quad \xi = \frac{r}{R}, \quad \tau = \frac{vt}{L},
\]

\[
\delta = \frac{D_{ef} L}{\varepsilon_2 R^2 v}, \quad Bi = \frac{k_f R}{D_{ef}}, \quad Pe = \frac{vL}{E_m}, \quad \gamma = 3Bi\delta \frac{1-\varepsilon_2}{\varepsilon_2} \frac{1-\varepsilon_1}{\varepsilon_1}, \quad K = \frac{(1-\varepsilon_1)q_f}{\varepsilon_1 C_f}.
\]

3. Input data for our study

The crystalline silicotitanate ion exchange column for Cesium removal has been chosen as a model system. The operating parameters were obtained from Hang (2003).

Table 3.1 Operating conditions

<table>
<thead>
<tr>
<th>Variables</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet concentration $C_f$</td>
<td>$3.19 \cdot 10^{-3}$ kg $\cdot$ m$^{-3}$</td>
</tr>
<tr>
<td>Flow rate $V$</td>
<td>$1.647 \cdot 10^{-8}$ m$^3 \cdot$ s$^{-1}$</td>
</tr>
<tr>
<td>Feed viscosity $\mu$</td>
<td>$0.0026$ Pa $\cdot$ s</td>
</tr>
<tr>
<td>Feed density $\rho$</td>
<td>$1150$ kg $\cdot$ m$^{-3}$</td>
</tr>
<tr>
<td>Column length $L$</td>
<td>$0.118$ m</td>
</tr>
<tr>
<td>Column diameter $D$</td>
<td>$0.008$ m</td>
</tr>
<tr>
<td>Bed porosity $\varepsilon_2$</td>
<td>$0.48$</td>
</tr>
<tr>
<td>Particle porosity $\varepsilon_1$</td>
<td>$0.23$</td>
</tr>
<tr>
<td>Particle radius $R$</td>
<td>$245.25$ $\mu$m</td>
</tr>
<tr>
<td>Axial dispersion $E_m$</td>
<td>$7.915 \cdot 10^{-7}$ m$^2 \cdot$ s$^{-1}$</td>
</tr>
</tbody>
</table>
Mass transfer rate $k_f$  
$2.613 \cdot 10^{-5}$ m $\cdot$ s$^{-1}$

Effective diffusion coefficient $D_{ef}$  
$5.353 \cdot 10^{-11}$ m$^2$ $\cdot$ s$^{-1}$

Langmuir coefficient $a$  
$7145$ m$^3$ $\cdot$ m$^{-3}$ BV

Langmuir coefficient $b$  
$48.3343$ m$^3$ $\cdot$ kg$^{-1}$

The following mass transfer parameters using empirical correlation were found in literature specified therein.

### 3.1 Axial dispersion coefficient

The axial dispersion coefficient for liquids in packed beds is determined from the correlation presented by Chung (1968)

$$P_e = \frac{L}{2 \varepsilon_2} \left(0.2 + 0.011 \cdot Re_p^{0.48}\right), \quad (14)$$

where $P_e$ is defined by equation (13 i) and $Re_p$ has the following form

$$Re_p = \frac{\nu \varepsilon_2 d_p D}{\mu}. \quad (15)$$

Using the data from Table 3.1 the $Re_p$ is calculated to be 0.071 which results in $P_e$ number of value 101.8. The axial dispersion coefficient is calculated from $P_e$ number using equation (14), its value was determined to be $7.915 \cdot 10^{-7}$ m$^2$ $\cdot$ s$^{-1}$.

### 3.2 Effective diffusion coefficient

The pore diffusion coefficient $D_p$ can be normalized with respect to the free stream diffusion coefficient $D_{AB}$. The inverse of this ratio is referred to as a tortuosity factor that is primarily dependent upon the internal structure of the porous material. The values $0.22$ and $1.058 \cdot 10^{-9}$ m$^2$ $\cdot$ s$^{-1}$ of the ratio $D_p / D_{AB}$ and diffusion coefficient for free stream $D_{AB}$, respectively, was found in Hang (2003). The effective diffusion coefficient $D_{ef}$ is then calculated from

$$D_{ef} = \varepsilon_i D_p. \quad (16)$$

### 3.3 Mass transfer coefficient

The mass transfer coefficient $k_f$ describes the external mass transfer resistance in the film surrounding the particle. The correlation of Wilson (1966)

$$\left( k_f \right) \frac{1}{\nu \varepsilon_2} S_{C^{2/3}} = 1.09 \frac{1}{\varepsilon_2} Re_p^{-2/3} \quad (17)$$

is used to determine mass transfer coefficient $k_f$, where $Re_p$ is defined by the equation (15) and $Sc$ has the following form

$$Sc = \frac{\mu}{\rho D_{AB}}. \quad (18)$$

Using the data from Table 3.1 the film mass transfer coefficient has the value $2.613 \cdot 10^{-5}$ m $\cdot$ s$^{-1}$.

