

Bioreactor Design and Analysis
Prof. Dr. Smita Srivastava
Department of Biotechnology
Indian Institute of Technology - Madras

Lecture – 26
Heterogenous Reactions in Bioreactors – Part 3

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9.3.5 Concentration Profiles in Other Shapes

The equations for flat-plate geometry are used to analyze bioreactions happening in cell films attached to inert solids. Even if the surface supporting the biofilm is curved rather than flat, if the film thickness b is relatively small compared with the radius of curvature, equations for flat-plate geometry are applicable.

To simplify mathematical treatment and keep the problem one-dimensional, the flat plate is assumed to be infinite length. In

Now if we need to determine, so we have been assuming from the beginning the for ease the particle shape as a spherical particle. Now let us see how will the concentration profile change with other shapes which we come across in various bioprocesses like your biofilms where the geometry will be like a flat plate. So, the equations for a flat-plate geometry they will be used to analyze the bioreactions happening in the cell films attached to inert solid surfaces.

Now if the surface supporting the biofilm is curved rather than flat and the thickness is relatively small in comparison to the radius of the curvature, we can still assume a flat geometry and extrapolate the results. To ease the mathematical calculations and to keep the solutions one dimensional, the flat plate is assumed to be of infinite length.

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Diffusion effects in surface bound enzymes on nonporous support materials

- Assume a situation where enzymes are bound and evenly distributed on the surface of a non-porous support material
- All enzymes molecules are equally active
- Substrate diffuses through a thin liquid film surrounding the support surface to reach the reactive surfaces
- At steady state, the reaction rate is equal to the mass transfer rate
- $J_s = k_L (S_b - S_s) = \underbrace{V'_m S_s / (K_m + S_s)}_{(1)}$

So, let us see if you want to characterize the diffusional limitations in a flat plate geometry or immobilized cells on flat surfaces, then we will begin with certain assumptions. Let us assume that the enzymes are bound and they are evenly distributed on the surface of a non-porous support material. Further all the enzymes are equally active and the substrate diffuses through the thin liquid film surrounding the support surface to reach the reaction surface.

So, at steady state, the reaction rate will be set equal to the mass transfer rate. So, again the mass transfer rate can be given as the mass transfer coefficient multiplied by the concentration difference at the surface and at some distance which is equal to if it is an immobilized enzyme system then let us assume it is following Michaelis-Menten kinetics. So, this should be equal to the rate of reaction.

So, whatever under steady state whatever substrate is diffusing in is what is getting consumed in the reaction. So, your equation shown at the bottom here demonstrates the steady state. So, this is the mass transfer of the substrate and the RHS is the reaction rate of the substrate.

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Diffusion effects in surface bound enzymes on nonporous support materials

- When the system is severely mass transfer limited ($S_s \approx 0$) then reaction rate is much rapid than mass transfer, in that case

$$v \approx K_L S_b \text{ (for } Da \gg 1 \text{) (mass transfer rate is less than reaction rate)}$$

$$v \approx V'_m S_b / (K_{m,app} + S_b) \text{ (} Da \ll 1 \text{) (mass transfer rate very high than reaction rate)}$$

$K_{m,app}$ is dependent on stirring speed as it is dependent on K_L

$$\text{With assumptions } K_{m,app} = K_m (1 + V'_m / (K_L (S_b + K_m)))$$

So, let us see what happens when this system becomes diffusion limited. Now if this system is severely mass transfer limited your S with a subscript s which was the concentration of the substrate reaching the surface where the enzyme is bound or is attached will become nearly equal to 0 because it is severely mass transfer limited and then in this case the reaction rate would be much rapid than the mass transfer.

And if that happens, then your reaction rate is being governed by the mass transfer rate and the mass transfer rate will be mass transfer coefficient multiplied by the bulk substrate concentration. This is the case when the Damkohler number is very high which means it is the mass transfer limited system than reaction rate limited. So, if you remember what was Damkohler number it was a dimensionless number which talks about whether the system is mass transfer limited or diffusion rate limited.

