

# Interfacial Engineering

Dr Manigandan S.

Department Chemical Engineering

Indian Institute of Technology, Ropar

## Lecture-18

### Micellar-enhanced ultrafiltration (MEUF): A surfactant-based separation technique

#### Micellar enhanced ultrafiltration (MEUF); contaminants removal; selection criteria

Welcome back! In today's video lecture, we will cover the applications of surfactants. We will see how the critical micellar concentration (CMC) and the ability of surfactants to form micelles can be used in various applications.

One such application we will explore is micellar-enhanced ultrafiltration. We will take an example of treating wastewater containing pharmaceutical and personal care residues or contaminants.

Timestamp: 1.25mins

Micellar-enhanced ultrafiltration (MEUF): A surfactant-based separation technique

Pharmaceutical and personal care products removal from water

MEUF process depends on surfactant type, CMC, and size of micelles.

✓ Above the CMC, monomers spontaneously aggregate into micelles whose size is in the same order as the pore size of UF membranes.

M. Schwarze, Environ. Sci.: Water Res. Technol., 2017, 3, 598–624

6:50 / 23:07

Scroll for details

Interfacial Engineering

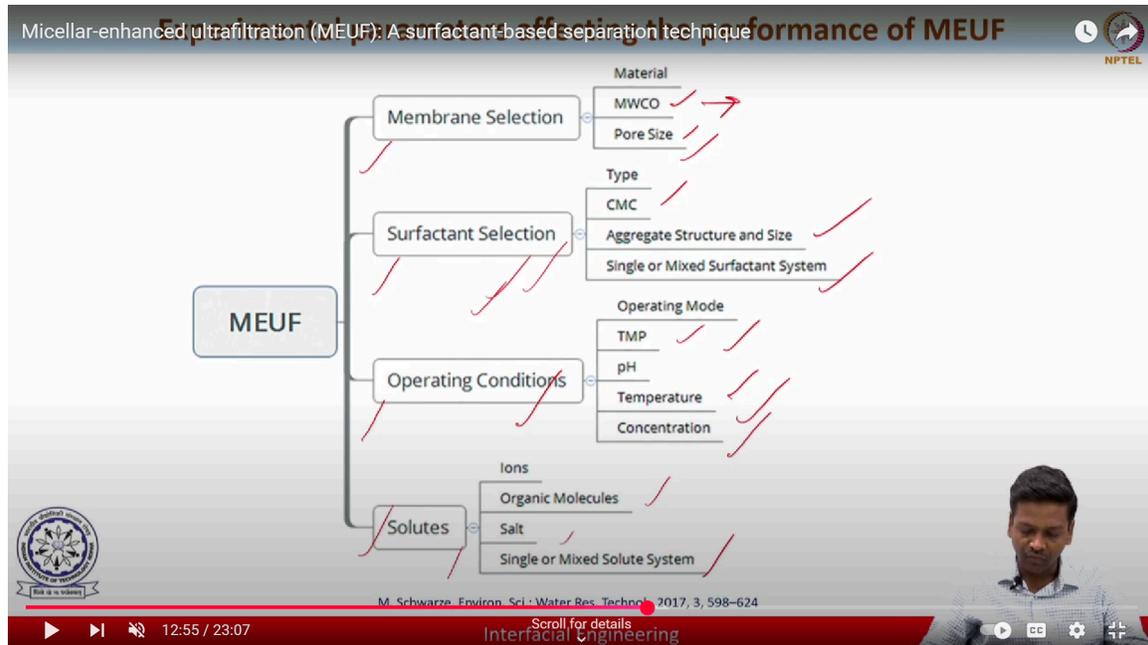
Let's begin. As we just described in today's video lecture, we are going to look at pharmaceutical and personal care products. So removal of these products from the wastewater stream. So we are going to use the ability to form micelles, the surfactant's ability to form micelles. That is going to be the key point for us to look at in today's lecture. So let's start with the let's say you want to remove the pharmaceutical and personal care products from the water. So we will have to choose the right surfactant. So, we know that whenever we add surfactant to the solution, so because there are, it has got hydrophobic and hydrophilic parts, the hydrophobic moieties or the hydrophobic parts would want to minimize their contact with the water. So they will self-assemble to form micelles in such a way that they will minimize their contact with water. So one such example is a spherical micelles. When they form, when they self-assemble to form spherical micelles, they will be arranged in this fashion, right? When they are arranged in this fashion, they leave the hydrophobic core or the oil core in which the organic matter, impurities, oil oil-soluble impurities are trapped.

