Physico-Chemical Processes for Wastewater Treatment Professor – V. C. Srivastava Department of Chemical Engineering Indian Institute of Technology, Roorkee Lecture – 44 Wastewater Treatment by Membrane Processes – IV

Good day everyone and welcome to these lectures on Physico-Chemical Processes for Wastewater Treatment. So, in today's lecture we will continue our discussion on the membrane processes which are used for water and wastewater treatment.

So, previously we have already discussed about the membrane processes which include ultrafiltration, nano filtration, micro filtration and reverse osmosis and we tried to learn regarding the different ways in which these membranes are made, how they are used further for water treatment. We tried to learn the different equations and other theories which are used.

So, in today's lecture we will try to solve one problem related to membrane processes and then further we will continue with the reverse osmosis. So, reverse osmosis is one of the techniques which is very very commonly used in the water and wastewater treatment. So, will be emphasizing and understanding reverse osmosis more in detail from today's lecture onward.

But before that we will try to solve one numerical problem and through that will try to see that there are different ways in which different design equations and other things can be used for solving. Also, many a times we require some basic understanding of chemical engineering, civil engineering, et cetera and those we can apply to solve our problem. (Refer Slide Time: 2:13)



So, will continue with the, first will start with one numerical and so in this numerical it is given that an emerging pollutant having 1 weight percent in the water is passed through a tubular ultrafiltration membrane module which is having a 2 centimetre internal diameter and it is 200 centimetre long and this is being done at a temperature of 25 degree centigrade.

Now, the rejection coefficient is 0.995 so, we are targeting that will performing the calculation at rejection coefficient of 0.995, the applied pressure difference is 2 bar. The diffusivity through the membrane force is 9 into 10 raised to minus 11 meter square per second and viscosity of the solute is 4 cP. Gel point concentration of the solute at the membrane interface is 10.5 percent.

So, we have to find out the flow velocity that has to be maintained in the tube in order to prevent formation of gel layer on the membrane surface. So, this is being asked, many times the problem may be solved differently. In actual scenario the data available in any problem where we have to solve the problem at any industry level or otherwise is very less and so any problem can be divided into three different sections.

So, one section is that, what amount of data is generally given by any industry. So, for which we are going to design the system. So, generally they will give is that, this is the flow rate and this is the concentration, so design a system for that. So, this is the first data which is available. Now as a design engineer, as an engineer our thing is that to take out other data.

So, now the second data that will come into picture that, what technique we are going to use. So, suppose we decide ultra-filtration membrane, so which module which we are going to use. So, this is our own decision. So, right now in this problem we are taking 2 centimetre internal diameter and 20 centimetre long. So, this is we have chosen.

It may be possible that this particular membrane nor may not do the duty that is required. So, we may have to change this data. Second thing is that, once we decide, this is the membrane module that we are going to use then we decide upon the operating parameter that we are going to work and under those condition whether we can achieve the targets also.

So, many times we can assume some of the operating parameters then try to find out other parameters, so this is possible. In between we have to correctly know other parameters also like viscosity of solute. So, may be the for that solute we will have to check into the literature or we will have to actually evaluate the viscosity of the solute. So, it has been given here but in the actual scenario these things we may have to determine differently. So, these are there.

Then some other parameters we assume, so under those condition and that is by experience. So, one data is given by the industry, many other data we have to find out by our own ideas or by different instruments etcetera. Some of the parameters we assume and cross check that if that assume assumed parameter is correct then whether the other parameters are also within the guidelines or not. So, this is the way we try to solve.

So, any problem can be always be broken into different sections for better understanding and this is how we should look into the problem. So, in this case we have to find out the flow velocity that has to be maintained in the tube to prevent the formation of gel layer and the membrane surface. So, this is there.

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Gel polarization model (Limiting flux):

 $\mathbf{J}_{w} = \mathbf{k}_{c} \ln \left(\frac{\mathbf{C}_{g} - \mathbf{C}_{p}}{\mathbf{C}_{b} - \mathbf{C}_{p}} \right)$

where, $k_c = mass$ transfer coefficient

Now, here what we has been given is that? The concentration of, concentration at the membrane surface at the incipient gelation, it is given again. So, this is there and membrane water permeability also is reported. This is also known to us. So, this is also maybe from literature we have found out. Now we start solving the problem. Now the gel polarization model which has been given earlier which we discussed as per that the Jw is Kcln Cg minus Cp upon Cb minus Cp where Kc is the mass transfer coefficient.

