

Membrane Technology
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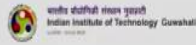
Lecture-18

Nanofiltration Basics, Transport Mechanism, Fouling Model and Applications

Good morning students, today is lecture 18th of module 6. In today's lecture we will basically discuss about Nanofiltration.

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Module	Module name	Lecture	Title of lecture
06	Reverse osmosis and Nanofiltration	18	Nanofiltration basics
			Transport Mechanism
			Fouling models and applications

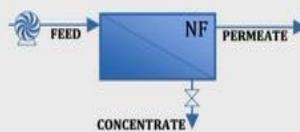


We will try to understand what is nanofiltration and I will tell you how nanofiltration and reverse osmosis overlaps each other. And what is the difference between them, we will try to see also learn also what is the transport mechanism of nanofiltration and systems and do various fouling models and the various applications of nanofiltration.

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Nanofiltration

- Nanofiltration refers to a specialty-membrane process that rejects dissolved solutes in the approximate size range of 1 nanometer (10 Angstroms).
- With respect to the size and weight of solutes that nanofiltration membranes reject, NF operates in the realm *between reverse osmosis (RO) and ultrafiltration (UF)*.
- Hydraulic pressure is used to overcome the feed solution's osmotic pressure and to induce diffusion of pure water (referred to as permeate) through a semi-permeable NF membrane.



So as you know, nanofiltration refers to a specialty membrane process that rejects dissolved solutes in the approximate size range of 1 nanometre of 10 Angstroms. So very small size solutes are being rejected. With respect to the size and weight of solutes that nanofiltration membranes reject nanofiltration operates in the realm between reverse osmosis and ultrafiltration. So actually, based on the range of the solute it rejects the membranes have been classified.

So nanofiltration can lie something somewhere between the cutoff of reverse osmosis, and ultrafiltration. Hydraulic pressure is used to overcome the feed solution osmotic pressure, and to induce diffusion of pure water, which we also called as permeate through a semi permeable membrane.

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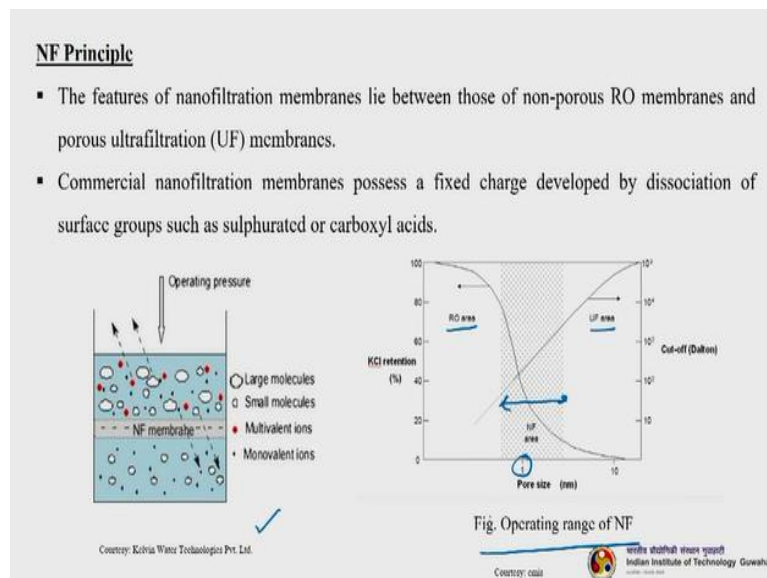
Nanofiltration

- The residual feed stream (referred to as retentate, concentrate, or reject) is concentrated by the process.
- Nanofiltration membranes can effectively reject dissolved organics, endotoxins/pyrogens, insecticides/pesticides, herbicides, antibiotics, nitrates, sugars, latex emulsions etc.
- NF may achieve moderate to low removal of monovalent ions (e.g., sodium, potassium, chloride).
- The ideal nanofiltration membrane has a very high water permeability, but the ideal permeability of solutes might be near zero or some higher value, depending on the solute and application.

The residual feed stream referred to as retentate, concentrate or reject is concentrated by the process. Nanofiltration membrane can effectively reject dissolved organics, endotoxins and pyrogens, insecticides and pesticides, herbicides, antibiotics, nitrates, sugars, latex emulsions etc. and nanofiltration may achieve moderate to low removal of monovalent ions. For example, sodium, potassium, chloride etc.

And ideal nanofiltration membrane has very high water permeability, right? But the ideal permeability of solutes might be near 0 or some higher value, depending on the solute and application. So, an ideal nanofiltration will pass as much as water, permeate as much as water, however, returning all source of solutes and ions.

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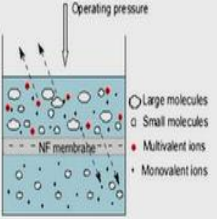
The features of nanofiltration membranes lie between those of non-porous RO membrane and porous ultrafiltration membranes; this is what we just discussed. Commercial nanofiltration membranes possess a fixed charge developed by dissociation of surface groups such as sulphurated or carboxylic acids. So you can see this particular figure here that how nanofiltration is rejecting large molecules, small molecules and multivalent ions.

However the monovalent ions, because of very small size are passing through the membrane along with water. Here this particular figure will tell you the operating range of the nanofiltration and you can see the pore size is 1 nanometre here, okay? Nanofiltration is range between here, RO here, this is RO, and this is ultrafiltration range. So, RO less than 1 nanometre mostly here, and UF greater than 1 nanometre almost into the range of 10 nanometre and higher size.

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NF Principle

- The properties of nanofiltration membranes, therefore, allow ions to be separated by a combination of the size and electrical effects of UF and the ion interaction mechanisms of RO.
- The size of pores in nanofiltration membranes is such that even small uncharged solutes are highly rejected while the surface electrostatic properties allow monovalent ions to be reasonably well transmitted while mostly retaining the multivalent ions.



The diagram illustrates the NF principle. It shows a cross-section of an NF membrane separating two chambers. Above the membrane, 'Operating pressure' is indicated by a downward arrow. The top chamber contains 'Large molecules' (represented by large blue circles), 'Small molecules' (represented by small blue circles), 'Multivalent ions' (represented by red circles with a minus sign), and 'Monovalent ions' (represented by red circles with a plus sign). The bottom chamber contains 'Small molecules' and 'Monovalent ions'. The membrane is labeled 'NF membrane'. A legend on the right side of the diagram identifies the symbols: a large blue circle for 'Large molecules', a small blue circle for 'Small molecules', a red circle with a minus sign for 'Multivalent ions', and a red circle with a plus sign for 'Monovalent ions'. Below the diagram, the text 'Courtesy: Kelvin Water Technologies Pvt. Ltd.' is visible. At the bottom right, there is a logo for 'Indian Institute of Technology Guwahati' with the motto 'एतन्निश्चयं विना नमो' and the year '1994'.

