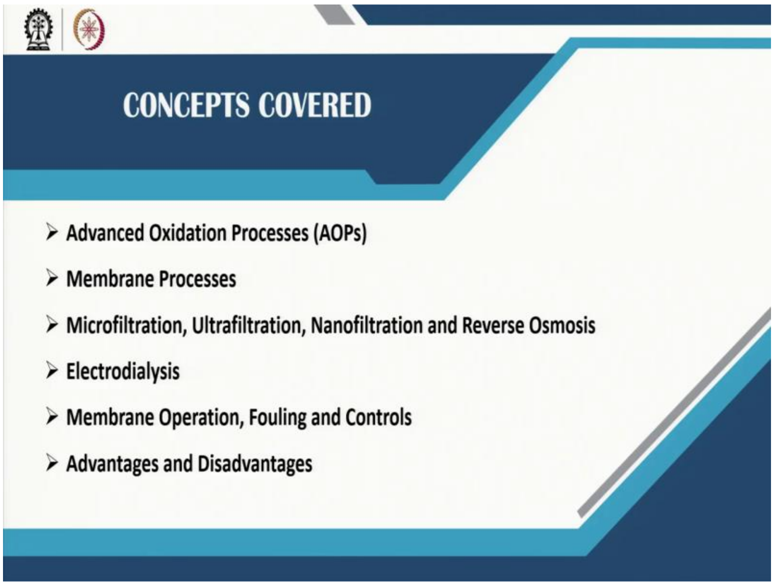
Water Supply Engineering
Prof. Manoj Kumar Tiwari
School of Water Resources
Indian Institute of Technology, Kharagpur

Lecture-40
Advanced Oxidation Processes and Membrane Process

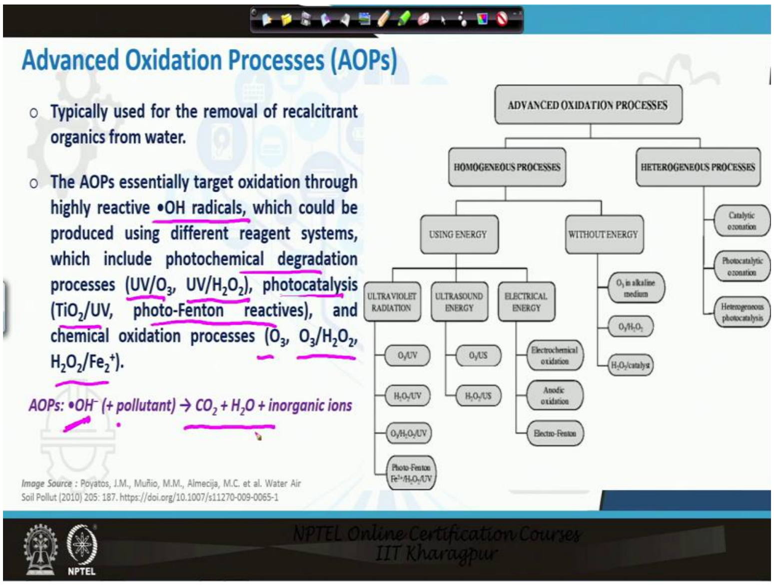
Hi everyone and welcome back. So, we will continue our discussion on the Advanced treatment processes. In the last class, we talked about we did discuss some processes including like absorption and iron exchange then dissolve your floatation or the softener systems. This class we are going to talk about the advanced oxidation process and the membrane process.

(Refer Slide Time: 00:39)



So, basically what we will be covering is the Advanced Oxidation process and then the different type of membrane process like microfiltration, Ultrafiltration, Nanofiltration, Reverse Osmosis, we will talk about electro dialysis as well. And then, we will touch upon the membrane operations, the problem of the membrane falling and how we control that and what are the advantages and disadvantages of these systems.

(Refer Slide Time: 01:04)



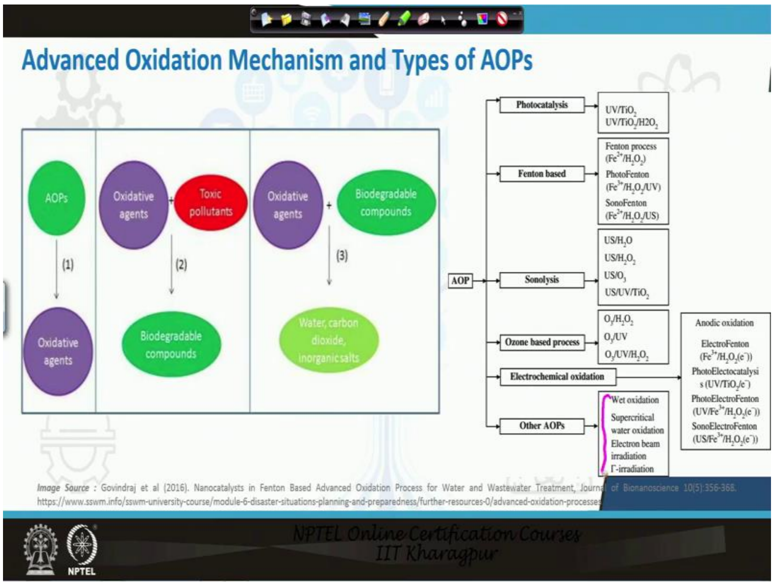
So, advanced oxidation processes are typically used for the removal of recalcitrant organics present in the water as just we were discussing in the last class that like lot of refractory organics or lot of the persistent organic pollutants emerging contaminants do come and many of them are organic in nature. So, advanced oxidation like through simple oxidation or simple approaches they cannot get there does not get oxidized. So, through advanced oxidation process, we can oxidize them break like in short the breakdown of those compounds.

However, this advanced oxidation process is more applicable to the wastewater systems. But few places in a water treatment also these type of systems are used. So, these advanced authorization systems typically rely on the oxidation through highly reactive OH radicals. So, which could produce like we can produce Voyage radicals through different means okay. It can be produced through like photochemical degradation process of ultraviolet and ozone of ultraviolet and hydrogen peroxide.

