Felleslab ST-7
Ultrafiltration
Report
Group B-16

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Contents

1 Introduction

This experiment has been conducted in order to obtain an understanding of the ultrafiltration-membrane process. To do so, the reduction of permeability of diluted milk has been measured and compared to that of deionized water.

2 Theory

The theory in this section is based on the curriculum written by Georg Voss available on professor Heinz Preisig's Felleslab web page [1].

In its most basic form, ultrafiltration is a pressure-driven process designed to remove solvent (typically water) and small solutes (e.g., salts and sugars) from larger macromolecules weighing between 10^3 and 10^6 Da (e.g. proteins). A membrane used in ultrafiltration typically has pores with a diameter of somewhere between 10 and 100 nm. More often, membranes are categorized by the term molecular-weight-cut-of (MWCO), defined as the molecular weight of dextran being 90% rejected by the membrane, given by the unit Da.

The two most common set ups for filtration are cross-flow and dead end filtration. The first set up is mainly used for industrially scaled processes, while the latter is more common in lab scale experiments. In this experiment only the dead end filtration technique will be used.

The flux is one of the most important characteristics of a membrane for filtration. Instantaneous flux is given by Equation (2.1):

$$J = \frac{1}{A}\frac{\Delta V}{\Delta t} \tag{2.1}$$

Here, A is the membrane surface area, V is the filtration volume and t is the filtration time. When comparing membranes with the same surface area it is sufficient to discuss the throughput of the membranes.

Also of interest in an ultrafiltration is the permeability, L_p, of the solvent:

$$L_p = \frac{J_v}{\Delta P} \tag{2.2}$$

In Equation (2.2), J_v is the volumetric filtration flux and ΔP is the trans-membrane pressure driving force. Because water is the typical solvent L_p is often referred to as the hydrodynamic permeability. The data are often

normalized by the solvent viscosity to account for the effects of temperature.

Many different units are used for filtration flux and permeability. In this experiment the unit for filtration flux will be [$\mathrm{L\,m^{-2}\,h^{-1}}$] and for the permeability [$\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$].

The mass transport through the membrane is dominated by convection. The rate of mass transport for both the product and for small impurities is proportional to the filtration flux and the corresponding solute sieving coefficients, S_i. S_i is equal to the ratio between the solute concentration in the filtrate over that in the feed solution. If R is the rejection coefficient the sieving coefficient is equal to 1-R. The apparent rejection for component i can be calculated from Equation (2.3):

$$S_i = \frac{c_{pi}}{c_{fi}} = 1 - R \implies R = 1 - \frac{c_{pi}}{c_{fi}} \tag{2.3}$$

The apparent rejection of component i is calculated from the concentration of i in the feed (c_{fi}) and in the permeate (c_{pi}). Due to concentration changes in the boundary layer between the membrane and the feed, the true membrane rejection is higher. Data for the boundary layer cannot be obtained.

2.1 Properties of milk

In this experiment a dilution of skimmed milk (0.1% fat) will be filtrated. The most important ingredients of milk besides water are proteins (mainly caseins) and sugars (lactose etc.). The industrial scale ultrafiltration processing of milk usually uses filters with a MWCO between 5000 kDa and 10 000 kDa to remove all proteins [2]. Milk proteins have a molecular weight described in Table 1. When using a membrane with MWCO at 30 000 kDa,

Table 1: Molecular weight of some milk proteins. Table gathered from [3]

Protein	Molecular weight [Da]
α-Casein	23000
κ-Casein	19000
β-Casein	24000
α-lactalbumin	14437
β-lactoglobulin	18000

the caseins should in theory go through the filter, but since they are relatively

close to the MWCO, they may not permeate properly. When analysing with UV/Vi-spectroscopy only the proteins in milk will be visible. This means that the minerals (such as calcium) and sugars will not contribute to the spectrum [4].

