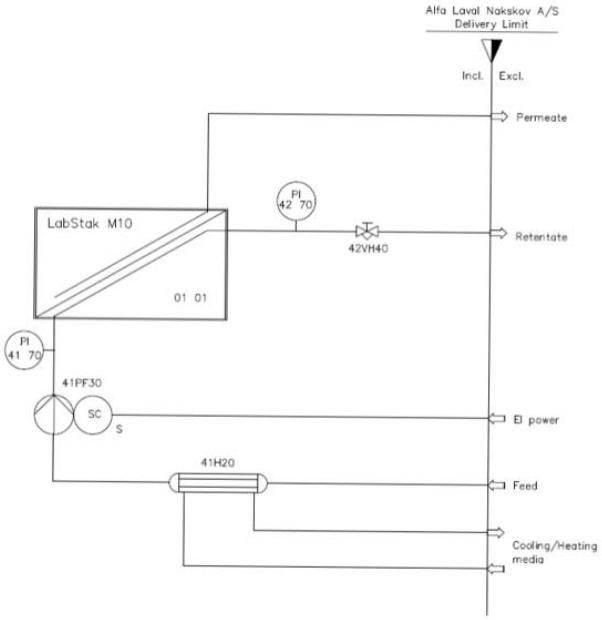
Screening of enzymatic cleaning of UF membrane fouled with oat slurry



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Abstract:

The demand for plant-based beverages, such as oat drink has been on an exponential increase in the past years due to their high content of dietary fibers, proteins, and sustainable production, and with dairy drinks high environmental impact, have left the consumers searching for alternative, sustainable and environmental-friendly beverages. However, the production of oat drink is not effective enough, with decantation yielding poor separation efficiency and high energy demand. Whereas, membrane filtration has low energy demand and high separation efficiency, but with fouling formation tendency. Enzymatic cleaning can remove fouling and restore the membrane to its original state, while operating at mild conditions, thereby minimizing the environmental impact. Therefore, this project aimed at investigating the cleaning parameters in order to ensure high cleaning efficiency and maximum pure water flux recovery in ultrafiltration membrane. Thus, producing oat slurry and selecting suitable enzymes to create a cleaning procedure with cleaning parameters such as temperature, cleaning time, multiple cleaning cycle, sequence, and concentrations of cleaning agents. The highest flux recovery was obtained by chemical alkaline cleaning with 21.65%, whereas for enzymatic agents the acidic enzymes followed by basic enzyme yielded 14% recovery.

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1 Introduction

The production and demand of plant-based substitutes to dairy products, including oat drink have increased the recent years, as consumer awareness and accountability for personal health and the environment have risen[1]. Oat drink is produced by mixing oat with water in the present of hydrolysis enzymes, and subsequently adding ingredients to enhance the sensory attributes of the drink. The oat slurry is filtered to remove unwanted insoluble solids. Decantation is the most used unit operation for removing solids in the plant-based industry. However, decantation has low efficiency and great environmental impact, due to its large pore sizes and high energy demand [2]. Therefore, a more efficient, consistent and environmental-friendly alternative is sought to replace decantation to separate solids from liquid. Membrane filtration is a promising candidate that fulfills the requirements due to its high selectivity and wide range of applications[3].

Membrane filtration is a widely used technology in the food and beverage industry for the production of high-quality products such as juices, dairy products, and plant-based drinks. However, fouling of membrane filters is a major challenge in the production process, as it leads to decreased filtration efficiency, in the form of fouling, and increased energy consumption[4].

Fouling is the accumulation of particles, microorganisms, and organic or inorganic substances on the surface or within the pores of the membrane filter [4]. Fouling can occur due to several reasons such as concentration polarization, adsorption, and cake formation. In oat drink production, fouling in oat slurry filtration is caused by the presence of soluble and insoluble components such as proteins, lipids, and fibers[5]. Fouling not only reduces the filtration efficiency but also affects the sensory properties and shelf life of the final product.

Enzymatic cleaning is a promising solution for fouled membrane filters, as it can effectively remove fouling without damaging the membrane[6]. Enzymatic cleaning is a process that involves the use of enzymes to break down the foulants on the surface of the membrane filter. Enzymes are biological catalysts that can accelerate the breakdown of complex molecules into simpler forms[7]. The enzymatic cleaning process involves the application of an enzyme solution on the membrane surface followed by a rinsing step to remove the degraded foulants. Enzymatic cleaning has several advantages over conventional cleaning methods such as chemical cleaning and physical cleaning. Enzymatic cleaning is a safer and more environmentally friendly method as it does not use hazardous chemicals, however the cleaning efficiency is typically lower compared to chemical cleaning. Enzymatic cleaning can reduce the energy consumption and downtime associated with cleaning the membrane filter, leading to increased productivity and reduced production costs[7].

The screening of enzymatic cleaning involves the selection of the appropriate enzyme, concentration, temperature, and time for effective cleaning[4]. Further research is needed to optimize the enzymatic cleaning process for specific oat drink formulations. In this project, screening of enzymatic cleaning for ultrafiltration membrane filters after fouling with oat slurry for the parameters; types of enzymes, concentration, temperature, cleaning sequence, cleaning cycles and time will be investigated, to answer the question ‘’What is the maximum water flux recovery that can be achieved with enzymatic cleaning of UF PES membrane in a plate-and-frame configuration fouled with oat slurry?’’

In this report following chapters will be covered oat structure and composition, membrane filtration, including membrane modules and operating parameters, fouling, cleaning, and factors effecting cleaning efficiency.

2 Oat structure and composition

Like most cereal crops, the oat grain consists of a complex food matrix. The matrix is the components' structure and hieratical (from molecule to tissue) organization. The arrangement and the relationship between the components in the plant matrix, can occur naturally (e.g. cellular structure of plant tissue) or be a result from processing (e.g. breadmaking). The oat grain complex contains the protective hull and the groat. The latter is the interesting component, containing three distinct parts: starchy endosperm, bran and germ (**Fejl! Henvisningskilde ikke fundet.**)[8].

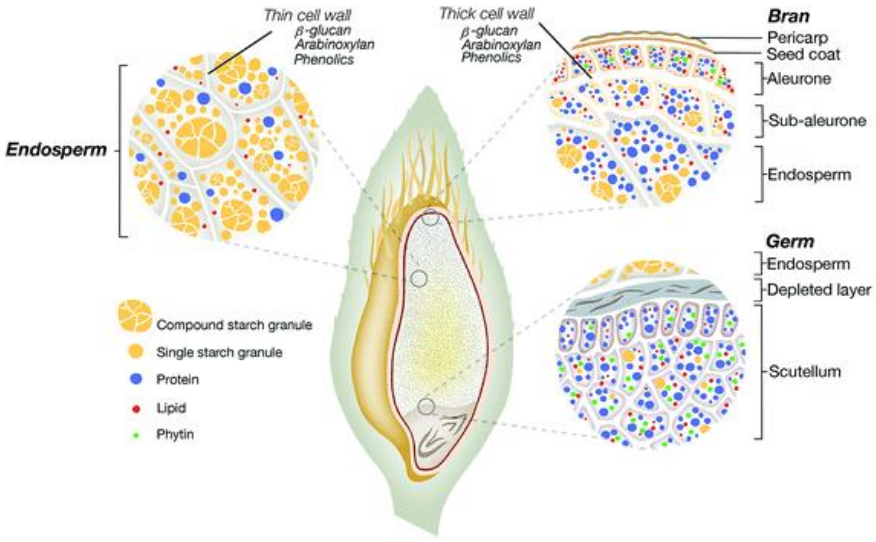

Figure 1: Structural representation of the oat grain presenting different oat [8]

The outer layer of the oat grain, called bran, is an essential component in the processing of oats. It is a rough texture layer that contains a high concentration of minerals, vitamins, and cell wall polysaccharides such as cellulose, arabinoxylan, and β-glucan, which are the vital compounds in the production of oat drink and other oat-base products[8]. The layers of aleurone and sub-aleurone are located beneath the pericarp and seed coat of the bran and are attached to the endosperm. The cells in these layers have thick cell walls that are difficult to digest, while the endosperm cells have thinner cell walls that contain high concentrations of β-glucan. The concentrations of oat protein and lipid increases from the center to the periphery of the groat, while the concentration of starch increases from the sub-aleurone region towards the center of the endosperm[8]. The proteins in oat grains (globulins, albumins, prolamins (avenin), and glutelins) have different structures and compositions depending on their location within the grain. The endosperm of the oat grain contains two types of starch granules: compound and single granules. The proportions of amylose and amylopectin, as well as the size of the granules, vary among different oat varieties[5].