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Now in this data what are the things that are known to us? So, concentration of the solute at the membrane it is already we have assumed to be 10.5 percent. So, here it will be 0.105 now the bulk solute concentration is one percent. So, it is 0.01. Now the permeate concentration which we have to find out, now already it is given that 99.5 percent is the rejection.

So, that means 1 minus 0.995 of the concentration will be rejected. So, based upon that we calculate and it is 0.0005. Now, if we apply this we are we are trying to find out the value within braces. So, that will be here and we solve it, it is 10.6.

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$$Iimiting flux: J_{w} = k_{c} ln \left(\frac{C_{g} - C_{p}}{C_{b} - C_{p}} \right) \Rightarrow exp \left(\frac{J_{w}}{k_{c}} \right) = \frac{C_{m} - C_{p}}{C_{b} - C_{p}} = \frac{C_{g} - C_{p}}{C_{b} - C_{p}}$$

$$\therefore exp \left(\frac{J_{w}}{k_{c}} \right) = 10.6 \Rightarrow \frac{J_{w}}{k_{c}} = 2.4$$
It is given that concentration at the membrane surface at incipient gelation $C_{g} = 0.021$ g mol/L

Now what we do is that, this was the limiting flux equation which was given Jw is equal to earlier we have. Now we little bit manipulate it, so the exponential Jw by Kc will become

equal to this and this is equal to this itself. So, only and now we have already found it to be 10.6. So, if you solve it, I will be finding that Jw by Kc which is like flux divided by the mass transfer coefficient is 2.4. So, it is given that. Now another data which is given is that, at the membrane surface the concentration is 0.021 gram mole per litre.

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So, using this data the concentration difference between the feed and the permeate side will be this. So, Cg is also known to us, Cp is also known to us. So, we can find out this is the gram per mole per... So, now osmotic pressure which will be there for this concentration will be based upon this concentration difference, so this is delta pi delta C RT and we find out to be 3.96 psi are 0.269 atmosphere.

But the applied pressure difference is 2 bar which is equivalent to 29.39 psi. So, the actual driving force which is there is delta p minus delta pi which is osmotic pressure. So, it is 29.39 minus 3.95, so we have 25.44 psi which is the pressure driving force which is available to us. Based upon the assumption that the applied pressure difference is 2 bar. Now under this condition, under this condition because the permeability is also given so we can find out after little bit correction.

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So, under this condition the water flux is 2.53 into 10 raised to minus 5 meter cube per meter square per second. So, this calculation we can perform because already the permeability data is given here. So, this is known to us, per unit psi so this is there. So, we multiply by the available psi to get the flux value. Now once this flux value is known then we can find out the value of Kc because Jw by Kc is 2.4 that we have found earlier.

So, from this data we can solve and we can find out the Kc value which is 1.05 into 10 raised to minus 6 meter per second. So, this data we have found out. Now once this data is known we can further go ahead and find out the minimum liquid velocity. So, already these values are known to us from the data itself. We are assuming this solution density to be 1000 kg per meter cube because the concentration is very less.

We are assuming the density to be of water only. The solute diffusivity value is also known, already known from given in the problem. It may be determined differently also. So, it is given here in the problem. So, under that condition if all these four parameters are known because tube diameter is also known. We can find out the Schmidt number. So, the Schmidt number is given by nu by rho D and all the diffusivity value, density and viscosity every term is known to us. So, this value is found to be 4.44 into 10 raise to 4.

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Now similarly, we can find out the Sherwood number and once Sherwood number is known we can find out the Reynolds number. So, Sherwood number is Kc small d by capital D which is diffusivity and the small d, the diameter is known to us. So, the Sherwood number has been found Kc value has been found. Now for mass transfer coefficient, there is a relationship between Sherwood number, Reynolds number and Schmidt number. So, this is known and using this relationship we can find out the Reynolds number and once the Reynolds number is known, we can find out the velocity also. So, Reynolds number is given by d v rho by nu and from that we can find out the Reynolds number is already known to us.

