## Physico-Chemical Processes for Wastewater Treatment Professor V. C. Shrivastava Department of Chemical Engineering Indian Institute of Technology, Roorkee Lecture 43 Wastewater Treatment by Membrane Processes - III

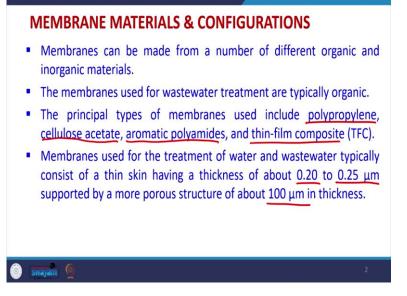
Good day everyone, and welcome to the Wastewater Treatment Processes that we are studying in all these lectures, understanding the membrane type of treatment processes which are used in wastewater treatment in the previous two lectures. And we understood that there are different types of membrane processes like microfiltration, ultrafiltration, nanofiltration and reverse osmosis, which are commonly used for water treatment, or wastewater treatment.

Among these membrane processes, the common things are that we have a membrane, semipermeable membrane which allows certain amount of, certain type of constituents to pass through it depending upon the pore size, which is there on the semipermeable membrane. Depending upon this pore size, and certain other parameters like the water the type of water that has to be treated, the viscosity of the water et cetera the performance of membrane processes varies.

Now, in the previous lecture, we studied the theory via which we can calculate the membrane the flux water flux through the semipermeable membrane in a membrane treatment process, and we found that that flux is highly dependent upon the pressure which is applied across the semipermeable membrane, then the radius of the membrane becomes very, very important because the flux is directly proportional to the pore size raised to power four.

So, the pore size of the membrane is important parameter, in addition the viscosity of the water that has to be treated also becomes very important parameter. So, equation was derived which is dependent like which is similar to Darcy's equation with some modification. So, we understood all those equations of flux et cetera in the previous lecture.

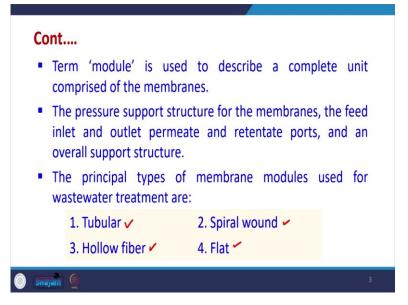
Now, we will continue further, we will try to understand the membrane, what are different types of membranes, their modules, how the operation is performed and what are the various issues with respect to membrane processes and their operations. Now, fouling is one of the important thing that happens during the filtration via membrane. So, how this is also incorporated in the equations et cetera that we will try to learn in this lecture.



So, different types of membrane materials are used for making different types of membranes, and these membrane materials may be organic or inorganic. So, for wastewater treatment generally the membranes which are used, they are made from organic materials. So, principal type of membrane used in the wastewater treatment include like that are made from polypropylene, cellulose acetate, aromatic polyamides, then we have thin-fin composites.

So, all these different types of membranes can be used for separation of different material from the water. Now, membranes used for the treatment of water or wastewater typically consists of very thin skin having a thickness of around 0.2 to 0.25 micrometre, and this is supported on a more porous structure that is about 100 micrometre in thickness. So, this is how the membrane configuration is there.

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Now, the term module is used to describe a complete unit comprised of the membrane itself. So, we have a different types of modules of membranes are used for water treatment, the pressure support structure for the membrane, and the feed inlet, outlet permeate and retentate ports where the reject come out. All these are there within the support structure itself.

So, there are different types of membrane modules which are used for wastewater treatment. And these membrane modules include, like the tubular ones, the spiral wound, the hollow fibre, and the flat type. So, all these types of modules are used for the water treatment.



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And these modules are shown here, we can see here the tubular module, where we can see the pores here and this is the tubes, we have different configuration you can see how the pores

are oriented within this modules, we can see here. Similarly, spiral wound membranes are there. So, this we can see the spiral wound, then the hollow fibre one. So, we can see the hollow fibre one, these are the modules which are there, then the flat ones are also there. So, different types of modules are possible with respect to membranes.

