12º Encontro Brasileiro sobre Adsorção
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Fotografia de Leonid Streliaev

Numerical solution of diffusion mass transfer model in adsorption systems

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1960

Agenda

- ✓ Mass Transfer Mechanisms
- ✓ Diffusion Mass Transfer Models
- ✓ Solving Diffusion Mass Transfer Models
- ✓ Parameter Estimation

Mass Transfer Mechanisms

Adsorption System

- ✓ Batch Operation
- ✓ Stirred-Tank
- ✓ Liquid Phase
- ✓ Spherical Adsorbent Particles

Mass Transfer Mechanisms

The overall rate of adsorption rate on a porous solid includes the following three simultaneous steps:

✓ External Mass Transfer

✓ Intraparticle Diffusion

✓ Adsorption on Active Site

External Mass Transfer

- ✓ It represents the moviment of the adsorbate (molecules/ions) from bulk solution to the external surface of adsorbent particle.

- ✓ It is governed by external mass transfer coefficient.

Interparticle Diffusion

- ✓ It representes the moviment of the adsorbate (molecules/ions) inside the particle.

- ✓ It occurs by:
  - ✓ Effective pore volume diffusion (Fick’s diffusion)
  - ✓ Surface diffusion
  - ✓ Combination of both mechanisms

Interparticle Diffusion

Effective pore volume diffusion

✓ It describes the transport of the adsorbate (molecules/ions) in the liquid phase inside of the particle.

✓ It is represented by the effective pore volume diffusion coefficient.

Interparticle Diffusion

Surface diffusion

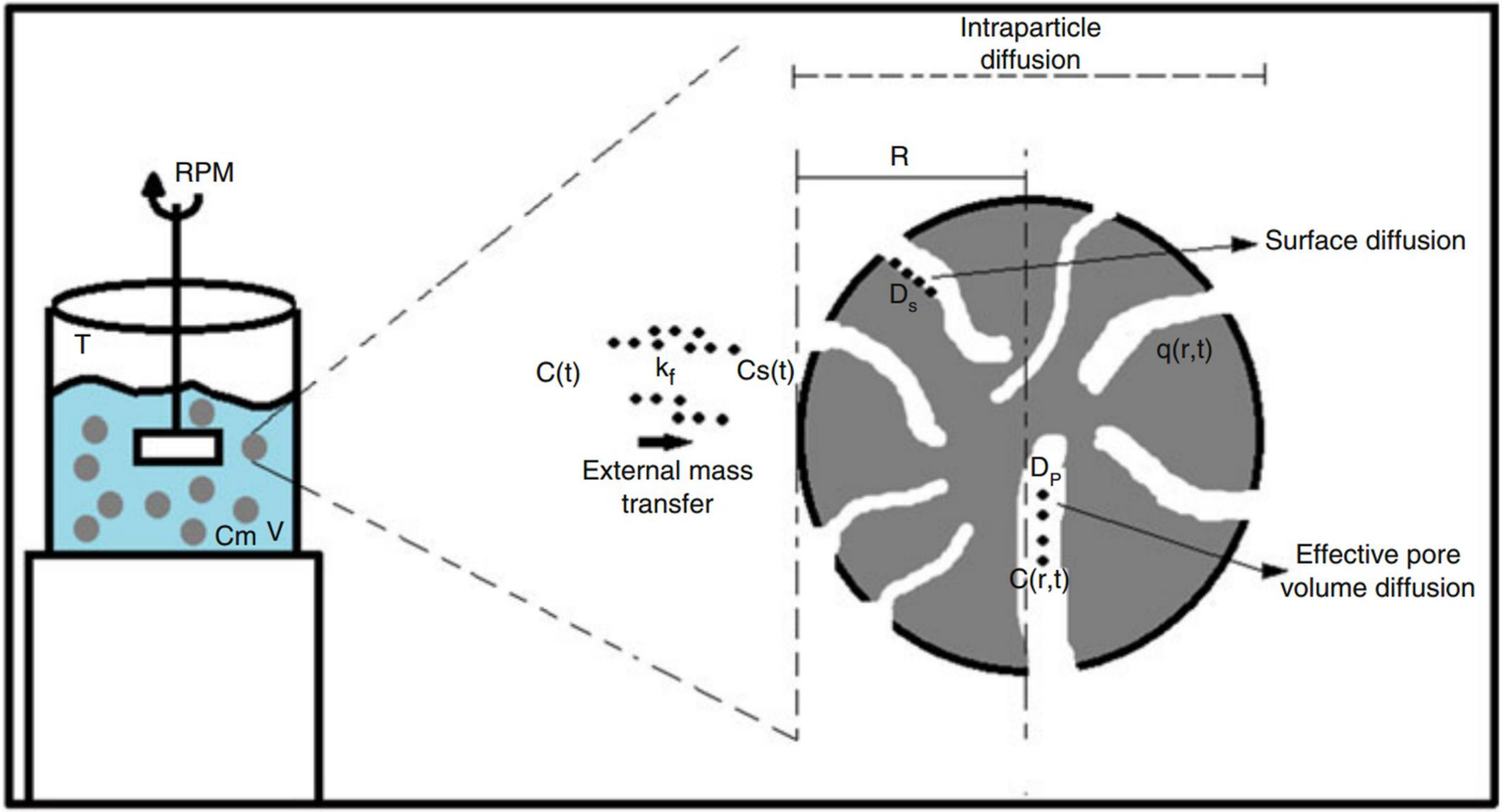
- ✓ It is relative to the transport of the adsorbate over the surface of the adsorbent particles, from sites of higher energy to sites of lower energy.
- ✓ It is represented by the surface diffusion coefficient.