It can be produced through photocatalysis process of TIO2 UV or photo Fenton reactives and it can be basically through chemical oxidation process of Ozone, ozone hydrogen peroxide or ozone and Iron. So, eventually the OS radical is produced by whichever means it is produced but advanced oxidation process usually produced the OS radical which reacts with the pollutant and converts them to CO2 and H2 and inorganic ions, okay.

These advanced oxidation processes could be like homogeneous process or heterogeneous process. So, heterogeneous process is say catalytic or ozonation then, photo catalytic ozonation or heterogeneous photocatalysis, whereas homogenous process might be with energy uses and without energy uses without energy uses again like ozone in alkaline medium or ozone O2 or H2O2 and some catalysts and with energy. So, we rely on the ultraviolet radiations or ultrasound energy or electrical energy. And again using these different constituents we can actually produce the radical.

(Refer Slide Time: 03:11)

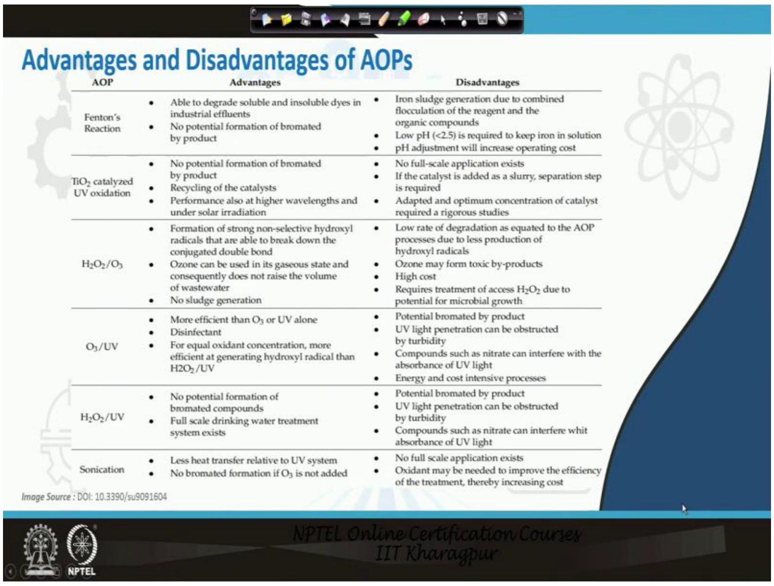


So if you see the mechanism of the oxidation. So, these advanced oxidation processes produce an oxidizing agent these oxidizing agent reacts to the toxic compounds they convert it to the like biodegradable compound or like it can actually lead to the complete mineralization as well. And then these oxidizing agents further reacts to these biodegradable compounds and convert them to simple like water carbon dioxide or in Organic.

And they are of different types as we are discussing the photo catalysis which is UV and TIO2 or H2O2 then Fenton processes which are iron based processes photo fenton, ozone Fenton or simple Fenton processes. Then, so analysis again ultrasound base ultrasound H2O2, ultrasound ozone, ultrasound UV and then, there are ozone based processes which are basically where OH is particularly produced from the ozone.

And then electrochemical oxidation processes are there okay which is basically electro found Fenton or photo electrolysis. So, these are and then there are other AOPs which are kind of supercritical water oxidation, Electron beam irradiation. So, these are the actually these are even more emerging technologies in the advanced oxidation processes okay.

(Refer Slide Time: 04:29)

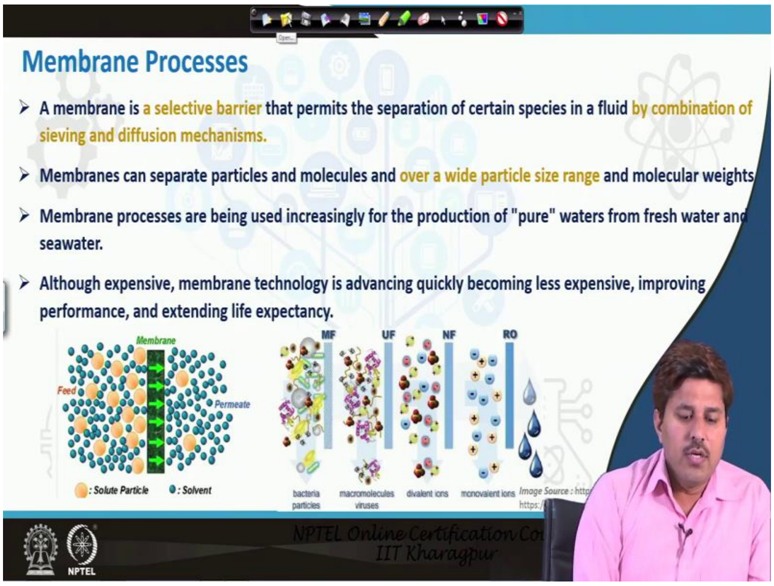


AOP	Advantages	Disadvantages
Fenton's Reaction	• Able to degrade soluble and insoluble dyes in industrial effluents • No potential formation of bromated by product	• Iron sludge generation due to combined flocculation of the reagent and the organic compounds • Low pH (<2.5) is required to keep iron in solution • pH adjustment will increase operating cost
TiO_2 catalyzed UV oxidation	• No potential formation of bromated by product • Recycling of the catalysts • Performance also at higher wavelengths and under solar irradiation	• No full-scale application exists • If the catalyst is added as a slurry, separation step is required • Adapted and optimum concentration of catalyst required a rigorous studies
H_2O_2/O_3	• Formation of strong non-selective hydroxyl radicals that are able to break down the conjugated double bond • Ozone can be used in its gaseous state and consequently does not raise the volume of wastewater • No sludge generation	• Low rate of degradation as equated to the AOP processes due to less production of hydroxyl radicals • Ozone may form toxic by-products • High cost • Requires treatment of access H_2O_2 due to potential for microbial growth
O_3/UV	• More efficient than O_3 or UV alone • Disinfectant • For equal oxidant concentration, more efficient at generating hydroxyl radical than $H2O_2$/UV	• Potential bromated by product • UV light penetration can be obstructed by turbidity • Compounds such as nitrate can interfere with the absorbance of UV light • Energy and cost intensive processes
H_2O_2/UV	• No potential formation of bromated compounds • Full scale drinking water treatment system exists	• Potential bromated by product • UV light penetration can be obstructed by turbidity • Compounds such as nitrate can interfere whit absorbance of UV light
Sonication	• Less heat transfer relative to UV system • No bromated formation if O_3 is not added	• No full scale application exists • Oxidant may be needed to improve the efficiency of the treatment, thereby increasing cost