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Membrane geometry	Suspended solids tolerance	Control of fouling	Cleaning easiness	Packing density	Cost for unit of volume
Tubular ✓	Good	Excellent	Excellent	Low- medium	Medium- high
Spiral- wound 1	Low	Limited	Medium	High	Low

Now, different membrane configurations which are there, they are compared here in this slide and further. So, the first and foremost membrane geometry is like tubular one, or spiral wound. So, what is the tolerance of these membranes with respect to suspended solids, can we control the fouling are not?

What is the easiness of cleaning with respect to these modules? What is the packing density and cost per unit volume? So, these are tentatively compared here. So, we can see here that the tolerance with respect to suspended solids is good for that tubular case, and they can very well control the fouling thing. And the easiness of cleaning is also excellent in the case of tubular case.

These are little bit limited in the case of a spiral wound module. So, this is there. Now, because of this good things the cost is also medium to high for these tubular module membranes. So, this is there, and certainly the cost is lower for the spiral wound module.

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Membrane geometry	Suspended solids tolerance	Control of fouling	Cleaning easiness	Packing density	Cost for unit of volume
Hollow fiber (external feed)	Scant (good)	Scant (good)	Scant (good)	Excellent	High (low)
Flat	Medium	Good	Medium	Medium	Medium- low
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Now, when further hollowfibre module, and flat module for this the suspended tolerance and the control of filing as well as the easiness of cleaning is sufficiently okay with them, the packing density is excellent, and the though the cost is high to low that will depend upon the type of hollow fibre and various other things. For flat membrane geometry, the suspended solids tolerance is like medium, they have good control of fouling, because they are like flat easiness of cleaning is also okay, and the packing density is medium only.

So, they have medium to low cost. So, depending upon the requirement type of water that has to be treated the membrane the pressure driven, how much pressure has to be applied? The depending upon all these parameters, any of these modules et cetera can be used.

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## MEMBRANE FOULING

- Membranes can be seen as sieves retaining part of the feed.
- As a consequence, deposits of the retained material will accumulate at the feed side of the membrane.
- In time this might hamper the selectivity and productivity of the separation process. This process is called **fouling**.
- Koros et al. gave the definition of fouling as "The process resulting in loss of performance of a membrane due to deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores".
- Membrane fouling is an important consideration in the design and operation of membrane systems as it affects pretreatment needs, cleaning requirements, operating conditions, cost, and performance.

Swayall 🔮 Source: Pandey et al. [2012]

Now, membrane fouling is one of the important considerations during any use of any membrane processes for water treatment or wastewater treatment. So, membrane can be sieves, they can be they are work as a sieve, and they retain some of the constituents from the feed itself. So, they are like a filtration unit.

And because of this, they have lot of deposition which happens on the membrane surface. So, deposition of the retained material always goes on accumulating at the feed side of the membrane itself. And so thus, this feed the cake deposition that happens, that starts accumulating and then that may become very, very high.

So, under those conditions, the selectivity and productivity of the separation process goes down. And this way, this process is called fouling. So, like the definition of fouling has been given by Koros et al, that the process resulting in loss of performance of a membrane due to the deposition of suspended or dissolved substance on its external surface at its pore opening or within its pore.

So that this is called as fouling, and this is the more one of the most important consideration in the design and operation of membrane systems. Because these membrane fouling affects depending upon the concentration of pollutants which are there in the feed stream. So, considering the membrane fouling, we may require a certain amount of pre-treatment that has to be done.

Now, pre-treatment whether it is done, or not done, how much cleaning will be required at the membrane, what is the periodic timing of cleaning that will be required, then what is the operating condition under which we will be operating, because the flux is going to decrease as the fouling will increase. Also because of the fouling, how much is that decrease in the performance of the membrane, and what is the additional cost that will be there because of the membrane fouling. So, because of all these parameter the membrane fouling is very, very important parameter.