According to [9], the biochemical composition of oat grains reveals that oats grains mainly consist of starch (60%), but also soluble- and insoluble fibers, proteins, and fats. β-glucan is one of the soluble fibers and varies depending on the variety of the oat. Oat bran contains lesser amount of insoluble fibers such as cellulose and hemicellulose compared to the husk. The study in [9]compares the biochemical composition of wheat- and oat bran (Figure 2). This comparison shows that oat contains higher content of proteins. Soluble dietary fibers (SDF) and fats compared to wheat bran.

Content (%)	Wheat bran	Oat bran
Moisture	7.1 ± 0.66	6.2* ± 0.66
Protein	13.0 ± 0.46	16.6* ± 0.56
Fat	3.7 ± 0.55	7.5* ± 0.65
Ash	5.8 ± 0.15	2.1* ± 0.04
TDF (n=3)	47.1 ± 1.10	16.5* ± 0.84
SDF (n=3)	2.4 ± 0.73 (5)	7.9* ± 0.49 (48)
IDF (n=3)	44.8 ± 0.45 (95)	8.5* ± 0.38 (52)
SFA	21.6	17.4
USFA	78.4	82.6
SFA/USFA ratio	1 : 3.6	1 : 4.8

*Significant ($p \leq 0.05$), (n=6)
Figures in parentheses indicate per cent of total dietary fiber
TDF: Total dietary fiber, SDF: Soluble dietary fiber, IDF: Insoluble dietary fiber, SFA: Saturated fatty acid, USFA: Unsaturated fatty acid

Figure 2: biochemical composition comparison between what- and oat bran[9]

Research on the structural and biochemical composition of oat unveiled high level of proteins, vitamins, minerals, and fibers such as β-glucan, which has several health benefits claims. Reduction in inflammation among others[1].

2.1 Oat drink production

In this section a brief explanation of how oat drink is produced will be described. A more detailed explanation can be found in [10]

Oat drink also known as oat milk is made by blending oats with water, then processing the mixture to create a smooth, creamy liquid.

There are three main steps involved in the production of oat drink: 1) oat slurry creation: The first step is to create an oat slurry by blending water with oats in a process known as gelatinization, where the mixture is heated to help break down the oats and release their starches. Resulting in the starch inside the oats to swell and gelatinize and increase of viscosity is observed. 2) Enzyme treatment; once the slurry is heated, hydrolysis enzymes are added to break down the starch into smaller sugar units and thereby decrease the viscosity. 3) deactivation of enzymes: in the final step the mixture is again heated to deactivate the enzymes and stop the starch breakdown process[11]. This ensures that the oat drink will have a consistent texture and flavor profile. After these three steps, the oat drink can be flavored, sweetened and packaged for sale.

According to the experiment of DSM on liquefication and saccharification of oat slurry [12]. In this study DSM investigated the influence of time on the production of branched sugars in the liquefication step at 70°C with 1000 ppm of Delvo Plant ALT (α-amylase)Figure 3. They also investigated the influence of β-glucosidase concentrations on the production of monomeric sugars by in the saccharification step at 50°C for 2 hours Figure 4. The maximum release of sugar was 3.8% (w) for liquefication and 5.3% (w) for saccharification[12].

Oat slurry contains, as mentioned earlier insoluble fibers, proteins, starch, which can be broken down to smaller parts. These parts can sediment down to the bottom, since they are not soluble, unlike milk, which doesn't sediment after being processed. The insoluble molecules need to be filtered to enhance the sensory attributes. Furthermore, proteins, starch and fibers that have been broken down can decrease the filtration efficiency of Ultrafiltration membrane, due to their molecule charges[13]. More about membrane filtration in the next chapter.

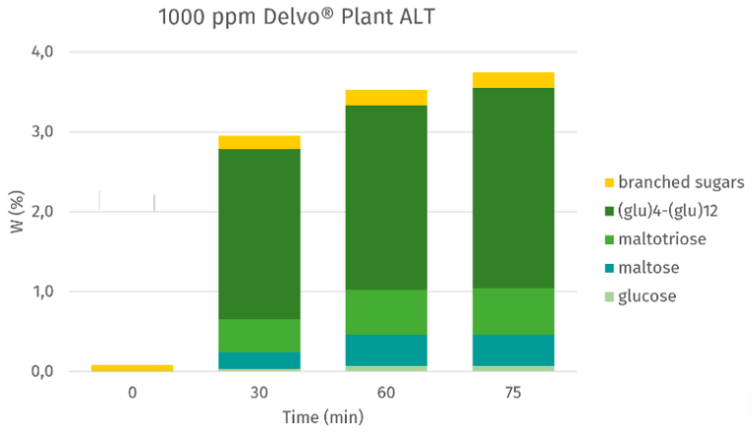

Figure 3) Liquefication of oat slurry[12]

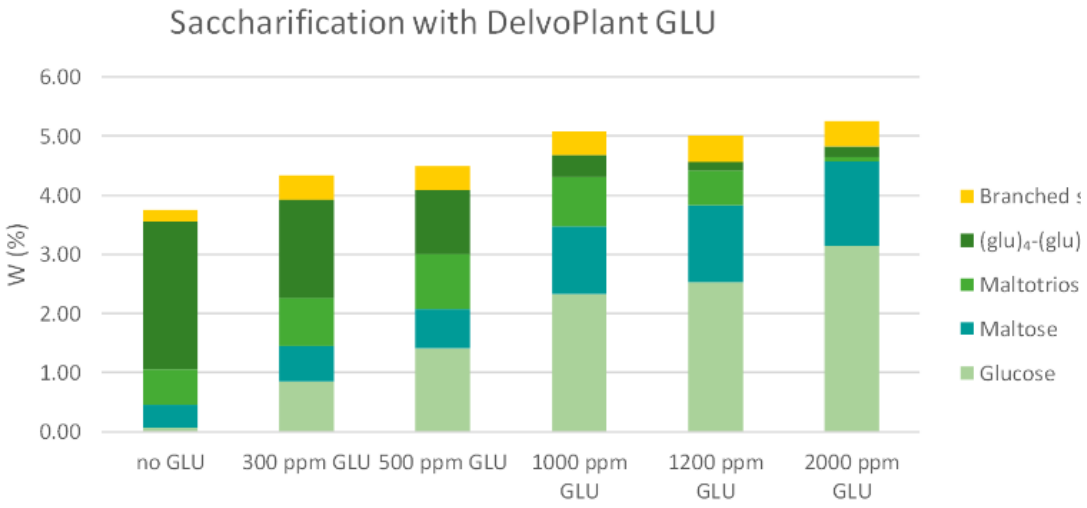

Figure 4) saccharification of oat slurry[12]

3 Membrane Filtration

Filtration is a term that refers to the separation of two or more components from a liquid or gas. Generally, it refers to the separation of solids from liquids or gases. In membrane separation, membranes are used to either purify products by removing dissolved solutes from the liquid or to concentrate solutes in a liquid by separating them from other solutes[8]. The membrane separation process is based on the presence of semi-permeable membranes, that act as very specific filters that will let water pass through, while catching suspended solids and other substances. There are several methods to enable substances to penetrate a membrane. Examples of these are the application of high pressure, the maintenance of a concentration gradient on both sides of the membrane and the introduction of an electric potential[14].