So, if you see the advantages and disadvantages of various processes of course, some work at low PH some work at high PH then the how like the cost might be different, the control over this is different, okay some are more effective than others. So, these are actually a comparison we are not we are not going to go into the detail of this but this is kind of a comparative summary of these various advanced oxidation processes.

Whatever process we choose remember we are ultimately going to use OH radicals for oxidation purpose. Now, how this OH Radical works is going to produce that depends on the what process we are using and what are like we can then see that advantages and disadvantages of all these different processes.

(Refer Slide Time: 05:14)



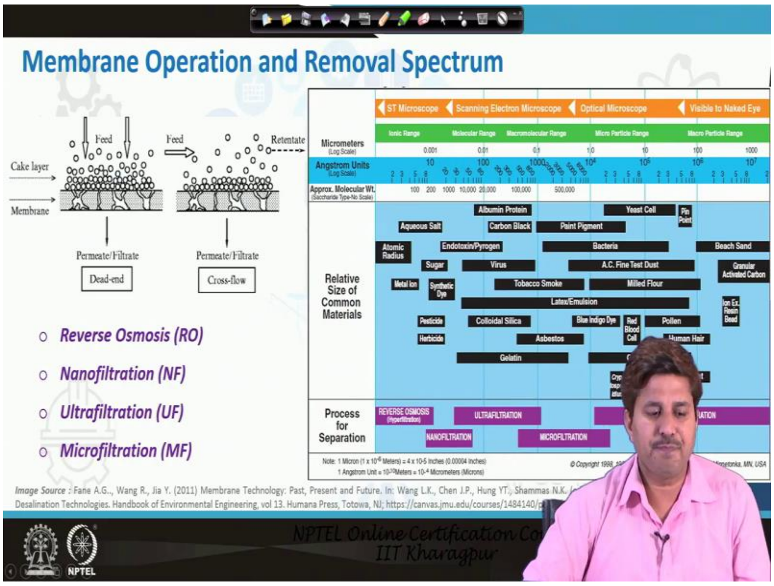
The other process which is by far considers the most advanced technology in water treatment are the membrane processes okay. These membrane processes is a selective barrier that permits the separation of certain species which basically can be either, only those compounds will not be treated which are size, which are of size finer than the membrane size, whatever membrane we are using okay.

Otherwise majority of them are removed by combination of sieving and diffusion mechanism. And this diffusion mechanism makes sure that even some smaller size particles then the membrane size are also removed. So, this membrane can separate almost like any impurity it can actually treat anything it can separate molecules over a wide particle size range, okay. These processes are being used increasingly in the production of pure water.

So, this is one of the way like these particularly the RO kind of units are getting more and more popular, for the production of pure water for drinking purpose, okay. These are very expensive but again advancing quickly to becoming less expensive and the performance is also being improved it is seen that way. So, the technology is simple you have a membrane you have basically feedwater one side and then there are say so contaminant particle and water particles.

So, water will penetrate through this membrane and this contaminant does not penetrate or does not pass through membrane, so they retain okay. So, depending on the size of the membrane we can see that the micro filter which can basically retain most of the bacteria particle ultra filter, which can retain the micro molecule viruses etcetera, nano filter, which can retain the divalent iron and RO in fact can retain almost anything even as low as monovalent iron. So, that the water we get is of very pure quality almost pure water we get okay.

(Refer Slide Time: 07:21)



If you see the; operate like the spectrum of the membrane removal, okay so as just we were saying, this is simple particulate filtration what we get through sedimentation and those things. So, they can filter up to a range of this is micrometer scale so up to a range of one micron then micro filtration which is up to a range of 0.1 micron okay. So, they can remove these as best as these two by cosmic pigment, some of the pigments and ultra filtration can removed gelatine, colloidal silica, virus, carbon, black albumin, protein.

These things can be removed up because the size is point zero one micron and or 100 angstrom range. Then, the nano filtration comes which is even finer than the ultra filtration of the range of around one nanometer okay so, they can remove majority of like pesticides, dyes, in these endotoxins compounds, colloidal this herbicides, sugar particles. So, all the divalent and those kind of iron and then even finer size is the reverse osmosis which can actually go to like even lower sizes and can remove the compounds like monovalent metal ions across all the atomic radius.

Everything can be filtered out through these processes. For application perspective, this is like, there are two approaches. There is one is the dead end filtration and then there is a cross-flow filtration regime. So, the cross-flow filtration regime is that the feed is provided here and it basically the filtration takes place not in the direction of feed through the basically cross flow. So, this is better inner terms like the contaminants present here and they will go as a lieutenant or kind of defuse materials.