### 4. Numerical solution

The mathematical model is described by the equations (1) - (4) and (9) - (12). Applying the method of lines (space discretization of the governing PDEs) we obtain a system of ordinary differential equation (ODE). The finite difference method (FDM) has been applied to discretize both the bulk-fluid phase equation and the particle equation.
Let the axial (i.e. for the column) and the radial (i.e. for the particle) interval \( (0, 1) \) be equidistantly partitioned into \((n - 1)\) and \((m - 1)\) subintervals, respectively, with 

\[
\{\eta_1, \eta_2, ..., \eta_n\} \text{ a set of nodes in the axial direction,}
\]

\[
\{\xi_1, \xi_2, ..., \xi_m\} \text{ a set of nodes in the radial direction.}
\]

Let us denote by

\[
U_i(\tau) \quad \text{- approximation of } C^*\left(\eta_i, \tau\right),
\]

\[u_{i,j}(\tau) \quad \text{- approximation of } C^*\left(\xi_j, \tau\right) \text{ in the } i\text{-th axial layer,}
\]

\[
h_a \quad \text{- mesh size in the axial direction, } h_a = 1/(n - 1),
\]

\[
h_r \quad \text{- mesh size in the radial direction, } h_r = 1/(m - 1).
\]

Discretizing the equations (1) - (4) with respect to the space variable \( \eta \) we obtain the set of ODEs. The equation corresponding to the first grid point is

\[
\frac{dU_1}{d\tau} = \frac{1}{Pe h_a^2} \left( U_0 - 2U_1 + U_2 \right) - \frac{1}{2h_a} \left( U_2 - U_0 \right) - \gamma \left( U_1 - u_{1,m} \right),
\]

where \( U_0 \) is approximation of concentration in a fictitious point \( \eta_0 \). Discretized form (20) of boundary condition (2)

\[
\frac{1}{2h_a} \left( U_2 - U_0 \right) = Pe \left( U_1 - 1 \right)
\]

was used to eliminate \( U_0 \) from equation (19). This results in

\[
\frac{dU_1}{d\tau} = \frac{2}{Pe h_a^2} \left( U_2 - U_1 \right) - \frac{2}{h_a} \left( U_1 - 1 \right) - \gamma \left( U_1 - u_{1,m} \right) - Pe \left( U_1 - 1 \right).
\]

The equations for \( i = 2, ..., n-1 \) are of the form

\[
\frac{dU_i}{d\tau} = \frac{1}{Pe h_a^2} \left( U_{i-1} - 2U_i + U_{i+1} \right) - \frac{1}{2h_a} \left( U_{i+1} - U_{i-1} \right) - \gamma \left( U_i - u_{i,m} \right)
\]

The equation corresponding to the last grid point is

\[
\frac{dU_n}{d\tau} = \frac{1}{Pe h_a^2} \left( U_{n-1} - 2U_n + U_{n+1} \right) - \frac{1}{2h_a} \left( U_{n+1} - U_{n-1} \right) - \gamma \left( U_n - u_{n,m} \right).
\]

Similarly as in the first grid point we used a fictitious point \( \eta_{n+1} \) in the discretized form (24) of boundary condition (3)

\[
\frac{1}{2h_a} \left( U_{n+1} - U_{n-1} \right) = 0.
\]

Substituting \( U_{n+1} \) in equation (23) using equation (24) we obtain

\[
\frac{dU_n}{d\tau} = \frac{2}{Pe h_a^2} \left( U_{n-1} - U_n \right) - \gamma \left( U_n - u_{n,m} \right).
\]

Analogously, for each fixed \( \eta_i, i = 1, ..., n \), the discretization of the equations (9) - (12) with respect to the space variable \( \xi \) yields the set of ODEs for the particles. The corresponding equation for the center of particle is derived applying L’Hopital’s rule to the boundary condition to eliminate the singularity.
\[
\frac{du_{i,j}}{d\tau} = \frac{6 \delta}{g_i h_r^2} (u_{i,j} - u_{i,j-1}), \quad (26)
\]