Solids that could block the flow channels of membrane modules in the subsequent stages are removed, for example by filtration or centrifugation (F&C) of the process stream. Suspended Solids and colloidal matter are separated by microfiltration (MF). Macromolecules, for example hemicelluloses and proteins, are concentrated by ultrafiltration (UF). Monosaccharides, multivalent inorganic ions and low molar-mass lignin are concentrated by nanofiltration (NF) and salt are removed by reverse osmosis (RO). The distinction between the three pressure-driven membrane processes MF, UF and NF, is somewhat arbitrary, however, they are commonly defined as; MF membranes retain suspended particles in the range 01 – 10 µm and UF membranes retain macromolecules in the rage 1 – 20 nm. NF membranes have smaller pores than UF but larger than RO membranes. The classification of MF membranes is based on nominal pore size and UF membranes of nominal molar-mass cut-off in the range of 1-1000 kDa. The driving force is usually 2 – 10 bars during UF and less than 2 bar during MF[15]

3.1 Membrane modules

The Selection of a membrane for a particular application relies on several factors, including its separation properties, as well as its mechanical and chemical durability. The membrane's ability to withstand pressure and temperature determines its mechanical stability, while its chemical stability is indicated by its resistance to different pH ranges and solvents. Therefore, when selecting a membrane, one must consider its separation characteristics, mechanical stability in terms of pressure and temperature limits, and chemical stability regarding pH range and resistance to solvents[13].

Membranes are manufactured from a variety of materials, both polymeric and ceramic (Figure 5). while temperature and pH resistance are generally higher for ceramic membranes, does polymeric membranes have higher maximum pressure. Among polymeric materials are polysulfone (PS), polyethersulfone (PES), polyvinylidene fluoride and generated cellulose the common ones. Ceramic membranes are usually made of Al_2O_3 and TiO_2[16].

Within each group of materials, there is a diverse range of membranes that exhibit different separation characteristics. The average pore diameter is used to describe the characteristics of MF membranes, while the cut-off value is used for UF membranes. However, the retention of solutes is not solely determined by size; factors such as molecular shape, inter-molecular interactions, and membrane-molecular interactions also play a role. Thus, the cut-off and pore size provide only an approximate indication of the membrane's separation performance[15]. The retention behavior of a substance in a multicomponent solution can differ significantly from that of a single solute of similar size. Additionally, even if two applications may seem similar, the optimal pore size for fractionation can vary due to variations in raw material heterogeneity and differences in

extraction process variables. Therefore, when designing a plant for a new application, it is advisable to conduct screening tests using multiple membranes to assess their suitability. This approach helps ensure that the chosen membrane meets the specific separation requirements of the application[17].

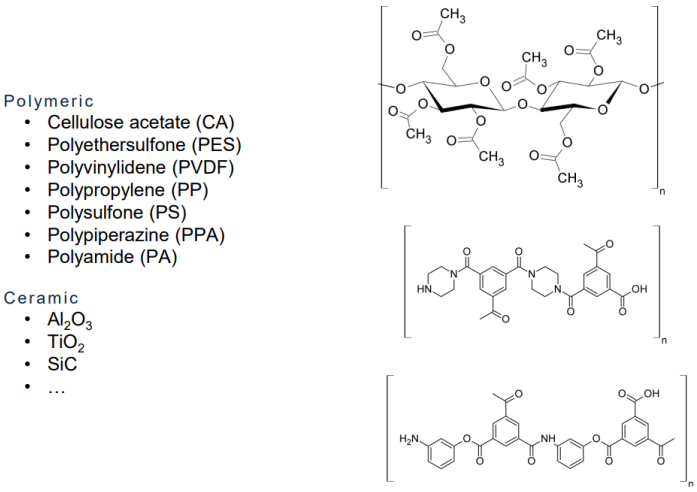

Figure 5) The two broad categories of membrane materials; polymeric and ceramic and their types[17]

Membranes are integrated into modules. Economic considerations, and chemical engineering aspects are of prime importance in the choice of membrane modules. A number of membrane module designs are possible, and all are based on two types of membrane geometry: *flat sheet membranes* and *capillary fibers.* In this chapter, two types of membrane modules will be described; spiral wound and plate-and-frame[16]

3.1.1 Spiral wound

Spiral wound module was initially developed for reverses osmosis applications and is nowadays also used in UF applications. Spiral wound modules have to be used where pressure drop has to be considered, and when counter flow is not needed to maximize separation efficiency. Higher pressure applications involving costly pressure vessels and piping make the hollow fiber modules more favorable because this reduces the component costs of the system by as much as a factor of ten in some cases[18].

The device is constructed of the same flat sheet membranes used In plate-and-frame modules. Each cartridge is made by wrapping alternate layers of membrane and separator screens concentrically around a hollow core as shown in Figure 6. The feed that needs to be filtered enters one end of the cartridge under pressure and flows tangentially down the central axis. The ultrafiltrate containing salts, water and molecules not retained in by the membrane flows through the membrane into the permeate channel and spirals all the way to the central core of the cartridge. The permeate is continuously removed from the central core while the retentate containing the rejected spiral cartridges made with different ultrafiltration membranes with varying cuts-off are available from filter suppliers. [19] reported that that the packing density of spiral wound modules are greater than that of the plate and frame module but is influenced by the channel height, which is determined by the thickness of the of the permeate and feed-side spacer material [20].

The advantages of spiral-wound modules are that they are simple, cost-effective construction they have good mass transfer due to feed spacer and they have relatively high packing density/membrane area to volume ratio (up to 1,000 m2/m3). The downside of spiral-wound membrane modules is their long permeate path and cleaning difficulty[20].

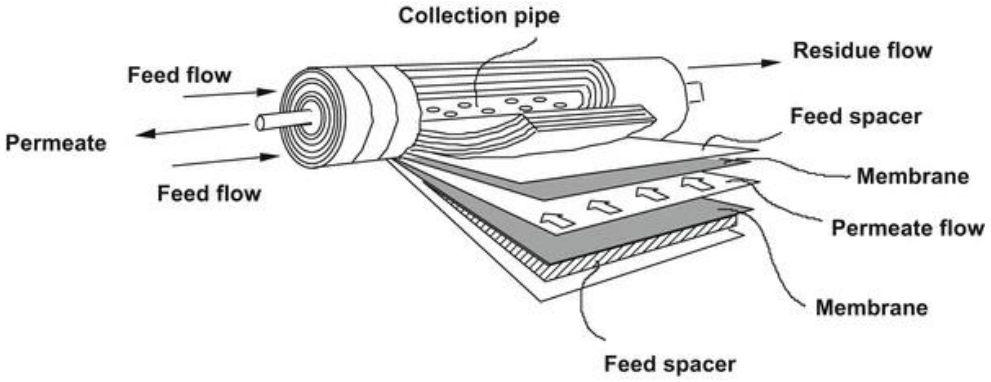

Figure 6: Schematic drawing of a spiral-wound module membrane and its components[20]

3.1.2 Tubular

A tubular membrane module utilizes tubular membranes, which share the same membrane geometry as capillary membranes and hollow fiber membranes but differ in size. Tubular membranes typically have an outer diameter ranging from 5 to 25 mm. Unlike capillaries and hollow fibers, tubular membranes lack self-supporting properties. Instead, they are inserted into porous tubes made of stainless steel, ceramic, or plastic, with the tube diameter typically exceeding 10 mm. The number of tubes incorporated into the module can vary, ranging from 4 to 18, but it is not limited to this range[21].

