

Introduction to Process Modeling in Membrane Separation Process
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Lecture – 20
Modeling of Dialysis (Contd.)

Welcome to the last session of this course, and we were looking into the chemical process enhanced separation in a batch dialysis process. We have written down we have take example of aniline separation from the feed using sulfuric acid in the dialysate side. And we have seen that how the sulfuric aniline reacts with sulfuric acid forming the anilinium ion maintaining the zero concentration of aniline in the dialysate side, where we can maintain the maximum concentration gradient or driving force so that we can have the maximum separation possible.

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Mass Balance

Solute balance in Feed:

Component 1: $V_F \frac{dC_F}{dt} = -A_m \frac{Dm}{L} (C_F - C_D)$

$\hookrightarrow \frac{dC_F}{dt} = \frac{A_m Dm}{L V_F} (C_D - C_F)$

Comp 1 balance in Dialysate side:

$\frac{dC_D}{dt} = \frac{A_m Dm}{L V_D} (C_F - C_D) - \frac{dC_{Sp}}{dt}$

$\frac{A_m Dm}{L} = k$

$$\frac{dC_F}{dt} = \frac{k}{V_F} (C_D - C_F)$$

$$\frac{dC_{Sp}}{dt} + \frac{dC_D}{dt} = \frac{k}{V_D} (C_F - C_D)$$

So, we have written down the governing equation of the solute one in the feed side. We have written down the governing equation of the solute one in the dialysate side, and now we look into the initial condition of this problem.

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Mass Balance

Solute balance in Feed:

Component 1: $V_F \frac{dC_F}{dt} = -A_m \frac{D_{12}}{L} (C_F - C_D)$

$\hookrightarrow \frac{dC_F}{dt} = \frac{A_m D_{12}}{L V_F} (C_D - C_F)$

Component balance in Dialysate side:

$\frac{dC_D}{dt} = \frac{A_m D_{12}}{L V_D} (C_F - C_D) - \frac{dC_{3D}}{dt}$

$\frac{A_m D_{12}}{L} = K$

$$\frac{dC_F}{dt} = \frac{K}{V_F} (C_D - C_F)$$

$$\frac{dC_{3D}}{dt} + \frac{dC_D}{dt} = \frac{K}{V_D} (C_F - C_D)$$

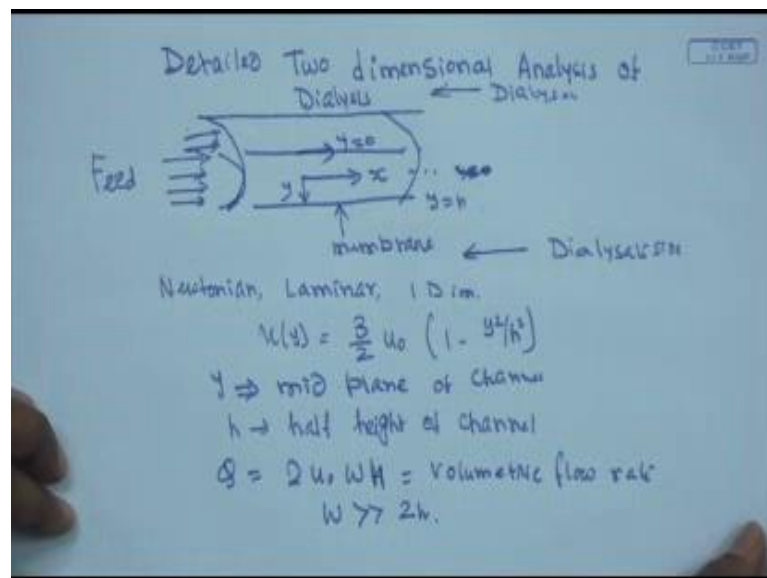
The initial conditions are at time t is equal to 0 we have C_{1F} is equal to C_{1F} naught and C_{1D} is equal to 0, because there is no solute initially and C_{3D} equal to 0 because there is anilinium ion also formed initially. Now, C_{3D} can be obtained by the equilibrium relationship because it is equilibrium govern reaction, so it is K equilibrium is equal to C_{3D} divided by C_{1D} times C_{2D} where C_{2D} is constant because this 2 is a sulfuric acid and this is constant because it is in excess; 2 is in excess. Now we take the Laplace transform and of both the equation like before and see what we get.