3 Experimental

3.1 Experimental Setup

The dead-end filtration was carried out using a Stirred Ultrafiltration Cell Model 8400 from Millipore with a total volume of 400 mL and a circular membrane with a total area of 41,8 cm^2. The feed side was connected to a container of pressurised air with a pressure gauge mounted on the tube leading the air into the apparatus. The mass of the filtrate was measured and logged with the corresponding time by a computer with Labview software connected to a scale. The filtration apparatus stood atop a magnet stirrer in order to keep the feed in constant motion and well mixed.

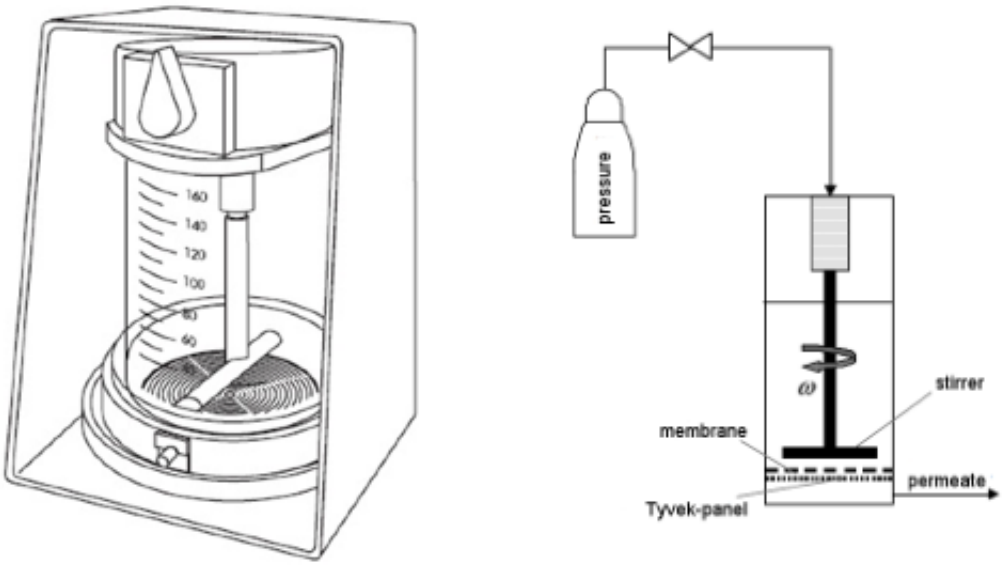

Figure 1: The apparatus used: A Stirred Ultrafiltration Cell Model 8400 from Millipore with a total volume of 400 mL and a circular membrane with a total area of 41.8 cm^2. Figure collected from the curriculum on the Felleslab web page [1].

Since ultrafiltration membranes can operate with low pressures as driving force, the transmembrane pressure for this experiment was set to 2 bar (gauge)

by inducing pressure with pressurised air at the feed side. During each filtration the rotation frequency of the stirrer was set to 140-150 rpm, and approximately 200 mL of feed was poured into the apparatus.

3.2 Experimental procedure

Originally the experiment would have been performed using a membrane with a MWCO of 100 kDa, and three filtrations would be performed. To begin with, deionized water would be filtrated twice to examine whether there would be a decrease in the membrane's performance using a feed containing so few impurities, and then a solution consisting of milk diluted with water would have been filtrated for comparison. However, during the experimental procedure a few unexpected situations arose. Due to various reasons, the results attained with the 100 kDa MWCO membrane were deemed so highly dubious that it was decided to scrap the entire data collection and redo the experiment altogether with a different membrane, this time with a MCOW of 30 kDa.

When the experiment was restarted there was not much time left for the day and so the procedure had to be ended prematurely. There was enough time to perform both of the filtrations with deionized water, but the data sampling from the filtration of the dilute milk had to be aborted after having time only to let slightly more than 10% of the feed to be filtrated.