In this module design, the feed solution always flows through the central region of the tubes, while the permeate passes through the porous supporting tube and into the module housing (Figure 7). Tubular modules are commonly employed for assembling ceramic membranes. However, the packing density of tubular modules is relatively low, measuring less than 300 m2/m3.

Currently, tubular modules are predominantly used in ultrafiltration applications, where their superior resistance to membrane fouling resulting from favorable fluid hydrodynamics outweighs the associated high costs[16].

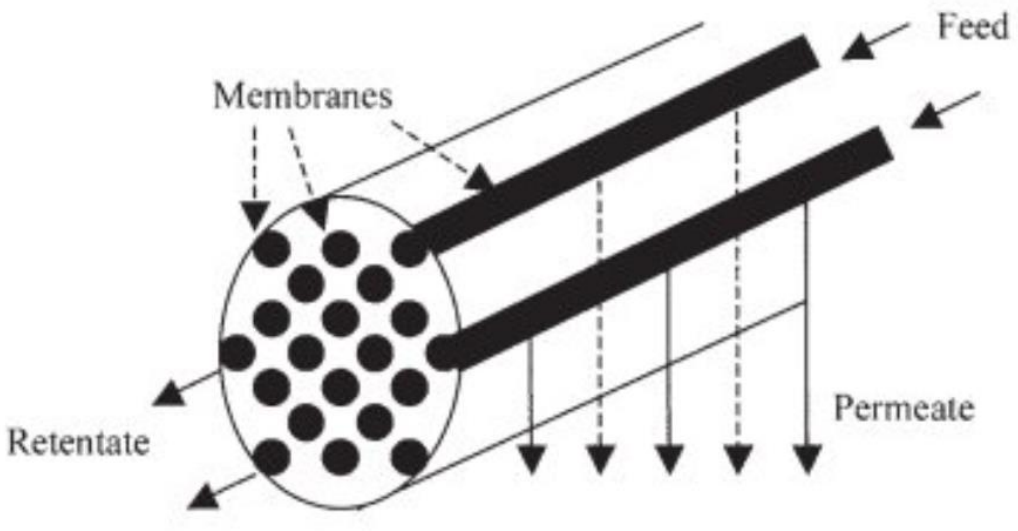

Figure 7) schematic drawing of a tuburlat membrane module

3.1.3 Plate-and-frame

The plate and frame module design closely resembles the flat membranes commonly used in laboratory settings [4]. The key components of this module construction include the flat membrane, membrane supporting plate/spacer, and feed distribution plate [22]

In the plate-and-frame module configuration (refer to Figure 8), two membranes are arranged in a sandwich-like manner with their feed sides facing each other. Each feed and permeate compartment is equipped with an appropriate spacer. To create a plate-and-frame stack, multiple sets of membranes are assembled, accompanied by sealing rings and two end plates, according to the desired membrane area. These modules have a relatively low packing density, typically ranging from 100 to 400 m2/m3[4]

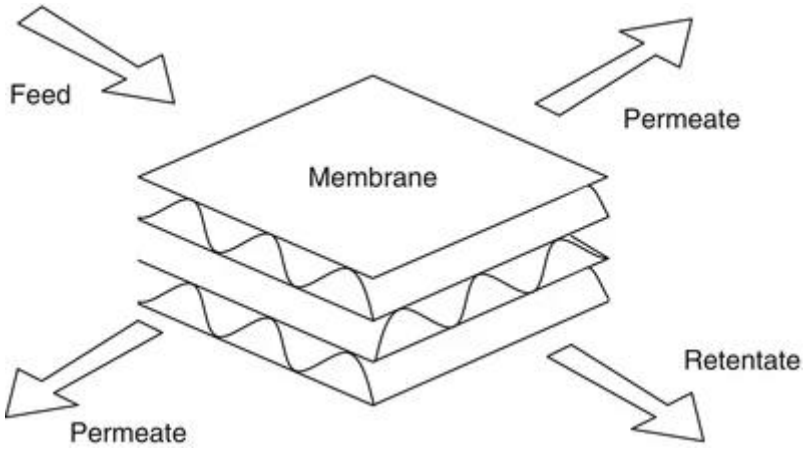

Figure 8: Schematic representation of a plate-and-frame membane module

Figure 9 illustrates a schematic flow path within a plate-and-frame module. Baffles are introduced to mitigate channeling, which is the tendency of the fluid to bypass certain areas of the membrane and take shortcuts. The inclusion of baffles helps establish a uniform flow distribution (Mulder, 1997).

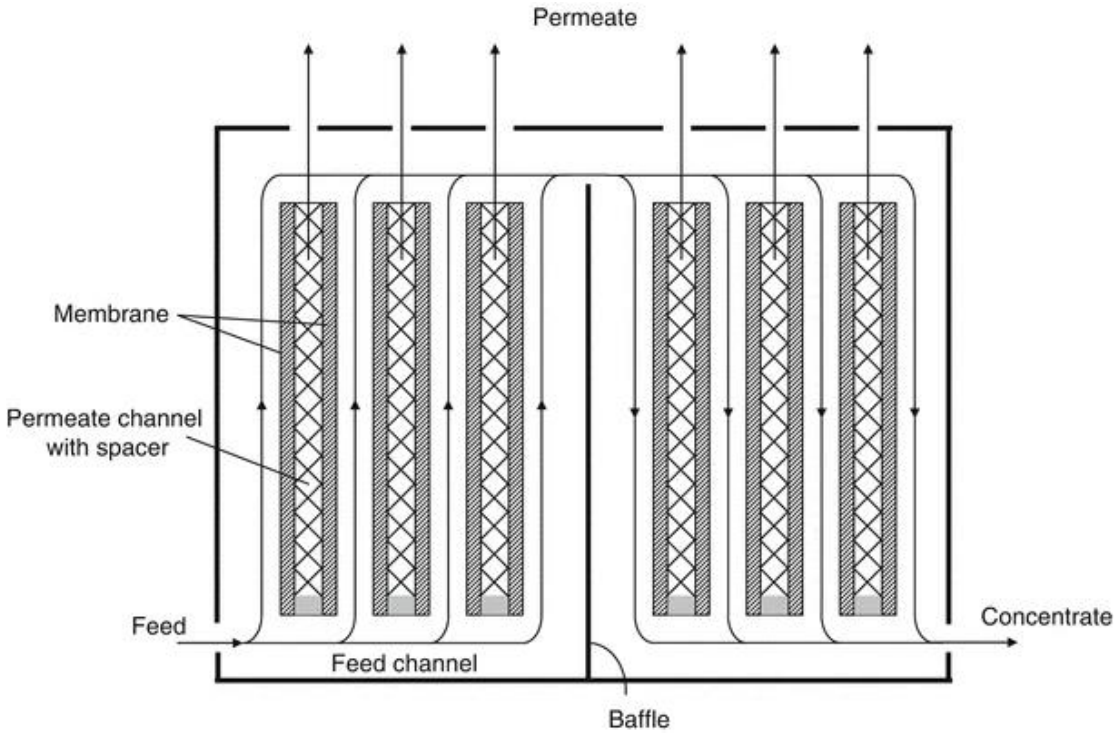

Figure 9: flow path for a plate-and-frame membane module

According to a study by Blackmer and Hedman in 1979, plate-and-frame membrane modules offer several advantages. They exhibit low sensitivity to blockage caused by particulate matter in the feed channels, and they can be assembled without the need for glue since they are solvent bonded. Additionally, these modules can be used repeatedly for several years after undergoing proper cleaning and sanitization. However, they also come with certain drawbacks. They require multiple sealings, which adds complexity. There is a pressure drop associated with their operation, and their packing density is comparatively low compared to other module types. Furthermore, achieving a thorough cleaning of the module requires disassembly, resulting in the need for manual labor and this increasing the operating costs [4].

3.2 Operating parameters

The cost and membrane performance are influenced by several operating parameters, that must be optimized in each specific application. In this section the most commonly used operating parameters for membrane performance will be investigated[15].

