Physico-Chemical Processes for Wastewater Treatment Professor V.C. Shrivastava Department of Chemical Engineering Indian Institute of Technology, Roorkee Lecture 42 Wastewater Treatment by Membrane Processes - II

Good day everyone, and welcome to these lectures on Physico-Chemical Processes for Wastewater Treatment. In the previous lecture, we started studying the membrane processes which are used for wastewater treatment. And in the previous lecture, we understood that there are different types of membrane processes which can be used, and they can be classified broadly under the size range of the constituents they are able to remove.

So, broadly the membrane processes which are used in the wastewater treatment they include microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Now, all these four processes have a semipermeable membrane which allows some of the constituents of the water to pass through it. So, it will certainly allow the water to pass through it, it may allow some other constituents depending upon the size of the pores on the semipermeable membrane to pass through it.

So, thus it will stop most of the other constituents on the and will not allow to pass through the semipermeable membrane. So, the permeate that we get across the membrane, it will be free of the constituents, but we get a reject stream also which is a like a concentrated solution which contains all the constituents which have not been able to pass through the semipermeable membrane. So, we have thus, we have a reject stream, or highly concentrated stream that has to be managed further. (Refer Slide Time: 2:30)



Now, in this lecture, we are going to understand the different mechanism or the theories which are related to the membrane filtration or how the system membrane works for this. So, in the membranes, so in the previous lecture, we studied that we have a membrane which is like this, and it is able to pass some of the constituents on this.

So, and we have a reject which is coming from here, and flux of water which coming from the there. Now, this membrane on which the filtration occurs. So, they have a different pores which are there. So, depending upon the size of pores, the straining will happen. So, this is one of the most common mechanism of filtration using the membrane processes, so straining. So, these are the pores which are there.

So, particles which are coming they are getting blocked here. So, we have a this membrane surface this is there, and particles are getting blocked because of the straining effect. Also the smaller size particles which are actually able to pass through these pores, they may get adsorb on the side of the pores also.

So, adsorption is another mechanism by which the removal happens. Now, cake filtration is another mechanism. So, all the particles which have been blocked, so they are able to now, they have been blocked because their size is bigger than the pore size itself.

Now, second layer of the particles will come, and because a number of layers formation may happen, so soon the size of the pores, because of this additional cake which has been deposited on this membrane surface that will make the pore size effectively much smaller than the usual pore size. So, the cake will also filter out the smaller size particles also certainly bigger sized particles as well.

So, finer particles, which are much lower than the size of the pores they are also getting blocked here. So, we can see here very easily the finer particles are getting blocked here as well. So, we have three common mechanism by which filtration occurs on the membrane surface. The first is straining, then we have adsorption, then we have cake filtration as well.

(Refer Slide Time: 4:57)



So going further, we can see here that some particles are getting removed because of the mechanical screening which is happening on like in figure a, because the particle is larger than the smallest opening through which the water flows, this is the dominant mechanism for

membrane filters. Now, additional mechanism that can remove the particles are like absorption and cake formation.

So, this is possible. So, for absorption like natural organic matter which is there that gets adsorbs on the membrane surfaces as shown in the figure b, which is which was shown here.

(Refer Slide Time: 5:37)



Now, further ahead in the early stages of filtration with a clean membrane on which there is have been no trapping of any particles, the first layer of particles will get formed because it will remove the soluble and insoluble materials that have dimension that are much smaller than the membrane pore size.

So, that will only go through others will be stopped, the absorption capacity will also quickly get exhausted because these materials had little absorption capacity. Now, adsorbed material

on the side of these pores, at least these also effectively reduce the pore size further. So, absorption also reduces the pore size, thus increasing the ability of membrane to capture particles that are smaller than the nominal pore size of the membrane itself.

(Refer Slide Time: 6:37)



Now, particles that are removed by straining, they build up as a cake on the membrane surface and as shown in the figure c, and that the cake itself starts acting as a filter medium, and it improves the efficiency of the filter because it collects the particles much, much smaller than the size of the membrane.

So, this is how it happens, but with the cake formation, the flux of the water which is passing through the membrane that also gets reduced. So, after certain time, the treatment the amount of treated water that we get also gets removed, though we are getting a better water as compared to earlier as in the permeate.