3.3 Analysis

A portion of the filtrate was collected for analysis by UV/Vis-spectroscopy. As a basis for this analysis, ten solutions of milk diluted in water with concentrations as described in Table 2 were prepared. From the sampling file, the units were converted to $[\mathrm{L\,m^{-2}\,s^{-1}\,bar^{-1}}]$ and the throughput and permeability was then plotted against time [s].

4 Results

The amount of filtrate by mass as function of filtration time is plotted in Figures 2 and 3. The permeate was almost colourless and did not resemble milk at all. By comparison to the prefabricated dilutions of milk in Table 2, it turned out to have a tint of light yellow/brown colour.

Table 2: Concentrations of milk diluted in water used for UV/Vis-spectroscopy.

Solution	Concentration [wt%]
1	0.065
2	0.26
3	0.38
4	0.65
5	0.85
6	1.37
7	1.8
8	2.0
9	5.1
10	9.6

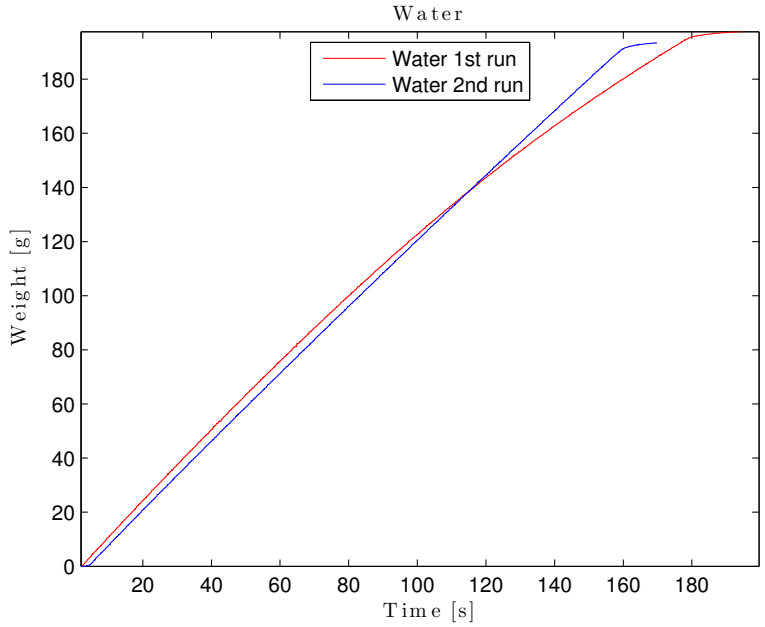

Figure 2: Plot of the amount of filtrate by mass as function of time during the filtrations of deionized water.

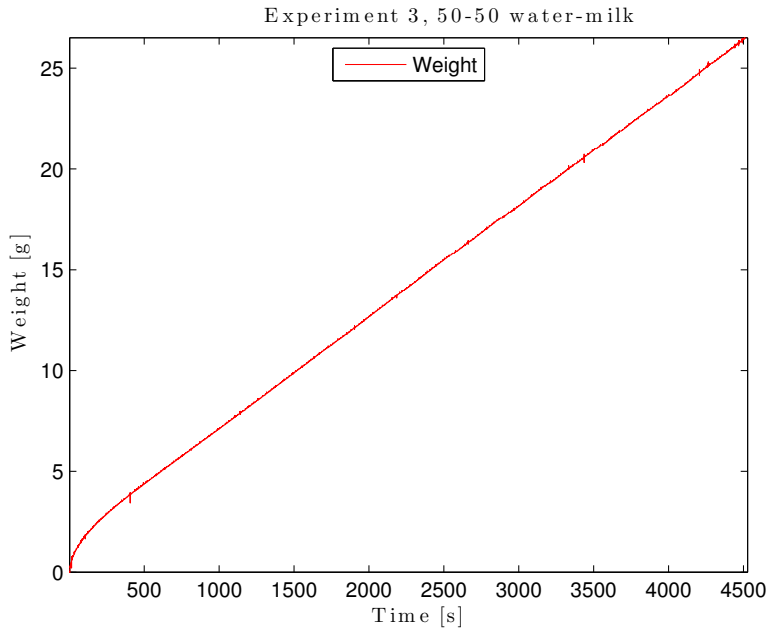

Figure 3: Plot of the amount of filtrate by mass as function of time during the filtration of a mixture of 50 wt% milk and 50 wt% water.