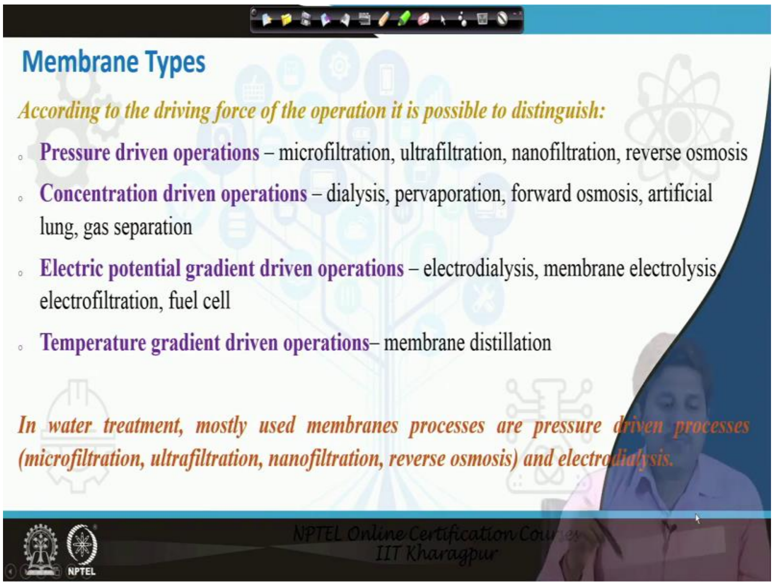
Whereas in the dead end it is basically feed is provided from the top and membrane is kept in between. So, if let's say you are having if this is my membrane and this is my feed direction this is my outlet okay so then, this is a dead end, because water has to pass through this some water comes here, but that is a contaminated stream. So, typically in membrane processes if you see okay so if this is my, if say, this is my membrane okay.

And I am allowing water to pass through this membrane so, the water which is basically comes out filtered through the membrane is known as permit or treated water okay which is water which has been treated. And the water which is not treated goes through as a concentrate or reject okay. This is known as concentrate or this is also people call it reject okay. So what these processes do the impurities that are present in the water will be filtered from this permit.

So permit will be basically contaminant free water and those contaminants are transferred to the concept to the water which is going as a concentrate. So, this concentrate water is in fact more polluted there, okay then the raw water. So, concentrate water will have higher level of contamination as opposed to the raw water which is basically being fed to the these membrane units okay. So, that is the written retentate or concentrate or whatever we call reject.

And in a cross flow module this direction of inflow is. this direction of permeate flow is this and the reject goes here. So, this is your cross flow module and in the dead end module as we said that the direction of feed is here and the direction of permeate is here okay. So, reject might go this way or might be collected separately. The major membranes which are used are in water treatment are the our own and of filtration ultra filtration and micro filtration kind of systems okay.

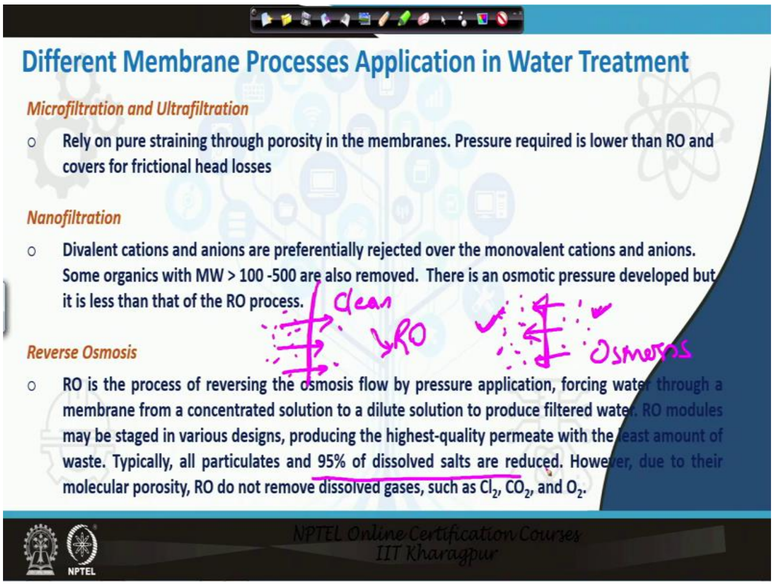
(Refer Slide Time: 11:34)



So, if you see these different membrane types we have pressure driven operations. So, the membrane which works with pressures microfiltration, ultrafiltration, nanofiltration, RO. There are concentration different operations, so dialysis or forward osmosis artificial these are not used in water treatment systems generally. Forward osmosis though is now being used as in a water treatment as well. Then electric potential gradient driven operations so electro dialysis membrane electrolysis okay these things.

And then, temperature gradient driven operations which is membrane distillation. So, in water treatment mostly like membrane processes, which are pressure driven are used, okay and electro dialysis is also used in water treatment systems though.

(Refer Slide Time: 12:22)



So, if you see the different membrane processes that are used in water treatment. so microfiltration and ultra filtration both rely on pure straining through porosity in the membrane. So, the like whatever the pore sizes they have the larger particles will be trapped and the water will pass through that okay. Pressure required is low because we will have just doing like pass through this.

And then, nano filtration where divalent cations and anions are preferably rejected over the monovalent cations and anions monovalent cations and anions can pass through this okay. Some organics of molecular weight in the range of 100 to 500 are also removed okay. These are also primarily works on the straining process okay. These also primarily rely on this training but there is some osmotic pressure developed but it is less than that of auto process.

So, it is not of like it does not impact much then auto process is different in a sense that it is not just this training process okay. The process is reversing the osmosis flow. So, like in a typical osmosis process what happens that if you have a semi permeable membrane say okay and you have a water like on both the side one side it is less contaminated and one side it is high contaminated.