(Refer Slide Time: 7:27)



The fraction of material removed from the permeate stream is described in the form of a simple efficiency equation:

$$R = 1 - \left(\frac{C_{\text{permeate}}}{C_{\text{feed}}}\right)$$

where

R = Rejection, dimensionless

 $C_{permeate} = Permeate concentration, mg/L or particles/L$

 C_{feed} = Feed water concentration, mg/L or particles/L

Now, there are different models, or the equations et cetera which are used in the membrane filtration. So, in today's lecture, we are going to discuss all these basic model equations et cetera which are used for describing the membrane processes and for there but better in understanding.

So made the basic model which is used for understanding or describing the membrane performance is based upon the concept of rejection, that how much amount of material is getting rejected by the membrane itself, the fraction of material removed from the feed stream it described in the form of simple efficiency equation which is given here. So, the here is that we can call it as rejection, and it is called as dimensionless

So, what is the concentration in the feed minus concentration in the permeate, so we can call it the concentration in the reject stream also divided by concentration in the feed. So, this is what is given here. So, that is why it is called how much of the concentration is getting rejected out of the system membrane process and it is called this is the basis on which different membranes can be compared also.

So, R is the rejection C permeate is the permeate concentration after the treatment, and C feed is the water concentration of the pollutants in the feedwater. So, this is there.

(Refer Slide Time: 9:14)



Now, there is another equation which is used, it is called in the logarithmic part, or it is called as log removal also. So, in this case we call is log of concentration in the feed divided by concentration in the permeate. So, this type of equation is also used for describing the rejection. Also percent removal efficiency can also be used. So, this equation is also very common, which is used for reporting the removal efficiency of the systems.

(Refer Slide Time: 9:50)



Rejection as a function of the particle size

$$\mathbf{R} = 1 - 2\left(1 - \frac{\mathbf{d}_{\text{part}}}{\mathbf{d}_{\text{pore}}}\right)^2 + \left(1 - \frac{\mathbf{d}_{\text{part}}}{\mathbf{d}_{\text{pore}}}\right)^4$$

where

 d_{part} = Particle diameter, m d_{pore} = Effective pore diameter, m

Now rejection as a function of particle size can be described using this equation which was given by Ferry and it has been reported in various papers including Yao et al., 1970, MWH, 2005. The details of these papers are given in the reference section. So, here it is like what is the diameter of the particle which are getting trapped or removed, and with respect to diameter of the pore.

So, what is the effective diameter of the pore, and what is the diameter of particles they are able to remove. So, this is how it is this equation has been given, and this is used as a equation for rejection as a function of particle size. This equation is also used many times for discussing the membrane utilities, or how they are working.

(Refer Slide Time: 10:55)

Theory of Membrane Filter Hydraulics

- Flux
 - Pure water transport across a clean porous membrane is directly proportional to the transmembrane pressure (TMP) and inversely proportional to the dynamic viscosity.
 - The volumetric flux (m³/h·m² of membrane surface area) is modelled using a modified form of Darcy's law.



Now, theory of membrane filter hydraulics. So, flux is very important parameter. So, with respect to this the pure water gets transported across a clean porous membrane and the flux will be directly proportional to the what is the transmembrane pressure which has been applied, and the flux is inversely proportional to the dynamic viscosity as per that.

So, as per this membrane filter hydraulic theory. So, flux is directly proportional to the transmembrane pressure, but it is inversely proportional to the dynamic viscosity, and that volumetric flux with respect to membrane which is described as meter cube per hour per meter square of the membrane surface area is modelled using a modified form of Darcy's law.

So, Darcy's law is modified and used in the membrane for determining the volumetric flux, and it is the volumetric flux in the membrane case is generally reported as meter cube per hour per meter square of the membrane surface area.