Adsorption on Active Site

- ✓ It relative to the interaction of the adsorbate with the active sites of the adsorbent.

- ✓ It can be considered instantaneous and represented by the isotherm model equation.

Mass Transfer Mechanisms



Diffusion Mass Transfer Models

Diffusional Models

- ✓ They are constructed on the basis in the three consecutive steps:
  - ✓ External mass transfer
  - ✓ Intraparticle diffusion (effective pore volume diffusion, surface diffusion, or a combination of both mechanisms)
  - ✓ Adsorption on an active site

Diffusional Models

- ✓ They represent realistically the adsorption kinetics.

- ✓ One of the most complete diffusional models is the pore volume and surface diffusion model (PVSDM).

PVSDM Assumptions

- ✓ Batch system adsorption occurs at constant temperature.
- ✓ Mass transport by convection within the pores is negligible.

PVSDM Assumptions

- ✓ Intraparticle diffusion can occur by both pore volume diffusion and surface diffusion.

- ✓ Values of effective pore volume diffusion coefficient and surface diffusion coefficient are constant.

- ✓ Adsorption rate on an active site is instantaneous.

PVSDM

$$V\frac{dC_t}{dt} = -mSk_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

$$t = 0, C_t = C_0$$

$$\varepsilon_p\frac{\partial C_r}{\partial t} + \rho_p\frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(D_p\frac{\partial C_r}{\partial r} + \rho_p D_s\frac{\partial q}{\partial r}\right)\right]$$

$$t = 0, 0 \leq r \leq R, C_r = 0$$

$$\left.\frac{\partial C_r}{\partial r}\right|_{r=0} = 0$$

$$D_p\left.\frac{\partial C_r}{\partial r}\right|_{r=R} + \rho_p D_s\left.\frac{\partial q}{\partial r}\right|_{r=R} = k_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

PVSDM

✓ To solve this model, it is considered that there exists a local equilibrium between the adsorbate concentration of the pore solution and the mass of adsorbate adsorbed on the pore surface.

✓ This equilibrium relationship is represented by the adsorption isotherm:

$$q = f(C_r)$$

PVSDM

- ✓ In case of Redlich-Peterson isotherm model equation:

$$q = \frac{k_{RP} C_r}{1 + a_{RP} C_r^{\beta}}$$

PVSDM

✓ From chain rule:

$$\frac{\partial q}{\partial t}=\frac{\partial C_r}{\partial t}\frac{\partial q}{\partial C_r} \longrightarrow \frac{\partial q}{\partial t}=\frac{\partial C_r}{\partial t}\frac{\partial}{\partial C_r}\left(\frac{k_{RP}C_r}{1+a_{RP}C_r^{\beta}}\right)$$

$$\frac{\partial q}{\partial r}=\frac{\partial C_r}{\partial r}\frac{\partial q}{\partial C_r} \longrightarrow \frac{\partial q}{\partial r}=\frac{\partial C_r}{\partial r}\frac{\partial}{\partial C_r}\left(\frac{k_{RP}C_r}{1+a_{RP}C_r^{\beta}}\right)$$

PVSDM

- ✓ Also, if the volume is constant, it is evident that adsorbate concentration from bulk solution and the mass of adsorbate per mass of adsorbent:

$$q_t = \frac{(C_0 - C_t)V}{m}$$

PVSDM

- ✓ Three models can be derived from the PVSDM model:
  - ✓ External mass transfer model (EMTM)
  - ✓ Pore volume diffusion model (PVDM)
  - ✓ Surface diffusion model (SDM)

EMTM

- ✓ It assumes that the movement of solute from the liquid phase to the adsorbent is only due to external mass transfer.
- ✓ Intraparticle diffusion is instantaneous.
- ✓ There is not a concentration gradient inside the particle.
- ✓ Intraparticle diffusion resistance is considered to be insignificant.

EMTM

$$V\frac{dC_t}{dt} = -mSk_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

$$t = 0, C_t = C_0$$

$$\varepsilon_p\frac{\partial C_r}{\partial t} + \rho_p\frac{\partial q}{\partial t} = \cancel{\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(D_p\frac{\partial C_r}{\partial r} + \rho_p D_s\frac{\partial q}{\partial r}\right)\right]}$$

$$\cancel{t = 0, 0 \leq r \leq R, C_r = 0}$$

$$\cancel{\left.\frac{\partial C_r}{\partial r}\right|_{r=0} = 0}$$

$$\cancel{D_p\left.\frac{\partial C_r}{\partial r}\right|_{r=R} + \rho_p D_s\left.\frac{\partial q}{\partial r}\right|_{r=R}} = k_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

EMTM

$$V\frac{dC_t}{dt} = -mSk_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

$$t = 0, C_t = C_0$$

$$\frac{m\varepsilon_p}{\rho_p}\frac{dC_r}{\partial t}\bigg|_{r=R} + m\frac{dq_t}{dt} = mSk_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

$$t = 0, C_t = 0, q_t = 0$$

PVDM

- ✓ It is a simplification of the PVSDM model, used when the intraparticle diffusion is controlled only by pore volume diffusion.

- ✓ Surface diffusion coefficient is neglected.