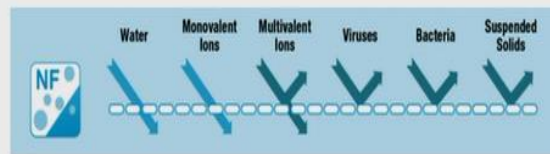
The properties of nanofiltration membranes, therefore, allow ions to be separated by a combination of the size and electrical effects of UF and the ion interaction mechanisms of RO. So that means note that, the NF actually works in the combined principle of UF and reverse osmosis, UF basically sizes represent membrane and process, as well as charged separation also affects.

However, in RO the ionic interaction plays a major role. So in NF both the all these things are playing in a while rejecting a solute or permeating the water, the size of pores in nanofiltration membranes is such that, even small uncharged solutes and highly rejected while the surface electrostatic properties allow monovalent ions to be reasonably well transmitted while mostly retaining the multivalent ions.

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Properties of NF

- The membranes are produced in plate and frame form, spiral wound, tubular, capillary, and hollow fiber formats from cellulose derivatives, synthetic polymers, inorganic materials, ceramics etc.
- NF can withstand very high or low pH environment.
- NF membrane tend to have a slightly charged surface, with a negative charge at neutral pH.



Country: Oltremare/abnase

Now, look at that, further properties and look at this particular schematic here. You can see this water and monovalent ions are mostly being transmitted or pass to the permeate side, whereas multivalent ions, most of the multivalent ions are developed as viruses, bacteria, suspended solids, all are we getting rejected. Some multivalent ions will occurs pass through the membrane because of the various non ideal semi permeable membranes that is actually existed.

So, NF membranes can be produced in plate and frame form, spiral wound, tubular, capillary and hollow fiber formats, from various membrane materials mostly cellulose derivatives, maybe there are some synthetic polymers, and then inorganic materials also, ceramics also available. Now, NF can withstand very high or low pH environment. NF membrane tends to have a slightly charged surface with a negative charge at a neutral pH.

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Transport mechanism in NF membrane

- Two major theories are adopted:

Sourirajan's sorption surface-capillary flow theory

- It describe the preferential sorption of water molecules in the membrane and the desorption of multivalent ions (by dielectric forces) causing exclusion of charged solutes, even smaller than the membrane pores, from movement into the membranes.
- Effective charge density, pore radii and the ionic strength determine the rejection of monovalent ions.
- For NF membranes, the rejection of monovalent ions range between 0% and 50%.

Two types of transport theories or models are basically adapted to describe the nanofiltration transport. So first one is the Sourirajan's sorption surface capillary flow theory and the second one is the usual solution diffusion model which we have discussed in detail in our previous classes. So, in Sourirajan's sorption surface Capillary Flow theory, so actually it describes the preferential sorption of water molecules in the membrane.

And then the desorption of multivalent ions by dielectric forces, causing explosion of charged solutes even smaller than the membrane pores, from movement into the membranes. So that means the membrane and the water molecules are getting served inside the membranes. Okay, then they are passing through the permeate cell, and that desorption of multivalent ions are happening due to the dielectric process because we just discussed that the membrane NF membranes are slightly negative in charge.

So, smaller than the pore size of the membranes, ions are also getting rejected. So the effective charge density, pore radii and ionic strength determine the rejection of monovalent ions. For nanofiltration membranes the rejection of monovalent ions ranges between 0% to 50%.

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Transport mechanism in NF membrane

Solution-diffusion theory

- It describes the membrane as a porous film into which both water and solute (ions) dissolve.
- The solute moves in the membrane mainly under concentration gradient forces.
- The water transport is dependent on the hydraulic pressure gradient.
- The transport of the solute through the membrane depends on hindered diffusion and convection.

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So the solution diffusion this way discussed, as I told you in detail earlier it is the same for the RO we have discussed, so it describes the membrane as a porous film into which both water and solute ions dissolve. Whatever is getting water has to be served inside the membrane material, and then only it will get to into the permeate side. Similarly, the solute ions which are supposed to be transmitted through the membrane must dissolve itself in the membrane material.

Then sorption will take place, the solute moves in the membrane mainly under the concentration gradient forces. The water transport is dependent on the hydraulic pressure gradient, so that means more you are giving supplying the ΔP , so more will be the water flow and the transport of the solute through the membrane depends on the hindered diffusion and convection.

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Transport mechanism of charged solutes

- Transport of solutes through NF is more complex than other membrane processes.
- Three modes of transport occurs:
 - 1) *diffusion* (due to concentration potential gradients, as in RO membranes),
 - 2) *convection* (as in larger pore size filtration such as microfiltration),
 - 3) *electromigration* (attraction or repulsion from charges within and near the membrane).

Solute transport mechanisms occurring simultaneously for each ion

DIFFUSION → Ion movement due to concentration gradient

CONVECTION → Ion movement with solvent flow

ELECTROMIGRATION → Ion movement due to potential gradient

Active layer thickness Δx

Courtesy: Yagnaseni et al., Desalination, 420, 2017, 241-257.

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So let us understand the transport mechanism of the charged salutes in NF, transport of solutions through NF is more complex than any other membrane processes, actually 3 different modes of transport occurs; the first is diffusion, which is due to the concentration potential gradient in the reverse osmosis membranes, then convection in the larger pore size filtration such as microfiltration or ultrafiltration, then electromagnetism, attraction or repulsion from charges within and near the membrane.

So you can see this particular image which was actually proposed or given by one of the paper in desalination given by Yagnaseni et.al. So this is the solute transport mechanisms occurring simultaneously for each ion. Now, the mechanism also depends upon the feed water, and its composition. This is your Of course this is the membrane, right? So activity or thickness given by Δx and the water flux and solid flux both in this direction.

So you can see diffusion is a ion movement due to concentration gradient, okay? So you can see this is given by this particular line. So you can see there is a concentration grant in the downstream side. So that is why movement of ions will happen to the diffusion. Then

conviction; so iron movement with solvent flow, so along with solvent that means, along with the water some ions are flowing through. So this indicates that the membrane are having some pores, so they are pores, some pores are existing, okay?

Otherwise, if there are no pores, absolutely no pores membrane then convention will not happen basically. So then there is electromigration, so that means ion movement due to potential gradient. So as you know that ion membrane is slightly negatively charged, you can see this, right, and then up stream side we are maintaining some positive charged, so ion movement takes place by the flow of cations and anions in both ways and ion movement will take place both ways.

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Transport mechanism of charged solutes

Donnan exclusion:

- Has a pronounced effect on the separation in NF compared to other pressure driven membrane processes.
- Due to the slightly charged nature of NF membrane, solutes with an opposite charge compared to the membrane are attracted.
- Solutes with a similar charge are repelled.
- At the membrane surface a distribution of co- and counter-ions takes place, thereby causing an additional separation.

IUPAC: Reduction in concentration of mobile ions within an ion exchange membrane due to the presence of fixed ions of the same sign as the mobile ions.

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So, transport mechanism of charged solutes can be explained by 3 things actually. One is, Donnan exclusion, the next is actually a dielectric exclusion and then there is also something called the steric exclusive. So we will learn what is all this things one by one. So Donnan exclusion, actually what is Donnan exclusion, if you see the IUPAC actually definition. It says reduction in concentration of mobile ions within an ion exchange membrane due to the presence of fixed ions of the same sign as the mobile ions.

