Biosorption model

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February 10, 2018

1 Conventions

Unknown function $\bar{L}_f(\bar{x},\bar{t})$, $\bar{q}(\bar{x},\bar{r},\bar{t})$, $\bar{S}_s(\bar{x},\bar{t})$, $\bar{S}_f(\bar{x},\bar{r},\bar{t})$, $\bar{S}_{fs}(\bar{x},\bar{t})$, $\bar{S}(\bar{x},\bar{t})$, $\bar{S_{av}}(\bar{x},\bar{t})$, the bar under the functions and functions variables means that they are not normalized and have their dimensions. Transformation to the dimensionless form is made by next equations:

$$x = \frac{\bar{x}}{L} \quad r = \frac{\bar{r}}{R} \quad t = \frac{\bar{t}}{T \cdot D_g} \tag{1}$$

$$\bar{x} = xL \quad \bar{r} = rR \quad \bar{t} = t \cdot TD_g \tag{2}$$

$$E_d = \frac{TD_sD_g}{R^2} \quad D_g = \frac{\rho_a q_0(1-\epsilon)}{\epsilon S_0} \quad D = D_g D_x \frac{T}{L^2} \quad St = 3k_f T \frac{1-\epsilon}{R\epsilon} \quad B_0 = \frac{L_{fmax}}{R} \tag{3}$$

Table 1: Naming convention

x, r, u, t	axial, radial substrate $(0, R)$, radial biofilm $(R, R+L_f)$, and time coordinate
M, M, M, N	grid size for x, r, u, t
i, j, j, k	grid index for x, r, u, t
m, p	upper-inner loop variables
$\bar{v}$	bar under variable mark that dimensionless procedure was not done yet
Ed	ration of the surface diffusion transport to bulk transport
τ	timestep t_{k+1} - t_k

2 Kinetic equation

Standard equation

$$\frac{\partial \bar{q}(\bar{x},\bar{r},\bar{t})}{\partial \bar{t}} = \frac{D_s}{\bar{r}^s} \cdot \frac{\partial}{\partial \bar{r}} \left(\bar{r}^s \frac{\partial \bar{q}(\bar{x},\bar{r},\bar{t})}{\partial \bar{r}} \right) \tag{4}$$

Using (3) and (2) we get dimensionless equation

$$\frac{\partial q(x,r,t)}{\partial t} = \frac{E_d}{r^s} \cdot \frac{\partial}{\partial r} \left(r^s \frac{\partial q(x,r,t)}{\partial r} \right) \tag{5}$$

$$\frac{\partial q(x,r,t)}{\partial t} = E_d \frac{s}{r} \frac{\partial q(x,r,t)}{\partial r} + E_d \frac{\partial^2 q(x,r,t)}{\partial r^2} \tag{6}$$

Table 2: Experimental data

R	radius of the particle, r_M or r_{max}	0.039	cm
L	length of the adsorber, x_M or x_{max}	40	cm
T	time of supervising, t_N or t_{max}; $T = \tau_{res} \cdot n_t$	$3.6 \cdot 10^4$	s
τ_{res}	adsorber resident time, or empty bed contact time, $\tau_{res} = L/V_x$		s
n_{res}	number of treatment cycles supervised $n_t = T/\tau_{res}$		–
Ds	surface diffusion coefficient of the substrate within the adsorbent particle	$9.12 \cdot 10^{-9}$	cm^2/s
s	symmetry of a particle, 0 - slab, 1 - cylinder, 2 - sphere	2	-
ρ_a	density of adsorbent particle	$7 \cdot 10^2$	mg/cm^3
$q0$	substrate concentration in adsorbent in equilibrium with the initial adsorber influent concentration S_0	$(S_0)^n$	mg/mg
ϵ	adsorber bed porosity	0.7	–
S_0	Initial substrate concentration	0.11	mg/cm^3

Initial and boundary conditions

$$q(x_i, r_j, t_1) = 0 \qquad \left.\frac{\partial q(x,r,t)}{\partial r}\right|^{(i,1,k)} = 0 \qquad q(x_i, r_M, t_k) = S_s(x_i, t_k)^n \tag{7}$$