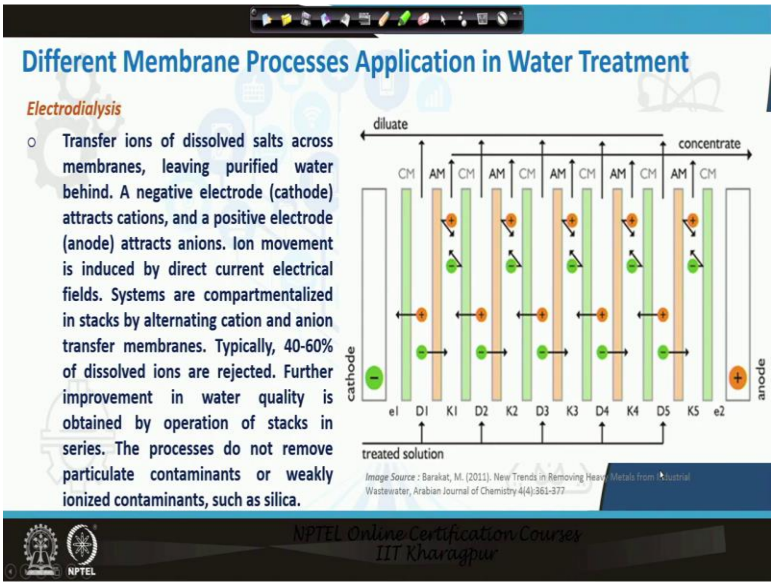
So, normally what happens that water from a high contaminant side to pass here in normal osmosis process okay so this is normal osmosis process. In order to maintain the concentration gradient equal on both sides, water will pass through this semi permeable membrane. This semi permeable membrane so it will not allow solute to pass so it actually water passes through here, so that this becomes diluted okay, sorry.

Water will actually pass through like if you have a semi permeable membrane here, there is a less solute and here there are more solute okay so water will pass from the less solute side to more solute side so that the you can get a dilution effect here okay in a osmosis process, you can get a dilution effect here and since water is passing here so this side will get more and more concentrated and this side will get more and more diluted till they come into an equilibrium.

So that is the osmosis process now what happens in a reverse osmosis process, you have contaminated part at one side and water with very less contaminant or say clean water at other side. So, in normal osmosis sense water will pass from here to here, but in reverse osmosis if we are talking about RO system so, in RO system water pass like through pressure we make the water pass from a more contaminated site to less contaminated site so that we get clean water here and contaminated water or reject water here.

So that is like we can remove around 95 percent of the dissolved salts this way. It does not work on the dissolved gases such as chlorine carbon dioxide and oxygen because of their molecular porosity. But all other kind of impurities may be removed through this auto process.

(Refer Slide Time: 15:47)



Now the electrodialysis is another type of membrane process okay so, what electro what happens in an electro dialysis, it is basically the transfer of ions that are present in the water. And how it happens let us say we are providing, we are feeding in solution here, so we are say feeding in solution here, now in this zone, we are having water present, okay. At one end we have cathode and at one end we have a node.

So cathode will attract the cations okay and anode will attract the anions. So, anions, all anions wherever it is there either this channel or say this channel wherever these are they will pass towards the anode side okay and cut and cations will pass towards the cathode side. Now we place the and selectively membranes, the membranes which can pass just one type of ion, in in a basically alternate sequence.

So here we have a cationic membrane and here we have anionic membrane. So, what will happen that because this is a cation and it is coming here. And this is a cationic membrane so it will allow cationic these cationic particles or cations to pass through. So, they will pass and come here. Similarly, these anions will pass and come here so what we get like cations move this way and I will move this way. And the water when comes out is free of these cations and anions so we get treated water here.

Now what happens in next channel, if you see in next channel there are like if you are feeding water there as well so, whatever water is here in next channel, these anions have moved here they have come here, okay. And similarly, from other channel the cations have come here so this is having anions and cations. Again now anions will like to enhance from here. We like to pass in this direction will be easily repelled from the cathode and attracted towards anode.

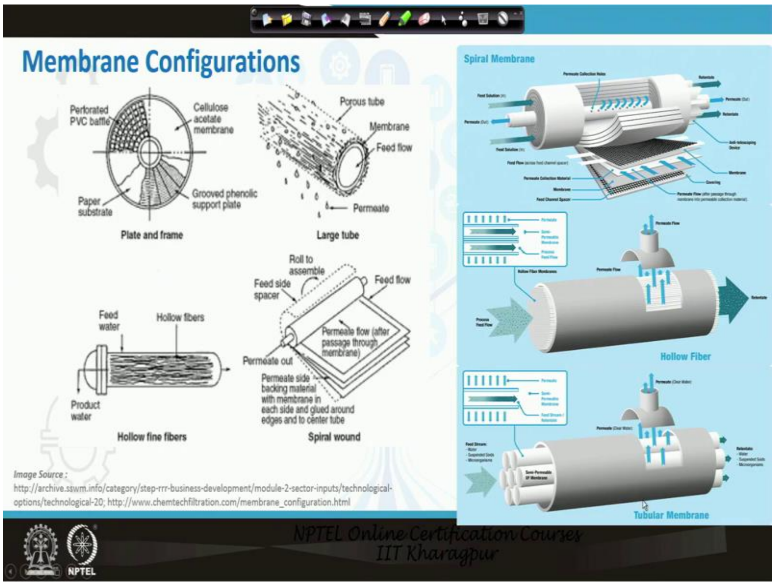
And cations will get repelled from the anode and attracted to cathode so the cations will like to move this way and anions would like to move this way. Now what happens because you have an anionic membrane here, it will not allow cation to pass through. The cation is willing to go this direction but it will not allow cation to pass through. So, it is going to remain here cation will not go this side because there is a repulsion of the anode.

So, it is going to remain in this channel itself. Similarly, for anions, the anions which has come in this, in this channel, will now like to go towards the anode. So, it will like to basically go this side, but there is a cationic membrane which will not allow anion to pass through. So, since the cationic membrane is not allowing anion to pass through so, they will again come in this channel and they cannot go this side although there is an ionic membrane but they cannot go this side because there is a cathode which is repelling them.

So cathode is not allowing them to come this side and this membrane is not allowing them to come to that side. So, they remain in this channel in bit in the middle channel itself. And they go as a concentrate okay whereas so this way, like in each alternate channel, whatever like ,we will see that in each alternate channel we get the treated water. So, this will have a treated water, this will have a treated water, this will have a treated water, which is can be collected together.