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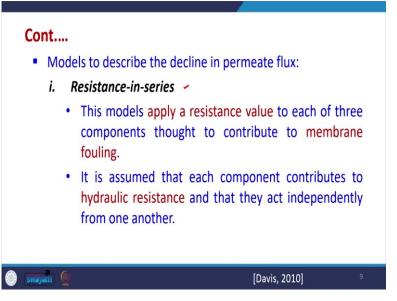
## 🍥 🚮 🔮 Source: Pandey et al. [2012]

Now, fouling of microfiltration and ultrafiltration membranes may be defined as that gradual reduction in the filtered water flow at a constant pressure. So, that means, what is done is that suppose, we have a semipermeable membrane is there, and this is the treatment unit which is there. So, if the same pressure difference is applied across this membrane, so because new type of cake resistance is coming into picture, so the water which is coming out the treated water will decrease with time if the constant pressure is applied.

Now, if we want to retain the same amount of permeate, that means, we have to gradually increase the transmembrane pressure with time. So, this is there, and this this has to be taken care of, if the permeate which is required has to be maintained at a certain level. Now, fouling of the membrane is caused, can be caused by particulate matter, dissolved organic matter, or because of the biological growth also which may happen because of the deposition of organic materials, bacterial materials et cetera on the membrane surface. So, this is there.

Fouling may be irreversible, but if it is irreversible, it is totally undesirable, but if it is reversible, it can be taken care of. The fouling is termed irreversible, if the loss in flux cannot be recovered by backwashing or cleaning operations. So, this is there.

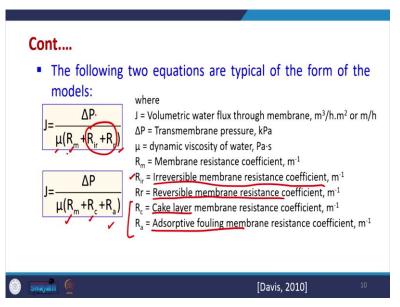
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There are different models which can be used to describe the decline in permeate flux. So, like we have now, two resistances which are coming into picture, one is the resistance of the membrane itself, and the resistance of the cake which is getting deposited. So, we have two resistances. So, one of the first models which is used to describe that decline in the permeate flux is using the resistance in series model.

So, what it does is that, it applies a certain resistance value for each of the three components through which contribute to the membrane fouling, and it is assumed that each component contributes to the hydraulic resistance, and that they act independently of each other. So, additional resistances are assumed.

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The following two equations are typical of the form of the models:

$$J = \frac{\Delta P}{\mu(R_m + R_{ir} + R_r)}$$
$$J = \frac{\Delta P}{\mu(R_m + R_c + R_a)}$$

where

J = Volumetric water flux through membrane, m<sup>3</sup>/h.m<sup>2</sup> or m/h

- $\Delta P$  = Transmembrane pressure, kPa
- $\mu$  = dynamic viscosity of water, Pa·s
- $R_m$  = Membrane resistance coefficient, m<sup>-1</sup>
- $R_{ir}$  = Irreversible membrane resistance coefficient, m<sup>-1</sup>
- Rr = Reversible membrane resistance coefficient, m<sup>-1</sup>
- $R_c$  = Cake layer membrane resistance coefficient, m<sup>-1</sup>
- $R_a$  = Adsorptive fouling membrane resistance coefficient, m<sup>-1</sup>

Now, these resistances are defined here, the following tree equations are typical, or the form of the model. So, like what we do that earlier we had only assumed that J is proportional to delta P, directly proportional to pressure which is applied, and the viscosity of the water and the proportionality constant was assumed to be a factor which is like a resistance coefficient, membrane resistance coefficient.

Now, this membrane resistance coefficient has been further being extended in this equation and this equation now, in this equation two additional terms have been added. So, these terms are R ir, irreversible membrane resistance coefficient. And then the reversible membrane resistance coefficient, irreversible membrane coefficient cannot be removed if we do the backwashing also.

So in the second cycle, irreversible coefficient will always be present along with the R m, but, reversible membrane resistance coefficient can be removed and so the flux will increase after the bypassing is done. Then other way also it can be defined, one is called cake layer membrane resistance, and another is adsorptive fouling absorption, because of absorption in the pores, how much resistance has been added.

So, in addition to the membrane resistance, two additional resistance may be added. One additional resistance is because of the cake layer which has been deposited on the surface of the membrane, and then there is a additional resistance because some adsorption may have occurred in the side of the pores also. So, because of this the size of the pores may have decreased. So, this is possible.