Parameters studies are often performed in a number of concentrations to simulate the conditions in different stages of multistage plant (number of feed-and bleed stages in series). The characteristics of the specific membrane and feed in question influence the importance of each operating parameter. The transmembrane pressure (TMP) and the crossflow velocity are the most important operating parameters and are therefore often optimized in pilot-scale investigations. The table below (Table 1) shows some general trends in UF[13].

Table 1: relationship between operation parameters and flux[15]

Parameters increase	Flux impact

Pressure (TMP)	Flux increases linearly initially, then levels off as pressure is raised further, and finally may even decrease at elevated pressure
Crossflow velocity	Flux increases, the effect reduces as velocity increases further
Temperature	Increase in flux
concentration	Decrease in flux

Pure water flux (PWF) is defined as the flux of deionized water, and the limiting flux is the highest flux that can be obtained when increasing the TMP within a given set of operating conditions. Three definitions of the concept of critical flux are extensively reviewed by [23]. a common definition of the critical flux is the flux at which the operation shifts from reversible to irreversible during the increase in pressure. In essence, the point below which the flux remains constant with the time[13].

The PWF is defined as:

$$PFW = \frac{\Delta P}{\mu \cdot R_m}$$

Where ΔP is the TMP, μ is the viscosity of water, and R_m is the hydraulic resistance of the membrane. The PWF can be used to determine the hydraulic resistance and to control the efficiency of cleaning. The PWF is a linear function of pressure until the maximum operating pressure of the membrane is reached. At this point compressibility of the membrane limits the flux increase.

UF membrane present at 1 bar and 25 ºC is usually in the interval of 10-500 $\frac{L}{m^2 \cdot h}$. There are two basic flux models. In the *osmotic pressure model*, the driving force is reduced by the flow resistance offered by material retained by the membrane on the surface. The flux for the model is given by:

$$J = \frac{\Delta P - \Delta \pi}{\mu_P \cdot R_m}$$

Where $\Delta \pi$ is the osmotic pressure difference across the membrane and μ_P is the viscosity of the permeate. The osmotic pressure of suspended solids and colloids retained by MF is negligible and the osmotic pressure in the bulk solution of macromolecules retained by UF is usually also insignificant. However, when there is a permeate flow through the membrane, solutes are transported together with the solvents to the membrane surface. This means that retained compounds will accumulate near the membrane. And the concentration at the membrane surface will be higher than the concentration in the bulk solution. This phenomenon occurs to varying degrees in all membrane processes and is commonly referred to as concentrations polarization (further detail in chapter 4.1). The osmotic pressure of macromolecules at the concentrations prevailing at the membrane surface can be significant, markedly reducing the flux[8].

In the *cake filtration model*, it is assumed that a layer of concentrated solute, a cake or gel, is formed at the membrane surface. The flux is then expressed as[3]:

$$J = \frac{\Delta P}{\mu_P (R_m + R_c)}$$

Where R_c is the hydraulic resistance of the filtercake. The effect of the osmotic pressure on the driving force is neglected since the additional resistance on the filtercake is large in comparison. The osmotic pressure model

applies fairly well when treating solution containing small, non-interacting solutes, whereas when treating solutes with a molar mass greater than 100kDa, the cake filtration model gives a better description of the concentration profile. The cake filtration model is thus often used during MF and osmotic pressure model during UF[24].

Flux declines with time due to fouling. The two mentioned models don't take cake into account with the decline of flux with time. The *resistance-in-series model* is often used to interpret and quantify flux decline behavior. This model is an extension of the cake filtration model, the resistance to flow is accounted for by several resistances in series with the membranes:[24]

$$J = \frac{\Delta P}{\mu_P (R_m + R_{cp} + R_f)}$$

Where R_{cp} is the reversible resistance to flow due to concentration polarization and R_f is the fouling resistance. The fouling resistance is divided into different components, presented in more detail in the later section on fouling[24].

3.2.1 Pressure

Pressure measurements are taken at different points in a membrane plant, including the inlet (P_{in}) and outlet (P_{out}) of the membrane module, as well as on the permeate side (P_p). The Transmembrane Pressure (TMP) serves as the driving force in UF and is calculated as the average pressure difference across the membrane:

$$\Delta P = \frac{P_{in} + P_{out}}{2} - P_P$$

The TMP against flux is depicted in Figure 10. The pure water flux (PWF) is a linear function of pressure until the maximum pressure is reached. Whereas, the flux of solution is different the flux decreases over time, and is flattening out after a period of time[24].

The TMP is often regulated by the retentate valve. However, when using ceramic membranes the TMP is often regulated by a valve on the permeate side of the module. If there is no permeate valve, the permeate pressure equals atmospheric pressure.

The frictional pressure drop is the pressure difference between the inlet and outlet of the module.

$$\Delta P = P_{in} - P_{out}$$

In small bench-scale membrane modules, the pressure drop is usually minimal, but it can become more significant in full-scale modules. In situations where the inlet pressure is elevated, such as in UF, the difference in pressure between the inlet and outlet is typically negligible. However, when dealing with viscous fluids and operating at high cross-flow velocities, the pressure drop can become substantial. This can result in a zero flux or even a reverse flow of permeate in the final section of the feed flow channel[24].

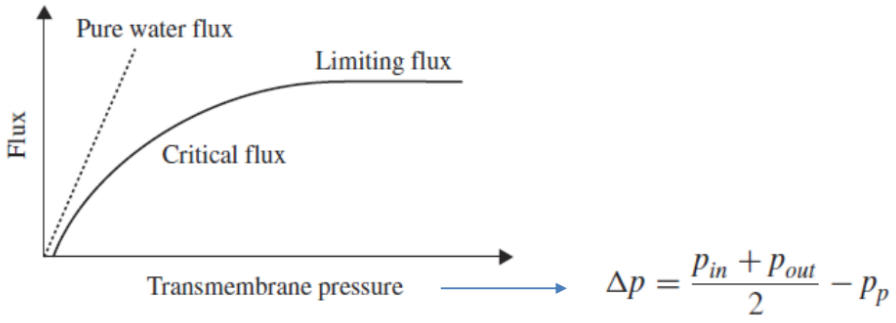

Figure 10) TMP vs flux curve.[24]

3.2.2 Cross-flow velocity

Cross-flow operation is utilized to mitigate concentration polarization and enhance mass transfer [92–94]. According to the film theory, the fluid flow in the boundary layer near the membrane surface is considered laminar, while the fluid flow beyond this layer is turbulent, facilitating thorough mixing of solute. Under steady-state conditions, the convective transport of solute within the boundary layer is balanced by the permeate flow and the diffusive transport of solute back into the bulk solution. The film theory model provides a correlation between flux and concentration at the membrane surface, expressed as follows:

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

The correlation provided by the film theory model relates the mass transfer coefficient ($k = D/\delta$), where D is the diffusion coefficient, and δ represents the thickness of the boundary layer. Within the equation, Cm, Cb, and Cp denote the concentrations at the membrane surface, in the bulk solution, and in the permeate, respectively. The actual thickness of the boundary layer depends on the rheological characteristics of the solution and the exerted shear forces.