PVDM

$$V\frac{dC_t}{dt} = -mSk_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

$$t = 0, C_t = C_0$$

$$\varepsilon_p\frac{\partial C_r}{\partial t} + \rho_p\frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(D_p\frac{\partial C_r}{\partial r} + \cancel{\rho_p D_s\frac{\partial q}{\partial r}}\right)\right]$$

$$t = 0, 0 \le r \le R, C_r = 0$$

$$\left.\frac{\partial C_r}{\partial r}\right|_{r=0} = 0$$

$$D_p\left.\frac{\partial C_r}{\partial r}\right|_{r=R} + \cancel{\rho_p D_s\left.\frac{\partial q}{\partial r}\right|_{r=R}} = k_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

PVDM

$$V\frac{dC_t}{dt} = -mSk_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

$$t = 0, C_t = C_0$$

$$\varepsilon_p\frac{\partial C_r}{\partial t} + \rho_p\frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(D_p\frac{\partial C_r}{\partial r}\right)\right]$$

$$t = 0, 0 \leq r \leq R, C_r = 0$$

$$\left.\frac{\partial C_r}{\partial r}\right|_{r=0} = 0$$

$$D_p\left.\frac{\partial C_r}{\partial r}\right|_{r=R} = k_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

SDM

- ✓ It is a simplification of the PVSDM model, used when the intraparticle diffusion is controlled only by surface diffusion.

- ✓ Effective pore volume diffusion coefficient is neglected.

SDM

$$V\frac{dC_t}{dt} = -mSk_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

$$t = 0, C_t = C_0$$

$$\varepsilon_p \frac{\partial C_r}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(\cancel{D_p\frac{\partial C_r}{\partial r}} + \rho_p D_s \frac{\partial q}{\partial r}\right)\right]$$

$$t = 0, 0 \le r \le R, C_r = 0$$

$$\left.\frac{\partial C_r}{\partial r}\right|_{r=0} = 0$$

$$\cancel{D_p\left.\frac{\partial C_r}{\partial r}\right|_{r=R}} + \rho_p D_s \left.\frac{\partial q}{\partial r}\right|_{r=R} = k_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

SDM

$$V\frac{dC_t}{dt} = -mSk_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

$$t = 0, C_t = C_0$$

$$\varepsilon_p \frac{\partial C_r}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(\rho_p D_s \frac{\partial q}{\partial r}\right)\right]$$

$$t = 0, 0 \leq r \leq R, C_r = 0$$

$$\left.\frac{\partial C_r}{\partial r}\right|_{r=0} = 0$$

$$\rho_p D_s \left.\frac{\partial q}{\partial r}\right|_{r=R} = k_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

PVDM & SDM

- ✓ If the external mass transfer is negligible, the boundary condition can be replaced by the adsorption isotherm, or by other boundary condition.

PVDM: $$D_p \frac{\partial C_r}{\partial r}\bigg|_{r=R} = k_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

SDM: $$\rho_p D_s \frac{\partial q}{\partial r}\bigg|_{r=R} = k_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

HSDM

- ✓ Homogeneous surface diffusion model (HSDM) is another important diffusion model.

- ✓ It considers a dual mass transport mechanism across the hydrodynamic boundary layer surrounding the adsorbent particle and intraparticle resistance within the particle in the form of surface diffusion.

HSDM

$$m\frac{dq_t}{dt} = mAk_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

$$t = 0, C_t = C_0$$

$$-m\frac{dq_t}{dt} = V\frac{dC_t}{dt}$$

$$\rho_p\frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(\rho_p D_s\frac{\partial q}{\partial r}\right)\right]$$

$$t = 0, 0 \le r \le R, q = 0$$

$$\left.\frac{\partial q}{\partial r}\right|_{r=0} = 0$$

$$\rho_p D_s\left.\frac{\partial q}{\partial r}\right|_{r=R} = k_F\left(C_t - C_{s(t)}\big|_{r=R}\right)$$

HSDM

✓ In the same way of the other models, HSDM requires a relation between the amount of adsorbate adsorbed on the adsorbent and the amount of the adsorbate in the bulk solution, which is given by the adsorption isotherm.

Solving Diffusion Mass Transfer Models

Solving Model Equations

- ✓ Numerical method of lines utilizes ordinary differential equations (ODEs) for the time derivative and finite differences on the spatial derivatives.