And this will have concentrated water these alternate channels will have concentrated water which will be basically collected together. So, typically 40 to 60% of dissolved ions are rejected and in if you want to improve the performance we can actually like do these process in series. So, we can operation the we can achieve the operation by stacking such units in the series, so that everything is removed okay.

(Refer Slide Time: 19:46)



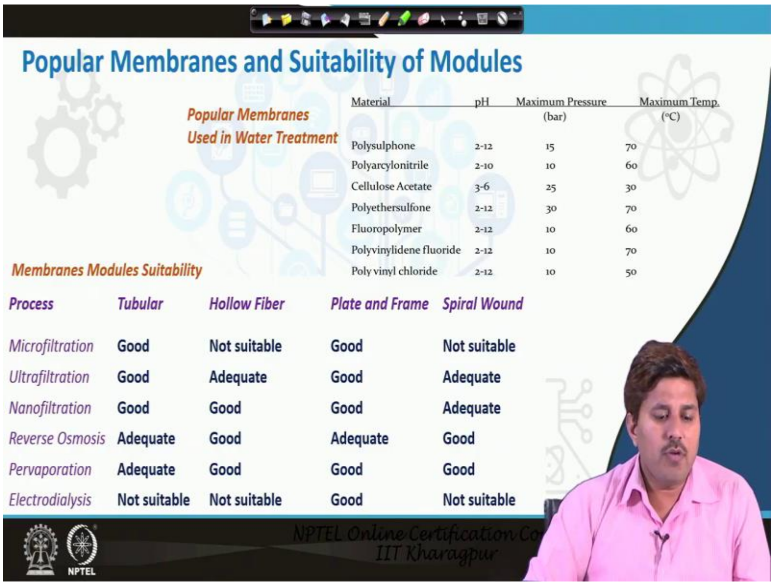
Weakly ionized contaminants like silica and those things are not removed through electro dialysis process. So, these membranes come in at different configurations okay, if you see the particularly, the like high-end RO membrane or these membranes, so there are like spiral-bound membranes so they will be bound in this and in between you have a membrane so water passes through this then permit is water is passes feed through these feed channel okay.

And then, it is basically it will be going through these pores and through these holes and the permit will be collected. So, this is basically a spiral-bound membrane. There are tubular flow membranes okay which is again water is passed in the tubes and then these tubes are having this semi permeable membrane. So, this is basically a membrane so water coming out of the tubes will be connect collected as a permit and whereas water that comes towards this side in the tube are reject.

We may have a hollow fiber membrane again very fine tubes very like several tubes, again these tubes are also having made of the, made of the membrane material. So, whatever permits comes through these is flow and whatever comes through this here is reject. So, that way we can have several membranes. All these are cross flow membranes. So, cross flow membranes are more popular because and particularly with high end like nano filtration or RO processes because reject pass away is easily.

But if you are having a dead end membrane so then, water has to pass through this and then reject passing becomes difficult. So, cross flow a membrane that is why are considered far more like they are more applicable in there.

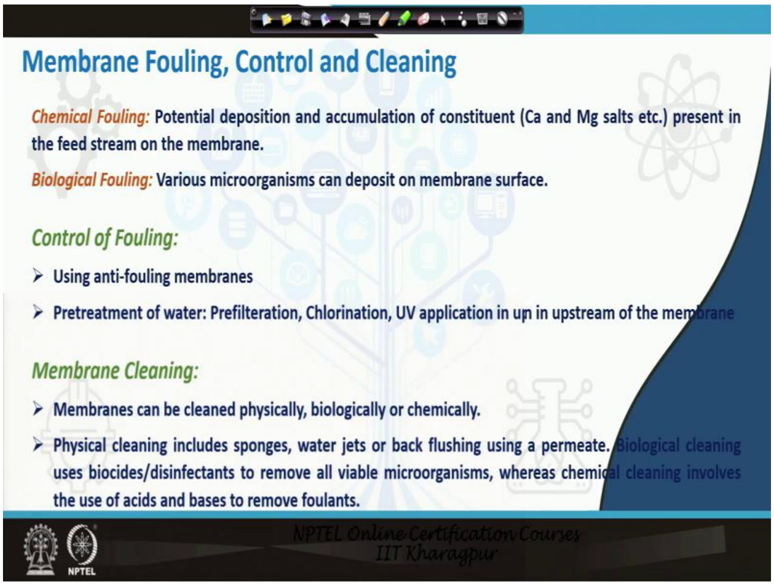
(Refer Slide Time: 21:33)



So, membrane modules and if you see like for microfiltration, ultrafiltration, nanofiltration, these different membrane models, tubular hollow fiber plate and frame spiral bone so which are good so far like reverse osmosis if you see the hollow fiber is very good okay. And this spiral bond is very good whereas these tubular and these are adequate okay. For electro dialysis tubular membranes or spiral bond membranes or hollow fibers are not suitable.

Plate and frame type of membranes are suitable because we have to place them as a form of plate okay. So that is why we have to control from other side so that that kind of adjustment is needed. For nano filtration almost all are good okay. This parallel wound is just adequate but other way these are some of the popular membrane material, they are working pH range pressure range and temperature ranges.They are so these are like the popular materials which are used for the membrane processes.

(Refer Slide Time: 22:34)



Then the membrane operation leads to the basically falling of the membrane because the contaminant is getting retained on the membrane. So, progressively there is potential deposition and accumulation of these constituents, Calcium and magnesium salts particularly if you are treating water so these present in the feed stream they will get deposited on the membrane okay.