So, we can find out the velocity, it is 3.42 meter per second. So, this is the minimum flow velocity that has to be maintained so that the wall mass transfer coefficient is always high enough for preventing any formation of gel layer on the membrane surface. So, this we have to see. So, as to avoid the formation of gel layer and further following etcetera.

So, this is how we can perform the calculation. We can use the same tricks to find out other parameters also. So, this is like an iteration type of thing where one of parameters is assumed then the second parameter is known. So, based upon this we can perform different calculations etcetera. Certainly we should know these correlations etcetera as well for finding out this parameter. So, we need to understand many other things for performing, various other calculations.

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Now as pointed earlier, reverse osmosis is very very commonly used in the wastewater treatment and it is used in the industry as well, as well as in the small water treatment units which are there, which are installed in the households as well. So, what is reverse osmosis? What are its details? Now we are going to study the reverse osmosis thing more in detail.

So, and reverse osmosis is opposite of osmosis. So, let us first understand osmosis and then will understand reverse osmosis. So, osmosis is defined as the spontaneous transport of a solvent like for water and wastewater case the solvent is water. From a dilute solution to a concentrated solution across a ideal semi-permeable membrane and that impedes the passage of solute but allows the solvent to flow.

So, this will not allow the solute to move across the interface but it will allow water to flow across the semi-permeable membrane. So, under usual condition because of osmosis always a spontaneous transport of solvent will occur. The system will reach equilibrium when the hydrostatic pressure on the saline water side balances the force which is like osmotic pressure, moving the water through the membrane. So, this osmotic pressure is noted. So, this is this is noted as osmotic pressure.

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- If pressure is exerted to overcome the osmotic pressure, the solvent (pure water) will flow from the saline side to the fresh water side.
 The semipermeable membrane will not allow the passage of molecules other than water and gases.
 - This is noted as reverse osmosis.
- Therefore, Reverse Osmosis (RO) is a membrane-based demineralization technique used to separate dissolved solids, such as ions, from solution (most applications involve waterbased solutions).

https://water.ma/media/documentationen/Principles%200f%20Reverse%200smosis%20Membrane%20Separation.pdf

So in the actual condition what will happen is that, we have fresh water, we have saline water and if we just keep them open, the fresh water will always move across the saline water until unless we have condition where it will stop.

So, equilibrium will be reached, under that condition some amount of water will be again filled up, up to this condition and we try to see what is this difference and from this difference we can find out the osmotic pressure which is there for this. So, this is called as osmotic pressure and because of this the fresh water will always go towards the saline water and try to dilute the concentration of this water.

So, this is there, so this is the osmotic pressure or osmosis. Now if pressure is exalted to overcome the osmotic pressure, the solvent will flow from the saline side to the fresh water side and the semi-permeable membrane which was earlier also that will not allow the passage of the molecules either other than water and gases.

So, this will be a reverse osmosis condition. So, therefore, reverse osmosis is a membrane based demineralization technique which is used to separate dissolved solids such as irons from solution. Most applications involve like water based solution. So, what we do is that, we apply certain amount of pressure on this and once we start applying pressure on this, the water starts moving from this side to this side.

So, because of the pressure because this semi-permeable membrane will only allow the water to move across it. Now because of that, the saline concentration which is there, it will become more concentrated because the water is going from this side. So, the amount of salt is still the same but water is going to the fresh water side.

So, that means this will become more concentrated and later on we can remove this and thus we are getting clean water from saline water. So, this is called as reverse osmosis but we have to apply very high amount of extra pressure to achieve this condition. So, this is the reverse osmosis.

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Principle of Reverse Osmosis (RO) In this way, osmosis is a natural phenomenon which can be defined as the movement of pure water through a semi permeable membrane from a low to a high concentration solution (discussed in previous figure). The membrane is permeable to water and some ions but rejects almost all ions and dissolved solids. This process (movement of water) occurs until the osmotic equilibrium is reached, or until the chemical potential is equal on both sides of the membrane.