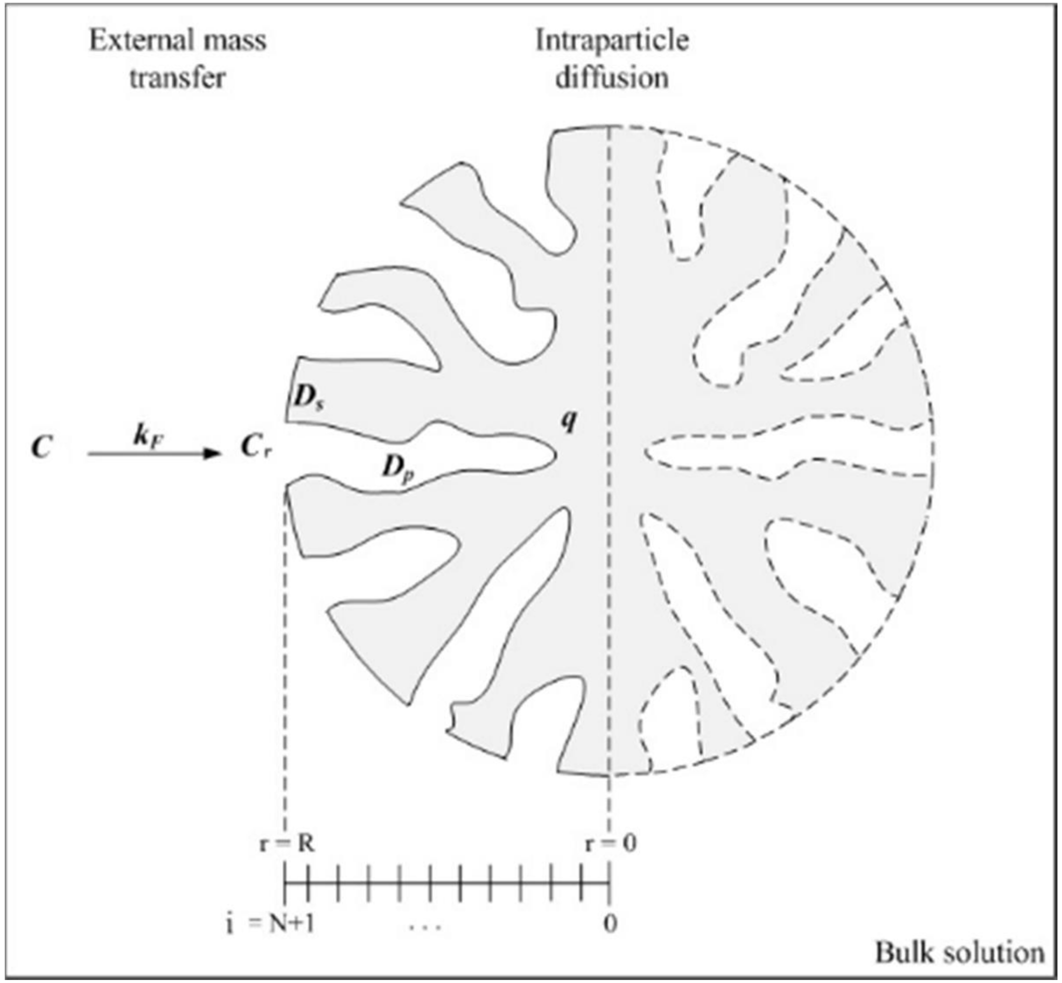
- ✓ In finite difference method, the derivatives in the partial differential equations (PDEs) are approximated by linear combinations of function values at the grid points.

Solving Model Equations

- ✓ Derivatives in the partial differential equation of diffusional transfer models are discretized into $N + 1$ points on the spatial derivatives (radius), where N is the number of grid points.

Discretization (grid points)

- ✓ Transport of adsorbate molecules from the bulk solution to the spherical particle.



Discretization (grid points)

- ✓ In this way, it has C_r in different points i where $i = 0$ is the grid point at $r = 0$ and $i = N+1$ is the grid point at $r = R$.

- ✓ Grid points are spaced equally with the step size given by:

$$h = \frac{R}{N+1}$$

Finite Approximation Functions

Difference	First-Order Formula	Second-Order Formula
Forward Difference for First Derivative	$\frac{d}{dx}f(x_i) = \frac{f(x_{i+1})-f(x_i)}{\Delta x}$	$\frac{d}{dx}f(x_i) = \frac{-3f(x_i)+4f(x_{i+1})-f(x_{i+2})}{2\Delta x}$
Central Difference for First Derivative	-	$\frac{d}{dx}f(x_i) = \frac{f(x_{i+1})-f(x_{i-1})}{2\Delta x}$
Backward Difference for First Derivative	$\frac{d}{dx}f(x_i) = \frac{f(x_i)-f(x_{i-1})}{\Delta x}$	$\frac{d}{dx}f(x_i) = \frac{3f(x_i)-4f(x_{i+1})+f(x_{i+2})}{2\Delta x}$

Finite Approximation Functions

Difference	First-Order Formula	Second-Order Formula
Forward Difference for Second Derivative	$\frac{d^2}{dx^2}f(x_i) = \frac{f(x_i)-2f(x_{i+1})+f(x_{i+2})}{\Delta x^2}$	$\frac{d^2}{dx^2}f(x_i) = \frac{2f(x_i)-5f(x_{i+1})+4f(x_{i+2})-f(x_{i+3})}{\Delta x^2}$
Central Difference for Second Derivative	-	$\frac{d^2}{dx^2}f(x_i) = \frac{f(x_{i+1})-2f(x_i)+f(x_{i-1})}{\Delta x^2}$
Backward Difference for Second Derivative	$\frac{d^2}{dx^2}f(x_i) = \frac{f(x_i)-2f(x_{i-1})+f(x_{i-2})}{\Delta x^2}$	$\frac{d^2}{dx^2}f(x_i) = \frac{2f(x_i)-5f(x_{i-1})+4f(x_{i-2})-f(x_{i-3})}{\Delta x^2}$

Finite Approximation Functions

- ✓ Temporal variation of the adsorbate concentration in bulk solution is rewritten in the discretized form:

$$\frac{dC}{dt} = -\frac{mSk_F}{V}\left(C - C_r^{N+1}\right)$$

Finite Approximation Functions

- ✓ Second-order central difference approximations of the first and second derivative can be used to solve the PDEs.

$$\varepsilon_p \frac{dC_r}{dt} + \rho_p \frac{dC_r}{dt}\frac{d}{dC_r^i}\left(\frac{k_{RP}C_r^i}{1+a_{RP}{C_r^i}^{\beta}}\right) =$$

$$\frac{1}{r^2}\left\{ 2r\left[D_p\left(\frac{C_r^{i+1}-C_r^{i-1}}{2h}\right) + \rho_p D_s\left(\frac{C_r^{i+1}-C_r^{i-1}}{2h}\right)\frac{d}{dC_r^i}\left(\frac{k_{RP}C_r^i}{1+a_{RP}{C_r^i}^{\beta}}\right)\right] + r^2\left[D_p\left(\frac{C_r^{i+1}-2C_r^i+C_r^{i-1}}{h^2}\right) + \rho_p D_s\left(\frac{C_r^{i+1}-2C_r^i+C_r^{i-1}}{h^2}\right)\frac{d}{dC_r^i}\left(\frac{k_{RP}C_r^i}{1+a_{RP}{C_r^i}^{\beta}}\right)\right]\right\}$$