If the Damkohler number is very low which would mean that the system is reaction rate limited. So, if the system is reaction rate limited which means mass transfer rate is very high than the reaction rate, so reaction rate is slow. So, in this case your substrate concentration which reaches the surface becomes equal to S_b , very rapidly it cross so the mass transfer rate was very high. So, the overall reaction will be guided by the reaction rate.

So, here if it is following Michaelis-Menten kinetics then it has been shown that the reaction rate will be given as the Michaelis-Menten form with the substrate concentration as S_b . Now here the Michaelis-Menten constants will be the apparent values because it is an immobilized system and it would depend on the stirring speed and other operating parameters.

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Diffusion effects in immobilized cell systems-Biofilms

- The presence and significance of diffusional limitations depend on the relative rates of bioconversion and diffusion as given by damkohler number.
 - A differential material balance for the rate-limiting substrate within the biofilm yields at steady state
 - $D \frac{d^2S}{dy^2} = \frac{1}{Y_{x/s}} (\mu_m S / (K_s + S)) X$ ①
 - Boundary conditions: $S=S_0$ at $y=0$; $dS/dy=0$ at $y=L$
 - Assuming negligible liquid film resistance (agitated liquid phase)
 - Maximum rate of substrate utilization = $r_m = \frac{\mu_m X}{Y_{x/s}}$
 - $D \frac{d^2S}{dy^2} = r_m S / (K_s + S)$ ②
 - In dimensionless form $D \frac{d^2S'}{dy'^2} = \phi^2 (S' / (1 + \beta S'))$ where $S' = S/S_0$; $y' = y/L$ and $\beta = S_0/K_s$ ③
 - $\phi = L \sqrt{(\mu_m X / (Y_{x/s} DK_s))} = L \sqrt{r_m / DK_s}$
 - The maximum rate of substrate flux in the absence of diffusion limitations is given by
 - $N A = DA \frac{dS}{dy} \Big|_{y=L} = r_m S_0 / (K_s + S_0) (LA)$ ④
- A = surface area of the biofilm for substrate flux; N = substrate flux; L = thickness of the film
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Now let us take an immobilized cell system on flat surfaces. We have been discussing the immobilized enzyme systems, let us assume a cell system and following a Monod kinetics. So, like in based treatments bacteria immobilized on the surfaces. Now the presence and the significance of diffusional limitations it depends on the relative rates of bioconversion and diffusion. This we determine using the dimensionless number which is Damkohler number.

So, if you do the material balance for the rate limiting substrate within this biofilm at steady state, you see the equation 1 here, your LHS using Fick's second law of diffusion so this is your rate of substrate transfer and your RHS is the rate of substrate consumed where $Y_{x/s}$ is your yield of x by s and this term is your Monod model which determines dx by dt . When you divide it by the $Y_{x/s}$ term.

So, your entire RHS here will become ds by dt which is the amount of substrate consumed in the growth. This should be equal to the amount of substrate transferred through the biofilm which is being demonstrated here by Fick's second law of diffusion. Now in order to solve this, we will be needing boundary conditions. What can be the boundary conditions? Let us assume that at the surface of this biofilm which the substrate concentration is S_0 .

Which is your bulk substrate concentration and the distance your axis starts from the surface so where your $y = 0$. Now L is the length of the biofilm. So at $y = L$, the substrate is bounded. So therefore, dS by dy becomes equal to 0. Now assuming negligible liquid film resistance

because it is an agitated liquid phase, so therefore whatever is in the bulk is at the surface. So now we will substitute in equation 1 the value of μ_m X by $Y \times$ by s as r_m .

This is nothing but the maximum rate of substrate utilization possible. So, if there is maximum rate of substrate utilization y because your culture is growing at its μ_{max} . So, then this has been substituted as r_m in equation 1 and your equation 1 can then become equation 2 as shown here. So, after doing the substitution it becomes equation 2. Now further if we convert the equation 2 in dimensionless forms.