So, this is how it is explained. So, osmosis is a natural phenomena which can be defined as the movement of pure water through a semi-permeable membrane. The membrane is permeable to water and some ions but rejects almost all the ions and dissolved. This process occurs until osmotic equilibrium is reached in the chemical engineering terms, when the chemical potential becomes equal on both sides of the membrane. (Refer Slide Time: 19:00)



The general form of the Gibbs function is:

 $\partial G = V \partial P - S \partial T {+} \sum \mu_i \partial n_i$

where, G = Gibbs energy, J

- $V = Volume, m^3$
- P = Pressure, Pa
- S = Entropy, J/K
- T = Absolute temperature, K
- μ_i = Chemical potential of solute i, J/mole

n_i = Amount of solute i in solution, moles

Now a difference of height is absorbed between both compartments when chemical potential is equalized. So, this difference in height is measured as the osmotic pressure which was given here. Now in the reverse osmosis, we apply pressure in addition to osmotic pressure. So, under that condition water is forced to flow from the concentrated to the dilute side and solutes are retained by the membrane on the concentrated sites itself.

This is the way, we can treat the water or we can get pure water out of a concentrated slurry. So, this is there. Now the driving force for diffusion in the osmotic pressure is typically described as a concentration gradient. So, a more rigorous explanation nation can be given by understanding the chemical engineering thermodynamics. So, in the chemical ranging thermodynamics we know Gibbs energy.

So, the general form of Gibbs function is given here and which is well known the delta G is equal to v delta p minus s delta t plus this potential term. So, in this the nu i, is the chemical potential of solute i and the amount of solute i in the solution is given by ni. So, this is the other terms are volume, pressure, entropy etcetera.

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Now, it is known that the chemical potential which is nu i is defined as the change in the Gibbs energy resulting from a change in the amount of component i, when the temperature and pressure are held constant. So, from here we can always define the chemical potential also, this is given by delta g upon ni. Now therefore under constant temperature conditions, so equilibrium will be achieved when this condition is met.

So, this is there, so under this this term is equal to 0. And we want to see that delta g equilibrium condition is reached. So, under equilibrium condition this term will be equal to 0. So, if we equate them, so v delta p must be equal to this. So, this is now we can see. Now going further the pressure delta p which is required to balance the difference in chemical potential of a solute it is called as osmotic pressure and it is by convention generally it is written as pi. So, this is how it is found.

Now the equation for osmotic pressure can be derived thermodynamically using assumptions of incompressible or ideal solution behaviour also and under that condition it will be given by pi is equal to i psi CRT where this term is osmotic coefficient which is dimensionless. C is the concentration of all solutes. R is universal gas constant, T is the temperature and i is the number of ions produced during dissociation of solute. So, through this we can find out the osmotic pressure also, this is there.

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So, here some examples are given that number of ions per mole i, would be 2 for NaCl, this is there. Now the osmotic coefficient psi depends upon the nature of substance and its concentration for NaCl like it ranges from 0.93 to 1.03 over a concentration range of 10 to 120 gram per litre of salt. Now sea water has an osmotic coefficient that varies from 0.85 to 0.95 for different concentration ranges. So, this is there.

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Now going further we will try to understand the flux. So, already we have defined that the flux for osmotic reverse osmosis case or for membrane processes, it is always given as meter square, meter cube per meter square per day where meter square is the membrane surface area. For solutes it may be given as kg per meter square per day or kg per day per meter square, again meter square is the membrane surface area.

So, in place of meter cube we are using kg in the case of solutes and there are different models which can be used like solution diffusion model, pore flow model, preferential sorption capacity flow models etcetera. They can be used for understanding the flux or determining the flux.

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i. Solution-diffusion model			
 Permeation occurs through a dense membrane where active layer is permeable but <u>nonporous</u>. 	the		
 Water and solutes dissolve into the solid membrane material, diffuse through the solid, and reliquefy on the permeate side of the membrane. 			
Separation occurs when the flux of the water is different from the flux of the solutes.	ent		
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So, here they are described so solution diffusion model, under this model it is assumed that the permeation will occur through a dense membrane where the active layer is permeable but it is essentially non-porous. It is allowing some amount of permeation but it is non-porous. Water and solutes dissolve into the solid membrane material, diffuse through the solid and re liquefy on the other side of the membrane.

Separation occurs when the flux of the water is different from the flux of the solute itself. So, both the fluxes are different and because of that the separation is occurring. So, this is called solution diffusion model. So, this is there.