So that means you see the cation ion matrices, which are having this negatively charged ions already onto them, so, it will repeal this same charge groups. Similarly, an ion exchange membrane which are having this fixed positive charge, for all the positive changes their way attracting the opposite charge. So this is, and then after some time some equilibrium will be observed here. So that is actually called on an equilibrium.

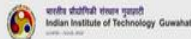
So, Donnan exclusion has a pronounced effect on the separation in NF compared to other pressure driven membrane processes because we are mostly dealing with the ions, so each ions are having some charges. Due to the slightly charged nature of NF membrane, salutes with an opposite charge compared to the membrane are attracted. Solutes with a similar charge are repelled. At the membrane surface, a distribution of co and counter ions takes place, thereby causing an additional separation.

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Transport mechanism of charged solutes

Dielectric exclusion:

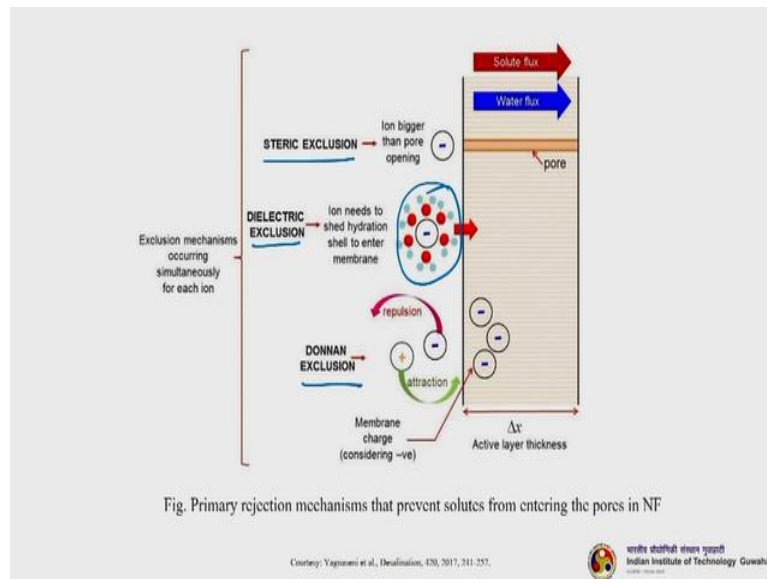
- Water molecules show a polarization in the pore due to the charge of the membrane and the dipole moment of water.
- The polarization results in a decrease in dielectric constant inside the pore, thereby making it less favorable for a charged solute to enter.
- Even in a situation that the dielectric constant inside the pore equal to the one in water, a change in electrostatic free energy of the ion occurs when the ion is transferred from the bulk into the pores.
- This also results in exclusion.



So the next one is dielectric exclusion; now water molecules show a polarization in the pore due to the charge of the membrane and the dipole moment of the water. The polarization results in a decrease in dielectric constant inside the pore, thereby making it less favorable for a charged solute to enter. That means, when the water is getting polarized inside the pores. It is hindering the diffusion of solutes inside that pore.

So this is what is actually known as dielectric exclusion. So even in a situation that the dielectric constant inside the pore equal to the one in water, a change in electrostatic free energy, of ion occurs when the ion is transferred from the bulk into the pores. So, this also resulted in exclusion.

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Let us see this particular figure again given by a Yagnaseni et.al, the desalination of this particular, you can refer to this nice publication actually, this materialistic so you can see this exclusion mechanisms occurring simultaneously for each ion, steric exclusion, this is nothing but side exclusion, than your dielectric exclusion, then Donnan exclusion. So you can see this at in steric exclusion, ion bigger than the pore opening, Okay?

They are trying to, they will be actually rejected on the surface of the membranes exclusion means we are talking about rejection how rejection is happening rejection of solutes from the membrane surface is happening then the dielectric exclusion something like this will happening. So, ion needs to shed hydration cell to enter the membrane. So it is difficult, because the membrane is already charged, some charge, Okay?

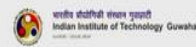
Then there are counter ions will be there, so they will try to form some groups on something like this is some, some structure something like this. So thereby there is rejection of the oppositely charge which is similar charged particles, ions will happen. So then we have Donnan exclusion, so here the repulsion expulsion happening due to the positive or negatively charged ions. So membrane charge considering it is negative.

So, we will see this, how the repulsion is happening, Okay? So, this particular figure tells us the rejection mechanism of the charge solutes on the nanofiltration membrane.

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Parameters affecting the performance of NF membrane

- **Pressure:** Pressure difference is the driving force responsible for an NF process.
Effective driving pressure is the applied hydraulic pressure less the osmotic pressure applied on the membrane by the solutes.
- **Temperature:** NF membrane flux increases with increase in temperature due to viscosity reduction.
- **Cross-flow velocity:** NF membrane flux increases with increase in cross-flow velocity because of efficient removal of fouling layer from the membrane surface.
The maximum cross flow velocity depend on the mechanical strength of the membrane and construction of the element and system hardware.
Operating a NF membrane at too high cross flow velocity may cause premature failure of membrane and module.



So let us now understand the different parameters that affect the performance of an nanofiltration membrane. So, there are various parameters we will see one by one. First one and foremost one is of course the pressure; pressure difference is the driving forces responsible for an nanofiltration membrane. So effective driving pressure is the applied hydraulic pressure, less the osmotic pressure, there is applied on the membrane and by the solutes, Okay?

Temperatures on nanofiltration membrane flux will increase with increasing temperature, due to the reason is that when the temperature increases the viscosity is reduced. That is where the flux getting's enhanced. Then cross flow velocity; so nanofiltration membrane flux increases also go along with that increasing the cross flow velocity. Why? Because if there is a higher cross flow velocity.

Then, here what it will do is basically the cell will wash away the concentrated concentration polarization layer, or we can say that the deposition whatever is happening on the surface of the membranes will be washed away due to a higher flow rate. So, thereby reducing the concentration polarization actually is falling. So the maximum cross flow velocity depend on the mechanical strength of the membrane and construction of the element and system hardware.

Operating a NF membrane at too high cross flow velocity may cause premature failure of the membrane and module. So, it is true that you cannot operate a NF system, beyond a certain pressure. Otherwise your system will failure and membrane will get rupture.

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Parameters affecting the performance of NF membrane

- **Solution pH:** Charged sites on NF membrane surface varied with pH (negatively charged at neutral pH and lose their charge at acidic pH).
- Most NF and RO membranes have lower rejection at low pH.
- However, the pH dependency of a membrane is determined according to the chemistry applied to produce the membrane.



So the next other parameter says solution pH, so you know solution pH is the one of the most important parameter, whenever you talked about any liquid systems. Okay, liquid phase systems, whether you were doing some separation carrying out some reaction, whatever. So, charged sites on the NF membrane surface varied with pH. So negatively charged at a neutral pH and lose their charge at acidic pH.

So most NF and RO membranes have lower rejection at low pH. Because of the surfaces are already charged and mostly it is negatively charged at neutral pH. However the pH dependence upon membrane is determined, according to the chemistry applied to produce the membrane.

