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Introduction: Opportunities and Challenges of Real Time Monitoring on Membrane Processes

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1.1

Introduction

Membrane technology applications today focus considerable interest on the continuous performance of a membrane. It is well known that fouling reduces the flux and changes the retention properties of membranes, which makes the process less economic. Characterization of protein fouling has been reviewed by Chan and Chen [1], Chen et al. [2, 3]. The goal would be a non-fouling process with a steady flux and retention.

The possible tools today to make this come true are: cleaning the membrane and running the process at constant flux; and, in order to avoid fouling, running at a subcritical flux [4]. To find the best long-term conditions some online monitoring is needed. It has been noticed that in many discussions with industry one of the most important items on their “wish list” is to monitor the membrane process and characterize the membrane, possibly on-/inline.

The membrane properties of interest would be: flux, retention (pore size and distribution), charge, wearing, pinholes, fouling and hydrophilicity, just to mention a few. Membrane stability during the process would contribute to a sustainable process. The best monitoring processes would be in real time, non-invasive, in situ/in vivo, at a molecular scale and using pattern recognition approaches.

1.1.1

Monitoring from Permeate and Concentrate Properties

Of the properties mentioned above, flux may be the easiest to monitor continuously. The monitoring could be done online by having a measurement device that could be connected to any membrane element. This device could also contain information on whether the flux is within acceptable limits or whether the module should go for cleaning. This type of device could also detect too high a flux and

thus maybe any wear or pinholes in the membrane. In the long run, too frequent cleaning does not increase the sustainability of a membrane.

One of the most difficult characteristics to handle is retention. In cases where the pore is much smaller than the retained molecules (ultrafiltration, UF; or microfiltration, MF,) the problem is not so delicate, but when the question comes to nanofiltration (NF), passage through the membrane can very easily be destroyed by a foulant (for instance calcium sulfate), making the fractionation in question impossible. The typical causes of changes in retention are fouling or other modifications of the membrane.

The cut-off of the membrane can be monitored with a standardized procedure, as developed in the FP4 CHARMME project for UF and NF and modified in the FP6 NanoMemPro project. Monitoring online faces the problem that the module in most cases should be taken out of use during the time needed for measurement. This could of course be done in connection with the cleaning of the module. Another way is to use tracers which could be analyzed from the normal permeate [5].

The following introduces the main methods available, online or not; and then they are further studied in the separate chapters of this book.

1.2

Microscopic Techniques in Membrane Characterization

In most microscopic techniques, characterization has to be done on dried samples and thus an online study is not possible. Normal *optical microscopy* might be done by direct observation if the sample of the membrane has big pores through which one can look at (for instance) fouling [6], using a camera (see Chapter 2). In this case you can only distinguish particles which are around a micrometer or larger. The method can be used to study bacterial or particle fouling or when looking at bubbles in the feed. With *confocal microscopy* (see Chapters 4 and 7) one can also look at the membrane in situ without having to dry it, since characterization can be performed on wet samples.

Multi-photon microscopy for in situ characterization is a fluorescence laser scanning technique (see Chapter 8). This technique can produce 3D images, which can be stacked to get time series for different interesting phenomena in UF and MF. Fouling inset can be characterized and thus also the critical flux can be measured. Fouling of membranes, especially by proteins, has been studied with this technique. Because the target substance needs to be fluorescent, not all kinds of filtration processes can be monitored in this way.

When attempting to see membrane structures below one micrometer the possible microscopic techniques are *electron microscopy* (EM), which can be supplied by an additional *elemental scanning* (EDS) device (see Chapter 3). In this case and also in *transmission electron microscopy* (TEM) [7] the samples need to be dry. It is often quite difficult to study polymer membranes with these microscopic techniques because the densities of most materials are the same. Therefore, marker systems should be used like radioactive tracers, fluorescent staining or dendrimeric staining. Today, in *environmental scanning electron microscopy* (ESEM) one can work also with wet samples.

Atomic force microscopy (AFM) is a technique where, in principle, you can also look at samples under water, but the images are usually sharper when done on dry samples. AFM is mostly used for UF membranes to look at pore size, but according to Bowen (see Chapter 6) one can actually see nanopores using AFM. When using AFM it is also possible to make scans on pore size distribution and on the roughness of samples [8]. Both of these characteristics would be important for online measurements because both fouling and wear of membranes could be observed as a function of time, which is of great value in industrial applications. Using AFM equipment, characterization of membranes used in gas separation processes can be performed (see Chapter 5) and also charge analysis of the surface can be made using its force balance analysis scheme, where repulsion or attraction between the tip of the instrument and the membrane can be analyzed and pictured as functions of interaction distance (see Chapter 6).