(Refer Slide Time: 12:12)



The volumetric flux $(m^3/h \cdot m^2)$ of membrane surface area) is modelled using a modified form of Darcy's law:

$$J = \frac{Q}{A} = \frac{\Delta P}{\mu R_m}$$

where

J = volumetric water flux through membrane, $m^3/h \cdot m^2$ or m/h

Q =volumetric flow rate of pure water, m^3/h

A = surface area of clean membrane, m^2

 ΔP = transmembrane pressure, kPa

 μ = dynamic viscosity of water, Pa·s

 R_m = membrane resistance coefficient, m⁻¹

Now, if this J which is called as membrane volumetric flux, that can be given as J is equal to Q by A. So, Q is the volumetric flow rate of pure water, and A is the surface area of the clean membrane. Now, this J is equal to Q by A is directly proportional to delta P. So, delta P is the transmembrane process across a semipermeable membrane, and mu is the dynamic viscosity of the water.

So, they may have different unit, so depending upon the units that we use, there is a term which is introduced which is like a proportionality constant, and it is called as membrane resistance coefficient and its unit is per meter in the SI case, and it is described by the term R m. So, R m is there, and this is called membrane resistance coefficient and, this found is similar to Darcy law, but it differs little bit differently as compared to that, because in the Darcy law, absolute value of pressure differential is used rather than the pressure gradient.

So, in the here we are using the absolute pressure whereas, in the Darcy law, the pressure gradient is used. So, this is little bit different than the Darcy's law, but it is similar to that.

(Refer Slide Time: 13:56)



The volumetric flow rate of water across a single pore can be modeled using Poiseuille's law:

$$Q_{pore} = \frac{\pi r^4}{8\mu} \frac{\Delta P}{\Delta z}$$

where

 $Q_{pore} =$ Volumetric flow rate of pure water across a single pore, m³/h

r = Radius of pore, m

 ΔP = transmembrane pressure, kPa

 μ = dynamic viscosity of water, Pa·s

$$\Delta z = Pore length, m$$

Now, the volumetric flow rate of water across a single pore can also be modelled by Poiseuille's law, and the Poiseuille's law is given here. So, the flow rate through a pore is proportional to here we can see it is like idyllic, we have a gradient here delta P by delta z, and pi r raised to 4 into eight mu. So, this is the Poiseuille's law.

Here, Q pore is the volumetric flow rate of pure water across a single pore, r is the radius of the pore, delta P is the membrane transmembrane pressure, and mu is the dynamic viscosity of the water, and delta z is the length of the water itself, though that is there. So, we have radius of the pore which is important, the pore length is also important and the delta P. So, if all everything all these 4 parameters are known, we can find out the flow rate through a single pore.

(Refer Slide Time: 14:57)

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 Because pores in commercial water treatment membranes are not perfectly cylindrical, a dimensionless tortuosity factor is added to previous equation. To represent the total flow rate, previous equation is multiplied by the surface area and pore density per unit area:		
[Davis, 2010] 12		

Because pores in the commercial water treatment membranes are not perfectly cylinder. So, the Poiseuille's law is for cylindrical pore. So, a dimensionless factor which is called as tortuosity factor is added to the previous equation of Poiseuille. So, here you can see here that tortuosity factor which is dimensionless is added to report the flow rate through a pore, to represent the total flow rate the previous equation is multiplied by the surface area, and pore density per unit area. So, through that if we can do so we can come to the overall total flow rate also so this is possible through this method.

(Refer Slide Time: 16:06)



The membrane resistance coefficient (R_m):



Now, by analogy, if we compare this equation and the previous equation, so we can say that the R m the membrane resistance coefficient can be described by this equation. So, by comparing both equation we can find out that R m is the resistance coefficient is given by this equation.

So, from here we can see that it is a function of the viscosity of the water that has to be treated, that tortuosity factor that will be there with respect to any membrane, then what is the length of the pores or we can call it what are the what is the width of the membrane itself, the

radius of the poor, and the density et cetera also. The most important factor affecting the flow rate is the pore size.

So, among all these thing, because flow rate is directly proportional to the fourth power of the pore radius, the pore size becomes the most important parameter among all these values. Now, a small increase in pore radius can result in large increase in the filtered water flow. So, this is possible. So, we had to manipulate that what size range of the pore that we want to use in the membrane.

So, through this we can balance whether we require the constituents to be removed more, or we want the water treated water flow rate at what amount so this is the factor.

