High flux ultrafiltration
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Membrane filtration is an attractive separation process, as it is usually performed under gentle conditions. Membrane processes have found wide application in especially the biochemical, food and beverage industry. Examples can be found in the treatment of waste water, desalination processes and concentration of protein solutions. Separation of different components is achieved by a combination of sieving, hindered transport through the narrow membrane pores and other specific interactions between the components and the membrane material (such as adsorption, electrical interactions). The process can be driven by different forces: a concentration difference on both sides of the membrane (dialysis), a pressure difference over the membrane (ultrafiltration, reverse osmosis) or by an (externally) applied electrical field (electrodialysis).

This thesis is on pressure driven membrane filtration (especially ultrafiltration). The different pressure driven membrane processes are usually classified based upon the size of the solutes that the membrane filters reject. This is summarised in table 1.

<table>
<thead>
<tr>
<th>type of process</th>
<th>particle size</th>
<th>particle type</th>
</tr>
</thead>
<tbody>
<tr>
<td>microfiltration</td>
<td>0.1-5 μm</td>
<td>yeast cells, bacteria, suspended solids</td>
</tr>
<tr>
<td>ultrafiltration</td>
<td>10-100 nm</td>
<td>proteins, polymers</td>
</tr>
<tr>
<td>nanofiltration</td>
<td>1-10 nm</td>
<td>amino acids, oligosaccharides, oligomers</td>
</tr>
<tr>
<td>reverse osmosis</td>
<td>&lt; 1 nm</td>
<td>sugars, salts</td>
</tr>
</tbody>
</table>
All these processes are driven by an externally applied pressure difference. However, during the process also concentration differences and, in case of electrically charged components, an electrical field may develop. These can strongly influence the filtration process.

The separation characteristics of membranes, especially for ultrafiltration membranes is often expressed in terms of the Nominal Molecular Weight Cut-off (NMWC). It is usually determined by measurement of a polymer with different sizes. The NMWC value is then equal to the molecular weight of that polymer that is rejected for more than 90%. Common macromolecules that are used are dextrans, PEGs or proteins. The problem is, however, that NMWC values are different for different substances. For example, dextrans are more linear molecules than PEGs and thus show a different rejection behaviour. It is even more difficult to interpret measurements with protein as the rejection of these components is not only a function of the size of the pores of the membrane and the solute but is also influenced by specific interactions between protein and membrane material.

**Fluxes**

The volume flux in a pressure driven membrane process depends on the hydraulic resistance of the membrane used and the pressure drop over the membrane. This is generally expressed by the following formula (Fane 1986):

\[
J = \frac{1}{\eta} \frac{\Delta P}{R_m}
\]

Here \( R_m \) is the hydraulic resistance of the membrane. In general the inverse of the resistance is used and defined as the hydraulic permeability \( H_p = 1/R_m \). This permeability depends on the pore size and structure, the porosity \( \varepsilon \) and the thickness of the membrane, \( \Delta z \). Especially in the Maxwell-Stefan based theoretical descriptions, it is useful to rewrite the hydraulic permeability in the following way:
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\[ H_p = \frac{\varepsilon}{\tau \Delta \tau} B_0 \]  

(2)

The effect of porous structure is now separated from the other parameters in the specific permeability, \( B_0 \). Membranes can have different structures, they may consist of different, more or less cylindrical pores or may be composed of a packed bed of various small particles (which are of the order of nanometers). If the membrane consist of pores, they are often considered cylindrical and straight. The permeability of the pores is usually described by the Hagen-Poiseuille equation for flow through cylindrical tubes (Bird 1960):

\[ B_0 = \frac{d_{\text{pore}}^2}{32} \]  

(3)

If the membrane consists of a packed bed of particles, the specific permeability is derived from the Carman-Kozeny equation (Elmaleh 1992):

\[ B_0 = \frac{1}{180} \frac{\varepsilon^2}{(1 - \varepsilon)^2} d_{\text{particle}}^2 \]  

(4)

Besides the hydraulic permeability of the membrane also the pressure difference over the membrane is important to determine the flux. Usually the pressure difference is applied externally to achieve filtration. During this process, solutes are separated from the solvent. These solutes accumulate near the membrane interface. The concentrations of these solutes are thus higher at the feed side than at the permeate side. This causes an osmotic pressure difference that reduces the effective pressure difference across the membrane.