4.1 Flux and permeability

The flux and the permeability of the three filtration parallels were calculated using Equations (2.1) for the flux and (2.2) for the permeability (Appendix A). The results are given in Table 3.

Table 3: Flux and permeability for the three filtration parallels. Note that the uncertainty in the permeability values is very high due to low precision in the pressure values.

Parallel	Flux $[\mathrm{mL\,s^{-1}\,cm^{-2}}]$	Permeability $[\mathrm{mL\,s^{-1}\,cm^{-2}\,bar^{-1}}]$
Water 1	0.27	0.14
Water 2	0.24	0.12
Water/Milk 50/50	$1.4 \cdot 10^{-3}$	$7.0 \cdot 10^{-4}$

It is important to note that the readings of the pressure used to calculate the permeability are unreliable. The pressure gauge normally read approximately 2 barg when pressure was applied, but it varied slightly throughout

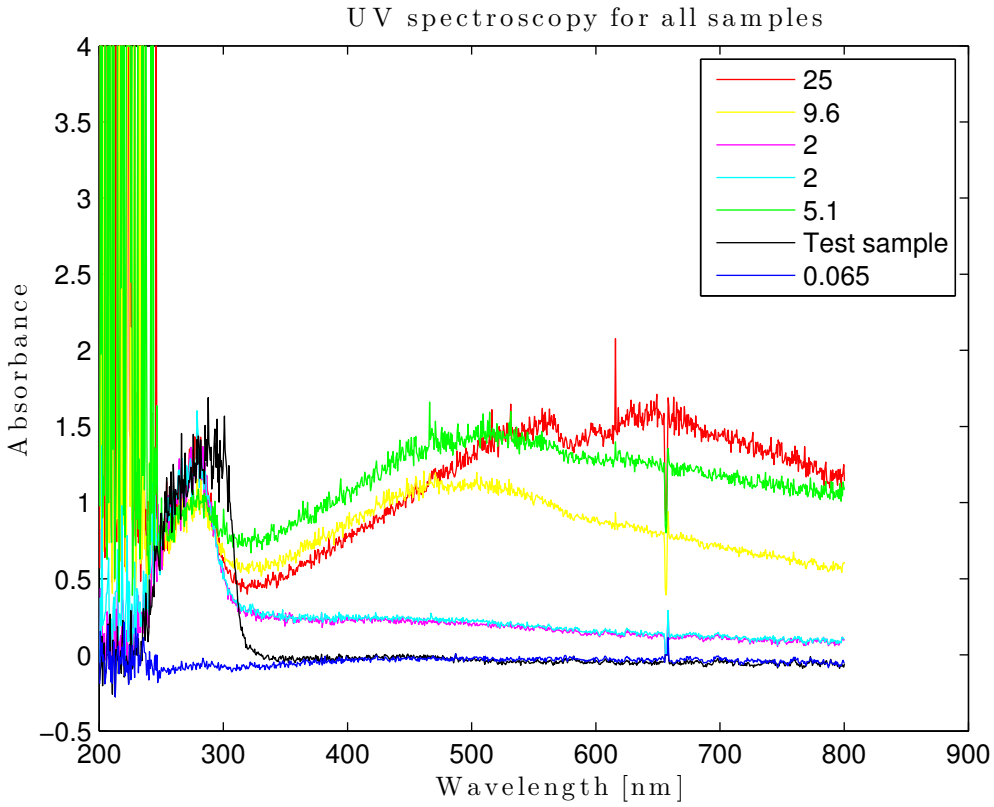

Figure 4: The UV-spectroscopy of the different samples, with the permeate in black. The concentration of the diluted samples are made marked in percent of pure milk.

the filtrations. Rather than trying to constantly log the pressure value, it was decided to set the value to 2 barg, which is a reasonable estimate of the mean value. However, this does mean that the calculated permeability values have within them a high degree of uncertainty and should be regarded merely as an indication of a trend.