So, from the first equation we will be get in K by $V_F C_{1D}$ bar is transform variable C_{1F} bar is equal $S C_{1F}$ bar minus C_{1F} naught. And from the second equation we get K by $V_D C_{1F}$ bar minus C_{1D} bar is equal to $S C_{1D}$ bar minus C_{1F} naught plus $S C_{3D}$ bar minus C_{3D} 0, which will be basically 0 at time t equal to 0. From these two equations what is resulted is that we can write down K by $V_F C_{1D}$ bar is equal to K by V_F plus S 1 plus V_D over K 1 plus C_{2D} ; C_{2D} is a constant times $S C_{1D}$ bar minus C_{1F} naught. And by simplifying we can get expression of C_{1D} bar is equal to C_{1F} 0 divided by A plus $B S$ square. Where, A is equal to V_D by V_F 1 plus C_{2D} and B is equal to V_D by K 1 plus C_{2D} .

And we can take an inverse Laplace and can obtain C 1D as a function of time. This is straight forward you can really do that I can get the profile of concentration of aniline in the dialysate side and how it values other function of time. So, this is the modeling of a batch cell which is or the dialysis is separation of dialysis enhance by an external chemical reagent. So, this must also be known to a student that how we can maximize the driving force during a dialysis process and how to model the situation.

Next will be going a detailed 2 dimensional analysis in actual dialysis operation or a continuous study stat system; so will be doing a detailed 2 dimensional analysis of dialysis process.

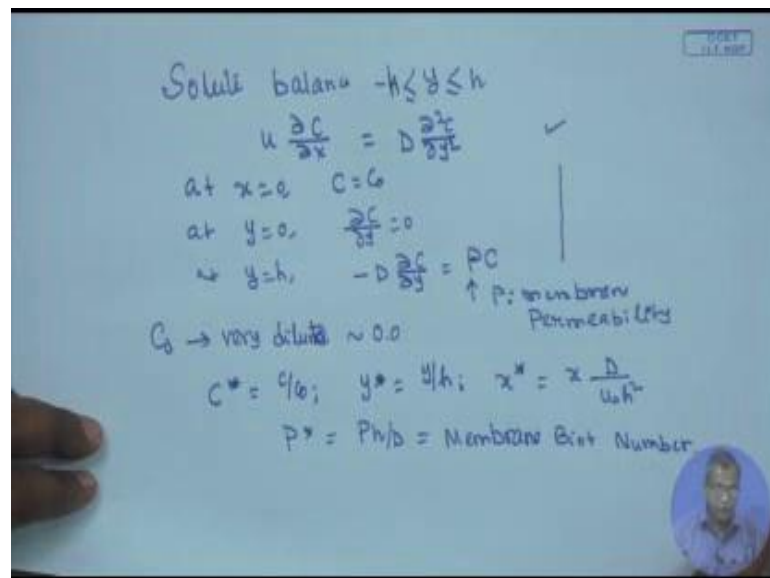
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So, let us say this is the feed side. The feed is flowing as a laminar flow; laminar parabolic profile so these feed going in to the system in the feed side and will be setting up your our x axis in the middle of the channel these y in these direction so this y equal to h this is y equal to 0. And we have placed a dialysis membrane and this is the dialysate side. So, there is a feed side, this is a dialysate side, and these are dialysate side as well both side and it will be having concentration profile something like this in the middle. It is basically the feed is like this, is a parabolic velocity profile.

So, if you consider a Newtonian fluid, laminar, and 1 dimensional flow the velocity profile as we have already know it is a parabolic velocity profile $1 - y^2/h^2$. So, y is the mid plane of the channel we invert this is fixed here, this is y equal to 0. Y is the mid plane of the channel and h is the half height. Next we write down the Q , Q is equal to $2 \int_{-h}^h u dy$ volumetric flow rates $2 u_0 w h$ is the volumetric flow rate. We are assuming that the channel is quite wide compared to the general height, w is much greater than $2 h$, and there is assumption. Now at the steady state we write down the solute balance with in the channel.