Osmotic pressure may be a problem especially at higher solute concentrations or with poor mixing of the feed solution. The latter case is discussed in more detail in the section on concentration polarisation. First it will be discussed how the degree of separation can be expressed by a useful quantity, the rejection (also called retention).
Chapter 1

Rejection

The rejection is generally expressed as the fraction of solute that passes the membrane filter. It is expressed in permeate concentration of that solute compared to the concentration in the feed:

\[
R = 1 - \frac{C_p}{C_f}
\]  

(5)

If the feed solution is poorly mixed, the concentrations at the membrane surface can be different from those in the feed solution. To separate the performance of the membrane filter itself from the degree of mixing in the feed, it is useful to define the so-called true rejection, \( R_{true} \). This compares the concentration in the permeate to that at the membrane interface of the feed side rather than to the concentration in the bulk feed. It is defined by:

\[
R_{true} = 1 - \frac{C_p}{C_m}
\]  

(6)

Here \( C_m \) is the concentration at the membrane interface (on the interface). In practice the concentration at the membrane interface cannot be measured directly and observed rejections are determined, \( R_{obs} \). These are relative to the concentration in the bulk feed, so \( R \) in eqn. (5) can be replaced by \( R_{obs} \):

\[
R_{obs} = 1 - \frac{C_p}{C_f}
\]  

(7)

To calculate the true rejection from observed rejection data, more information is needed on how the degree of mixing affects the concentrations at the membrane surface.
Separation mechanisms

The rejection of solutes by the membrane is determined by different mechanisms:
- distribution of components between liquid phase and membrane phase
- interaction of solutes with the wall
- interaction of solutes with other components in the solution
These mechanisms are briefly discussed below.

Distribution

Ferry (Ferry 1936) showed how the distribution of solutes over liquid and membrane phase was determined by geometrical factors. He considered the situation of a spherical solute rejected by a membrane with cylindrical pores. The situation under consideration is visualised in fig. 1. It is shown that a solute that is not much smaller than the size of the pores cannot be distributed evenly over the whole pore cross sectional area. Its centre cannot get closer to the pore wall than to a distance equal to the radius of the solute. So the actual space that is available to the large solute is bounded by the dashed line in fig. 1. The cross sectional area of this space is equal to \( \pi (r_p - r_s)^2 \). If a solute approaches the pore with its centre being outside this area the solute collides against the outer membrane surface and will be rejected. Smaller molecules (e.g. the solvent) can get much closer and can thus occupy almost the whole pore cross section. So a jump in the concentration is observed going from outer liquid to the solution inside the pores. Ferry expressed this concentration jump in terms of the cross sectional area this solute can occupy compared to the total pore cross sectional area. The distribution of components over membrane and liquid is then written as:

\[
C_s^* = C_s \left(1 - \frac{r_s}{r_p}\right)^2 \quad \text{or:} \quad C_s^* = C_s K_s
\]

by which \( K_s \) is defined as the sterical distribution coefficient of solute \( s \). \( C_s^* \) is the equilibrium concentration in the membrane pores.
The distribution described above has been deduced from purely geometrical considerations, but this is not the only factor that affects the distribution. Specific interactions between solute and membrane material may be very important. Examples are preferential adsorption of components on the pore surface or electrical interactions between a charged pore surface and ionic components. The latter has been described by Donnan (Donnan 1995) and is visualised in fig. 2. Membrane material is often weakly charged, e.g. due to specific adsorption of small ions onto the surface. If a membrane is negatively charged and a solution of ionic components is filtered, a concentration jump is induced due to electrical interaction with the pore wall. Positively charged ions are attracted by the membrane and will obtain a higher concentration inside the pore than in the outer liquid. Negatively charged ions are repelled however and will have a low concentration inside the pore. Besides the concentration jumps also a jump in electrical potential is expected. In the case of a negatively charged membrane this potential in the pore will be lower (or more negative) than in the outer liquid.

Interaction with wall

Inside the membrane, the separation process continues. Larger solutes will experience friction with the pore wall, more than smaller components. Where the smaller components pass relatively freely through the pores due to the pressure gradient, the larger components are retarded and separated from the
fast moving smaller ones. The hindrance that components experience from the pore wall can be due to geometrical factors or to specific interactions such as adsorption and electrical effects.