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NF Advantages

- Lower discharge volumes, lower retained concentrations than RO for low value salts.
- Reduced salt content and dissolved solid content (TDS) in brackish water.
- Reduction in heavy metals.
- Reduced nitrates and sulphates.
- Reduction in color, tannins and turbidity.
- Softens hard water with the use of specific softening membranes.
- Chemical-free, i.e. needs no salt or chemicals during operation.
- pH of water after nanofiltration is normally non-aggressive.
- Disinfection.

Courtesy: Kavin Water Technologies Pvt. Ltd.



So let us understand the nanofiltration advantages. So, it has lower discharge volumes, lower retained concentrations than RO for low value salts. Reduced salt content and dissolved solid

content in brackish water. Reduction in heavy metals, reduced to nitrates and sulphates, reduction in color, tannins and turbidity, Softens hard water with the use of specific softening membranes. Chemical free, that is needs no salt or chemicals during the operation.

And pH of water after nanofiltration is normally non aggressive and disinfection. So, these are the thing that is being done by the nanofiltration membrane.

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NF Disadvantages

- Higher energy consumption than Ultrafiltration and Microfiltration (0.3 to 1 kWh/m³).
- Pre-treatment is needed for some heavily polluted waters (pre-filtration 0.1 - 20 microns). This is always the case with spiral-wound membranes.
- Limited retention for salts and univalent ions.
- Nanofiltration membranes are a little more expensive than reverse osmosis membranes.
- Membranes are sensitive to free chlorine (life-span of 1000 ppmh).
- An active carbon filter or a bi-sulphite treatment is recommended for high chlorinic concentrations.

Country: Kivita Water Technologies Pvt. Ltd.

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So, it has certain disadvantages also. So higher energy consumption than ultrafiltration and microfiltration and so almost 0.3 to 1 kilowatt hour per meter cube. So, another important thing is that pre-treatment is required for some heavily polluted water, so pre-filtration 0.1 to 2 microns. The all these things needs to be removed. Otherwise, your membrane will be blocked, and it will not give the targeted performance.

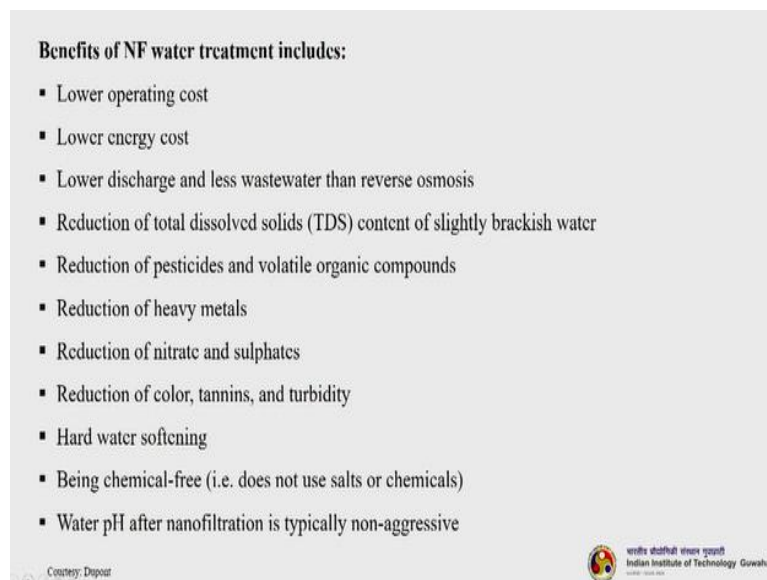
So this is always the case with spiral wound membranes, see the spiral wound membranes typically frames as it leaves you, we have understood how spiral wound actually work in our membranes module discussion as well as in RO also. So you know the how it is being fabricated. So the space in between is to less. So they are more pore to fouling. So, it is important that there is a statement before nanofiltration, okay?

For heavily polluted it is not that every water streams are paid water has to be pre-treated. So limited retention for salts and univalent ions, nanofiltration membranes are little more expensive than reverse osmosis membranes. So membranes are sensitive to free chlorine, so

most of the time chlorine is present in water and water streams. So they are not very good chlorine resistance membranes, so life span of 1000 ppmh, Okay?

So an active carbon filter or a bi-sulphite treatment is recommended for high chlorine concentrations.

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Benefits of NF water treatment includes:

- Lower operating cost
- Lower energy cost
- Lower discharge and less wastewater than reverse osmosis
- Reduction of total dissolved solids (TDS) content of slightly brackish water
- Reduction of pesticides and volatile organic compounds
- Reduction of heavy metals
- Reduction of nitrate and sulphates
- Reduction of color, tannins, and turbidity
- Hard water softening
- Being chemical-free (i.e. does not use salts or chemicals)
- Water pH after nanofiltration is typically non-aggressive

Courtesy: Depozar

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Let us understand the benefits of the NF water treatment; so most of the times, NF is actually used to produce potable water. So in that case, what are the advantages; so the operating cost actually is very less, energy costs also less, lower discharger and less wastewater than reverse osmosis and the principal produces. Then reduction of total dissolved solids content of slightly brackish water.

Reduction of pesticides and volatile organic compounds, reduction of heavy metals, reduction of nitrates and sulphates, reduction of color, tannins and turbidity, hard water softening. Being chemical free say does not use any salts or chemicals. Water pH after nanofiltration is typically non-aggressive.

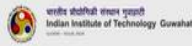
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NF Applications

Typical applications of NF includes:

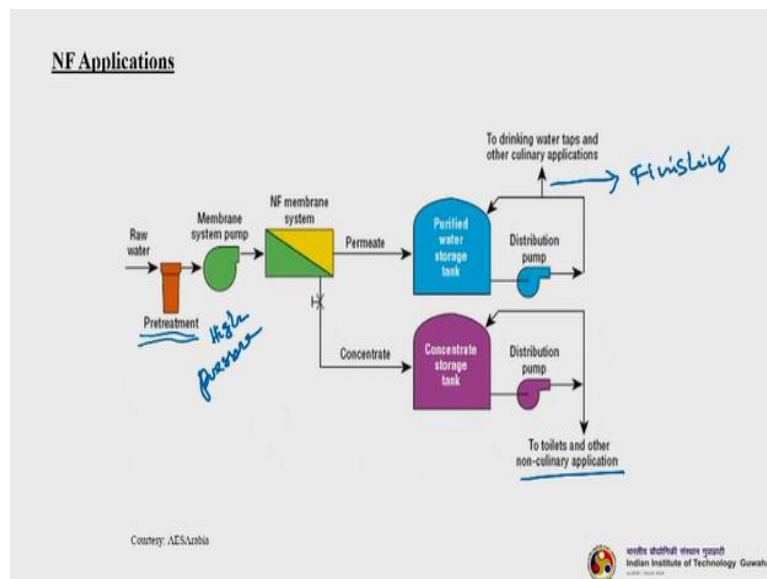
- Desalination of food, dairy and beverage products or byproducts
- Partial Desalination of whey, UF permeate or retentate as required
- Desalination of dyes and optical brighteners
- Purification of spent clean-in-place (CIP) chemicals
- Color reduction or manipulation of food products
- Concentration of food, dairy and beverage products or byproducts
- Fermentation byproduct concentration.