So, through these two equations, we can define the flux, or we can cater to the like take care of the fouling in the flux equation. So, both of these are possible ways.

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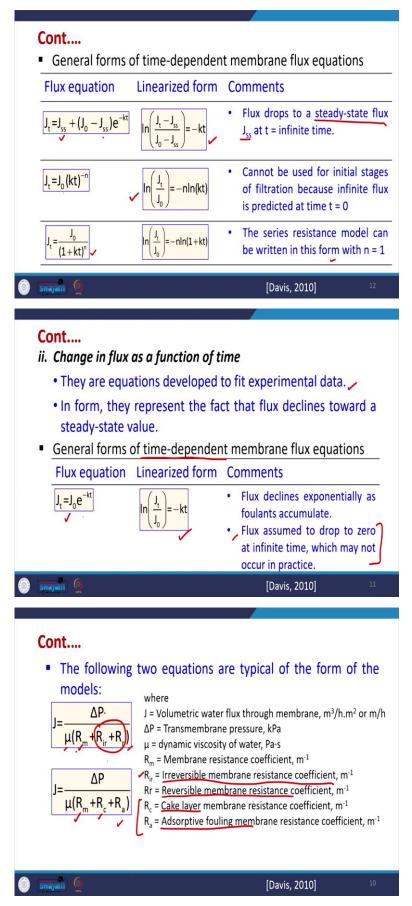
<b>Cont</b> ii. Change in flux as a function o	of time
<ul> <li>They are equations develop</li> </ul>	ed to fit experimental data.
<ul> <li>In form, they represent the steady-state value.</li> </ul>	fact that flux declines toward a
<ul> <li>General forms of time-depen</li> </ul>	dent membrane flux equations
Flux equation Linearized for	rm Comments
$\int_{J_{0}} \frac{J_{0}e^{-kt}}{\sqrt{J_{0}}e^{-kt}}$	<ul> <li>Flux declines exponentially as foulants accumulate.</li> <li>Flux assumed to drop to zero at infinite time, which may not occur in practice.</li> </ul>
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Now, then, there is another model which is called as change in flux as a function of time. So, in this case, the equations are developed to fit the experimental data, and they represent the fact that the flux declines towards a steady state value. So, this is there. So, what we do is that, we carry out experiments, we fit the experimental data to certain equations, and in fitting these we take care that okay the flux will decline to a certain steady state value with time.

So, this is there. So, flux equation can be given like one of the equations is this, generalized forms of time dependent membrane flux equation. So, membrane flux equation has been made time dependent in these equation. So, here the first one is J at any time t is equal to J 0 e raise to minus kt. So, this is there, and we can always use a linear form also.

So, in this case what we are assuming is that, the flux is declining exponentially as the fouling, foulants are getting accumulated. So, and flux is assumed to drop to 0 at infinite time. So, in this case we are assuming that flux will ultimately totally stop, and which may not occur actually in practice. So, this is the drawback of using this equation, but this may true up to a certain time.

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Then there is another type of flux equation, where we have a J ss, where plus J 0 minus J ss e raise to minus kt and its linear form is like this. So, in this case, we are assuming the flux drops to a steady state flux which is J ss at infinite time. So, we are not assuming this to be dropping to 0. Now, we are assigning a certain value which is a steady state value.

So, then there is another equation which is like J t is equal to J 0 kt raise to minus n. So, in place of exponential we are writing like this and its linear form is given here. So, this equation cannot be used for initial stages of filtration, because in this equation infinite flux has been assumed at time t equal to zero which is not possible. So, this is also wrong.

So, but it can be used later on well, then another type of equation which is like J t is equal to J 0, 1 plus kt raise to n. And the series resistance model can be written in this form with n is equal to 1. So, if you put n is equal to 1, like it is a the series resistance equation, which was given earlier that can be converted it they are very similar equation. So, we can write like this. So, these are the different equation.