**Interaction with other solutes**

Inside the pore a velocity difference is induced between the retarded larger molecules and the fast moving smaller components. The latter therefore have to slip past the retarded components and will experience friction with them. Conversely, the larger molecules are dragged along by the smaller components. The forces acting on the large solutes are visualised below in fig. 3.

The arrow pointing to the left symbolises the friction this solute experiences from the smaller molecules, the one pointing to the right indicates the friction between the large solute and the smaller (solvent) molecules. The balance between these forces determines, in addition to the distributions at the entrance and exit of the membrane, the rejection of the large solute.

**Fig 3.** Friction between solute and pore wall and between solute and solvent molecules.

**Behaviour of the true rejection**

At low permeate fluxes $R_{true}$ increases with increasing flux (and thus with increasing pressure drop). This is partly due to the distribution at the entrance and exit of the membrane and partly due to the velocity difference that is induced between the solute and the solvent. This difference is due to the
friction that the solute experiences from the pore wall. At higher fluxes the velocity difference between solute and solvent becomes so important that the solute is dragged along by the solvent. Finally the friction between the solute and solvent completely balances the friction of the solute with the wall and $R_{\text{true}}$ approaches a constant value.

**Concentration polarisation**

So far we have only dealt with the role of the membrane. Equally important or even more important at high fluxes is the degree of mixing in the feed solution. Let us consider flow past a flat membrane. If this flow is turbulent, it will be well mixed, except near the membrane surface where the velocity of the fluid is reduced and a so-called laminar layer or boundary layer is developed. This layer is relatively poorly mixed. This has consequences: in the filtration process the components that are rejected accumulate near the membrane surface. This accumulation near the surface is defined as concentration polarisation and has serious consequences especially in ultrafiltration (Blatt 1970). If the degree of mixing is high enough, these rejected components are quickly transported back to the bulk feed and accumulation of rejected components near the membrane surface is limited. If this mixing is poor, however, the transport of rejected solutes back to the bulk is not fast enough and the rejected solutes may accumulate near the surface to unacceptable levels.

This accumulation continues until the concentration near the surface is high enough to provide enough potential for diffusion of this component back into the bulk. This process is visualised in fig. 4. The lower the degree of mixing, the higher the concentration has to be to give enough potential for back transport. This process is usually described by a steady state mass balance, which states that the diffusion of an accumulated rejected component from the interface back to the bulk must balance the difference between the convective transport of this components towards the interface and the amount of the component that passes the membrane.
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Fig. 4. Concentration polarisation in ultrafiltration. A concentration gradient is built up over the liquid boundary layer, $\delta$.

This balance is presented by the following equation:

$$J \cdot C = J \cdot C_p - D \frac{\partial C}{\partial z}$$

(9)

The resistance to back diffusion is located in the thin liquid layer adjacent to the membrane interface that is nearly stagnant. The thickness of this layer, $\delta$, is important for model calculations, such as the integration of eqn. (9). It can be obtained by application of an empirical dimensionless relationship between mass transfer and hydrodynamic properties:

$$Sh = ARe^b Sc^c$$

(10)

The constants $A$, $b$ and $c$ have been determined for various flow systems, the value of $c$ is in most of the cases reported to be 0.33.

Integration of equation (9) over the liquid boundary layer, with boundary conditions, $C = C_b$ at $z = 0$ and $C = C_w$ at $z = \delta$, yields the well-known concentration polarisation equation:

$$J = k \ln \left( \frac{C_w - C_p}{C_b - C_p} \right)$$

(11)
Here $C_w$, $C_p$, and $C_b$ are the concentrations of solute at the membrane interface, in the permeate stream and in the bulk respectively, $k$ is the mass transfer coefficient in the boundary layer.

Concentration polarisation is a serious problem that has consequences both for the rejection of the component and for the flux. Both will be discussed below.

![Fig. 5. Typical plot of true rejection and observed rejection as a function of flux.](image)

**Observed rejection**

The dependency of the true rejection on the volume flux has been described above. Now the effect of concentration polarisation on the rejection that is observed during experiments will be discussed. This is visualised in fig. 5 in which typical plots of the observed rejection vs. flux (or pressure drop) is shown by the solid line. For comparison the true rejection also has been plotted with a dashed line. Concentration polarisation causes the concentration near the interface to rise. It is this concentration, rather than that of the feed solution, that determines the performance of the membrane filter. From eqn. (11) it can be deduced that for low fluxes the concentration near the membrane surface is not too different from the bulk so that the observed rejection, that is related to the concentration in the bulk follows the same pattern as the true rejection which is related to the concentration at the interface. The higher the flow gets the more the two will diverge and at sufficiently high fluxes a maximum in the observed rejection is experienced. This is near to the point where the true
rejection reaches its plateau value. Beyond that point the observed rejection drops. The concentration at the membrane interface is now so high that the component begins to break through; its concentration inside the membrane and in the permeate is increased and the observed rejection thus lowered.