The equations for \(j = 2, \ldots, m-1\) are
\[
\frac{du_{i,j}}{d\tau} = \frac{\delta}{g_i h_r^2} \left[ \left( 1 - \frac{1}{j-1} \right) u_{i,j-1} - 2u_{i,j} + \left( 1 + \frac{1}{j-1} \right) u_{i,j+1} \right], \quad (27)
\]

The equation corresponding to exterior surface of the particle is
\[
\frac{du_{i,m}}{d\tau} = \frac{2 \delta}{g_i h_r^2} \left[ u_{i,m-1} - \left[ 1 + \left( 1 + \frac{1}{m-1} \right) h_r Bi \right] u_{i,m} + \left( 1 + \frac{1}{m-1} \right) h_r Bi U_i \right]. \quad (28)
\]

The term \(g_j\) for \(j = 1, \ldots, m\) is
\[
g_j = 1 + \frac{KA}{\left[ 1 + (A-1)u_{i,j} \right]^2} \quad (29)
\]

The resulting set of ODEs (21), (21), (25) - (28) is solved using an existing ODE solver provided by MATLAB.

5. Results and discussion

An accurate value of the surface concentration is needed to calculate the flux at the particle surface. The equations (9) - (12) has been solved for fixed bulk-phase concentration \(C^*\) to determine a convenient discretization of the particle (the optimum number of grid points). Grid refinement with more than 30 nodes does not significantly affect concentration \(C_p^*\) on the surface of the particle (see Fig. 5.1). It has been observed that using 20 grid nodes in the particle gives the breakthrough curve almost identical with that obtained when using 30 grid points.

![Fig. 5.1 Concentration profile on surface of particles. Effect of number of nodes in particles m on surface](image-url)
The shape of the breakthrough curve in dependence on the number of nodes in the column is depicted in Fig. 5.2. Higher number of the nodes in the column (over 50) does not affect significantly the shape of the breakthrough curve. Our results correspond very well with the results published by Hang (2003), where the method of orthogonal collocation on finite elements was applied.

![Breakthrough Curve](image)

**Fig. 5.2 Breakthrough curve. Effect of number of nodes in the column on breakthrough curve. n = 20, 50, 100; m = 20**

6. Conclusions

The mathematical model of isothermal adsorption in fixed bed has been solved using method of lines. This method is shown to be an accurate and stable for solving the equations describing adsorption processes.

Acknowledgements

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Notation

- \(a\) Langmuir coefficient, \((m^3 \cdot m^{-3} \text{ B.V.})\) (B.V.: Volume of the fixed bed)
- \(A\) dimensionless parameter of Langmuir’s isotherm defined by Eq. (7)
- \(b\) Langmuir coefficient, \((m^3 \cdot kg^{-1})\)
- \(Bi\) Biot number defined by Eq. (13 h)
- \(C\) bulk-phase concentration, \((mol \cdot m^{-3})\)
- \(C_p\) pore-phase concentration, \((mol \cdot m^{-3})\)
- \(D_{ef}\) effective diffusion coefficient, \((m^2 \cdot s^{-1})\)
- \(E_m\) axial dispersion coefficient, \((m^2 \cdot s^{-1})\)
- \(k_f\) mass transfer coefficient, \((m \cdot s^{-1})\)
- \(K\) dimensionless parameter defined by Eq. (13 k)
- \(L\) bed length, \((m)\)
$Pe$  Peclet number defined by Eq. (11 i)
$r$  radial position from center of adsorbent particle, $(m)$
$R$  particle radius, $(m)$
$t$  time, $(s)$
$v$  interstitial velocity, $(m \cdot s^{-1})$
$x$  position in axial direction, $(m)$

Greek symbols
$\delta$  dimensionless parameter defined by Eq. (13 g)
$\gamma$  dimensionless parameter defined by Eq. (13 j)
$\varepsilon_1$  intra-particle porosity
$\varepsilon_2$  bed porosity
$\eta$  dimensionless position in axial direction defined by Eq. (13 d)
$\mu$  feed viscosity, $(Pa \cdot s)$
$\rho$  feed density, $(kg \cdot m^{-3})$
$\tau$  dimensionless time defined by Eq. (13 f)
$\xi$  dimensionless radial position from the center of adsorbent particle defined by Eq. (13 e)

Subscripts
$f$  feed

Superscripts
*  dimensionless variables

References