Courtesy: AES/Arabia



So NF applications includes; the desalination of food, dairy and beverage products or by-products. Partial desalination of whey, UF permeate or retentate as required. Desalination of dyes and optical brighteners. Purification of spent clean in place chemicals, CIP chemicals. Color reduction or manipulation of food products. Concentration of food, dairy and beverage products or by-products. Fermentation byproduct concentration.

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Let us see one; this is one application, in which the nanofiltration membrane is used to produce clean water, even for drinking water taps as well as other culinary applications. So you can see the schematic here, so raw water is coming as I told you that, one of the disadvantages, in nanofiltration is that it needs a pre-treatment and not always, but most of the times. Depending upon what is your feed water composition and what it contents basically.

So then it goes to high pressure pump, basically this is a high pressure membrane system pump is a high pressure pump, okay? So this high pressure pump will pump the raw water or filter to the nanofiltration system. So you get permeate and a concentrate. So the permeate is goes to the purified water storage tank, Okay? Then it can be taken for the culinary or drinking water taps, or there is purified water, or it may be recycled by partly to maintain the volume.

see many times, here also, this one needs another finishing step, this finishing step is basically required because most of the ions are divide. When we are doing the nanofiltration, so it is actually when we are talking about the potable water system or potable water applications. So you need to sometimes re-mineralization, re-mineralize the NF water. So the concentrate which is coming here and getting stored here, so, this concentrate is also can be used to toilets and other non-culinary application.

You can use it for watering your plants in the garden and all these things. So you have been used in the toilets many of the big hotels star hotels are now are doing are adopted this technology, and you will see this in the wash room many times it is written that, especially in your commodes you can see the color of the water is slightly, slightly greyish or a little yellowish it is written within that, because this is treated water. So, there is some color

So you can remove the color also completely but it will be unnecessarily above the process what of course so it is not required. So, whatever you are using for your bathing or your drinking purposes or washing, so you will get them, you will obviously being supplied with the good water.

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NF Applications

- A combination of resin and membrane processes is especially attractive for plant locations where the waste disposal is a critical issue.
- In the future, NF is expected to find application in recovery of water and salt from waste brine at a sugar decolorization plant in sugar industry.
- In addition, the volume of toxic wastes discharged from sugar refinery columns can be lowered.

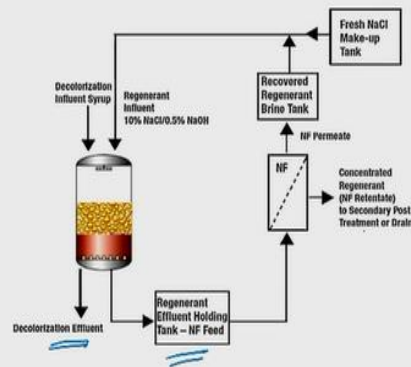


Fig. Schematic of NF process for purifying anion-exchange resin regeneration effluent in the sugar industry.

Courtesy: Fakhrudin Saleh, Food and Bioproducts Processing, 92 (2014) 161-177.



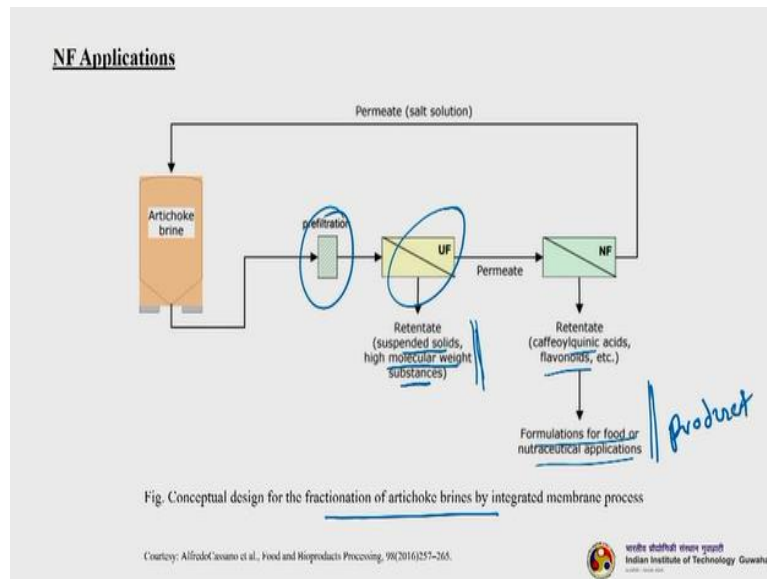
So another NFL application is the NF process for purifying anion exchange resin regeneration effluent in the sugar industries. So, here what is happening actually a combination of a resin and membrane processes is especially attractive for plant locations, where the waste disposal is a critical issue. Now most of the industries that do not have land for waste disposal, and the rest of them to rules, of course waste disposal also being imposed.

So it is imperative that they need to treat it. So in the future, NF is expected to find applications in the recovery of water and salt from waste brine at a sugar decolorization plant in sugar industry. So these are also getting adapted now a day. So in addition, the volume of toxic wastes discharged from sugar refinery columns can be lowered. So you can see how it is happening, actually.

So, this regenerate effluent that is the first is coming and you are adding some decolorizations. So, the decolorizations effluent is being taken here, and it regenerated effluent, Okay? Which is being stored here. So this is basically NF feed, it goes to the nanofiltration system, where you are getting the concentrate the region, which is the NF retentate to secondary post treatment of drain, or you can just use it again, as I told you, for watering garden and all this purposes, non-culinary purposes, and the NF permeate. Okay?

So this is nothing but recovered regenerate brine tank goes and stored there, so this will be recycled brine.

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So there is this is another application. This is a conceptual design for the fractionation of artichoke brines by integrated membrane process. Now here, this is a hybrid system you can say, okay, usually we say a hybrid system is something where two different unit operations are plugged together. Okay? But here two different, two different membrane systems are plugged together.

So you can say integrator membrane process, so you can see here, there is an ultrafiltration membrane, there is nanofiltration membrane, Okay? Why it is being used so let us try to understand so artichoke brine is stored here. See our artichoke brine is being feed to the ultrfiltration membrane. So before being to the ultrfiltration membranes some, some sort of prefiltration happens to remove the floating solids, suspended solids have certain, certain other larger molecular compounds.

So, that the UF membrane will not, UF membrane being porous it should not get clogged. So this filter artichoke brine then goes to the UF membrane, where we are getting the retentate, so the retentate is getting artichoke brine, suspended solids, higher molecular weight substances, okay? But now we will try to understand that why we are using UF here. If you do not use the UF here, directly feeding the artichoke brine after this brief filter, okay?

To hear, them all these whatever the UF is getting rejected will be rejected here but the membrane performance will decrease drastically, Okay? So that is why there is a need to actually refilter, as well as there is a need to place a UF, so that the UF will remove most of the suspended solids and the high molecular weight components. So the permeate divide all these

things, Okay? and having only smaller molecular weight compounds and ions is being feed to the NF.