Simplify and make expansion in (i, j, k) point

$$\left.\frac{\partial q(x,r,t)}{\partial t}\right|^{(i,j,k)} = E_d \frac{s}{r} \cdot \left.\frac{\partial q(x,r,t)}{\partial r}\right|^{(i,j,k)} + E_d \left.\frac{\partial^2 q(x,r,t)}{\partial r^2}\right|^{(i,j,k)} \tag{8}$$

Lagrange polynomial approximation

$$q(x,r,t) = \sum_{m=1}^{M} \prod_{p=1}^{M} \frac{r - r_p}{r_m - r_p} \cdot q(x, r_m, t) = \sum_{m=1}^{M} l_m(r) \cdot q(x, r_m, t) \tag{9}$$

$$\left.\frac{\partial q(x,r,t)}{\partial r}\right|^{(i,j,k)} = \left.\sum_{m=1}^{M} l'_m(r) \cdot q(x, r_m, t)\right|^{(i,j,k)} = \sum_{m=1}^{M} A_{jm} \cdot q(x_i, r_m, t_k) \tag{10}$$

$$\left.\frac{\partial^2 q(x,r,t)}{\partial r^2}\right|^{(i,j,k)} = \left.\sum_{m=1}^{M} l''_m(r) \cdot q(x, r_m, t)\right|^{(i,j,k)} = \sum_{m=1}^{M} B_{jm} \cdot q(x_i, r_m, t_k) \tag{11}$$

$$\left.\frac{\partial q(x,r,t)}{\partial t}\right|^{(i,j,k)} = \frac{q(x_i, r_j, t_k) - q(x_i, r_j, t_{k-1})}{\tau} \tag{12}$$

Insert (10), (11), (12) into (8)

$$\frac{q(x_i, r_j, t_k) - q(x_i, r_j, t_{k-1})}{\tau} = E_d \frac{s}{r_j} \cdot \sum_{m=1}^{M} A_{jm} \cdot q(x_i, r_m, t_k) + E_d \sum_{m=1}^{M} B_{jm} \cdot q(x_i, r_m, t_k) \tag{13}$$

$$\tau E_d \sum_{m=1}^{M} \left(\frac{s}{r_j} A_{jm} + B_{jm} \right) q(x_i, r_m, t_k) - q(x_i, r_j, t_k) + q(x_i, r_j, t_{k-1}) = 0 \tag{14}$$

Upper boundary equation

$$q(x_i, r_M, t_k) = S_s(x_i, t_k)^n, \qquad r_M = 1 \tag{15}$$

Inserting equation (15) into (14) we will get

$$\tau E_d \sum_{m=1}^{M-1} \left(\frac{s}{r_j} \cdot A_{jm} + B_{jm} \right) q(x_i, r_m, t_k) + \tau E_d \left(s A_{jM} + B_{jM} \right) S_s(x_i, t_k)^n - q(x_i, r_j, t_k) + q(x_i, r_j, t_{k-1}) = 0 \tag{16}$$

for each slice of column $x_i \in [x_1, x_2 ..., x_i, ..., x_{H-1}]$ (roots of Legendre polynomial of $H-1$ degree)
for each time layer $t_i \in [t_2, t_3, ..., t_k, ..., t_N]$, where $t_k = \tau * (k-1)$
for each radial layer $r_j \in [r_2 ..., r_j, ..., r_{M-1}]$ (roots of Legendre polynomial of $M-2$ degree) we use (16)
for t_1 we have already known q from initial conditions $q(x_i, r_j, t_1) = 0$
The last equation are added from lower boundary condition

$$\left. \frac{\partial q(x,r,t)}{\partial r} \right|^{(i,1,k)} = \frac{q(x_i, r_2, t_k) - q(x_i, r_1, t_k)}{r_2 - r_1} = 0 \quad \Rightarrow \quad q(x_i, r_2, t_k) - q(x_i, r_1, t_k) = 0 \tag{17}$$

Depends on $S_s(x,t)$.