Traditionally, the estimation of the mass transfer coefficient involves the use of the Sherwood number [95], which can be expressed as:

$$Sh = \frac{k \cdot d_h}{D} = A \cdot Re^a \cdot SC^b$$

Here, Re represents the Reynolds number, Sc is the Schmidt number, and A, a, and b are constants determined empirically. To enhance the flux, it is common practice to increase the mass transfer coefficient by reducing the thickness of the boundary layer. In most modules, the shear rate is intensified by elevating the cross-flow velocity. The relationship between the mass transfer coefficient and cross-flow velocity is described as follows [96]:

$$k \propto u^{0.33} \text{ (for laminar flow)}$$

$$k \propto u^{(0.69-0.8)} \text{ (for turbulent flow)}$$

In the equations, u represents the cross-flow velocity, and typically, the flow within the feed channel is turbulent [8.20] [8.21]. The mass transfer coefficient is also influenced by viscosity, which is in turn affected by the concentration of the feed solution. Under turbulent flow conditions, the impact of bulk viscosity on the mass transfer coefficient can be described as [97]:

$$k \propto \mu^{(-0.33b)}$$

3.2.3 Temperature

Increasing the temperature of the feed solution has three positive effects on enhancing the flux in membrane processes. Firstly, it reduces the viscosity of the permeate, resulting in a higher flux. Secondly, the lower viscosity of the solution on the feed side of the membrane improves the mass transfer coefficient. Lastly, the decreased viscosity of the bulk solution increases the Reynolds number, leading to a lower frictional pressure drop. This reduction in pressure drop further contributes to an improved flux[21].

3.2.4 Concentration

The concentration of feed solutions in membrane processes is inherently limited. It is important to note that no membrane process can achieve complete solute concentration to dryness. in processes involving microfiltration (MF) and ultrafiltration (UF), it is typically the low mass transfer rate of high-molar-mass substances retained by these membranes and the resulting high viscosity that pose challenges in pumping the retentate, thereby limiting the final concentration[9].

4 Concentration polarization and fouling

The flux of a solution will always be lower than the PWF. This is because of two phenomena known as concentration polarization and fouling. The two phenomena are distinguished by the reversibility of the flux decline. concentration polarization is the part of the flux decline that is reversible simply by changing the operating conditions. Whereas, for the fouling membrane, cleaning is required to restore the flux[13] . In this chapter, concentration polarization and fouling of the membrane will be investigated and linked to their influence on the membrane[17].

4.1 Concentration polarization

Concentration polarization occurs when the concentration of a specific component increases or decreases at the boundary layer close to the membrane surface due to the selective transport through the membrane. In case of pressure-driven processes such as MF and UF, the macromolecule solute is typically retained by the membrane, leading to a concentration profile similar to Figure 11A. This profile can also be found in processes such as membrane-based extraction or membrane-based absorption. In other membrane processes where the transport of through the membrane takes place by diffusion rather than by convection, a concentration profile similar to Figure 11B will be obtained since the component will permeate faster through the membrane, being the boundary layer where the transport is limited by diffusion. This concentration profile can thus appear in processes such as gas Concentration polarization gas separation, pervaporation, dialysis, electrodialysis, membrane crystallization, membrane distillation, etc[40].

Concentration polarization produces a decline in the transmembrane flux, which may be very severe, such as in microfiltration or ultrafiltration, or negligible, such as in gas separation. Regarding the retention, it may lead to a lower retention if low molecular weight solutes (e.g., salts) are considered, or it may lead to a higher retention, which is the case of mixtures of macromolecular solutes. Concentration polarization can be mathematically described by specific [25]models that have been described in the literature, for example, gel layer model, osmotic pressure model, boundary layer resistance model [40]

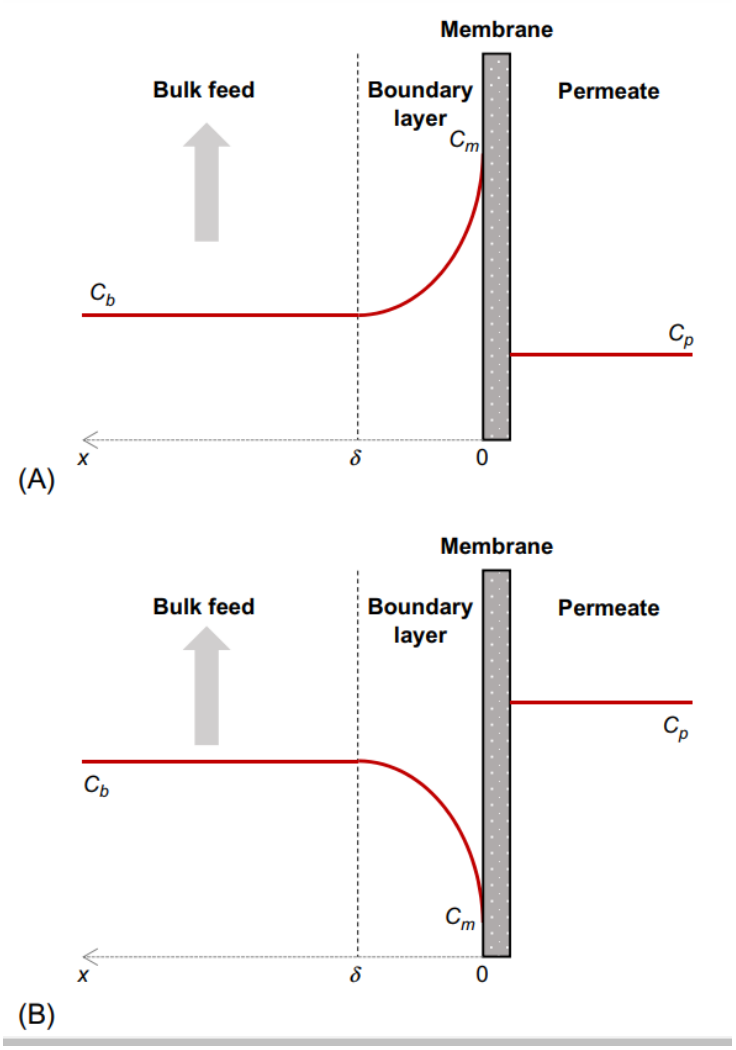

Figure 11) Concentration profile with concentration polarization: (A) mass transfer limited by the membrane and (B) mass transfer limited by the boundary layer.[10]

4.2 Fouling

Over time, the permeability and selectivity of UF membranes deteriorate due to the accumulation of solids, suspended particles, colloids, and bacteria on the membrane surface and within its pores. This phenomenon is commonly referred to as membrane fouling. Fouling occurs when particles, colloids, macromolecules, salts, biomolecules, and other substances deposit on the membrane surface or inside the pores, leading to a reduction in membrane flux, either temporarily or permanently. The main mechanisms of fouling include the adsorption of partially rejected matter within the pores (pore constriction), the blocking of individual pores by particles similar in size (pore blocking), and the accumulation of completely rejected particulate matter on the membrane surface (cake formation). Fouling is a result of concentration polarization, adsorption, and the deposition of a cake layer[13], [26], [27].

The fouling phenomenon arises from the interaction between the membrane surface and various foulants, which can be inorganic, organic, or biological substances occurring in different forms. These

foulants not only physically interact with the membrane surface but can also chemically degrade the membrane material. For instance, colloidal particles like natural organic matter (NOM) not only physically interact with the membrane surface but also chemically deteriorate the membrane material. In both MF and UF processes, the separation performance and membrane fouling are strongly influenced by the pore structure of the skin layer (size, shape, length, and porosity) and the chemistry of the membrane (functionality, charge, and hydrophilicity). It is important to note that not all MF or UF membranes exhibit fouling at the same rate, suggesting that differences in polymer composition and other membrane surface properties (e.g., hydrophobicity, roughness, pore size and geometry, charge density) play a role in determining the rate at which foulant matter initially attaches to the surface[28].

In the appendix 12.1) detailed descriptions on the various types of foulants, effects of morphology on UF fouling, the principles of the commonly used instrument techniques in predicting these factors and measures that can be taken in fouling control will be covered.