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Cont iii. Mechanistic	
cake formation as fur	be <u>pore adsorption</u> , <u>pore blocking</u> , or nction of time. e been termed the <b>blocking laws</b> .
Blocking filtration law	S
Flux equation	Major features and assumptions
Pore sealing (completed blocking filtration law	•
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Then there is a third way of modelling the fouling, and in this case what we assume is that, that it attempts to describe the pore adsorption, pore blocking and cake formation as a function of time. So, we try to see that, how we can model the pore adsorption, because this is one of the mechanism then pore blocking and cake formation as a function of time, and collectively they are termed as blocking filtration laws.

So, this is called as blocking laws, or blocking filtration laws. And these are the different flux equation and major features and assumptions which are there. So, one of the first is called as

pore sealing, or complete blocking filtration law. So, in this model, it assumes that the model's blockage of the entrance to the pores by particle is retained at the membrane surface itself only. So, this is there.

• Each retained particle blocks an and membrane surface equal to the part sectional area.	
<ul> <li>C = concentration of particles</li> <li>Flux declines in proportion to the mem that has been covered.</li> <li>No superposition of particles occurs.</li> <li>Each particle lands on the membrane s not on other particles, </li> <li>Flux reaches zero when a monolayer has been retained.</li> </ul>	brane area

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And the flux equation can be given by this, where C is the concentration of particles in the feed stream. So, this is there. And G 0 the initial flux. So, these are the major features and assumption which have been given for this particular equation. So, in this case it is assumed that each retain particle blocks an area of membrane surface equal to the particle cross sectional area. So, this is the first major feature of assumption of this, then the second flux declines in proportional to the membrane area that has been covered.

So, whatever membrane area that has been covered, so flux will decline proportional to that. No superposition of particle occurs. So, here we are assuming that no superposition, each of the particles are different. So, no superposition, each particle lands on the membrane surface and not on the particle, which may not be very true. And flux reaches 0 when a mono layer a particle has been retained. So, this is the, there are basic equation assumptions of this, so many of the assumptions may not be very true. So, this is there. (Refer Slide Time: 22:07)

Cont	
Flux equation	Major features and assumptions
Internal pore constriction (standard blocking filtration law)	Models the reduction of the void volume within the membrane.
$J_{t} = \frac{J_{0}}{(1 + CJ_{0}t(\rho P)^{2})}$ , L=membrane thickness, m	<ul> <li>Assumes the membrane is composed of cylindrical pores of constant and uniform diameter.</li> <li>Particles deposit uniformly on the pore walls; pore volume decreases proportionally to the volume of particles deposited.</li> </ul>
swayam 🔮	[Davis, 2010] 15

Then there is a second type of model is that were internal pore construction, or standard blocking filtration law, it is called as. So, in this case, the model it models the reduction of the void volume within the membrane. So, whatever is the void volume within the membrane that will occur because of adsorption also.

So, it is modelled, and this is the equation and here L is the membrane thickness in the this. So, in this case, it is assumed that the membrane is composed of cylindrical pores of constant and uniform diameters. So, we are assuming the pores to be of constant and uniform diameter.

Particles, then it is assumed that particles deposit uniformly under pore walls so particles are getting deposited. So, this is like cylindrical pores, we have particle which are getting deposited on the pore walls and because of which the pore volume decreases proportionally to the volume of particles getting deposited. So, this is the decrease in pore volume.

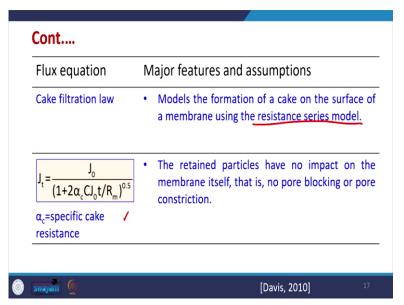
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$J_t = J_0 e^{-(1.5CJ_0 t/\rho_p d_p)}$	Major features and assumptions <ul> <li>Each retained particle blocks an area of the</li> </ul>
C = concentration of particles	<ul> <li>membrane surface equal to the particles cross-sectional area.</li> <li>Flux declines in proportion to the membrane area that has been covered.</li> <li>No superposition of particles occurs.</li> <li>Each particle lands on the membrane surface and not on other particles, </li> <li>Flux reaches zero when a monolayer of particles has been retained.</li> </ul>

Then there is a third type of equation which is also called as model, which is also called as intermediate blocking filtration law. So, in this case the pore ceiling with superposition is assume, and in this model, the blockage of the entrance to the pores by the particle retained at the membrane surface is modelled.