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Solute balance in the channel that means the channel is arranged from minus h ; h is the half height minus h^2 plus h and we write down the governing equation $u \frac{\partial C}{\partial x}$ is equal to $D \frac{\partial^2 C}{\partial y^2}$. Now this is an ideal dialysis process where the only driving force that is appearing in the system is the concentration of gradient. And unlike the earlier cases is the pressure driven membrane process is we did not have any pressure gradient pressure operating into the system so therefore there is no convective flux in the y direction. We will be having the solute flux in the x direction only, there is no $v \frac{\partial C}{\partial y}$ term is present in this equation.

So, at x equal to 0 we have C is equal to C naught and at symmetry in the mid plane at y is equal to 0 we have $\frac{\partial C}{\partial y}$ will be equal to 0 and at y is equal to h we have molar flux minus $D \frac{\partial C}{\partial y}$ should be equal to P times C , here P is the membrane permeability towards the solute. So therefore, we are assuming that the dialysate concentration is extremely dilute; C_d is very dilute and can be considered to be 0 at any point of time.

So, these system is a typical Eigen value problem and let us make it non dimensional and how the solution can be obtained. So, C^* we defined as C by C naught y^* we defined as y over h x^* we defined as x d divided by $u_0 h^2$ and P^* is membrane biot number they called it; so this will be ph over D and this is also known as the membrane biot number. So, let us look into the governing equation and the boundary conditions in the non dimensional version.

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$$\frac{3}{2} (1 - y^{*2}) \frac{\partial C^*}{\partial x^*} = \frac{\partial^2 C^*}{\partial y^{*2}}$$

BC: at $x^* = 0$, $C^* = 1$
 at $y^* = 0$, $\frac{\partial C^*}{\partial y^*} = 0$
 at $y^* = 1$, $\frac{\partial C^*}{\partial y^*} + P^* C^* = 0$

Sturm-Liouville or Eigenvalue Problem

Sepn of variables:
 Analytical Soln:

$$C^*(x^*, y^*) = \sum_{n=1}^{\infty} A_n \exp\left(-\frac{2}{3} \lambda_n^2 x^*\right) \sum_{m=0}^{\infty} a_{nm} y^{*m}$$

Eigenvalues $\rightarrow \lambda_m$

So, $\frac{3}{2} (1 - y^*^2) \frac{\partial C^*}{\partial x^*}$ is equal to $\frac{\partial^2 C^*}{\partial y^*^2}$, these is a governing equation. The boundary conditions become at x^* equal to 0 C^* is equal to 1 at y^* is equal to 0 $\frac{\partial C^*}{\partial y^*}$ equal to 0 and at y^* is equal to 1 we have $\frac{\partial C^*}{\partial y^*} + P^* C^*$ equal to 0. Now we can able to solve this equation by using separation of variable, and all of you must be knowing the

separation of variable and analytical solution can be obtain. The analytical solution will be in the form of C star as a function of x star y star will be summation it will be represented in the summation series m is equal to 1 to infinity Am exponential minus 2 by 3 lambda m square x star and summation of a nm y star where the n trans from 0 to infinity.

So, the Eigen value of the systems, these are a standard Eigen value problem and the standard Eigen value problem was Sturm Lourille problem. So, Eigen value of the systems are lambda m, lambda m are the Eigen values of the system and then we will see how the solution will involve. If that is the case then rate of removal of the solute can be written as.

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Rate of removal of solute:
 $M \text{ (kg/s)} = 2 u_0 h w (C_0 - C_{cm})$
Channel width

$C_{cm} \rightarrow$ cup mixing concentration of solute in the channel

$$C_{cm} = \frac{\int_0^h \frac{3}{2} u_0 \left(1 - \frac{y^2}{h^2}\right) c(x, y) dy}{\int_0^h \frac{3}{2} u_0 \left(1 - \frac{y^2}{h^2}\right) dy}$$

$C_{cm} = \frac{C_{cm}}{C_0} = 3 \left[\sum_{m=1}^{\infty} A_m \exp\left(-\frac{2}{3} \lambda_m^2 x^*\right) \sum_{n=0}^{\infty} \frac{a_{nm}}{(n+1/2)^2} \right]$