**Flux decline by concentration polarisation or gel formation**

High concentrations near the membrane surface have serious consequences for the flux as well. Higher concentrations at the feed side induce an osmotic pressure gradient that is opposed to the externally applied pressure gradient (Kozinski 1972). The effective pressure gradient over the membrane, i.e. the driving force for the process, is thus reduced and the flux decreases. Another phenomenon that can occur is formation of a so called gel layer. The concentration of certain components can become so high that the solubility limits are exceeded. Then the solute will form a deposit layer on top of the membrane, which acts as an extra hydraulic resistance. This also results in a lowering of the flux. In model descriptions, the concentration of the solute at which a gel layer is formed, $C_{gel}$, is assumed to be constant (Blatt 1970, Porter 1972). The gel layer regime is visualised in fig. 6. A general plot of the flux as a function of pressure drop is shown in fig. 7. In both osmotic pressure limitation and gel formation the flux finally becomes independent of pressure and attains a plateau value at high transmembrane pressure drops.

![Fig. 6. Formation of a gel layer on the membrane. The concentration of solute at the membrane interface is assumed to reach a constant value (Blatt 1970, Porter 1972), which is equal to the solubility of the solute.](image)
**Chapter 1**

![Diagram: Flux vs. Pressure Drop](image)

**Fig. 7.** Typical plot of the flux vs. the pressure drop that is applied over the membrane. Due to concentration polarisation or gel formation the flux finally attains a limiting value.

**Fouling**

In addition to concentration polarisation and gel formation, other mechanisms also reduce the flux. They can generally be ascribed to fouling. The different fouling mechanisms are visualised in fig. 8. In fact, gel layer formation is one form of fouling and is in principle reversible: rinsing with clean water should solve the problem. Fouling can become irreversible if the components in the gel layer react with each other and form a dense cross-linked layer on top of the membrane, which is not easy to remove. Also adsorption of components at the pore wall influences the performance of the membrane. The pore radius is reduced and the hydraulic resistance increased, with a lower flux as the result. The rejection of components, that have passed freely before, may be increased, which is unfavourable if a separation of two differently sized solutes is to be achieved. Another mechanism of fouling is pore blocking which can be highly irreversible.

Possibilities for cleaning depend on the fouling type. If fouling is reversible, like gel formation, rinsing with pure water might cure the problem. If irreversible, other solutions have to be sought, rinsing with strongly alkaline or acidic agents at elevated temperatures may help in case of adsorption or irreversible fouling layer formation. A successful technique that can be applied when a fouling layer or pore blocking occurs is back flushing. In this technique the pressure gradient is periodically reversed for a short period of time to remove the fouling.
Prevention is better than cure, however, therefore on-line techniques are preferred. Back flushing is in practice almost an online method. Other possibilities are to apply a high degree of mixing in the feed solution, such as a high recirculation rate of the feed or the application of turbulence promoters. This mainly helps if the fouling that has formed is reversible, but it also reduces the concentration near the membrane interface and reduces the risk of induction of fouling. Another prevention measure is of course a careful control of process conditions such as pH, for example to prevent scale formation in solutions containing calcium. As the costs of membrane material are still substantial, achieving high fluxes is essential. Therefore reduction of fouling and concentration polarisation is still one of the main issues in membrane technology.
Outline of the thesis

This thesis deals with high flux ultrafiltration. **Chapter two** starts with the processes that take place inside the membrane pores. At high fluxes viscous flow becomes important besides diffusive transport. An overview of various descriptions of high flux transport inside the pores is given. The work on Maxwell-Stefan descriptions of Mason and others is expanded and connected to the hydrodynamic theory of Bungay and Brenner and Deen. The description thus developed is compared to data on falling spheres through cylindrical tubes, diffusion of uncharged solutes through membrane pores and pressure driven transport of these solutes through membranes.