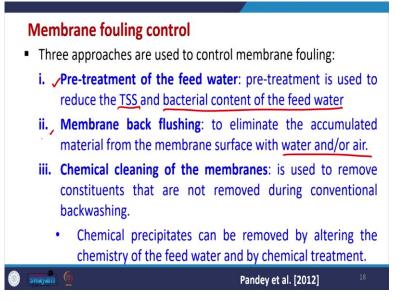
And now, in this case, the assumption is that, in this equation which has been given the extension of this is like complete blocking filtration law. So, earlier whatever the complete blocking filtration law was given, it is a extension of that, it relaxes the mono layer assumption, in the complete blocking filtration law. And this is done by allowing particle to land on the previously retained particles also and also or on the membranes surface by evaluating the probability that a particle will block a pore or not.

So, if it is lending on already. Suppose, these are the different pores which are there, and if the particle is already blocking any of the pores, and so if the second is landing on that, so the probability whether it is landing here or whether it is landing here, where a second pore is there, so depending upon that this model has been given. And this is so you can use any better book for understanding more of these thing. (Refer Slide Time: 24:44)



Then we have a cake filtration law. It under this cake filtration law, the formation of cake on the surface of the membrane using the resistance series model is assumed. So, this is the type of equation, the retained particles have no impact on the membrane itself. And that is no pore blocking, or the pore construction is assumed to this is there. So, these are the different models and others modelling approaches.

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We will try to solve some equations in the next lecture, but before that, we will try to see that how the membrane fouling et cetera can be controlled. So, there are three approaches are used to control the membrane fouling and these approaches are given here. And these approaches are like, if we have to avoid the membrane fouling and if the water contains lot of particles, so we have to pre-treat it the feedwater.

So, pre-treatment is used to reduce the total suspended solids, and bacterial content of the feedwater. So, if it is then, we will be able to avoid more amount of suspended particles to be passing through the semipermeable membrane. So, this way, the fouling will be reduced. Also if the bacterial content is removed beforehand, so bacterial growth et cetera, will not be there.

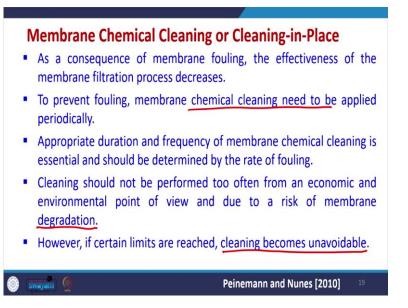
And so this way, we can avoid the bacterial growth also which ultimately blocks the membranes et cetera. Then the second method is called membrane back flushing. So, this is like backwashing, to eliminate the accumulated material from the membrane surface, some backwashing with water or air may be used.

So, through this we are able to remove the fouled whatever materials that have been accumulated on the membrane surface, and thus we clean the surface, then we can use the chemical cleaning of the membranes also. So, this is also possible, it is used to remove the constituent that are new, not removed during conventional backwashing.

So, it is possible that some of the simple backwashing technique which is used, and that is not able to remove some other material, which have been which may have got attached to the surface. So, if we use some chemicals, which has more affinity towards the fouling materials. So, this way the fouling material will be attracted toward that chemical, and thus we can do that cleaning. So, this is possible.

So, chemical cleaning of the membrane can be used to remove constituent that are not removed during conventional backwashing. Chemical precipitates can be removed by altering the chemistry of the feedwater by chemical treatment. So, suppose the retention has happened at a certain pH. Now, for backwashing if we use a pH which is different than that, under with the removal was happening.