λ_m are roots of polynomial of form:
 $0 = P^2 - \left(\frac{2}{3} + \frac{5}{12} P^2\right) \lambda_m^2 + \left(\frac{1}{30} + \frac{1}{45} P^2\right) \lambda_m^4$

Let us say this is the mass per unit time that will be in kg per second we removed will be $2 u_0 h$ times w ; w is the width channel width multiplied the C_0 minus C_{cm} . What is C_{cm} ? C_{cm} is the cup mixing concentration across the channel. So, it is some kind of average concentration of solute in the channel. So, C_0 is the feed concentration, h is the half height, $2 h$ is the total height usually is the velocity, w is the width. Now next will be finding out what is the cup mixing concentration. Cup mixing concentration is given as by these expression it is some kind of cross section average concentration; 0 to

$h^3 \int_0^1 (1-y^2)^2 dy$ and there will be 0 to $h^3 \int_0^1 (1-y^2)^2 dy$. C is the function of x and y .

These expression can be integrate quite easily there is absolute no problem in that, we have already found out what is the expression of C as a function of x and y that can be integrate across the y . So, the (Refer Time: 15:26) will be intact so I will be getting ultimately C_{cm} as a function of concentration. How the cup mixing concentration of the average concentration in the feed side will be varying along the x that expression can be obtain by these.

So, if we looking to the expression of that 1 dimensional version of that C_{cm} star is equal to nothing but C_{cm} divided by C_{naught} and this will be after integration will be getting this expression summation of m is equal to 1 to infinity $A_m \exp(-\lambda_m^2 x)$ summation of n equal to 0 to infinity $a_{nm} \frac{1}{n+1}$ into $n+3$ at the Eigen values or the are roots of the polynomial. λ_m are roots of polynomial of the form $0 = P^2 - \frac{2}{3}P + \frac{5}{12}P^3 + \frac{1}{20} + \frac{1}{45}P^4$. So, this will be the polynomial that the roots or the Eigen values. So, what is a λ_1 ?

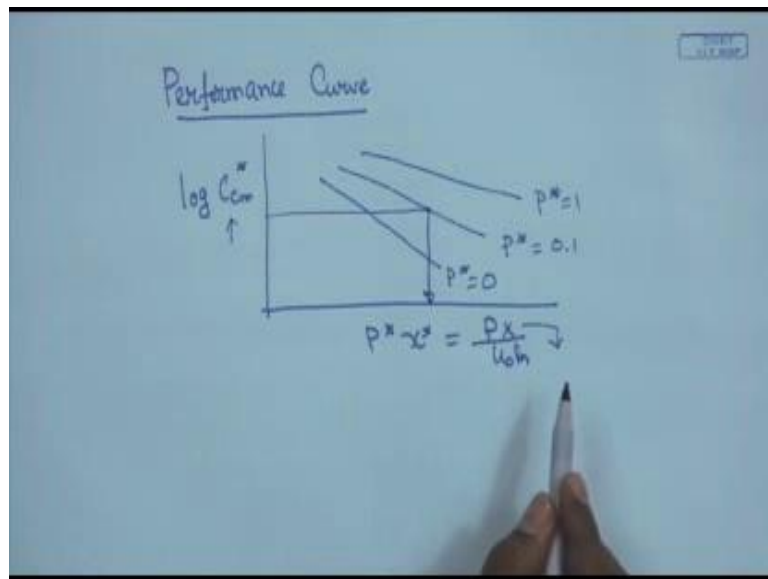
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$a_{0m} = 1; a_{1m} = 0; a_{2m} = -\frac{\lambda_m^2}{2}; a_{3m} = 0$
 $a_{4m} = \frac{\lambda_m^4}{24}; a_{5m} = 0 \dots$
 $A_m = \sum_{n=0}^{\infty} \frac{a_{nm}}{(n+1)(n+3)}$
 $\sum_{n=0}^{\infty} \sum_{p=0}^{\infty} \frac{a_{pm} a_{n-p,m}}{(n+1)(n+3)}$
Simplification: exponent decay is fast
 First eigen value
 $\lambda_1^2 = \frac{P^2}{\frac{2}{3} + \frac{5}{12}P^2}$
 Consider 1st term of series