So that is going to be the advantage of this structure okay so we'll start with the let's say if we want to remove the pharmaceutical and personal care product we will have to consider that we have the wastewater containing the target pollutants or the solute molecules then what we have to do we have to add surfactant of decide surfactant so depending on the which products that you want to remove sometime you may choose depending on the ionic you know target contaminants sometime non-ionic target contaminants. Let us say we choose the surfactant you know that you will remove the pharmaceutical and personal care products via the two micelles right so when they form micelles they will interrupt these organic solutes at you know the core hydrophobic core right so these are the solute molecules that we are talking about so when you add sufficient quantity of surfactant let's say above CMC they will form these micelles right so that is idea. Now after this, you will have some free monomers that are not you know taking which are not participating in this entrapment process and you will also have free organic you know solutes right? So, the next step that we have to employ is the ultrafiltration unit. So, this will contain pore size in the nano range, right? So that when you employ them, when this micelle loaded the water stream, the aqua stream passes through this ultrafiltration unit, the free monomer and the solid will you know will come out of this membrane as a permeate whereas the micelles and the entrapped right you know the solid molecules right the micelles solid molecules entrapped within the micelles will be collected as retentate right so you got two streams in this so in this way you can collect or remove the free solute and the free monomer but the important problem for us will be how to deal with this one because you want to remove the solute molecules but we also added another component in this problem, that is the surfactant molecules. So if

we cannot remove the surfactant and solute from the micelles, the process will become a costly affair because you would not be able to reuse the surfactant molecules.

So ideally we need to recover the surfactant and once again it has to be reused only then the process will be economical. So, for that what one has to do is what we are going to look at as we move further right.

Timestamp: 6.55mins



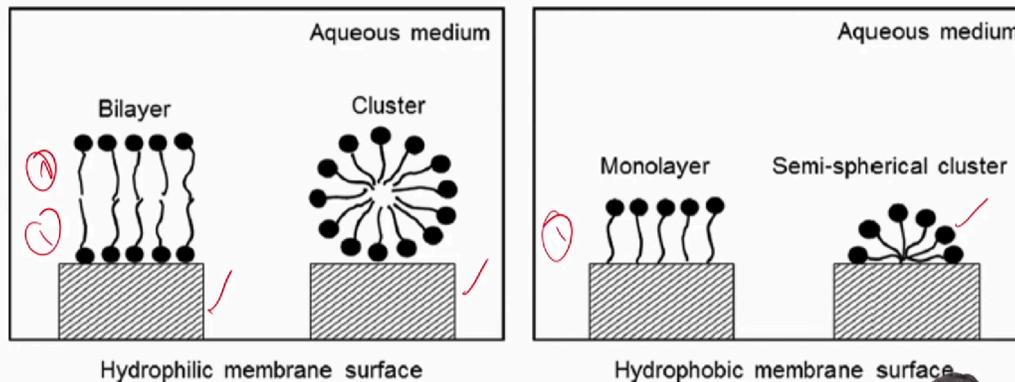
So next is going to be, we can explain before we explain the technique to separate the surfactant from the, you know, the contaminants, target contaminants, we will first look at the various experimental parameters affecting the performance of this membrane, right, this process. So, there are several key parameters that we need to keep in mind. One is the membrane selection, surfactant selection, operating condition, and different types of solute molecules that we are dealing with. When we talk about membrane selection, the material of construction, the material of, I mean, using which membranes are made upright that is very important for example there are two parameters that one has to look at you know very critically the molecular weight cutoff right so molecular weight cutoff is related to the pore size distribution and retention capability and then the pore size so what is the pore size of the membrane that we deal with for example the pore size should not be such that it is you know the larger than the size of the micelles right themselves so what will happen is in such case micelles also will be passing through the membrane so one has to choose the right pore size and molecular weight cut off. So, the general rule of thumb I mean general thumb rule is that the molecular weight cut-off should be at least

three times smaller than the molecular weight of the solute that we are dealing with. Next comes the surfactant solution here as you know CMC plays a very crucial role so generally we should choose a surfactant for which the CMC is minimal right at minimal so that you don't end up consuming too much surfactant right say for example if you choose a surfactant for which the CMC is you know on the higher side which means that you have to use a lot of quantities right for the operation so that will lead to a costlier affair. One has to uh choose the right surfactant which has very low CMC so that economically the process will be viable. The second point to cover is the aggregate structure and size. So what is the size of the micelles that we are dealing with? The size should be a little larger than the pore size that we are dealing with. So, one has to choose accordingly, and the next point that we should uh you know worry about is whether to use the single or mixed surfactant system sometimes using co-surfactant will be economical because the efficiency of the process may be better when we operate with the mixed surfactant system. So, these are various guidelines when you want to choose the surfactant solution. Next comes the operating conditions.