4.3 Analytical techniques for studying fouling

4.3.1 Water contact angle

The water contact angle is used to determine the hydrophilicity or hydrophobicity of a membrane surface. A contact angle less than 90° indicates a hydrophilic surface, while an angle greater than 90° suggests a hydrophobic surface. Hydrophobic membrane surfaces are formed by disrupting intermolecular bonds within the polymer matrix, resulting in a low surface energy. Factors such as surface roughness, porosity, and pore size distribution can also affect the contact angle. Contact angle measurements provide insights into surface hydrophilicity, roughness, and porosity, which influence fouling behavior. The contact angle values of MF and UF membranes depend on their surface hydrophilicity (or hydrophobicity), roughness, porosity, pore size, and pore size distribution. A highly porous membrane may exhibit a very low contact angle, even if it is not necessarily hydrophilic. Similarly, a membrane with higher surface roughness will have a higher contact angle compared to a membrane with lower surface roughness, even if both membranes are similarly hydrophilic.4 It is believed that a membrane with a lower contact angle will have a stronger affinity for water. When the membrane comes into contact with the feed solution, a hydrated layer is formed, which prevents the further accumulation of hydrophobic foulants.

4.3.2 Zeta-potential

Zeta potential is an electrokinetic potential that quantifies the charge present on the membrane surface. It is commonly used to study fouling interactions, particularly the electrostatic interactions between charged membrane surfaces and charged foulants. The ζ potential can be measured using streaming potential measurement, which evaluates charge modifications on the membrane surface. The ζ potential is influenced by the pH of the feed solutions and can provide insights into fouling behavior. According to Lawrence et al.,[46] the interactions leading to fouling, specifically the electrostatic interactions between charged membrane surfaces and charged foulants, can be predicted through ζ-potential studies. If the measured ζ potential remains similar before and after fouling and cleaning, it suggests that the membrane surface has been restored close to its original condition after the fouling and cleaning process.

5 Cleaning

Maintaining the permeability and selectivity of a membrane process requires regular membrane cleaning. Cleaning is defined as the removal of substances that are not inherent to the membrane material itself [9]. Presently, membrane cleaning techniques can be broadly classified into three categories: physical, chemical, and enzymatic methods, with the first two being the most used. In this chapter the different types of membrane cleaning, as well as cleaning protocols and parameters influencing cleaning efficiency will be investigated. There are two types of cleaning; *reversible*- and *irreversible* cleaning.

Reversible cleaning refers to the process of removing fouling or deposits from a membrane or surface in a manner that allows the membrane or surface to regain its original performance without any permanent damage or loss of functionality. Reversible cleaning methods typically involve the use of mild cleaning agents or techniques that can dissolve or dislodge foulants without causing significant changes to the membrane structure or surface properties. These methods aim to restore the membrane's performance and allow it to continue operating efficiently.

On the other hand, irreversible cleaning involves the use of more aggressive cleaning agents or techniques that may cause permanent changes or damage to the membrane or surface being cleaned. Irreversible cleaning is typically employed when fouling is severe or when reversible cleaning methods have failed to restore the membrane's performance. In some cases, irreversible cleaning may be necessary to remove stubborn or strongly adhered foulants that cannot be easily removed by gentle means. However, the downside of irreversible cleaning is that it may lead to alterations in membrane structure, surface properties, or performance, resulting in reduced membrane lifespan or decreased separation efficiency. in this project, one of objective is to use reversible enzymatic cleaning agents.

5.1 Physical

Physical cleaning methods utilize mechanical forces to dislodge and eliminate fouling substances from membrane surfaces. The initial step of physical cleaning involves stopping permeation or TMP and allowing the foulant layer to relax and dissolve back into the recirculating feed stream[29].

For specific membrane types such as hollow fibers and certain flat sheet membranes, backflushing or reversing the flow of permeate through the pores can be employed intermittently during filtration or as part of a cleaning cycle to remove particle cakes and internal fouling. While this method can be highly effective, backflushing may not ensure uniform distribution across all pores as the majority of the flow tends to follow the path of least resistance, resulting in incomplete removal of foulant cake. If permeate is used in backflushing, any soluble foulant remaining in the permeate has a second chance to deposit internally within the membrane pores. To enhance the efficacy of physical cleaning, pulsed flow or aeration can be employed to induce higher turbulence. Ultrasonic cleaning has been proposed for membranes in the dairy industry; however, challenges exist in terms of large-scale implementation and energy requirements. In the case of tubular membranes, physical removal of surface foulants can be achieved using sponge balls, but it is not effective for addressing internal fouling[30].

5.2 Chemical

Chemical cleaners are employed to break down the structure of fouling substances and enhance their solubilization. The breakdown of foulant structure can occur through the cleavage of bonds within macromolecules or between aggregates present in the fouling material. Solubilization of the fouling substance can be increased by chemically degrading the species into more soluble forms, such as saponification, which involves breaking ester bonds between fatty acids and glycerol[31]. Additionally, surfactants or other dispersant agents can be utilized to sequester hydrophobic groups into micellar or emulsified forms, promoting their solubility. Surfactants are effective in displacing or preventing the precipitation of foulant residues, which is particularly important in membrane cleaning for food and bioprocess applications where proteins, lipids, and their degradation products tend to be hydrophobic and prone to precipitate in aqueous cleaning solutions. Wetting agents are also employed to enhance the penetration of cleaning agents into the membrane pores[32].

Sanitization and disinfection are crucial steps at the end of the cleaning process to eliminate or reduce biofilm formation by destroying pathogenic microorganisms and reducing the overall microbial count. These steps also protect the membrane surface from microbial attack and minimize the risk of product contamination[33].

When multiple cleaning agents are used in a cleaning regimen, rinsing between the different cleaning agents is necessary to flush and remove any residual buildup in the membrane module and on the membrane surface. Without proper rinsing, even if bulk foulants are removed from the surface, residual proteins and other macromolecular components can lead to re-fouling of the membrane or penetrate deeper into the pore structure. Commonly employed cleaning agents in various industries include acids, bases, surfactants, disinfectants, and enzymes[6].

5.3 Enzymatic

Enzymes serve as catalysts that accelerate reaction rates without being consumed in the process. Although most enzymes are protein-based, there are a few exceptions with catalytic RNA molecules. Enzymes exhibit specificity towards particular substrates and reactions and perform effectively under mild conditions and temperatures[30].

Enzymes function optimally within specific temperature and pH ranges. Changes in temperature and pH can induce alterations in intermolecular bonds, leading to modifications in enzyme structure and properties. Denaturation occurs when a protein loses its biological function, including the catalytic activity of enzymes. Denaturation can be caused by increased solvation of nonpolar amino acids and charged groups within the hydrophobic core of the protein under pressure. Exposure to temperatures outside the optimal range can also result in denaturation. Enzymes are classified into high (thermophilic), moderate (mesophilic), and low (psychrophilic) working temperature groups[34].

Enzymes such as proteases, lipases, and amylases have the potential to act as cleaning agents for the removal of fouling agents containing proteins and polysaccharides, which are prominent in hydrolyzed oat. These enzymes can break specific bonds within protein chains, leading to protein degradation and facilitating their removal from the membrane. However, the effectiveness of enzymatic cleaning depends on determining the optimal pH, concentration, and temperature for each specific enzyme-foulant combination to ensure efficient cleaning performance[25].

Enzymatic cleaning has shown promising results in the cleaning of membranes fouled with abbatoir effluent, utilizing lipases and proteases as enzymes. Lipase is typically used first to prevent degradation by protease. The combined use of lipase and protease has resulted in nearly 100% flux recovery. Novozymes, DSM and other manufactures have started producing enzymes and other cleaning agents to break down plant-based compounds such as, cellulose, β-glucan, plant proteins and etc[4].

5.4 Cleaning protocol design

The efficiency of cleaning is influenced by various factors including the concentrations of cleaning agents, cleaning time, temperature, and hydrodynamic conditions during the cleaning process. The presence of mass transfer barriers within the fouling layer often acts as the limiting factor for chemical and biochemical cleaning. When designing a cleaning regimen, it is important to consider the balance between process turn-around time, membrane lifetime, generation of cleaning effluent, and economic costs. Wilson identified several factors that should be taken into account when designing and implementing an appropriate cleaning regimen for food and bioprocess applications.