3 Adsorbent phase material balance

$$\frac{\partial}{\partial t} \int_0^R q(x,r,t) 4\pi r^2 dr = \frac{k_f A_p R^3}{3 V_c \rho} (S(x,t) - S_{fs}(x,t)) - \frac{R^2 k X_f}{\rho Y} L_f(x,t) \frac{S_{f,av}(x,t)}{k_s + S_{f,av}(x,t)} \tag{18}$$

where

$$S_{f,av}(x,t) = \frac{1}{M} \sum_{j=1}^{M} S_f(x, r_j, t) \tag{19}$$

Let's introduce new function

$$S_{av}(x,t) = \frac{S_{f,av}(x,t)}{k_s + S_{f,av}(x,t)} = \frac{\frac{1}{M}\sum_{j=1}^{M} S_f(x,u_j,t)}{k_s + \frac{1}{M}\sum_{j=1}^{M} S_f(x,u_j,t)} = \frac{S_s(x,t) + \sum_{j=2}^{M-1} S_f(x,u_j,t) + S_{fs}(x,t)}{M k_s + S_s(x,t) + \sum_{j=2}^{M-1} S_f(x,u_j,t) + S_{fs}(x,t)} \tag{20}$$

Dimensionless form:

$$S_{av}(x,t) = \frac{S_{f,av}(x,t)}{k_s / S_0 + S_{f,av}(x,t)} \tag{21}$$

Then material balance equation will look like

$$\frac{\partial}{\partial t} \int_0^R q(x,r,t) 4\pi r^2 dr = \frac{k_f A_p R^3}{3 V_c \rho} (S(x,t) - S_{fs}(x,t)) - \frac{R^2 k X_f}{\rho Y} L_f(x,t) S_{av}(x,t) \tag{22}$$

Dimensionless form:

$$\frac{\partial}{\partial t} \int_0^1 q(x,r,t) r^2 dr = \frac{T D_g A_p k_f S_0}{12 \pi V_c \rho} (S(x,t) - S_f(x,t)) - \frac{T D_g k X_f L_{max}}{4 R \pi \rho Y} L_f(x,t) S_{av}(x,t) \tag{23}$$

I got another result than in the paper. You can use any result that you like.

$$K_1 = \frac{T D_g A_p k_f S_0}{12 \pi V_c \rho} \quad K_2 = \frac{T D_g k X_f L_{max}}{4 R \pi \rho Y} \tag{24}$$

We get the equation

$$\frac{\partial}{\partial t} \int_0^1 q(x,r,t) r^2 dr = K_1 (S(x,t) - S_f(x,t)) - K_2 L_f(x,t) S_{av}(x,t) \tag{25}$$

Depends on L_f, S_f, S

As we use Legandre polynomials with weight function $W(x) = r^\alpha(1-r)^\beta$, with $\alpha = 0$ and $\beta = 2$ we get $W(x) = r^2$, that is why in (i, j, k) we get

$$\frac{\partial}{\partial t}\int_0^1 q(x_i, r, t) r^2 dr = \frac{\partial}{\partial t}\sum_{m=1}^{M} W_m q(x_i, r_m, t) = \sum_{m=1}^{M} W_m \frac{\partial q(x_i, r_m, t)}{\partial t} = \sum_{m=1}^{M} W_m \frac{q(x_i, r_m, t_k) - q(x_i, r_m, t_{k-1})}{\tau} \tag{26}$$

All together in (i, j, k) we get

$$\sum_{m=1}^{M} W_m \cdot \frac{q(x_i, r_m, t_k) - q(x_i, r_m, t_{k-1})}{\tau} = K_1 S(x_i, t_k) - K_1 S_f(x_i, t_k) - K_2 L_f(x_i, t_k) S_{av}(x_i, t_k) \tag{27}$$

$$\frac{1}{\tau}\sum_{m=1}^{M} W_m [q(x_i, r_m, t_k) - q(x_i, r_m, t_{k-1})] - K_1 S(x_i, t_k) + K_1 S_f(x_i, t_k) + K_2 L_f(x_i, t_k) S_{av}(x_i, t_k) = 0 \tag{28}$$