**Chapter three** describes the ultrafiltration of ionic solutes. Experimental data on the ultrafiltration of phosphate are presented and modelled by the Maxwell-Stefan theory. The pores of ultrafiltration membranes are normally far too wide to reject salts such as phosphate. Desalination therefore used to take place by reverse osmosis. It is shown however that even ultrafiltration membranes can provide considerable rejection, the main mechanism of separation being electrical interaction between the salt ions and the charged membrane pore surface. As the fluxes obtained in ultrafiltration are much higher (up to 500 L m\(^{-2}\) hr\(^{-1}\) at pressures lower than 5 bar) than in reverse osmosis (up to 10 L m\(^{-2}\) hr\(^{-1}\) at pressures up to 50 bar), ultrafiltration can be a quite attractive alternative to the latter process for the treatment of dilute salt solutions. In concentrated solutions the beneficial effects of ultrafiltration disappear however, as the electrical forces between ions and pore wall are then strongly reduced.

**Chapter four** deals with protein filtration and desalination of protein solutions. Again electrical forces are very important. At pH values higher or lower than the iso-electric point, protein molecules are strongly charged. These charged molecules repel each other. The accumulation of rejected protein molecules near the membrane surface is then strongly reduced, which has a positive effect on the flux during the process and the speed of protein concentration is greatly enhanced. The protein forces the salt (especially the co-ion) to move faster through the membrane phase and negative rejection of the co-ion is observed. The results indicate the importance of pH control during protein concentration.
and/or desalination in order to obtain high fluxes of both solvent and salt and to achieve a fast process.

**Chapter five** discusses the application of turbulence promoters to reduce concentration polarisation. As turbulence promoters fluidised beds of glass or steel particles have been used. In this way higher fluxes can be obtained in ultrafiltration of polymers and proteins. Mass transfer is increased considerably by addition of fluidised particles. This results in an increased diffusion of rejected solutes from the membrane interface back to the bulk solution. Improvement of mass transfer is shown to be only a weak function of particle size and density. Therefore the particles can be chosen as light and small as possible. This reduces the energy consumption in the system and the risk of membrane damage, which may be a problem. Application of fluidised bed systems can be especially attractive in highly viscous systems, in which energy consumption can be a problem.

**Chapter six** deals with low flux rather than high flux membrane filtration. It describes the drawback of application of fluidised particles: a considerable flux decrease in time due to the continuous bombardment of the membrane by fluidised particles. Measurements of the pure water flux in time in the presence of fluidised particles are presented. These show that the flux is reduced by collisions of spheres with the membrane. The flux decline can be described by a model which is based upon the theory of elasticity of Hertz.

**Chapter seven** describes another technique using the effect of solid particles to improve fluxes. It is shown that insoluble soy bean particles have a positive effect on the flux and on the concentration rate. It is shown that the particles can clean the membrane by a scouring mechanism in addition to enhanced diffusion. In addition, the particles have a positive effect on the reversibility of fouling.
Symbols

$B_0$ : membrane permeability, m$^2$
$C$ : concentration mol m$^{-3}$
$d$ : diameter, m
$D$ : diffusivity, m$^2$ s$^{-1}$
$D_t$ : tube diameter, m
$H_p$ : hydraulic permeability, m
$k$ : mass transfer coefficient, m s$^{-1}$
$J$ : volume flux through the membrane, m s$^{-1}$
$P$ : pressure, bar
$r$ : radius, m
$R$ : rejection, fraction of solute that is retained
$R_m$ : resistance of the membrane, m$^{-1}$
TMP : transmembrane pressure drop, bar
$v$ : velocity m s$^{-1}$
$z$ : distance, m

$Re$ : Reynolds number in empty tube flow, $\rho \cdot v_{cross} \cdot D_t / \eta$
$Sc$ : Schmidt number, $\eta / \rho \cdot D$
$Sh$ : Sherwood number, $k \cdot D_t / D$

$\varepsilon$ : porosity of membrane
$\eta$ : viscosity, Pa s
$\rho$ : density, kg m$^{-3}$
$\tau$ : tortuosity of membrane

subscripts

cross : cross flow
$f$ : feed
$obs$ : observed
$p$ : permeate
$true$ : true rejection, intrinsic property of the membrane
$s$ : solute
$w$ : wall (membrane interface)
References

Ferry, J.D., 1936, Statistical evaluation of sieve constants in ultrafiltration, J. Gen. Physiol. 20, 95-104.