One of the new techniques to scan membranes and determine pore size distributions is *positron annihilation spectroscopy* (PAS). With this method also the free spaces in nanofiltration membranes can be determined. For instance in a study by Boussu et al. [9] it was found that some much-studied NF membranes (like Desal-5 DL, NTR7450) have two sizes of spaces, one size about 0.12–0.15 nm and the other between 3 nm and 4 nm. It could be speculated that diffusive transport would happen through the smaller spaces (the size of a water molecule), depending on the hydrophilicity properties of the membrane, and convective transport through the larger spaces, depending on size and charge conditions.

1.3

Electrical, Laser, Magnetic and Acoustic Techniques in Membrane or Membrane Process Characterization

The methods using electrodes to register phenomena on membrane surfaces may be the ones that are already available online or could very easily be adapted to an online situation (see Chapter 9). One of the already available techniques measures *streaming potential* (SP) online through the pores of the membrane. From the streaming potential the zeta potential can be calculated [10–12]. The measurement can be done both during pure water flux experiments and during fouling or cleaning. The result shows changes on the surfaces of the pores during the process. Nanofiltration membranes are better characterized for charge with SP measurements along the surface. Today these measurements are not yet well adapted for online measurements, but commercial devices are available for SP measurements along the membrane surface and it is most probable that it would not be very difficult to build them into a running process. It is important to notice that the charge on the pores within the membrane is not always equal to the charge on the membrane surface. A very good example of that is the track-edged membrane [13].

Another electrical measurement available is the *membrane potential* (MP) measurement [12, 14], which tells about the charge inside the membrane. MP

measurements are still very tedious and will probably not be available online yet. *Impedance* measurements can also be made showing fouling, or different membrane layers (see Chapter 9) [15].

X-ray photon spectroscopy (XPS) is a technique which has been available for a long time. It needs dry samples, but is especially good for characterization of the top layers of membranes. Today, a new technique, *X-ray tomography* can be applied for 3D characterization of membranes (see Chapter 10). The tomography technique is very challenging for visualizing pore structures and fouling because, in the 3D mode, one can feel like a molecule passing from feed to permeate and realize the obstacles in the way.

New ways to build microelectrodes have made it possible to “implant” electrodes inside the membrane or on both sides of it. This makes measurements using *acoustics* possible (see Chapter 11) [16]. The acoustic waves can give a wave pattern that differentiates a clean membrane from a fouled membrane because the fouling spots can be identified as a new resistance. In a similar way cleaning can be studied as the removal of these resistive spots. The electrodes can be placed in such a way or be part of the membrane so that also membrane pore size could be measured or (at least with the techniques available today) pinholes could be found. Measurements made with acoustics seem to be very promising online measurements.

Ultrasonic treatments also belong to the acoustic methods. Already, for more than ten years ultrasound has been used for the cleaning of membranes. In most cases the transducers have been situated outside the membrane, but the membrane has sometimes also been used as the transducer. Of crucial importance are the frequency of the waves and the way the waves have been applied (see Chapter 11). The method has mostly been used to prevent the build-up of a concentration polarization layer. Polarization of dense particles has been easier to prevent than fouling or polarization of small particles [17, 18].

The ultrasound technique today can also be put up in 3D so that a fouling pattern of the membrane can be visualized continually and modeled through different statistical programs. This method is called *ultrasonic time domain reflectometry* and can be used for fouling and cleaning in situ (see Chapter 15). The system can also be used to study infrasonic sound (1–20 Hz) as waves in the study of flux characteristics like pulsing.

Ultrasound can also be used to enhance chemical processes, for instance instead of UV; or transducers and sensors can be used together for different kinds of processes. The ideal future state would be implanting micro-electrodes in the membrane and visualizing the state of the membrane and its expected life-time. Problems could arise to keep the transducers/sensors clean.

1.4 Process Oriented Monitoring Techniques

The methods mentioned above for characterization all involve some kind of process aspect as the membranes, virgin or fouled, are to be used in some process.