4 Liquid phase material balance

$$\frac{\partial S(x,t)}{\partial t} = D\frac{\partial^2 S(x,t)}{\partial x^2} - V_x \frac{\partial S(x,t)}{\partial x} - \frac{3k_f(R + L_f(x,t))^2(1-\epsilon)}{R^3\epsilon}(S(x,t) - S_{fs}(x,t)) \tag{29}$$

$$\frac{\partial S(x,t)}{\partial t} = D \cdot \frac{\partial^2 S(x,t)}{\partial x^2} - n_t D_g \frac{\partial S(x,t)}{\partial x} - D_g St(1 + B_0 L_{max})^2 (S(x,t) - S_{fs}(x,t)) \tag{30}$$

Initial and boundary conditions

$$S(x, t_1) = 0 \qquad S(x_1, t) = 1 \qquad \frac{\partial S(x_H, t)}{\partial x} = 0 \tag{31}$$

Depends on $S_{fs}(x,t)$

Let $D_1 = D_g St(1 + B_0 L_{max})^2$ and use extension in (i, k)

$$\left.\frac{\partial S(x,t)}{\partial t}\right|^{(i,k)} = D \cdot \left.\frac{\partial^2 S(x,t)}{\partial x^2}\right|^{(i,k)} - n_t D_g \left.\frac{\partial S(x,t)}{\partial x}\right|^{(i,k)} - D_1(S(x_i, t_k) - S_{fs}(x_i, t_k)) \tag{32}$$

Using for (32) the same Lagrange polynomial expansion (11) and finite difference scheme (12) as for kinetic equation (8) we get:

$$\frac{S(x_i, t_k) - S(x_i, t_{k-1})}{\tau} = D\sum_{m=1}^{M} B_{im} \cdot S(x_m, t_k) - n_t D_g \sum_{m=1}^{M} A_{im} \cdot S(x_m, t_k) - D_1(S(x_i, t_k) - S_{fs}(x_i, t_k)) \tag{33}$$

$$\begin{split}\tau D\sum_{m=2}^{M} B_{im} \cdot S(x_m, t_k) + \tau D B_{i1} S(x_1, t_k) - \tau n_t D_g \sum_{m=2}^{M} A_{im} \cdot S(x_m, t_k) - \tau n_t D_g A_{i1} S(x_1, t_k) \\ - \tau D_1(S(x_i, t_k) - S_{fs}(x_i, t_k)) = S(x_i, t_k) - S(x_i, t_{k-1})\end{split} \tag{34}$$

With lower boundary condtions (31) and remember $D = D_k D_g$ we get

$$(1 + \tau D_1) S(x_i, t_k) - \tau D_g \sum_{m=2}^{M} (D_k B_{im} - n_t A_{im}) S(x_m, t_k) - \tau D_1 S_{fs}(x_i, t_k) = \tau D B_{i1} - \tau D_g n_t A_{i1} + S(x_i, t_{k-1}) \tag{35}$$

for each time layer $t_i \in [t_2, t_3, ..., t_k, ..., t_N]$, where $t_k = \tau * (k-1)$
for each slice of column $x_i \in [x_2, x_3..., x_i, ..., x_{H-1}]$ (roots of Legendre polynomial of $H-2$ degree) we use (35), for t_1 we have already known $S(t_1, x)$ from initial conditions $S(t_1, x) = 0$
The last equation are added from upper boundary condition (31)

$$\left.\frac{\partial S(x,t)}{\partial x}\right|^{(i,k)} = \frac{S(x_i,t_k) - S(x_{i+1},t_k)}{x_2 - x_1} = 0 \qquad \Rightarrow \qquad S(x_i,t_k) - S(x_{i+1},t_k) = 0 \tag{36}$$

5 Biofilm equations of diffusion and biodegradation

diffusion and biodegradation

$$\frac{\partial}{\partial t} S_f(x,r,t) = D_f \frac{\partial^2}{\partial r^2} S_f(x,r,t) - \frac{kXS_f(x,r,t)}{Y(ks + S_f(x,r,t))} \tag{37}$$