Finite Approximation Functions

- ✓ Isolating $\frac{dC_r}{dt}$ and simplifying:

$$\frac{dC_r}{dt} = -\left[r\left(-C_r^{i+1} + 2C_r^{i} - C_r^{i-1}\right) + h\left(C_r^{i-1} - C_r^{i+1}\right)\right] \frac{\left\{-D_p a_{RP}^2 C_r^{i\,2\beta} + \left[\rho_p D_s k_{RP}(\beta-1) - 2D_p\right] a_{RP} C_r^{i\,\beta} - D_p - \rho_p D_s k_{RP}\right\}}{h^2 r \left\{-\varepsilon_p a_{RP}^2 C_r^{i\,2\beta} + \left[\rho_p k_{RP}(\beta-1) - 2\varepsilon_p\right] a_{RP} C_r^{i\,\beta} - \varepsilon_p - \rho_p k_{RP}\right\}}$$

Finite Approximation Functions

- ✓ Second-order forward difference approximations of the first derivative can be used to solve the boundary condition at *r* = 0:

$$C_r^0 = \frac{4C_r^1 - C_r^2}{3}$$

Finite Approximation Functions

- ✓ Second-order backward difference approximations of the first derivative can be used to solve the boundary condition at *r* = *R:*

$$D_p\left(\frac{3C_r^{N+1}-4C_r^{N}+C_r^{N-1}}{2h}\right)+$$

$$\rho_p D_s\left(\frac{3C_r^{N+1}-4C_r^{N}+C_r^{N-1}}{2h}\right)\frac{d}{dC_r^{N+1}}\left(\frac{k_{RP}}{1+a_{RP}{C_r^{N+1}}^{\beta}}\right)$$

$$=k_F\left(C\;\;-C_r^{N+1}\right)$$

Boundary Condition

- ✓ Boundary condition at $r = R$ has no has no analytical solution, i. e. it is not possible to solve explicitly the equation to obtain C_r^{N+1}.

- ✓ An implicit method to solve non−linear equation is required.

- ✓The most common method for solving nonlinear algebraic equations is the Newton’s method.

Boundary Condition

fsolve

✓ MatLab function that attemps to solve equations of the form:

$$f(x) = 0$$

✓ Based on trust-region modification of Newton method.

ODE’s Integration

- ✓ Discretized PDEs yield ODE equation systems that are very stiff.
- ✓ To avoid a very small time step, an implicit method can be used, as the backward difference formula (BDF).

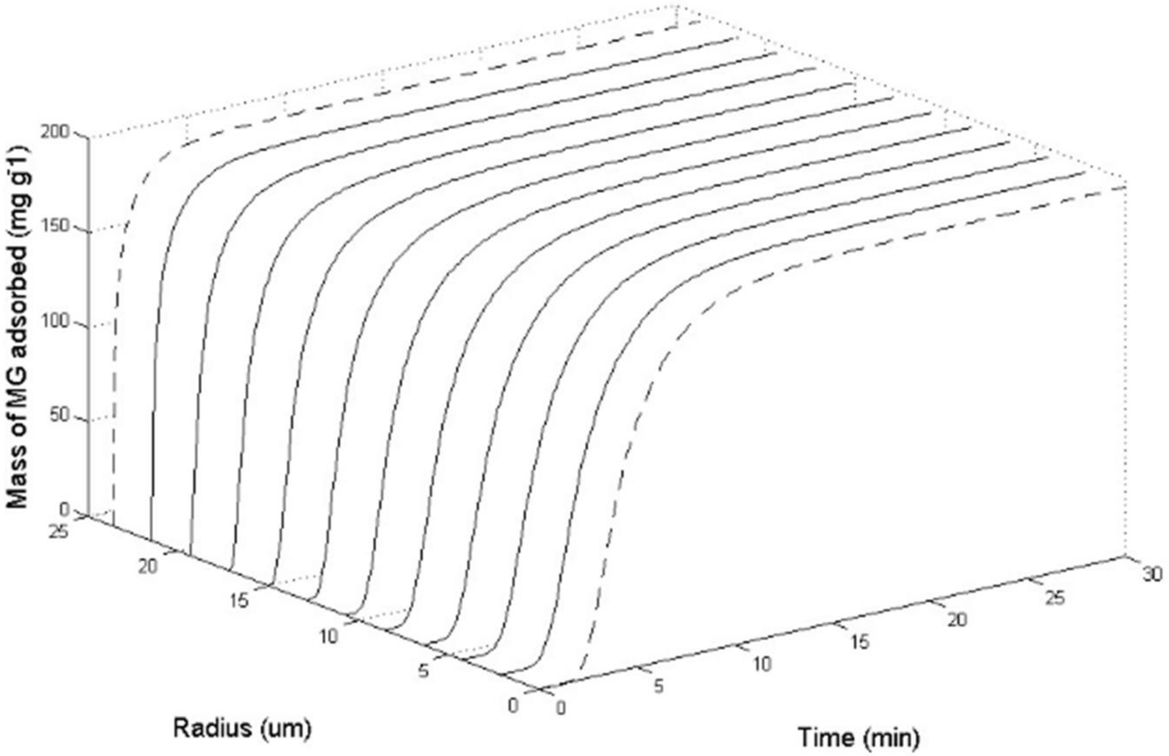
ODE’s Integration

ode15s

- ✓ MatLab function that attemps to solve stiff differential equations and DAEs, variable order method.
- ✓ Based on the numerical differentiation formulas (NDFs). Optionally, it uses the backward differentiation formulas (BDF, also known as Gear method) that are usually less efficient.