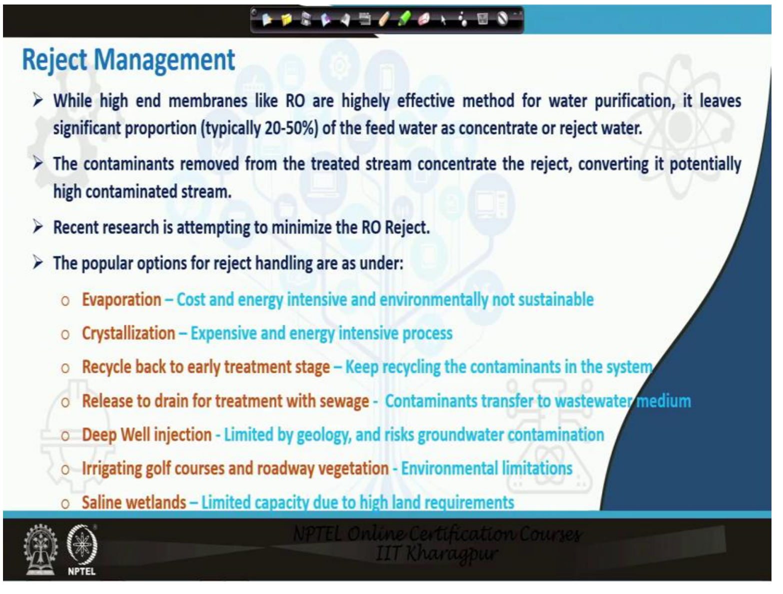
The biological falling also there so if there are microorganisms they can also deposit on the membrane surface so that if like that way, we can say whether falling is of chemical nature if it is by the chemical agents or if microorganism has deposited, so we call that as a bio falling or biological falling. Now, we can control this falling by two approaches one is we provide adequate pre-treatment okay we provide adequate pre-treatment like filtration chlorination, UV application, okay or in-stream.

So, before water fed to the member to the membrane system we provide certain pretreatment applications either pre filtration or chlorination so that the microbes are killed or inactivated so that they cannot proliferate on the membrane surface all those like UV applications. So, these kind of processes helps in controlling the falling process, specifically, biofalling process. There are some NT falling membranes which are being discovered okay this this is an still under R&D, so we can use anti falling membranes for the purpose of for the kind of purpose of controlling the falling.

So these membranes have a nature that they get self clean, okay they do not get fall easily. So, we can use either NT falling membrane or we can adopt pretreatment or a combination or both if membrane has found. So, we need to clean that and for cleaning purpose then we can clean it physically biologically or chemically. So, membrane cleaning process includes like we can use spawns or water jets or back flushing using a permit for physical cleaning.

Biological cleaning is we use bio sites or disinfectant to remove all viable microorganisms present in the membrane and then again use physical cleaning to clear them out or clean that out. And chemical cleaning also involves the use of acid and bases to remove the whatever chemical fallen that has been creating problem on the membranes.

(Refer Slide Time: 25:14)



So, these are about the like falling control then the other issue is the reject that comes out of these membranes so while high end membranes like ro are highly effective for water purification. But like as we go high so they produce more reject also. The reject coming out of a nano filtration module or ultra filtration module will be much lesser as opposed to reject coming out of the RO module.

So, RO membranes typically like produce significant portion typically in the range of 20 to 50 percent. Nowadays in fact some membranes are coming which claim to be very efficient in that way that they can convert ninety percent of water to permit and only ten percent or some even claim less than 10 percent reject. But generally majority of the membrane rejects almost twenty to fifty percent of the feed water okay that comes as a reject water.

Now the contaminant removed from the treated stream, as we discussed earlier, goes into the reject and that is why the reject is potentially more contaminated than the influent stream itself okay. There is lot of research going on in attempting to minimizing this RO reject. The major options that are taken for reject handling as of now are the evaporation so the reject water is evaporated so that salt is retained and water evaporates.

But this is again a cost and energy intensive process and environmentally not sustainable because a lot of heat and then carbon footprint is there associated with the evaporation process. Crystallization is another option where but again it is a very expensive and energy intensive process where we try to crystallize the solids present in the concentrate. Ah There is option that we recycle back to the early stage treatment, okay so that that is again commonly used.

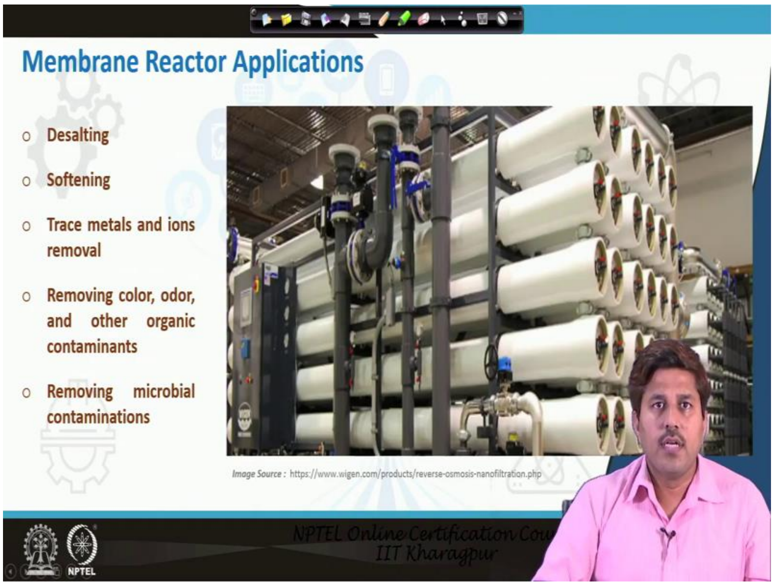
But if we keep on recycling the contaminant then the actually the contaminant is still in the system. We are not allowing contaminant to leave the system so eventually it is going to increase the concentration and decrease the effect of the successive units okay. So that is another issue. But it still it is by far like very popular in the water treatment systems. Then release to drain for the treatment with the sewage in many places like the RO treated water is collected and then reject is just drained.

So fewer networks it reaches through the sewage treatment facility. Deep well injection is another option. But again it is limited by the geology and risk of groundwater contamination is also there. So if we inject it into the deeper wells so, whatever the contaminant is coming they may pollute groundwater contamination and injecting them into the groundwater like what kind of like profiles, well profile or subsurface profile we have, that will also govern the deep well injection process.