We use in model simpler version for stationary conditions

$$D_f \frac{\partial^2}{\partial r^2} S_f(x,r,t) - \frac{kXS_f(x,r,t)}{Y(ks + S_f(x,r,t))} = 0 \tag{38}$$

Boundary condition for S_f

$$S_f(x, r = R, t) = S_s(x,t) \qquad S_f(x, r = R + L_f(x,t), t) = S_{fs}(x,t) \tag{39}$$

S_f defines only on interval $(R, R + L_f(x,t))$ and q only on the interval $(0,1)$. For me it is seems more logical totally separate this variables, introducing a new variable on the interval $(0,1)$. That will make possible to use orthogonal collocation and normalize result. The linear transformation $u = \frac{(r-R)}{L_f(x,t)}$ maps the interval $(R, R + L_f(x,t))$ to the interval $(0,1)$, replace r with u using $r = R + uL_f(x,t)$ we get Using dimensionless variables we get

$$\frac{\partial^2 S_f(x,u,t)}{\partial u^2} = \frac{kXL_f^2(x,t)S_f(x,u,t)}{YD_f(ks + S_f(x,u,t))} \tag{40}$$

Boundary condition for S_f

$$S_f(x, u = 0, t) = S_s(x,t) \qquad S_f(x, u = 1, t) = S_{fs}(x,t) \tag{41}$$

Use dimensionless transform we get

$$\frac{\partial^2 S_f(x,u,t)}{\partial u^2} = \frac{kXL_{max}^2 L_f^2(x,t)S_f(x,u,t)}{YD_f(ks/S_0 + S_f(x,u,t))} \tag{42}$$

To be consistent with paper, substitute $A_2 = \frac{kXL_{max}^2}{YD_f}$ and $B_1 = ks/S_0$

$$\frac{\partial^2 S_f(x,u,t)}{\partial u^2} = A_2 \frac{L_f^2(x,t)S_f(x,u,t)}{B_1 + S_f(x,u,t)} \tag{43}$$

Depends on $S_s(x,t)$ and $S_{fs}(x,t)$
Let's for u the collocation discretization be the same as for r, and we will use the same notation just for convenience. Using (11) and expansion in (i,j,k) we get

$$\sum_{m=1}^{M} B_{jm} \cdot S_f(x_i, u_m, t_k) = B_{j1} S_s(x_i, t_k) + \sum_{m=2}^{M-1} B_{jm} S_f(x_i, u_m, t_k) + B_{jM} S_{fs}(x_i, t_k) \tag{44}$$

$$B_{j1} S_s(x_i, t) + \sum_{m=2}^{M-1} B_{jm} S_f(x_i, u_m, t_k) + B_{jM} S_{fs}(x_i, t_k) = A_2 \frac{L_f^2(x_i, t_j) S_f(x_i, u_j, t_k)}{B_1 + S_f(x_i, u_j, t_k)} \tag{45}$$

6 Biofilm equations of grows and decay

$$\frac{\partial L_f(x,t)}{\partial t} = k\frac{S_{f,av}(x,t)}{ks + S_{f,av}(x,t)} - k_d L_f(x,t) = kS_{av}(x,t) - k_d L_f(x,t) \tag{46}$$

Initial and boundary conditions

$$L_f(x,t_1) = L_{f0} \qquad L_f(x,t_N) = L_{max} \tag{47}$$

Dimensionless form of that below, where $A_3 = kT$

$$\frac{\partial L_f(x,t)}{\partial t} = D_g A_3 \frac{S_{f,av}(x,t)}{B_1 + S_{f,av}(x,t)} - D_g A_3 L_f(x,t) = D_g A_3 S_{av}(x,t) - D_g A_3 L_f(x,t) \tag{48}$$

where $S_{av}(x,t) = \frac{S_{f,av}(x,t)}{B_1 + S_{f,av}(x,t)}$ and $B_1 = k_s/S_0$ substitute (20) to (48) and make expansion in (i,k) we get

$$\frac{L_f(x_i,t_k) - L_f(x_i,t_{k-1})}{\tau} = D_g A_3 S_{av}(x_i,t_k) - D_g A_3 L_f(x_i,t_k) \tag{49}$$