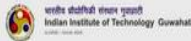
So the NF retentate is basically like caffeoylquinic acids, flavonoids etc., and this goes for the formalization for food or nutraceutical application. So this is actually our product of interest. Okay? And, whatever the permeate is, there it is getting recycled here. Oka? So it is the salt solution, mostly right so again going artichoke filter tank.

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NF Applications: Fractionation of artichoke brines by integrated membrane process

- The exhausted brines are submitted to a preliminary UF step aimed to remove most of suspended solid compounds.
- The UF permeate is a clear solution containing more than 95% of the compounds of interest.
- The subsequent treatment with spiral-wound membranes of 300 Da allows to obtain a retentate fraction enriched in phenolic compounds and with a salt content able to stabilize the retentate itself.
- This fraction is of interest for food or nutraceutical applications.
- The NF permeate is a salt solution free from caffeoylquinic acids which can be designed for reuse in the processing cycle or replenishing of fresh brines with a consequent reduction in the volume of water used in the process.

Courtesy: Fakreddin Salehi, Food and Bioproducts Processing, 92 (2014) 161-177.



So, the artichoke brines are submitted to a preliminary ultrafiltration step, aimed to remove most of the suspended solid compounds. This is what I already told you, so the ultrafiltration permeate is a clear solution containing more than 95% of the compounds of interest. So, it takes out all the larger molecular weight components as well as your TDs, most of the suspended solids.

So, components which are smaller molecular weight components this caffeoylquinic acids, flavonoids etc. So they will be fed to the nanofiltration system. So the subsequent treatment with spiral wound membranes of 300 Da allows to obtain a retentate fraction enriched in phenolic compounds, and with a solid content able stabilize the retentate itself. So, this fraction of interest for food nutraceutical applications.

So the NF permeate is a salt solution free from caffeoylquinic acid, which can be designed for reuse in the processing cycle or replenishing of fresh brines with a consequent reduction of the volume of water used in the process.

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NF Applications

- A typical system consist of a feed tank, a membrane cell, a pump, a temperature controller to keep the feed temperature at a specific value, a back pressure regulator, and a bypass valve to adjust the applied pressure and cross-flow velocity.
- A weighing balance or a digital flowmeter are used to measure the permeate flow rate. Permeate and retentate are recycled to the feed tank to maintain a constant feed concentration over time.

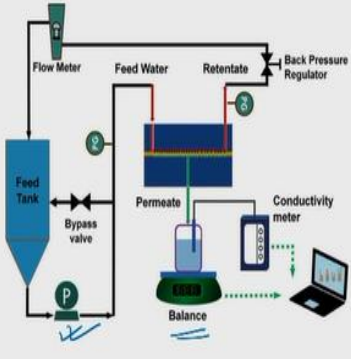


Fig. Bench scale cross-flow NF setup for the treatment of oil sands-produced water.

Country: Mohinda Satrazdeh et al., Nanofiltration for the Treatment of Oil Sands-Produced Water, IntechOpen.

weirika shikshak vikas sanghat
Indian Institute of Technology Guwahati

So this is another classic example of the scale cross-flow NF setup, Okay? For the treatment of oil sands produced water. So you can see this, there is a tank, Okay? So then it is high pressure pump is here, so it is pumping the feed water to the membrane cell, where they are getting permeate here. Okay. And then the retentate is again being recycled to the feed tank or it can be taken out also, okay?

A typical system consists of a feed tank, a membrane cell, a pump, a temperature controller to keep the feed temperature very specific value, a back pressure regulator and a bypass valve to adjust the applied pressure and cross flow velocity. So weighing balances here you can see this, or a digital flow meter used to measure the permeate flow rate. Permeate and retentate are recycled to the feed tank to maintain a constant feed concentration over time.

(Refer Slide Time: 27:49)

NF Applications

- Several types of viral removal devices are available as self-contained and disposable capsules and cartridges that can be subjected to integrity tests.
- With such devices, protein solution can be filtered in a dead-end flow filtration mode under a constant pressure mode as shown.

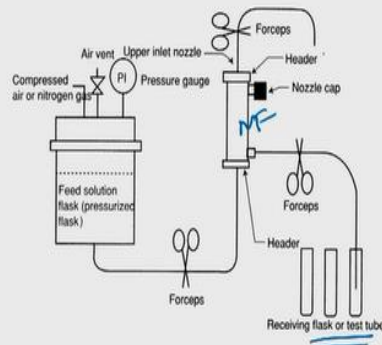
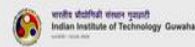


Fig. Schematic diagram of dead-end NF under constant pressure

Copyright: T. Banaei et al., Membranes (2003), 9, 24-37.



Another application, this is dead-end nanofiltration under constant pressure. You can see this is several types of viral removal devices are available as self contained and disposable capsules and cartridges that can be subjected to integrity tests. So with such devices, protein solution can be filtered in a dead-end flow filtration mode under constant pressure mode, you can see. So you can see this, this is NF system actually Okay?

So the proteins solutions are getting actually filter here. Okay, so you are getting the receiving flask or you have the test tube, whatever the permeate can be collected here.

(Refer Slide Time: 28:31)

Nanofiltration Fouling Model

- The water flux in RO and NF can be expressed as:

$$J_w = \frac{\Delta P - \Delta \Pi}{R_{tot}}$$

where, J_w is the water flux, ΔP is the applied pressure difference, $\Delta \Pi$ is the osmotic pressure difference and R_{tot} is the total resistance.

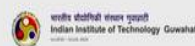
- The total resistance of the membrane is composed of three separate resistance in series:

R_m : resistance of a clean membrane to permeation of clear water and is time independent.

R_i : initial fouling resistance caused by concentration polarization and fouling of the membrane during start up of the process and is time independent.

R_f : time independent fouling resistance.

$$\frac{1}{R_{tot}} = \frac{1}{R_m} + \frac{1}{R_i} + \frac{1}{R_f}$$



So let us now understand the nanofiltration fouling mechanisms and the models. So, the water flux in RO and NF can be expressed as; J_w equals to Δp minus $\Delta \pi$ by R_{tot} . So J_w is the water flux, Δp is the applied pressure difference, $\Delta \pi$ is the osmotic pressure difference

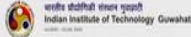
and R_{tot} is the total resistance, Okay?. Now the total resistance of the membrane is composed of three separate resistances in series, Okay?

So R_m , R_i and R_f , so R_m is the resistance of a clean membrane to permeation of clean water, and is time independent. Okay? So R_i is initial fouling resistance caused by concentration polarization, and fouling of the membrane, and, it is time independent, Okay? R_f is time independent fouling resistance. So you can write this, actually, we can write 1 over R_{tot} equals to 1 over $R_m + 1$ over $R_i + 1$ over R_f . this is how you right actually, this one the resistances.

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- Van Boxtel correlated R_i empirically with cross flow velocity (v), upstream pressure (P), and concentration ratio (C_r) by:
$$R_i = a \cdot v^b \cdot P^c \cdot C_r^d$$

where a, b, c, d are empirical constants.
- Example: Fouling becomes a major issue when dealing with fermentation broth as it contain salts, colloidal particles, bacterial cells and proteins which may causes fouling.
- By treatment of fermentation broth by ultrafiltration, protein and bacteria can be removed and fouling properties of the solution can be changed thereby reducing the overall resistance also.