Where S prime is the dimensionless form for the substrate, so your S is being divided by the bulk substrate concentration as we did earlier if you remember for Michaelis-Menten kinetics in immobilized enzyme systems for spherical pellets. Similarly, your distance traveled through the film is again converted into a dimensionless variable Y prime by dividing it Y by the length of the biofilm, the thickness of the biofilm.

And another constant after doing these substitutions will come into the picture called as β . So, your equation 2 will then take the form given here as equation 3. And your ϕ is again a form of Thiele's modulus in such systems where this stands for the thickness of the biofilm and the ratio of the maximum reaction rate or substrate utilization to diffusion rate. So, if there are no diffusional limitations, then your reaction rate is being governed by Michaelis-Menten kinetics and your mass transfer rate is very fast.

So, your overall reaction rate will be governed by the Michaelis-Menten kinetics given as $r_m \frac{S_0}{K_s + S_0}$ shown in the RHS because now your S in the Michaelis-Menten kinetics becomes equal to the bulk substrate concentration. And this rate of reaction or substrate utilization at steady state is equal to the rate of substrate transfer at the surface where the enzyme is attached. So how do we determine that? Using Fick's law, D is the diffusivity, A is surface area and dS by dy at $Y = L$ as shown here.

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- In the presence of diffusional limitations, the rate of substrate consumption or flux =
- $N = D \frac{dS}{dy} \Big|_{y=L} = \eta r_m S_0 / (K_s + S_0) (L)$ ——— (5)
- η = effectiveness factor defined as the ratio of substrate consumption in the presence of diffusional limitation to the rate of substrate consumption in the absence of diffusional limitation

So, in the presence of diffusional limitation the rate of substrate consumption or flux can be given by this equation as shown here let us call it as equation, so this was equation 4 four, let us call it as equation 5. So, efficiency factor is nothing but the rate at which actually the substrate is getting consumed in the reaction which can be determined as $DA \frac{dS}{dy}$ by dy at $Y = L$ when there is some diffusional limitation divided by the reaction rate in the absence of any diffusional limitations which was $r_m S_0$ by $K_s + S_0$.

So, the volume can be given as L times A . So here the A gets cancelled, so your efficiency factor can be given as this expression which is nothing but your equation shown here as 5. So, your η is your efficiency factor which can be defined as the ratio of the substrate consumption in the presence of diffusional limitation.

So, your numerator talks about the substrate consumption in the presence of diffusional limitation to the rate of substrate consumption in the absence of any diffusional limitations where your S_s will become equal to S_0 at the surface as shown here. So, at $y = S L$, your S becomes equal to S_0 in the absence of any diffusional limitations.

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Table 9.1 Steady-state concentration profiles

First-order reaction: $r_A = k_1 C_A$

Sphere	$C_A = C_{AS} \frac{R \sinh(r\sqrt{k_1/D_{Ae}})}{r \sinh(R\sqrt{k_1/D_{Ae}})}$
Flat plate	$C_A = C_{AS} \frac{\cosh(z\sqrt{k_1/D_{Ae}})}{\cosh(b\sqrt{k_1/D_{Ae}})}$

Zero-order reaction: $r_A = k_0$

Sphere*	$C_A = C_{AS} + \frac{k_0}{6D_{Ae}}(r^2 - R^2)$
Flat plate*	$C_A = C_{AS} + \frac{k_0}{2D_{Ae}}(z^2 - b^2)$

If you see this table for first-order reaction if we consider a spherical pellet or a flat plate geometry, this is how the concentration profile would look like with a change in the distance. If it is a sphere from the surface of the pellet to the inner core defining the radii as R that distance otherwise the length. Similarly, for zero-order kinetics the expression has been given here.

So, in this table here we can see in the consolidated form how the concentration profile changes due to the diffusional limitations in a spherical geometry and in a flat plate geometry if the kinetics are being governed by first order or by the zero order.