Case Study

- ✓ Mass of adsorbate adsorbed on each radial position over time.



Parameter Estimation

Isotherm Parameters

- ✓ In case of Redlich-Peterson isotherm model equation:

$$q = \frac{k_{RP} C_r}{1 + a_{RP} C_r^{\beta}}$$

Isotherm Parameters

✓ The nonlinear least-square objective function to be minimized is defined as the sum of the differences between the experimental and model data of mass of adsorbate adsorbed on the pore surface:

$$\min \left| f(p) \right| = \sum_{j=1}^{NE} \sum_{i=1}^{NY} \left[q_{(i,j)} - \hat{q}_{(i,j)} \right]^2$$

Model Parameters

- ✓ Calculated mass transport parameters:
  - ✓ External mass transfer coefficient (PVSDM, PVDM, SDM, HSDM)
  - ✓ Molecular diffusivity (PVSDM, PVDM)
  - ✓ Effective pore volume diffusion coefficient (PVSDM, PVDM)
  - ✓ Tortuosity factor (PVSDM, PVDM)

Model Parameters

- ✓ Estimated mass transport parameters:
  - ✓ Surface diffusion coefficient (PVSDM, SDM, HSDM)
  - ✓ External mass transfer coefficient (EMTM)

Model Parameters

- ✓ The nonlinear least-square objective function to be minimized is defined as the sum of the differences between the experimental and model data of adsorbate concentration.

$$\min|f(p)| = \sum_{j=1}^{NE} \sum_{i=1}^{NY} \left[C_{(i,j)} - \hat{C}_{(i,j)} \right]^2$$

Parameter Estimation

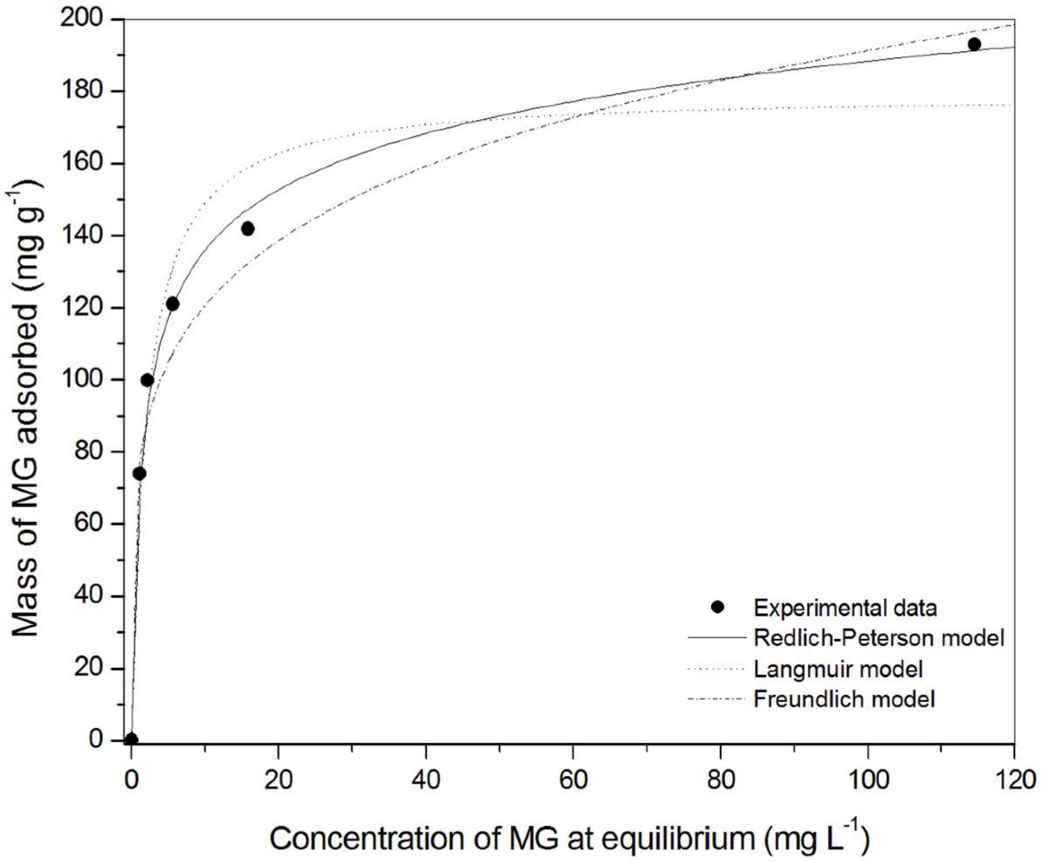
- ✓ Nonlinear least-square optimization can be used to estimate the isotherm and mass transport parameters.