So, what is the TMP trans membrane pressure it is going to be the driving force of the membrane so one has to choose the TMP accordingly pH. So, sometimes pH is going to be very crucial in addition to temperature and concentration because when you want to remove the ionic impurities we might employ the ionic surfactant, in this situation when you lower the pH probably we will generate a lot of protons around the micelles which will help us keep the cations away from the micelles you know naturally so that it is easier for us to separate the cations from the micelles. So, in such case, pH will be a very crucial parameter of temperature you know if you want to operate above or below the Krafft point or third point controlling temperature will be a very you know crucial aspect than the concentration because one has to work around the CMC critical micellar concentration and you cannot I mean one should also vary of using the concentration because if you use too much of concentration also, probably the solution becomes more viscous. So, it will end up, you know, you might end up, you know, there will be more pumping costs, right? So that will become a costlier affair. So that's why one has to choose the right operating conditions for the process that we are, you know, talking about. Then comes the solutes here. Whether you are going to remove the ions or organic molecules, okay, or sometimes heavy metals in the form of salt, right, or the singular mixed solute system, whether you are going to target only one particular type of pollutant or multiple pollutants. So, these are various questions that one should ask before, you know, any application, right?

Timestamp: 12.55 mins

## Surfactant adsorption on hydrophilic and hydrophobic membrane surfaces



M. Schwarze, Environ. Sci.: Water Res. Technol., 2017, 3, 598–624

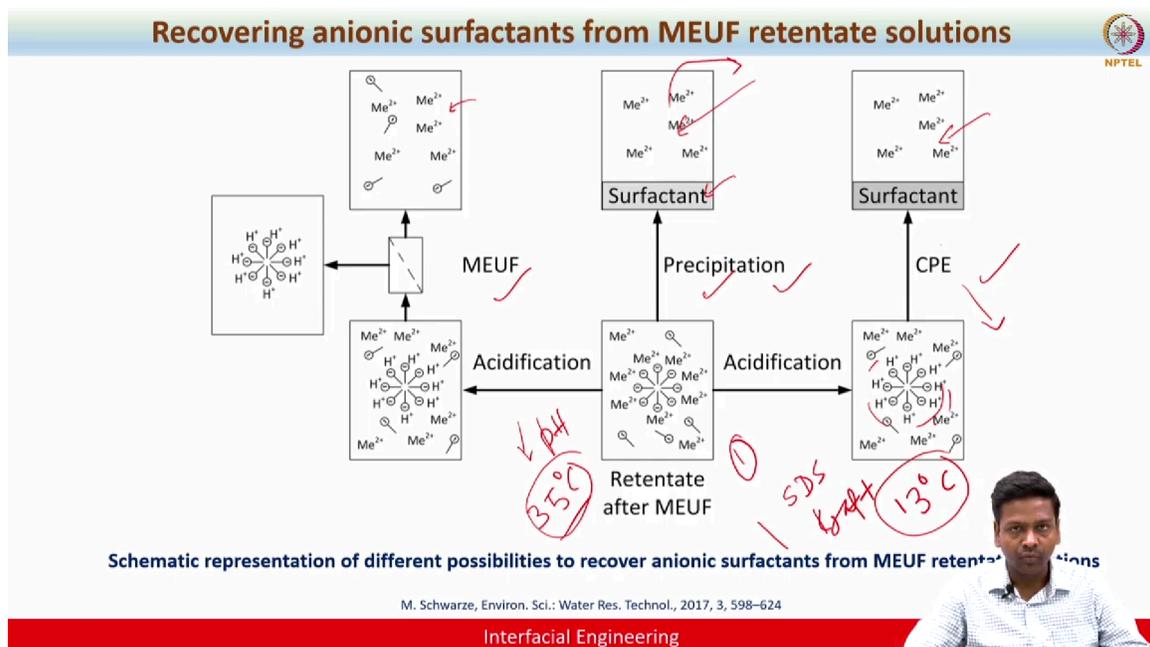
Interfacial Engineering

So, we will look at another mechanism through which the membrane clogging will take place. So, this is a very important aspect. So, before we look at the strategy that we will use to recover the surfactant we will have to also understand the mechanism through which the clogging of the membrane takes place. So, let's say we deal with two kinds of membrane one could be a hydrophilic membrane another type of membrane that we may often deal with is a hydrophobic membrane in the case of a hydrophilic membrane let's say the membrane that we use sometimes is functionalized membrane. To make the surface hydrophilic so surfactant sometimes you know some surfactant that we use often you know because it has got a head group and tail group head group carries some charge you know on it so there can be a hydrogen bonding between the head group and the surface of the membrane itself so you can expect the monolayer of the surfactant you know formation on the membrane surface as well as the monolayer forms because the tail is hydrophobic it can attract another layer okay of surfactant through hydrophobic attraction interaction between two tail groups. In this way, you can expect a bilayer formation on the membrane but there will be no further growth on this because between head groups there will be electrostatic repulsion so most likely there will be no growth further.