(Refer Slide Time: 17:57)

Temperature and Pressure Ef	fects
 Flux is inversely proportional to Viscosity changes due to change an important design consideration water where the water temper 20°C over the course of a year. µ=1.777-0.052T + 6.25×10⁻⁴ (where 	the viscosity., ges in water temperature are on in the treatment of surface rature may range from 1°C to T_{2}^{1}
μ = Dynamic Viscosity of Water (mPa·s T = Temperature °C)
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Viscosity changes due to changes in water temperature are an important design consideration in the treatment of surface water where the water temperature may range from 1°C to 20°C over the course of a year.

 $\mu=1.777 - 0.052T + 6.25 \times 10^{-4} (T)^{2}$ where $\mu = Dynamic viscosity of water (mPa \cdot s)$ T = Temperature °C

Now, there are certainly some temperature and pressure effects. So, in addition to these things, pressure certainly affects the flux as well as the temperature also affects the flux

because viscosity is dependent upon the temperature. So, thus both temperature and pressure have lot of effect on the flux itself. So, flux is inversely proportional to the viscosity in the previous slides we saw.

Now, viscosity changes due to change in water temperature, and thus the water temperature becomes important design consideration or the viscosity becomes a way, your design consideration in the treatment of surface water whether, where the water temperature may change from 1 to 20 degree centigrade over a course of a year.

So, it is possible that at many places, we have 20 degree variation, 30 degree variation with respect to temperature at in the same region during a course of year. So, the viscosity will vary a lot, and since viscosity will vary a lot, flux will also vary a lot. So, now, the viscosity with respect to temperature the effect of temperature on the viscosity can be described by this equation, or similar equations.

So, here the mu is the dynamic viscosity of the water, and that T is the temperature in degrees centigrade directly. So, this is a empirical type of equation, which can be used to model the variation in the viscosity with temperature. So, through that thing we can see the effect of temperature also on the flux.

(Refer Slide Time: 19:36)



Now, going further, we will try to solve one or two problem, and then understand the uses of these equations we have discussed in today's lecture. Now, the first and foremost important here one of the problems is given here, that what is the percentage change in the flux that will result from a temperature change from 16 degree centigrade to 24 degrees centigrade.

If the transmembrane pressure which is applied across the semipermeable membrane remains the constant. So, through this example we can see that, how the only small change in the temperature can significantly change the permeate flux or otherwise. So, we can cross-check through this method.

So, the variation is from 16 degree centigrade to 24 degree centigrade. So, this is the viscosity equation with respect to temperature that was given earlier. So, if we keep the value of 16 degree centigrade and 24 degree centigrade in this equation, we can solve it and we will get the these values 1.105 millipascal second, 0.889 millipascal second. So, this is the variation in viscosity will happen. Now, the transmembrane pressure and everything is constant.

(Refer Slide Time: 20:51)



Now, the flux was earlier discussed that flux is directly proportional to pressure and inversely proportional to viscosity, and R m was the resistive coefficient. Now, for at 16 degree centigrade let us write it like this because the transmembrane pressure is constant, and since we are using the same membrane, so R m will also be constant. So, we are keeping them same. So, here it is J, mu 14, here mu 16.

Now, if we divide this, we are able to remove all these parameters and we have inversely proportional parameters which are listed here. Now, if we put the values of here, we find that 1.243. So, that means, the percentage change is around at 24 degree centigrade the flux is 1.243 times of the flux at 16 degree centigrade.

So, what is the percentage change we can see here, and it is approximately 25 percent increase in the flux when the temperature is only changing from 16 degree centigrade to 24 degree centigrade, which is like approximate change of 8 degree centigrade. So, we can understand that any place where there is a significant change in the temperature, because in many places within India, or many other places all over the world, the variation in the temperature from winter season to summer season is highly significant.



So, if suppose we design the thing with respect to only 24 degree centigrade, so in the winter season the flux will be much, much lower as compared to in this summer season. So, whenever we are designing the temperature becomes very, very important parameter and we should design the system mostly on the most difficult situations that will be better because we will be getting and because significant decrease will be there with respect to after filter cake formation et cetera also.