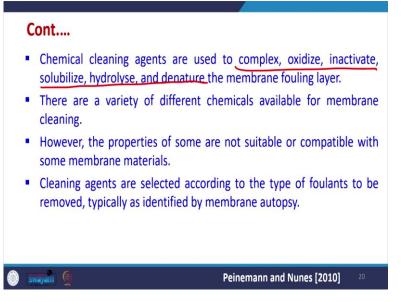
So it is possible that because of the change in the water chemistry, that adsorbed materials, or the materials which have been retained or the surface of membrane, they may get removed, because the water which is being used for backwashing it has completely different pH. So, that means the chemistry has been altered, and because of that, the treatment happened. Similarly, we can use some other chemicals also for removing of the foulants et cetera. (Refer Slide Time: 28:46)



Membrane chemical cleaning as a consequence of membrane fouling the effectiveness of the membrane filtration process decrease. So, to prevent fouling, some chemical cleaning may be done. So, appropriate duration and frequency of chemical cleaning is essential, and it will depend upon the rate of fouling or rate of deposition of the cake.

So, we should have all those data and if those data are available, we can design our system or we can determine beforehand that how much chemicals will be required, after how much we have to, after how much periodic time we have to do this chemical cleaning.

The cleaning should not be performed too often, from economic point of view, as also from the environmental point of view. So, and also because of the chemical cleaning the membrane degradation may also happen. So, we have to cross see and optimize this chemical cleaning time et cetera. However, if certain time limits are raised, so sometimes the cleaning becomes unavoidable and we have to use this chemical cleaning. (Refer Slide Time: 30:16)



Now, different types of chemical cleaning agents are used. So, these chemical cleaning agents are like they are able to form sometimes complexes, sometimes they will oxidize the material which is has been deposited on the membrane surface, sometimes they will inactivate or solubilize the material, or hydrolyse, or denature the membrane fouling layers. So, any of these things may happen, if we are using any chemical cleaning agent.

So, depending upon the type of material which is getting deposited, we may use different types of cleaning agent. So, there are different types of chemicals available for membrane cleaning. However, the properties of some are some of these agents are not suitable or compatible with some other membrane materials. So, this is possible.

Cleaning agents are selected according to the type of foulants that have to be removed. And so this is there, and for doing this, the fouled membrane its autopsy or the detailed characterization may have to be carried out. So, this is possible, and we may have the requirement of all these physico-chemical characterization of fouled membrane that has to be done. (Refer Slide Time: 31:39)

So, there are different types of cleaning agents like acids, oxidizing compounds, then antiprecipitating agent, because precipitation may have happened on the membrane surface. So, we have anti-precipitants, then different types of detergents maybe possible some alkaline acid, or alkaline materials depending on the foulant, then complexing agents which may form complex with the foulants and they are then removed away some biocides or enzymes to avoid the biological fouling which may happen.

Example is that suppose weak acids are known to remove iron and metal oxide. So, whereas the biofilm is usually cleaned by an alkaline base cleaner, so depending upon the foulant, we may have to use different types of chemical cleaning agent. So, this is there. So, we may have to use different types of cleaning material.

So, in this lecture we have tried to understand the fouling in detail. So, we understood that there are different methods via which we can the fouling may happen, and for modelling these things, different types of model equations, and some models et cetera have been given in and reported in the literature. So, we can use the model equations for actually getting the value of flux.

Certainly, we have to find out the parameters that may happen the additional resistive coefficient that have to be determined for modelling these types of fouling behaviour in the actual case. Now, after that we learned regarding the various ways under which the fouling can be avoided or clean. So, the simplest case is that to pre-treat the water beforehand, so that fouling can be avoided.

Second case is that can be used a simple backwashing to remove the fouling thing. So, this is also possible. But if these things are not possible, then we have to go for chemical cleaning. And for chemical cleaning, we have to cross-check that what type of constituents were originally present in water, how much amount of constituents, and what are the physico-chemical characteristics of deposits that have happened on the membrane surface.

So, we have to perform the autopsy. And depending upon that, and by basic understanding of the chemistry, we can determine that what type of chemical cleaning agents can be used for removing these foulants from the membrane surface. So, through this we can avoid this. So, we will go further ahead with the membrane treatment processes.

And we will try to determine, solve some problems and also understand the reverse osmosis process, which is very, very commonly used in the treatment process, more in detail in the next few lectures. Thank you very much.