Finally, we get

$$L_f(x_i,t_k) - \tau D_g A_3 S_{av}(x_i,t_k) + \tau D_g A_3 L_f(x_i,t_k) = L_f(x_i,t_{k-1}) \tag{50}$$

Initial and boundary conditions

$$L_f(x,t_1) = \frac{L_{f0}}{L_{max}} \qquad L_f(x,t_N) = 1 \tag{51}$$

7 all together

Initial conditions

$$\begin{gathered} L_f(x,t_1) = L_{f0}/L_{max} \quad L_f(x,t_N) = 1 \qquad q(x,r,t_1) = 0 \\ S_s(x,t_1) = 0, \qquad S_f(x,r,t_1) = 0, \qquad S_{fs}(x,t_1) = 0, \qquad S(x,t_1) = 0 \end{gathered} \tag{52}$$

Boundary conditions

$$\begin{gathered} \left.\frac{\partial q(x,r,t)}{\partial r}\right|^{(i,1,k)} = 0 \qquad q(x_i,r_M,t_k) = S_s(x_i,t_k)^n \\ S(x_1,t) = 1 \qquad \left.\frac{\partial S(x,t)}{\partial x}\right|^{(H,j,k)} = 0 \\ S_f(x,u_1,t) = S_s(x,t) \qquad S_f(x,u_M,t) = S_{fs}(x,t) \end{gathered} \tag{53}$$

For each time step $t = [t_2, t_3, ..., t_N]$. Do not forget that on t_N the $L_f(x,t) = L_{fmax}$, so it is already known. for each slice of column $x_i \in [x_1, x_2..., x_i, ..., x_H]$ and for each radial layer $r_j \in [r_2..., r_j, ..., r_{M-1}]$ and for $u_j \in [u_2..., u_j, ..., u_{M-1}]$ we have discretization. So it's big non linear equation and we need to solve it. Just do it, man!
For x_1 due to boundary conditions we get simpler system, so $S(x_1,t) = 1$ and $S_{fs}(x_1,t) = 1$ are already known. We get:

$$\tau E_d \sum_{m=1}^{M-1}\left(\frac{s}{r_j}\cdot A_{jm} + B_{jm}\right) q(x_1,r_m,t_k) + \tau E_d \left(sA_{jM} + B_{jM}\right) S_s(x_i,t_k)^n - q(x_1,r_j,t_k) + q(x_1,r_j,t_{k-1}) = 0 \tag{54}$$

$$\sum_{m=1}^{M} W_m \cdot q(x_1,r_m,t_k) - \tau D_1 D_g L_f(x_1,t_k) S_{av}(x_1,t_k) = \tau D_1 + \sum_{m=1}^{M} W_m \cdot q(x_1,r_m,t_{k-1}) \tag{55}$$

$$L_f(x_1,t_k) - \tau D_g A_3 S_{av}(x_1,t_k) + \tau D_g A_3 L_f(x_1,t_k) = L_f(x_i,t_{k-1}) \tag{56}$$

$$\left(B_{j1} S_s(x_1,t_k) + \sum_{m=2}^{M-1} B_{jm} S_f(x_1,u_m,t_k) + B_{jM} \right) - A_2 \frac{L_f^2(x_1,t_k) S_f(x_1,u_j,t_k)}{B_1 + S_f(x_1,u_j,t_k)} = 0 \tag{57}$$

$$S_{av}(x_1,t_k) = \frac{S_s(x_1,t_k) + \sum_{j=2}^{M-1} S_f(x_1,u_j,t_k) + 1}{MB_1 + S_s(x_1,t_k) + \sum_{j=2}^{M-1} S_f(x_1,u_j,t_k) + 1} \tag{58}$$

We can found out extra boundary conditions

$$S_{fs}(x_1,t) = 1 \tag{59}$$