A 0 m is equal to 1 a 1 is equal to 0. So, basically the even terms will survive of the series minus lambda m square by 2 and a 3 m is equal to 0, likewise a 4 m will be equal to lambda m square 2 plus lambda m square divided by 24, a 5 m is equal to 0 likewise it will go. And capital Am will be given as summation of n equal to 0 to infinity a nm divided by n plus 1 into n plus 3 and there will be double summation in the denominator n equal to 0 to infinity P is equal to 0 to n and this will be a pm a n minus P times m divided by n plus 1 into n plus 3.

Now, let us do a certain simplification. Simplification is that as we can see that the solution as x dependence in form of exponential minus lambda square x star, so lambda m will be large value and x square will be large. So therefore, exponential decay will be faster, so if you that if you if you take care of that. And we considered the since the exponential decay is faster we can take the first term as the first Eigen value. Decay is fast and we can consider the first Eigen value that will be lambda 1 square is equal to P star divided by 2 by 3 plus 5 by 12 P star, and considered the first term of series. If we do that than a typical nth plot log C cm star verses P star x star and will be getting a performance curve.

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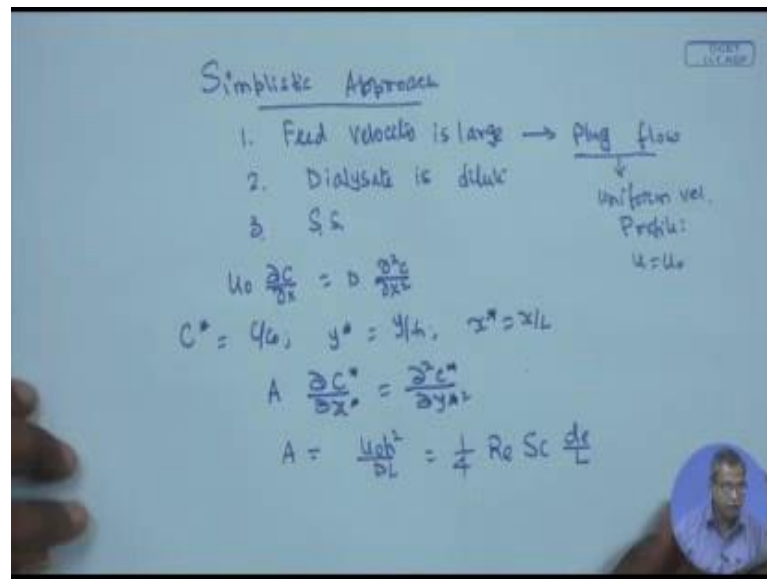
We compute taking the first Eigen value and the performance curve will be looking something like this. We will be having $\log C_{cm}$ star here and P star x star will be nothing but $P \times u_0 h$ and the curves will be like this for different value of P star; these for P star is equal to 1, these for P star is equal to 0.1, these for P star equal to 0. That means, there is no permission of the solute to the membrane it is impermeable.

So now, if you like to design what is the length of the dialyzer length for a particular removable of the solute then from that particular removable of solute we can estimate the value of C_{cm} star we can directly go of the value of P star if P star is 0.1 we can directly come here and get the value of x star. We know this coordinate system, so P is known to us, usually known to us, channel height is known to us, so you can get the value of x .

Likewise, for different type of membrane where the P star will be known we can get the curve for a 99 percent separation 98 percent separation of the solute from the feed side. You can get the length of the dialyzer. If the length of the dialyzer is known then from here one can find out what will be the each of the height of the dialyser. So, if the P star is not known we can then you have to interpolate between the two known values can find out the design of the dialyser or can find out the length of the dialyzer or the height of the dialyzer. If you one of them is fixed then other can be evaluated. So, thus in a continuous system for a 2 dimensional model which will be a basically and a very realistic model can be obtained, can be utilized to design a dialysis.

Next what will be looking, we will be looking into a very simplified version of this of this model so that the analytical solution will be will be in front of us. So, let us look into a simplistic approach.