Parameter Estimation

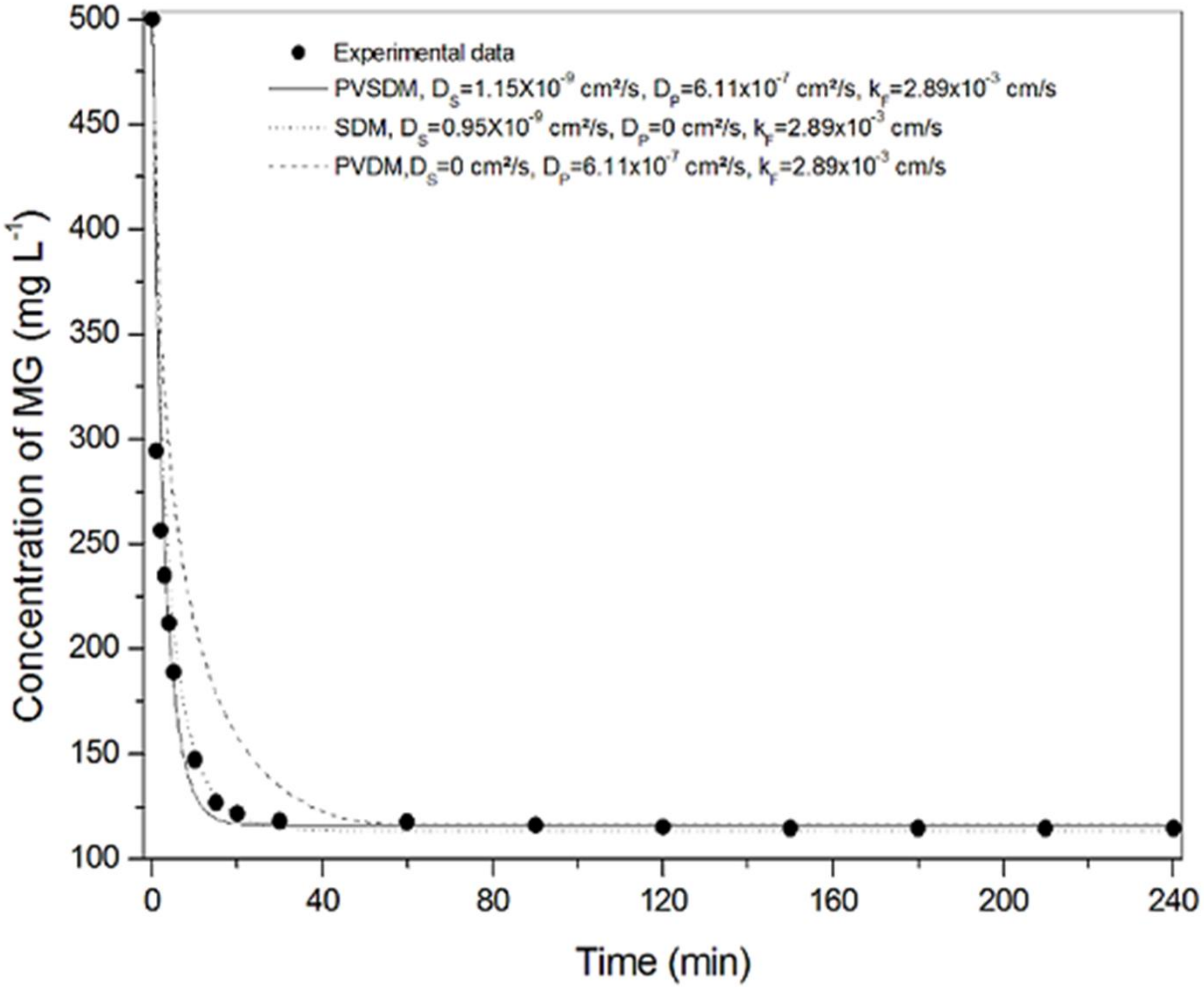
lsqnonlin

- ✓ MatLab function that solves non-linear least squares problems (nonlinear data-fitting) problems with optional lower and upper bounds on the parameters.
- ✓ It implements two different algorithms:
  - ✓ Trust region reflective
  - ✓ Levenberg-Marquardt