(Refer Slide Time: 23:11)



Now, going further we have a second question, a membrane which is having a thickness of 75 micrometre, and average porosity of 0.38. So, we are using this particular membrane. Now, pure water flux through the membrane is 36 meter cube per meter square per hour at a pressure drop of 1.4 at 25 degree centigrade.

Already it is given that the water flux that we are getting is 36 meter cube per hour per meter square of the surface area of the membrane at 1.4 bar. Now, the average pore size has been estimated to be 1.2 micrometre for this membrane, calculate the value of tortuosity factor of the pore and the resistance to the flow offered by the membrane, the viscosity of the water has been estimated to be 0.9 centipoise at 25 degree centigrade.

So, we have two factors to determine, one is tortuosity factor of the pores, and the resistance of the flow. So, this R m and tau value we can use in any other calculation. So, this is possible.

(Refer Slide Time: 24:33)



So, here the equation was given like this. So, with respect to single pore it was given like this where the tortuosity factor was given. Now, the flux for this case will be given like Q into porosity divided by A. Now Q is given here, so we can see here, so if we put all the values the equation will become like this.

So, and if you solve the final equation is this, and where epsilon is the porosity of the membrane itself. Now, in the present case we have been given certain values, now, all these units have been converted into basic SI units. So, here so that we can easily cut the unit and solve the question very easily.

So, diameter was 1.2 micrometre. So, it has been multiplied by 10 raised to minus 6, the radius or the pore size is 0.6 micrometre, it is given here. Pressure is 1.4 bar, so it has been converted into Pascal, viscosity is 0.9 centipoise. So, it is equivalent to 9 into 10 raise to 4 kg per meter second, then the delta z is 75 micrometre.

So, it is again given here. Now, the J flux has been given to be 36 meter cube per meter squared per hour. So, it has been converted into per second, because here in the viscosity we have per second unit, and the porosity was 0.38. Now, if we have to keep all these units here to find out the value of tortuosity factor.

(Refer Slide Time: 26:12)



So, we write all the units so 36 divided by 3600 this is the flux, and epsilon r square delta P, delta z everything is there, and if you solve it will be finding that okay tortuosity factor for this particular membrane is 3.325. Now, flux can also be given like this. So, in this case if you solve it, will get the resistance which is offered by this membrane. So, this value we can solve it easily you can see here, the value comes out to be 15.56 into 10 raised to 10 per meter.

So, this examples gives us that if we have made any membrane in a industry, so what we have to do is that, we have to find these parameters both tortuosity and R m, and we have to report these values to any person or any company which is purchasing these membrane for their uses. So, for them to use these membrane, they will always insist the manufacturer to tell us the tortuosity factor and the resistive coefficient.

(Refer Slide Time: 26:12)



So, for this we have to perform experiments in the industry itself or send some any other laboratory and this they can do these experiments they can perform at different pressures at different temperatures. And through this they can report what is the tortuosity factor, and what is the resistance offered.

Certainly, the flux has to be measured experimentally that how much amount of the water is coming per hour. And similarly, the surface area of the membrane also has to be measured. So, through these methods we can find out. Similarly, the porosity also has to be determined.

So, through these methods, we can find out these parameters and whenever we are selling these membranes, we can report and tell these values to the buyer and they can then the design the system at the actual condition using all these parameters, may be at certain other pressures, other temperatures et cetera. So, this is the example that gives an idea how to report these parameters, because these are very common thing, and they have to be reported.

So, in this today's lecture, we tried to learn different equations and little bit mechanisms by which the membrane processors work, and what are the different how we can determine the flux, we saw that the flux is a like a it is a it is dependent upon different parameters including the pressure difference, the size of the pores, the length of the pores, and then the viscosity of the water viscosity.

Viscosity in turn is a temperature dependent parameter. So, change in the temperature from one season to another season affects the flux a lot. And so we have understood the basics of the theory of the movement of the water across the membrane. So, in today's lecture, we understood the basic numerical that we can solve, or the basic understanding how we can go ahead with calculation of some of the important parameter with respect to membrane treatment. So, we will continue further with the membrane processes in the next lecture onwards. Thank you very much.