How well the process has been running can thus be distinguished by the use of methods characterizing the membrane itself. Another way to monitor the process is to use markers and sensors to measure (besides fouling) the permeate flux of compounds of interest.

The first markers to be used were radioactive markers, especially tritium or isotopic iodide-labeled proteins. The problems with this kind of markers were that radioactivity was not generally allowed to be used in experiments. Thus in order for a marker to be accepted it would have to be neither toxic nor harmful to nature. Naturally, also a marker should be easily detected, non-reactive and easily applied in the process.

Markers are very much needed for monitoring the cut-off of a membrane. For MF some monodisperse substances are available that can be monitored by microscopical methods because of their density. They are mainly used for the measurement of pore sizes, but they are very expensive. Good particles of this kind do not exist for nanofiltration today.

Online fluorescence monitoring is used in membrane bioreactors to see how well the biofilm is working (see Chapters 12 and 14). In this case the biofilm is studied through the module glass wall, using an optical well. The incoming excitation light makes the biofilm fluoresce and the emission light tells the intensity of the response. From a 2D image a 3D time-image is built up and the “fingerprint” of the biofilm can be monitored. Different fingerprints can be compared and growth or growth problems can be identified. The same type of set-up can be used using fluorescent markers or naturally fluorescent materials to study the fractionation of molecules, especially proteins.

Some of the fluorescent markers (like for instance tryptophane) change their fluorescence pattern as a result of the polarity of their environment (see Chapter 12). In this case an increase in polarity gives rise to a red shift and a decrease to a blue shift. The shifts can also be produced through adsorption of the molecule and thus fouling could be studied. Also some proteins change their structure after passing through a membrane pore. Today there exist very sensitive analysis methods for these small structural changes.

1.5

Future Scope of Sensors in Membrane Process Characterization

The techniques to measure and to handle data are developing very rapidly today. Computer technology has developed for mathematical simulations, equation solving and statistical analysis, so that different images can be analyzed at ever higher resolution, which makes it possible to analyze data from 2D levels to 3D or 4D levels. The limits of what can be done seem to be surpassed from year to year. This situation will be used in online monitoring of processes to make them sustainable and run at optimal conditions.

For online monitoring it is already possible today to make such monitoring where you take samples from feed and permeate and calculate how well the

process is going. What is not yet done is to use this data for regulating the process conditions. If this kind of online optimization of process parameters is done, the costs and the intervals of cleaning could be regulated. Also, all the methods used to monitor the fouling layer could be used in this respect. What is needed is a window to look at the membrane so that different measurements can be done. Measurement of fluorescence was mentioned above; but also the newly marketed *particle image velocimetry/laser induced fluorescence* (PIV/LIF) equipment could be used to look at streamlines, concentration polarization and fouling on the membrane. Fluid velocity mapping for investigation of fouling has been done by Delauney et al. [19, 20].

Today, microelectrodes can be prepared and used as electrical, magnetic, or acoustic probes or sensors. In a future process the membranes, spacers or modules could be equipped with a pattern of microelectrodes for different types of measurements and the collected data would be used for optimizing the process conditions within the membrane process. It could also be possible that, in an industrial process, there would for instance be one test module equipped in this way that could be placed somewhere in the process design.

In the text above some fluorescent protein molecules have been used as markers. If the molecules to be analyzed are not fluorescent, another way to mark the molecule in the feed would be to use an implanted molecule that reacts with a target molecule and gives a complex which can be seen or which emits some measurable electrical light. These nanosensors could also be contained in controlled release packages and thus be delivered over time to find the targeted molecules in the feed or on the membrane. If the sensors are implanted molecules they could function like functionalized affinity membranes are doing today.

New types of markers are the self-assembling particles, e.g. dendrimers [21]. These molecules can be made in different sizes, even nano-sizes, and they can be spherical or have other 3D structures. They can be made with layers on the outside which have a different charge or hydrophilicity; and they can also be made to contain metals or fluorescent groups (dansylated dendrimers). In that way they can (by size) be markers for pore size, (by charge) be markers for membrane charge and (by hydrophilicity) be markers for membrane hydrophilicity interaction. By covering the markers with gadolinium (water-soluble gadomers) they become good in vivo markers, as they are inert and not visible to body reactions. These markers can be used in very different ways in monitoring. Today they are still not all on the market (if available, they demand high prices) but in the future they would probably be very useful in monitoring membrane processes.

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