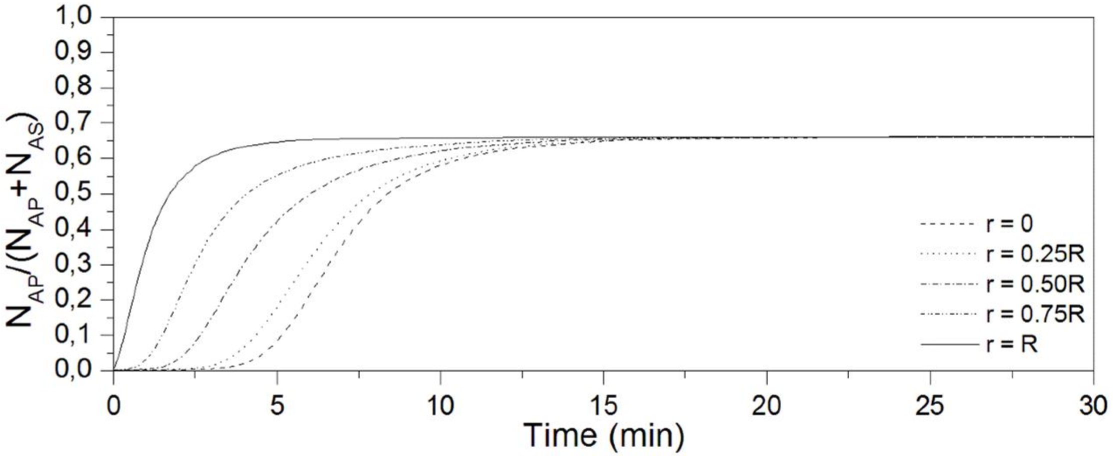
Case Study

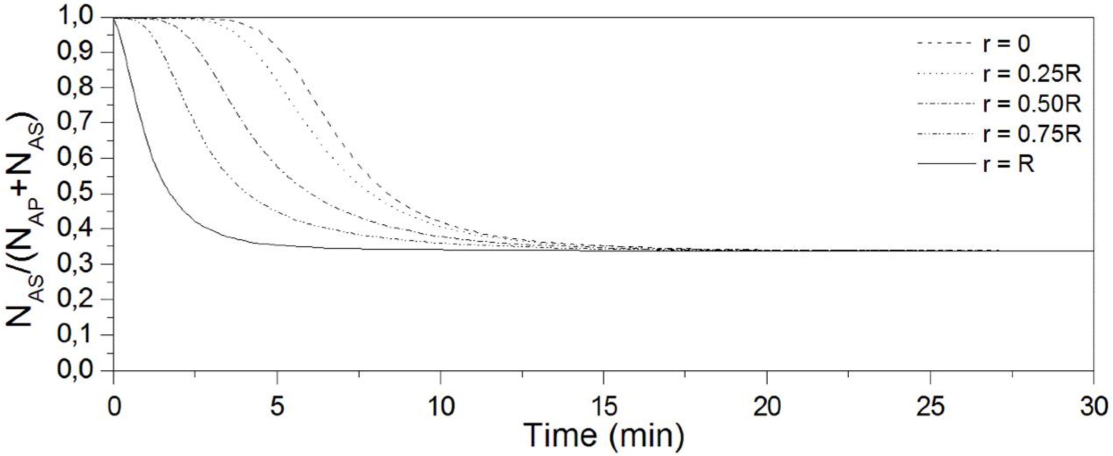

Mass of MG adsorbed (mg g^{-1})
200
180
160
140
120
100
80
60
40
20
0
0
20
40
60
80
100
120
Concentration of MG at equilibrium (mg L^{-1})
● Experimental data
Redlich-Peterson model
Langmuir model
Freundlich model

Case Study


● Experimental data
PVSDM, D_S=1.15X10^{-9} cm²/s, D_P=6.11x10^{-7} cm²/s, k_F=2.89x10^{-3} cm/s
SDM, D_S=0.95X10^{-9} cm²/s, D_P=0 cm²/s, k_F=2.89x10^{-3} cm/s
PVDM,D_S=0 cm²/s, D_P=6.11x10^{-7} cm²/s, k_F=2.89x10^{-3} cm/s
Concentration of MG (mg L^{-1})
500
450
400
350
300
250
200
150
100
0
40
80
120
160
200
240
Time (min)

Case Study


$N_{AP}/(N_{AP}+N_{AS})$
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
0
5
10
15
20
25
30
Time (min)
r = 0
r = 0.25R
r = 0.50R
r = 0.75R
r = R


$N_{AS}/(N_{AP}+N_{AS})$
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
0
5
10
15
20
25
30
Time (min)
r = 0
r = 0.25R
r = 0.50R
r = 0.75R
r = R

Any questions?

More information?

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Detailed numerical solution of pore volume and surface diffusion model in adsorption systems

P.R. Souza ✉, G.L. Dotto ✉, N.P.G. Salau ✉

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https://doi.org/10.1016/j.cherd.2017.04.021

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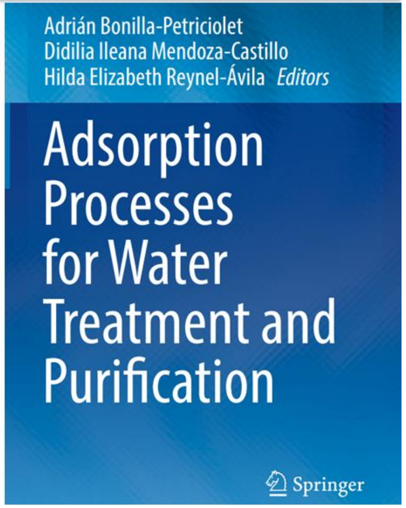

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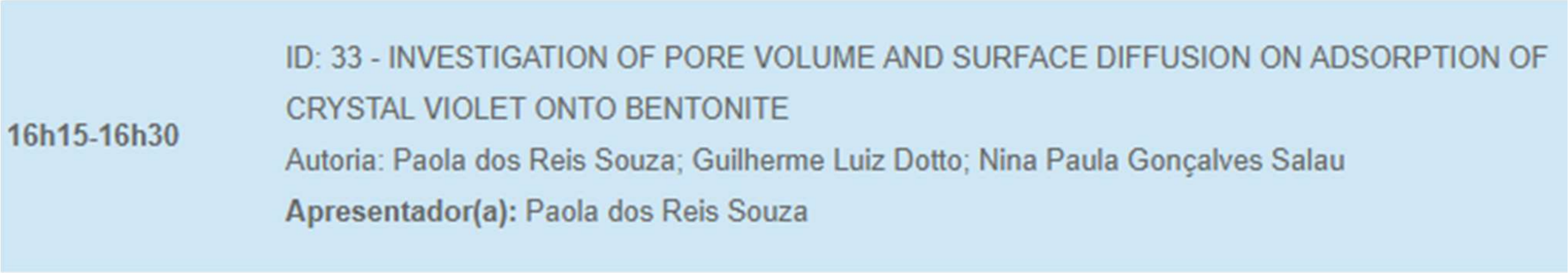

16h15-16h30

ID: 33 - INVESTIGATION OF PORE VOLUME AND SURFACE DIFFUSION ON ADSORPTION OF CRYSTAL VIOLET ONTO BENTONITE

Autoria: Paola dos Reis Souza; Guilherme Luiz Dotto; Nina Paula Gonçalves Salau

Apresentador(a): Paola dos Reis Souza

Thank You

<u>Contact</u>:

Prof. Nina Paula Gonçalves Salau, D.Sc.

email ninasalau@ufsm.br