4.2 UV/Vi-spectroscopy

The permeate was analysed using UV/Vi-spectroscopy and compared to the test samples in Table 2. The results are found in Figure 4. Wavelengths below 250 nm is mostly noise.

5 Discussion

One thing that is very striking is that the flux through the membrane was higher the second time the deionized water was filtered through is than the first time. This was unexpected to say the least, as the membrane performance would normally be likely to sink after use. With deionized water, though, it would be natural to expect a so small change that the flux would turn out to be practically the same. What caused the flux to drop during the second filtration is not very clear, but it could simply be down to that the pressure inside the container has been different. There was a breakage in the O-ring in the lid, and this could have caused the pressure to be lower the second time, resulting in a lower flux.

It is clear from Figure 3 that the mixture of 50% milk and 50% water went much slower through the membrane than the pure deionized water. This is a logical result since milk contains many big molecule substances, namely proteins, which would be likely to be held back by the membrane. The experiment on the diluted milk confirmed this, as a creamy white substance was detected on the membrane after the experimental procedure had been ended.

5.1 Difference in colour

The light yellow/brown tint in the permeate of the 50/50-filtration is probably a bit difficult to explain, but it is perhaps possible that it could be due to pollution from the coffee that many other groups have performed the same filtration experiment with. The supervisor claimed this to be impossible, but it is hard to imagine a different explanation. Is seems logical that some colour might have stuck from the coffee experiments, especially since coffee is known to leave colour in f.ex. Thermoses.

The main difference between the permeate and the diluted test samples is that the permeate should contain fewer large protein molecules as these should be stopped by the membrane. Since the test sample was colourless, this means that some of the milk proteins (which give milk it's white color) either has been denatured or didn't permeate through the membrane. This was therefore as expected.

5.2 UV-Spectroscopy analysis

The baseline in the plot is calibrated towards pure water, and every peak represents the UV spectrum of a substance. All wavelengths below 250 nm are considered noise and are therefore ignored.

As can be seen from Figure 4, the test sample peak at 280 nm is higher than the rest, especially compared to the 0.065% milk sample, which is very close to water in terms of concentration. The rest of the test sample is on the baseline, meaning that there is nothing but water present. Since only the proteins will be visible in the UV/Vi spectrum [4], it is likely that there are some milk proteins left in the permeate, as these are not present in the 0.065% solution. There are however some other sources of error, as the 25%, 9.6% and 5.1% samples show large absorbance in the > 300 nm area. A possible explanation for this is that the aluminium foil covering the UV/Vi sensor was not completely lightproof, as these are the wavelengths of visible light. An argument that supports this source of error is that since these were the first tests, another layer was added after these tests were conducted. These are therefore not usable for comparison. Compared to the UV/Vi-spectrum at page 11 in [4], only the sample test and the 0.065% and 2% tests are valid, as these follow the known spectrum of milk. The sample test follows [4] briefly, but with lower absorbance.

6 Conclusion

In this experiment the flux and the permeability of a solution of 50% skimmed milk in deionized water has been tested. The flux through the membrane was found to be $1{,}4 \cdot 10^{-3}\,\mathrm{mL\,s^{-1}\,cm^{-2}}$ and the permeability was found to be $7 \cdot 10^{-4}\,\mathrm{mL\,s^{-1}\,cm^{-2}\,bar^{-1}}$, both is much lower than that of deionized water (Permeability: $0{,}12\,\mathrm{mL\,s^{-1}\,cm^{-2}\,bar^{-1}}$).