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First, we considered the feed velocity is large and will be having a plug flow, dialysate is dilute, and third it is a steady state operation. So, if it is a plug flow or will be having a uniform velocity profile u is equal to u_{naught} , then our own analysis become simplified and will be having $u_0 \frac{\partial C}{\partial x}$ is equal to $D \frac{\partial^2 C}{\partial x^2}$. And take the non dimensional version C^* equal to C by C_{naught} y^* is equal to y by h and x^* is equal to x by L . If that is the case it becomes $A \frac{\partial C^*}{\partial x^*} = \frac{\partial^2 C^*}{\partial y^{*2}}$, so these equation are easy to solve and there will be a analytical solution is obtained here.

So, A is equal to $u_0 h^2$ by $D L$ this can be written as $\frac{1}{4} Re Sc \frac{d}{L}$ as we have done earlier.

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BC: at $y^* = 0$, $\frac{\partial C^*}{\partial y^*} = 0$
 $y^* = 1$, $\frac{\partial C^*}{\partial y^*} + P_m C^* = 0$
 $P_m^* = P h / D$
 $x^* = 0$, $C^* = 1$
Sepn of variable:
 $C^* = X(x^*) Y(y^*)$
 $\frac{A}{x} \frac{dx}{dx^*} = \frac{1}{Y} \frac{d^2 Y}{dy^{*2}} = -\lambda_n^2$
 $X = C \exp\left(-\frac{\lambda_n^2 x^*}{A}\right)$

The non dimensional version of the governing the boundary conditions we can write directly that at y star is equal to 0 my del C star del y star will be equal to 0 and y star is equal to 1, we have del C star del y star plus P_m C star is equal to 0. So, what is P_m star? P_m star nothing but $P h$ over D , D is the diffusivity of solute through the membrane matrix and at x star equal to 0 we have C star equal to 1.

Now, you can use a separation of variable type of solution and we can assume the concentration can be a function of sol function of x and sol function of y . And if you really do that and put into the governing equation these will become A by x dx star is equal to 1 over y d square y dy star square. The left hand side is the function of x alone the right hand side is a function of y alone they will be equal and they will be equal to some constant let us say, this constant is minus λ_n square.

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$$\frac{d^2 Y}{dy^{*2}} + \lambda_n^2 Y = 0$$

at $y^* = 0$, $\frac{dY}{dy^*} = 0$

at $y^* = 1$, $\frac{dY}{dy^*} + P_m Y = 0$

$$Y = C_n \cos(\lambda_n y^*)$$

Eigenvalue: $\lambda_n \tan \lambda_n = P_m$

$$C^*(x^*, y^*) = \sum C_n \cos(\lambda_n y^*) \exp\left(-\frac{\lambda_n^2}{\alpha} x^*\right)$$

$x^* = 0$, $C^* = 1$

$$1 = \sum C_n \cos(\lambda_n y^*)$$

$$C_n = \frac{\int_0^1 \cos(\lambda_n y^*) dy^*}{\int_0^1 \cos^2(\lambda_n y^*) dy^*}$$

So, the solution is x is equal to $C_1 \exp(-\lambda_n^2 x^*)$ and the varying part is $\frac{d^2 y}{dy^{*2}} + \lambda_n^2 y$ will be equal to 0 and will be having the boundary condition that at $y^* = 0$ $\frac{dy^*}{dy^*} = 0$ and $y^* = 1$ will be having $\frac{dy^*}{dy^*} + P_m y = 0$. This will be having a solution y is equal to some $C_n \cos(\lambda_n y^*)$ and the Eigen values will be nothing but the roots of the transcendental equation of $\lambda_n \tan \lambda_n = P_m$.

So, from this transcendental equation roots of this equation will be the Eigen values and one can get the final solution as $x^* y^*$ is summation of all these solutions, so this becomes $C_n \cos(\lambda_n y^*) \exp(-\lambda_n^2 x^*)$. So, from by using boundary condition initial condition that at $x^* = 0$, $C^* = 1$ we can get the value of C_n by using the orthogonal properties of the sin and cos function. If you really do that the C_n will become $\int_0^1 \cos(\lambda_n y^*) dy^*$ divided by $\int_0^1 \cos^2(\lambda_n y^*) dy^*$.