The favorable arrangement will be a binary arrangement on the membrane surface so in this way you can expect that the surface of the membrane will be clogged, which will hinder the process of transport this is one mechanism the other mechanism is it can also be sometimes clustered so micelles can also get attached to the surface through the hydrogen bonding so in this way you can expect the hindrance. The other way of hindrance is when you deal with the hydrophobic membrane surface, you will have the

surface share the hydrophobic interaction with the tail groups of the surfactants so in this way you will expect the monolayer formation on the surface but there will be no further layer above this monolayer because the head groups will experience electrostatic repulsion so there will be no you know attraction or between the head group as well as head to tail group because so it will not you know share great affinity between the head group and then the tail group or between the head groups. So you would expect a more layer formation on the surface and the other way could be a semi-spherical cluster as soon as the surfactant self-assembled to form micelles before even the complete process of micelles takes place because these tail groups are hydrophobic, they can get attracted to the membrane surface so in this way also you can expect you know the hindrance you know to happen so in various in this where these mechanisms the membrane surface get clogged you know from time to time so these are something that we should understand before we deal with the treatment process right.

Timestamp: 17.09mins



Here, we will look at recovering the anionic surfactants from micellar-enhanced ultrafiltration. We talked about you know we were here actually; we'll start from here there are three ways you can perform the recovery. Here in this example, we have taken the ionic you know surfactant and the ionic pollutants this example is not given for the micellar enhanced but the same strategy can be applied you know even for the case of the micellar enhanced separation. Now our starting point is going to be this one so let's say we have got the ionic surfactant so micelles are based upon I mean micelles are formed due to the self-assembly of the let's say anionic surfactant and we can take an example of SDS, in this case, okay and around it you can see the cationic pollutants or cationic

impurities okay so it can be any cationic pollutants so then you will see that when you perform the acidification which means that when you lower the pH right of the solution basically what will happen is it will generate a lot of protons, when a lot of when protons are generated around the micelles naturally these cations will be detached from the micelle because this proton will ripple cationic impurities because they share electrostatic repulsion between the two, right? So, if we employ, you know, the ultrafiltration again, you will be able to, you know, separate the micelles and the free monomer and the free cationic impurities. The disadvantage of this method is like, you know, high pumping cost here. At the same time, you will also have to you know, end up with the free monomers, free surfactant molecules along with the cationic impurities. So, this might again, you know, lead to some, add to, you know, further operating cost, right? So the other method is based on the precipitation. Here what we will do is we do SDS.

The Krafft point of the SDS is going to be 13 degrees Celsius. Whereas the Krafft point of the entire unit which is SDS combined with the cationic impurities is something let's say 35 degrees Celsius so these examples I am just giving for you to understand better. These values are taken from the literature right so data you, actually you can follow these data so that you can understand this mechanism and a little bit more in detail right so let's say we have we start from here now what we will do we know the Krafft point of the SDS which is 13 degree Celsius and the Krafft point of this entire unit is 35 degree Celsius. If I lower the temperature such that it falls below the solubility of the surfactant. Now what will happen is surfactants settle at the bottom naturally they will precipitate out from the solution what you will have been in the true solution, you will have the free ions alone so it is very easy to separate these free ions from the mixture. Last but not least is going to be the cloud point extraction method in this case what one has to do is from here you have to perform the acidification again which means that you have to lower the pH so that protons will be generated right around the micelles which will keep the cations away from the micelles right then by operating the temperature such that you are above the cloud point. So, what will happen in this mechanism is surfactant will phase separately from the two solutions and what we will have in the mixture in the solution will be just the free cationic ions. In this way it is easy for us to separate surfactant from the cationic impurities and this surfactant can be again fed used reutilized for the removal of the application of you know treatment wastewater treatment containing pharmaceuticals in healthcare products. The same strategy can also be used for the micellar-enhanced process okay so I think you know it would have given a good insight into the recovering of the anionic surfactants in this example. We will stop here we will continue from the next lecture

Thank you