Then, option is irrigating, golf course roadways vegetation, this kinds of things. Again there are environmental limitations to this because the water is not pure it is a contaminated water. Of course it can be used for normal irrigation in these things. But if there are like salt concentration is high eventually it might turn the places infertile okay. So, that is another problem. It can be taken to the saline wetlands. Again the capacity of these is limited because there will be lot of land requirement for creating a wetland.

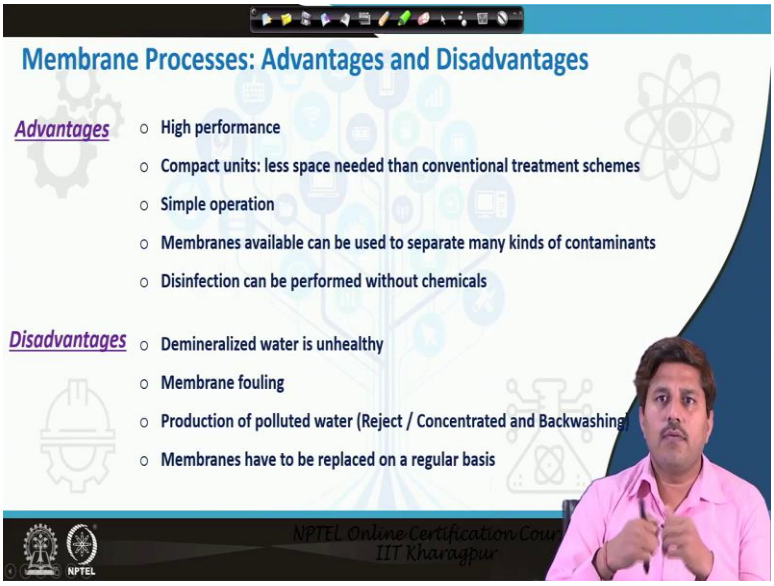
So these they like there are multiple options, but all options have their own limitations. And that is one of the problems like, still people are trying to opt or to device the methods for better reject management.

(Refer Slide Time: 29:06)



The applications of the membrane systems are for desalting, for softening purpose, for the trace metal and ion removal, removal of color order, other organic compound, removal of microbial contaminants. So, as we just discussed, RO is practically can remove any sort of contaminant okay and that is why like it is by far the most popular most safe treatment method which is usually recognized worldwide okay.

(Refer Slide Time: 29:30)



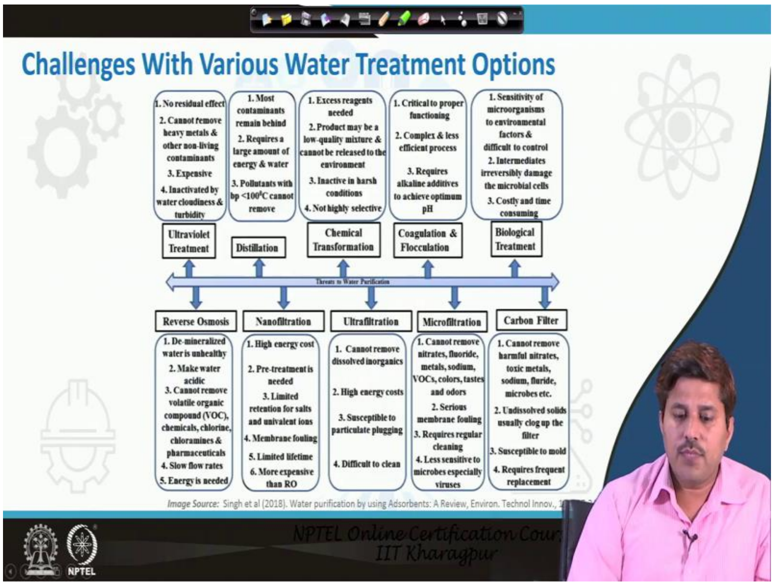
Again there are advantages and disadvantages associated with these membrane processes. The advantage is that performance is very good. They are generally compact unit so they need very less space as opposed to the conventional treatment systems. The operation is simple the membrane available can be used to kind of separate any kind of contaminant. Disinfection can also be achieved without chemical.

On the flip side the major one of the very major problem is that particularly with the RO system is that it kinds of remove the essential nutrients also from the water. So, the demineralized water or water treated from RO is not considered healthy and this is actually like the scientific community is now focusing on this, this is becoming one of the very basic problems that the essential nutrients that are present in the drinking water are removed through the RO process.

So it is not a healthy water for drinking purpose. We get some nutrient supplement through the drinking water and if those nutrients are removed through these RO or high end treatments so then there are health effect associated with that okay and people are facing severe health effects because of relying on the RO water which is devoid of the basic nutrients. The other disadvantages as we discussed is membrane falling.

It produces the polluted water in form of reject or concentrate and these kind of have to be replaced on a regular basis. Their whatever their life cycle is again the different process has different life cycles though.

(Refer Slide Time: 31:15)



So with this we conclude the discussion. These are the challenges of various water treatment options so, we have already discussed while discussing each of them individually. So what are the issues with ultraviolet distillation, then cognition flocculation process, carbon filter, and then, various other membrane processes. So, with this we conclude this class. We practically conclude the discussions also for this week.

And we have discussed so far the abstraction of water, the then like through intake systems estimation of the demand and know how much water is to be abstracted and then how we abstract that water through water intake, we discussed about the intermediate storage systems as well and then, we discussed about the treatment systems in last two three weeks. So, these are the like major treatment options which are used.

Of course, there are a few more techniques that are being developed recent techniques that are coming into the market. But these are by far the most common and like most known techniques for treatment of drinking water okay. The research and innovation is still on. So, we might see like more, more and more techniques coming into the market or the amended or improved systems like the the demerits of several of these techniques like the RO and those things we were discussing might actually get handled in a better way in the due course of time. So thank you for joining and see you for the next classes.