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$$C_n = \frac{2 \sin \lambda n}{\lambda n} \frac{P_m^2 + \lambda^2}{P_m^2 + P_m + \lambda^2}$$

$$C^*(x^*, y^*) = \sum_{n=1}^{\infty} C_n \cos(\lambda n y^*) \exp\left(-\frac{\lambda n^2 x^*}{A}\right)$$

$$C_{cm}^* = \frac{\int_0^1 u_0 C(x, y) dy}{\int_0^1 u_0 dy}$$

$$= \sum_{n=1}^{\infty} C_n \exp\left(-\frac{\lambda n^2 x^*}{A}\right) \frac{\sin \lambda n}{\lambda n}$$

$$M = \text{Rate of removal of pollutant} = 2 u_0 h w (C_0 - C_{cm})$$

And one can really do a calculation and evaluate the integrals and these becomes that C_n becomes $2 \sin \lambda n$ divided by λn P_m square plus λ square divided P_m square plus P_m plus λ square. And ultimately we can get the expression of C^* as function of x^* and y^* is equal to summation of $C_n \cos \lambda n y^*$ exponential minus $\lambda n^2 x^*$ divided by A ; n equal to 1 to infinity. Then we can evaluate the cup mixing concentration and by definition as we have done earlier the cup mixing concentration in this case will be we carry out the integration. And let us write down the expression first; so this uniform here $u_0 C(x, y) dy$ from 0 to 1 and here it will be 0 to 1 $u_0 dy$.

So, we will be getting the expression of cup mixing concentration as C_n exponential minus $\lambda n^2 x^*$ by times $\sin \lambda n$ divided by λn that will be expression of C_{cm}^* . And mass removed is rate of removal of pollutant will be $u_0 h$ times $w C_{naught} - C_{cm}$. Then after multiplying the C_{naught} if you can put this expression one can get the rate of removal of the pollute through the dialysis process. So, this is how the dialysis process can be model either by 1 dimensional model or detailed 2 dimensional models we have discussed.

I hope now you have really come down to the end of our course so let us summarize whatever we have learned in this course. In this course we have learned the basic principles and the various membrane based fundamentals of various moment based processes their underline transport mechanism. Then we have categorized various processes in terms of reverse osmosis, nano filtration, micro filtration, ultra filtration, and then membrane modules, we have discussed membrane modules as well as the dialysis process. We have looked into the various the important terms and definitions those were required tremendously for modeling the systems. We have looked into the how from irreversible thermodynamics the transport loss in case of reverse osmosis through the plus membrane can be obtained.

Then we have looked into the fouling, irreversible fouling and as well as the concentration polarization. Then we have looked into the 1 dimensional analysis of concentration profile, concentration polarization, and summarize the short coming of 1 dimensional model, and looked into the osmotic detailed 2 dimensional model for the osmotic pressure control filtration.

We looked into details of the osmotic pressure control filtration for dilute solution, for concentrate solution, for developing, for 1 dimensional model 2 dimensional model things like that. And then we moved into the gel layer polar polarization filtration system and we have looked into the detailed modeling of gel air controlling filtration. After that then went forward to the membrane modules, and how to covered, how to do the modeling, and how to format the design equations to model the membrane module, and how to obtain the solutions as well.

Again in this case as we have gone into step by step complicated step initially first the very first instance we consider a very simplistic case for constant permeate flux. Then we have taken the complexity to a second level where the permeate flux is proportional to the ΔP or the pressure gradient and then we got the solution. Then went into the next step there is a most complicated step where it is proportional to ΔP minus $\Delta \pi$ where the osmotic pressure is not negligible at all.

Solve that case then we have gone into the dialysis process and looked into the design equation for the basically batch dialysis, continuous dialysis, then batch dialysis with enhanced chemical reaction, enhance separation. And then finally we have looked into the 2 dimensional model of a continuous dialysis process.

I hope you have got a fair idea how to model and design the membrane based separation pressure systems starting from the pressure driven processes up to the dialysis operation. And I hope that this course will be of eminence help for you to your future career in research or in industry.

Thank you very much.