Van Boxtel correlated R_i empirically with a cross flow velocity, upstream pressure and concentration ratio and propose this particular equation. So, R_i equals to $a \cdot v$ to the power of b . P to the power of c and C_r to the power d . So C_r actually concentration this, so a, b, c, d are empirical constants. For example why this is being necessary and we were talking about this actually fouling problems becomes very severe.

So for example, we are taking fermentation broth. So, the fouling becomes a major issue when we are dealing with fermentation broth as it contain salts, colloidal particles, bacterial cells and proteins, which may cause fouling, most of the marble apartments. So, by treatment of fermentation by ultrafiltration, some protein and bacteria can be removed and fouling properties of the solution can be changed thereby reducing the overall resistance also. Then again it can be sent to the nanofiltration system.

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Fouling model

$$\frac{dR_f}{dt} = A \cdot J_w - B \quad R_f(t=0) = 0$$

where $A = \frac{\varepsilon \cdot C_{b,pr}}{\rho}$ and $B = \frac{\varepsilon \cdot k_{pr} \cdot C_{b,pr}}{\rho} \ln \frac{C_{g,pr}}{C_{b,pr}}$

- ε is the specific gel layer resistance, $C_{b,pr}$ protein concentration in the bulk,
- $C_{g,pr}$ is the protein concentration in the gel and k_{pr} is the mass transfer coefficient of protein in boundary layer.
- The above equation predicts a flux dependent increase of R_f with time and can only be applied with a constant $C_{b,pr}$ as in continuous system.

So, a fouling model can be expressed by this particular equation in the terms of R_f . So dR_f/dt equals to $A \cdot J_w - B$. So, R_f at $t=0$ equals to 0. That means R_f at $t=0$ equals to 0. So where A is given by $\varepsilon \cdot C_{b,pr} / \rho$ and B equals, B is given by this particular equation. So, ε is the specific gel resistance. $C_{b,pr}$ is the Protein Concentration in the bulk.

$C_{g,pr}$ or is the protein concentration in the gel and k_{pr} is the mass transfer coefficient of protein in boundary layer. The above equation predicts the flux dependent increase of R_f with time, and can only be applied with a constant $C_{b,pr}$ as in continuous system.

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Fouling model

- In case of a changing $C_{b,pr}$ that occurs during batchwise concentration of solutions, the above equation can be transformed into:

$$\frac{dR_f}{dt} = C_r \cdot A \cdot J_w - k_{pr} \ln \frac{C_{g,pr}}{C_{b,pr,t}} - \ln C_{r,l}$$

where, $C_r = \frac{V_0}{V_0 + J_w A w dt}$

- If proteins are absent, as in ultrafiltered fermentation broth, the gel layer model can not be applied.
- A precipitation model or colloidal fouling model is more appropriate in this situation.
- Cohen and Probstein developed a model in which deposition of colloidal particles caused fouling.

So, in case of a changing $C_{b,pr}$ that occurs during batchwise concentration of solutions, the above equation can be transformed into this particular equation, where dR_f/dt equals to C_r into $A \cdot J_w$ minus, this particular equation minus $\ln C_{r,l}$. So where C_r is given by this, this

equation V_0 by V the integration of this $J_w \cdot A_w \cdot dt$. So if proteins are absent, as in ultrafiltered fermentation broth, the gel layer model cannot be applied because it is not required, because there will be no gel formation, Okay? On the membrane surface.

So, a precipitation model or colloidal fouling model is more appropriate in this situation. So Cohen and Probstein developed a model in which deposition of colloidal particles caused fouling.


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Fouling model

- They discovered that colloidal fouling was convection controlled and using the law of mass conservation, they derived a equation as given below.

$$\frac{dR_f}{dt} = \frac{\phi_0 J_{w0} R_c}{1 - \epsilon_c}$$

- Where ϕ_0 is the foulant volume fraction in feed,
- J_{w0} is the water flux determined by extrapolating the flux-time curve to time zero,
- ϵ_c is the effective foulant layer resistance.
- The model shows that the increase in long term fouling is constant and linearly dependent on the foulant volume fraction.



So they discovered that colloidal fouling was convection controlled and using the law of mass conservation, the derived a question as given below; so dR_f by dt across to this ϕ_0 not J_w not R_c by $1 - \epsilon_c$. So we are find out is the foulant volume fraction in feed. J_w is the water flux determined by extrapolating the flux time curve to time 0, Okay? So basically it is the flux at zero.

So ϵ_c is the effective foulant layer resistance and this model shows that the increase in long term fouling is constant linearly dependent on the foulant volume fraction.

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Fouling model

- For a given feed which is processed at different C_r , and when it is assumed that J_{w0} shows the same pressure dependence, the above equation can be transformed into:

$$\frac{dR_f}{dt} = \frac{D}{R_{w0}} \cdot C_r \cdot (\Delta P - \Delta \Pi)$$

$$\text{where, } D = \frac{\phi_0 R_c}{1 - \epsilon_c}$$

- R_{w0} is the resistance at intercept of the flux-time curve at time zero.

So for a given feed which is processed at different C_r and when it is assumed that J_{w0} shows the same pressure dependence, the above equation can be transformed into dR_f by dt equals to D by R_{w0} . $C_r \cdot \Delta P - \Delta \Pi$, where D equals to this $\phi_0 R_c$ into $1 - \epsilon_c$. R_{w0} is the resistance, is the resistance at intercept of the flux time curve at time equals to 0.

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Fouling model

- The R_{w0} put into the concept of initial and long-term fouling is equal to the sum of R_m and R_f .
- By performing experiments at different C_r and ΔP , the first factor on the right-hand side of above equation can be evaluated.
- The factor D should be independent of process conditions.
- In the case of batch wise concentration, the assumption of a quasi-steady flux made by Cohen and Probstein does not hold.
- For this case J_{w0} in the above equation is replaced by J_w .

So, the R_{w0} put into the concept of initial and long term fouling is equal to the sum of R_m and R_f . By performing experiments at different C_r and ΔP , the first factor on the right hand side of the above equation can be evaluated. The factor D should be independent of the process condition. In the case of batch wise concentration, the assumption of quasi- steady state of flux made by Cohen and Probstein does not hold. For this case J_{w0} in the above the question is replaced by J_w .

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Fouling model

- An example of continuous experiment with lactic acid fermentation broth are shown in here.
- It is clear that during continuous NF of the UF-broth, R_i is the largest resistance to water permeation.
- Time dependent fouling (R_f) hardly contributes to the overall resistance to water permeation.
- This shows that osmotic effect and concentration polarization effects during continuous NF and UF-broth cause the main mass transfer resistance.

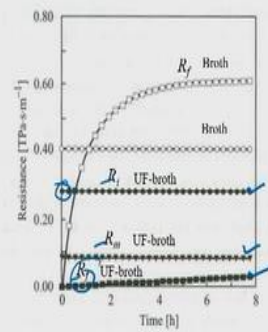


Fig. Resistances as a function of time of a continuous experiment with UF-broth and broth.