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Then there is a pore flow model. So, under this model it is assumed that the RO membranes have wide spaces pores through which the liquid water travels. So, it is assumed that the membrane have void spaces are pores through which the liquid water travels. It considers the water and solute fluxes to be coupled and rejection occurs because the solute molecules are strained at the inter ends to the pores.

So, this is as earlier also this assumption have been there in various models in the membrane processes because the solute and water molecules are similar in size, the rejection mechanism is not a physical saving but rather a chemical effect such as electrostatic repulsion. So, this this is also possible and this is also assumed.

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Then there is a third type of model, the major assumption this is model is called as preferential sorption-capillary flow model and in this model again it is assumed that the membrane has pores. The separation occurs when one component of the feed solution either solute or water is preferentially adsorbed on the pore walls and is transported through the membrane by surface diffusion.

So, it is absorbed but surface diffusion occurs on the pore walls and because of that the separation is occurring. So, these are the different types of models which are there for reverse osmosis case.

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 The coer 	se models express flux fficient and a driving for	as the product of a mass ce.	transfer
 The 	n, the water flux is: J_w	$=k_w(\Delta P - \Delta \pi)$	
where $J_w = V_0$ $\checkmark k_w = N_0$ $\Delta P = N_0$ $\Delta \pi = 0$, olumetric flux of water, m ³ /d 1ass transfer coefficient for v let transmembrane pressure Difference in osmotic pressu	l·m ² vater flux, m ³ /d·m ² ·kPa e, kPa re between the feed and the pe	rmeate, kPa
swayam		[Davis, 2010]	

The water flux is:

$$J_{w} = k_{w}(\Delta P - \Delta \pi)$$



The solute flux:

 $J_s = k_s(\Delta C)$

where,

 $J_s = Mass$ flux of solute, kg/d·m²

 k_s = Mass transfer coefficient for solute flux, $m^3/d \cdot m^2$

 ΔC = Concentration gradient across the membrane, kg/m³

The flux of solutes through the membrane is:

 $J_s = C_p J_w$

where,

 C_p = Solute concentration in the permeate, kg/m³.

Now these models express flux as the product of mass transfer coefficient and the driving force. So, under that condition if it is given, the water flux will be given as Jw is equal to Kw delta p minus delta pi. Now this equation already we have used in the numerical that we have discussed. So, delta pi is the osmotic pressure and delta p is the actual pressure which has been applied. So, net transmembrane pressure which has been used and Jw is the volumetric flux of the water and Kw is the mass transfer coefficient for the water flux.

So, this equation already we have used and so we have discussed it in the numerical itself. Then now the driving force for the solute flux and this is true for the water flux. Now for the solute, what is the condition? Now for the solute, the flux is because of the concentration gradient. So, delta C is the concentration gradient and for solute the s term is being used and here we are using the mass transfer coefficient Ks for solute flux.

So, it is given, so, this is the solute flux. So, flux of solutes through the membrane can also be given here. So, Js is equal to Cp into Jw which is there. So, this way also we can define, so, Cp is the solute concentration in the permeate itself. So, through the membrane how the solute moves will be this and these are the equation which are there with respect to solute flux.

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The recovery (r) is the ratio of permeate flow to feed water flow:

$$r = \frac{Q_P}{Q_F}$$

Rejection (R) is defined as:

$$R=1-\frac{C_{P}}{C_{F}}$$

Now the recovery for reverse osmosis case is the ratio of permeate flux to the feed water. So, this recovery is Qp upon Qf and the flow balance if we do, will be like this because we have feed water, we have permeate and we have concentrate which is there. So, with respect to overall flow rate this will be the mass balance and with respect to a solute itself the mass

balance will be this where Cf is the concentration in the feed waters, p is the concentration in the permeate and cc is the concentration in the concentrate or reject water.

So, this is there and through these balances we can find out the concentration etcetera. Now rejection is defined as R is equal to 1 minus Cp upon Cf. So, this is there, so like Cp upon Cf so, we can find out the rejection also, recovery also and these are the mass balance equations. So, we can use these equations to solve many problems and understand the reverse osmosis in detail.

So, further things with respect to reverse osmosis and other things we will learn in the next lecture onwards and we will try to understand that what are the different modules which are used? What are the characteristics which are required with respect to reverse osmosis for the whole system etcetera in the next lecture. Thank you very much.