The permeate was nearly colourless, indicating that most of the white proteins did not permeate through the filter, even though they have a smaller molecular weight than the membrane's MWCO. According to the UV/Vi-spectroscopy the permeate did contain some proteins, but this analysis had multiple sources of error and should therefore not be considered very reliable.

Trondheim, November 1, 2013

Signatures: _____ _____

Symbols

Symbol	[Unit]	Explaination
A	cm^2	Area of membrane
J	$\mathrm{L\,m^{-2}\,h^{-1}}$	Flux
$J_{50/50}$	$\mathrm{L\,m^{-2}\,h^{-1}}$	Flux during filtration with a mixture of 50% milk and 50% water
J_{W1}	$\mathrm{L\,m^{-2}\,h^{-1}}$	Flux during first filtration with deionized water
J_{W2}	$\mathrm{L\,m^{-2}\,h^{-1}}$	Flux during second filtration with deionized water
L_p	$\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$	Permeability
ΔP	bar	Transmembrane pressure
Δt	s	Filtration time
ΔV	mL	Filtration volume

References

[1] Curriculum by Georg Voss on professor Preisig's web page about the Felleslab, downloaded 22. September 2013. http://www.nt.ntnu.no/users/preisig/Repository/TKP_4110_Felles_Lab/experiment%20descriptions/Membrane_Ultrafiltration_Script.pdf

[2] Koch Membrane Systems http://kochmembrane.com/PDFs/KMS-Dairy-2012.aspx visited: 21.10.13

[3] Univeristy of Illionis http://classes.ansci.illinois.edu/ansc438/milkcompsynth/milksynth_proteinbiochem.html visited: 21.10.13

[4] Hansen, Per W., *Spectroscopic Analyses on Dairy Products*, Denmark, **1998**

A Calculation of flux and permeability

Equations (2.1) and (2.2) were used to calculate the flux and permeability of the three filtrations.

$$J_{\mathrm{W1}} = \frac{1}{41{,}8\,\mathrm{cm}^2} \cdot \frac{197{,}5\,\mathrm{mL}}{193{,}2\,\mathrm{s}} = 0{,}2446\,\mathrm{mL\,s^{-1}\,cm^{-2}}$$

$$J_{\mathrm{W2}} = \frac{1}{41{,}8\,\mathrm{cm}^2} \cdot \frac{193{,}4\,\mathrm{mL}}{169{,}0\,\mathrm{s}} = 0{,}2737\,\mathrm{mL\,s^{-1}\,cm^{-2}}$$

$$J_{50/50} = \frac{1}{41{,}8\,\mathrm{cm}^2} \cdot \frac{26{,}51\,\mathrm{mL}}{4527\,\mathrm{s}} = 1.401 \cdot 10^{-3}\mathrm{mL\,s^{-1}\,cm^{-2}}$$

$$L_{\mathrm{p\ W1}} = \frac{0{,}2446\,\mathrm{mL\,s^{-1}\,cm^{-2}}}{2\,\mathrm{bar}} = 0{,}1223\,\mathrm{mL\,s^{-1}\,cm^{-2}\,bar^{-1}}$$

$$L_{\mathrm{p\ W2}} = \frac{0{,}2737\,\mathrm{mL\,s^{-1}\,cm^{-2}}}{2\,\mathrm{bar}} = 0{,}1369\,\mathrm{mL\,s^{-1}\,cm^{-2}\,bar^{-1}}$$

$$L_{\mathrm{p\ 50/50}} = \frac{1.401 \cdot 10^{-3}\mathrm{mL\,s^{-1}\,cm^{-2}}}{2\,\mathrm{bar}} = 7.005 \cdot 10^{-4}\mathrm{mL\,s^{-1}\,cm^{-2}\,bar^{-1}}$$