So, let us see this particular figure here. So this is a resistance as a function of time of a continuous experiment with the UF broth, and only broth, Okay? So UF broth means ultrafilter broth, Okay? So an example of a continuous experiment with lactic acid fermentation broth is shown here. So it is clear that the continuous NF of the UF-broth R_i is the largest resistance.

So this is the UF broth, this is UF broth, this is UF broth, this is UF breath, and this is for R_i , this is for R_m . This is for R_i , Okay? You can see this is for R_m , this is for R_i . So you can see this, so it is clear that during this, nanofiltration of the ultrafiltration broth R_i is the largest a distance where you can see, Okay? So time dependent fouling R_f hardly contributes to the overall resistance of the water permeation.

So R_f is almost negligible, so you can almost neglect the R_f , Okay? Now this shows that osmotic effect and concentration polarization effects during continuous NF, and UF broth cause the main mass transfer resistance, Okay?

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NF Membrane and Module

There are two types of membranes:

Spiral membranes, cheapest but more sensitive for pollution.

Tubular/ straw membranes, the most used membranes seen the costs and effect, shall not easily be polluted.

The surfaces from the filter determine the capacity from the filter. Spiral membranes have the biggest surface area in general and are therefore the most cheapest in use. The surface area from Tubular/ straw membranes is less in general.

The pre-purifying of the feeding water has a influence on the performance of the installation.

The need of pre purifying depends on the feeding water quality.



So, NF membrane and module; so there are two types of membranes actually available commercially the spiral wound and the tubular membranes. Spiral membranes are cheapest but more sensitive to pollution. Tubular and straw membranes, the most used membranes seen the costs and effect, shall not easily be polluted. The surfaces from the filter determine the capacity from the filter.

Spiral membranes have the biggest surface area in general, and are therefore the most cheapest in use. The surface area from tubular or straw membranes is usually less in general. So the pre-purifying of the feeding water has influence on the performance of the installation. The need of pre-purifying depends on the feeding water quality.

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Difference between RO/NF

While RO and NF are very similar, they can be distinguished based on the size of particulates that each is able to remove. Comparatively, RO and NF are capable of removing finer contaminants than MF and UF, with applications including the removal of hardness, nitrates, sulfates, total dissolved solids (TDS), heavy metals, radionuclides, and organic macromolecules from process and waste streams.

RO	NF
extremely small pores capable of removing particles as small as 0.1 nm	slightly coarser filtration than RO, with the ability to remove particles as small as 0.002 to 0.005 μm
Old technology, since 1950	Recent technology
used chiefly for desalination, as in potable water generation from seawater or brackish water sources	developed mainly for potable water generation
very efficient at removing all ions, large and small	NF removes harmful contaminants, such as pesticide compounds and organic macromolecules, while retaining minerals that RO would otherwise remove. Nanofiltration membranes are capable of removing larger divalent ions such as calcium sulfate, while allowing smaller monovalent ions such as sodium chloride to pass through.

Courtesy: SAMCO



So let us now try to understand, before we wind up. What is the difference between RO and NF. So you know that we have discussed this that RO and NF, they are very much similar to each other, but they can be distinguished based on the size of the particulates or solute that each is able to remove.

So comparatively, RO and NF are capable of removing finer contaminants than micro filters and ultrafilters, with applications including removal of hardness, nitrates, sulphates, total dissolved solids or TDS, heavy metals, radionuclides and organic macromolecules from process and waste streams. So, this is just this tabular format to try to understand the differences.

So RO is rejecting a small then having small pores. So they are capable of removing particles as small as 0.1 nanometer, but NF range is almost point 0.002 to 0.005 microns, Okay? So, RO is old techniques existing almost since 1950s. However, NF is a very recently developed technology. So RO was used chiefly for the, mainly for the desalination purposes, as in potable water from seawater or brackish water sources and NF is exclusively developed mainly for the potable water generation.

So RO is extremely efficient in removing all ions, large and small, and NF removes harmful contaminants such as pesticide compounds and organic macromolecules, while retaining minerals that RO would otherwise remove. So, Nanofiltration membranes are capable of removing larger divalent ions such as calcium sulphate, while allowing smaller monovalent ions such as sodium chloride to pass through.

(Refer Slide Time: 37:38)

Criteria	Description/Rationale
Status of technology	Mature & robust technology
Applications	Water softening, metals removal and produced water treatment
Feed water quality	TDS 500 - 12000 mg/L can be handled with high concentrations of divalent ions, multivalent metal ions and radionuclides
Product water quality	Depends on feed water quality & operating conditions. >90% rejection of larger divalent ions and metals Moderate rejection of monovalent ions
Recovery	Ranges between 75% - 90%
Pre-treatment of feed water	Required to reduce scaling & fouling
Post-treatment of product water	Required re-mineralization to maintain sodium adsorption ratio (SAR) values
Energy use	Less energy than RO for same feed water quality
Chemical use	To prevent scaling and fouling, scale inhibitor and caustic may be required
Lifetime	3-7 years depending on use and operating conditions

So, this is a technical assessment of NF technology, so you can just go through it. So, the status of technologies, it is an expression is quite mature and it is a robust technology. So applications are wide, the most of the important applications are water softening, metal removal and produced water treatment. The feed water quality; it handles almost 500 to 12,000 milligrams per liter of a TDS. Okay? And product water quality; that depends on the feed water quality and operating conditions.

However, greater than 90% rejection of a larger divalent ions and metals are possible. Moderate rejection of monovalent ions are possible in nanofiltration. So the recovery range is almost 75% to 90%. This is one of the most important parameter. When you talk about industrial applications, the pre-treatment of feed water is necessary as we have learned in today's lecture. So it is required, so as to reduce scaling and as well as fouling.

Post treatment of product water sometimes required, especially we are talking about potable water because it is divided up all sorts of minerals. So re-mineralisation of sodium adsorption ratio that is SAR value is actually required. So energy uses quite less than the RO for the separate water quality. There is no chemical use however sometimes we use at the scaling and antifouling inhibitors, Okay? This is the caustic may be required.

And the lifetime depends actually, so it is anytime between 3 to 7 years, depending on use and operating conditions. So thank you very much.

(Refer Slide Time: 39:26)

Text/References

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So today's lecture, mostly is taken by a taken from, from Professor Nath's book, as well as some other journal sources. Please go through it and in the next class,

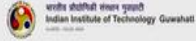
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(Overview of next lecture)

Module	Module name	Lecture	Title of lecture
07	Ultrafiltration basics, transport models, applications	19	Basic principles, advantages of UF, membranes and modules, various UF configurations

Thank you

For queries, feel free to contact at: kmohanty@iitg.ac.in



বিশ্ব শান্তিৰ মনস গুৱাহাটী
Indian Institute of Technology Guwahati
2013-2014

We are starting ultrafiltration, and the next module. So we will try to understand the basic principles and advantages of ultrafiltration, different types of membranes and modules that is required for the ultrafiltration, and various types of ultrafiltration configurations. So thank you very much. In case you have any queries, please feel free to write to me at kmohanty@iitg.ac.in. Thank you.