Although different plants may employ variations of cleaning sequences, it is common for acid cleaners to follow alkali cleaners, with appropriate rinses before and after each step. The duration of individual steps can range from 30 to 60 minutes. The effectiveness of alkali/acid or acid/alkali sequences has been studied in various dairy plants, but detailed comparisons have not been extensively conducted.

A commonly used approach to evaluate the cleaning efficiency of the cleaning process is to compare the particulate weight fraction (PWF) before and after cleaning. Cleaning efficiency is often assessed by measuring either the flux recovery or the removal of resistance to compare the effectiveness of different cleaning protocols. The flux recovery is typically estimated as follows:

$$Flux\ recovery = \frac{J_{wc}}{J_{wi}} \cdot 100\%$$

Where J_{wc} is the water flux after cleaning, and J_{wi} is the initial water flux. Resistance removal is estimated as:

$$Resistance\ removal = \frac{R_r - R_c}{R_r} \cdot 100\%$$

Where R_c is the resistance after rinsing, and R_c is resistance after cleaning. This type of assessment involves measurement of membrane fluxes prior to the filtration process, the initial water flux (J_{wi}), membrane flux at the end of filtration process (J_{wf}), membrane flux after rinsing (J_{wr}), and membrane flux after cleaning (J_{wc}). Comparison with normalized water fluxes of virgin membranes with certain tolerances (10-20%) can be made to establish the effectiveness of cleaning methods[13].

5.5 Factors influencing cleaning efficiency

The effectiveness of chemical cleaning is influenced by various factors that affect the interactions during diffusion within the foulant layer. These factors include temperature, pH, concentrations of cleaning agents, and contact time between the cleaning solutions and the membrane.

Water rinsing

Water rinsing is considered an effective method for cleaning the membrane surface. Flushing the membrane surface with purified water or water for injection at atmospheric pressure helps remove loosely bound deposits.

Studies on membrane cleaning fouled by whey protein solution have shown that rinsing can remove up to one-third of the total protein deposit. Increasing the ionic strength in the rinsing solution can enhance calcium removal, possibly due to calcium/sodium ion exchange[17].

pH, ionic strength and concentration of cleaning solution

The pH, ionic strength, and concentration of the cleaning solution also play a role in the cleaning process. While higher concentrations of cleaning solution can lead to improved reaction rates between the cleaning agent and the foulant, there is often an optimal concentration for specific cleaning applications. Exceeding the optimum concentration does not result in improved cleaning efficiency and can even have adverse effects on the cleaning process. Adjusting the pH to a level that changes the charge of the foulant from its original deposition conditions has been shown to improve cleaning efficiency[17].

Cross-flow velocity

Cross-flow velocity can enhance cleaning efficiency by improving the mixing of the cleaning solution and increasing the shear rate on the fouled membrane surface. Higher cross-flow velocity and the addition of air sparging during cleaning promote better mixing and shear rate, which facilitates the removal of hydrolyzed foulants from the surface. Appropriate shear stress has been reported to assist in removing particulate fouling and foulant aggregates.

Cleaning time

The cleaning time required depends on the specific foulants present. Adequate cleaning time should be provided to ensure sufficient contact between the cleaning agents and the foulants. Enhanced removal of the reacted top layer increases the contact between the cleaning agents and subsequent foulant layers, thereby reducing the cleaning time. Each specific application has an optimized cleaning time, and exceeding this optimized time may not provide significant cleaning benefits. In fact, longer cleaning times can be detrimental due to excessive denaturation or redeposition of foulants. In the case of enzyme cleaning, prolonged cleaning times can result in the enzyme fouling the cleaned membrane.

Temperature

Temperature also plays a role in cleaning effectiveness. In general, higher temperatures enhance mass transport and reduce viscosity, leading to improved cleaning effectiveness. However, the operating temperature may be limited by factors such as membrane material and module construction. Higher temperatures can also cause changes in protein structure, making it more difficult to clean. Higher temperatures can improve the efficiency of cleaning agents by increasing reaction kinetics, and many cleaning agents disperse better at higher temperatures.

Multiple cleaning cycle

Limited laboratory studies have been conducted on the effects of repeated cleaning treatments on membrane integrity and performance at cleaning temperatures and environments. The interactions between cleaning and sanitizing agents with clean UF membranes can have varying effects on membrane life and performance, even if the mechanical integrity of the membrane remains uncompromised[24].

In the case of ceramic membranes fouled by rough [14]. observed that harsh chemical cleaning methods were unable to completely remove the foulant due to strong adsorption forces, such as electrostatic and hydrophobic

attraction, as well as hydrogen bonds. Another study investigated the fouling and cleaning cycles of a 30kDa PES membrane using whey protein isolates (WPI) as the feed solution in cross-flow filtration. The researchers performed repeated cycles of fouling and cleaning using a NaOH followed by HCl cleaning sequence. The flux recovery due to NaOH remained relatively constant throughout the four repeated cycles, while the flux recovery due to rinsing, NaOH, and HCl cleaning cycle increased with the number of cycles and eventually reached a constant value of 90%. The enhanced cleaning efficiency of HCl may be attributed to the accumulation of residual inorganic components on the membrane surface over the repeated cycles, which could be effectively removed by HCl in the subsequent cleaning sequences[15].

Sequential cleaning

Sequential cleaning involves multiple stages, and the specific order and duration of each step can significantly impact cleaning effectiveness. A typical cleaning process includes rinsing, chemical cleaning, rinsing between different chemical agents if multiple agents are involved, and a final rinsing step. Initial rinsing and alkaline cleaning stages often recover the majority of the flux (around 80-90%). Sayed et al. conducted a study on the cleaning of membranes used in UF of an aqueous extract of soy flour. They found that caustic cleaning was more effective than acid cleaning, but the best results were achieved using an enzymatic cleaner containing protease, even though the flux was not fully restored. Sequential cleaning with water rinsing, NaOH, protease detergent, and NaClO, followed by a final rinsing step, resulted in complete flux recovery. Optimization of the order and duration of each cleaning step is essential for maximizing cleaning effectiveness in sequential cleaning processes[32].

6 Problem statement

One of the conventional methods to filter oat slurry for suspended solids and other unwanted substances is through decantation, which is an easy and relatively efficient method. However, as more sustainable, and environmental-friendly solutions are getting desired, membrane filtration can be a good alternative since less energy and water are required compared to traditional decantation. However, the fouling of membrane, especially UF remains a significant challenge that hinders their long-time efficiency and effectiveness in oat drink processing. Although chemical cleaning of fouled membrane has been studied excessively and been established as a cost-effective way to reduce fouling and recover flux to its initial state, the water effluent needs to be neutralized and the producers overall desire a more environmental-friendly, and sustainable production.

This can be achieved with enzymatic cleaning, that utilizes enzymes that selectively, and efficiently cleaves macromolecules into smaller molecules. While enzymatic cleaning has shown promise in mitigating fouling in various applications, its effectiveness and feasibility specifically for UF membrane fouling after oat drink filtration have not been thoroughly investigated. Therefore, this report will focus on screening of enzymatic cleaning of fouled UF membranes after oat drink production. PES flat sheet membranes in plate-and-frame module will be used to investigate fouling characteristics and cleaning efficiency, since plate-and-frame module configuration provides a versatile and controlled experimental platform to investigate and optimize enzymatic cleaning efficiency.

Furthermore, due to what was mentioned in Chapter **Fejl! Henvisningskilde ikke fundet.** 5.5, several cleaning parameters such as types of enzymes, pH, cleaning time, cleaning sequence will be adjusted while the rest will be held constant. Hence the report's problem statement is formulated as:

What is the maximum water flux recovery that can be achieved with enzymatic cleaning of UF PES membrane in a plate-and-frame configuration fouled with oat slurry?

To obtain that, certain objectives will be investigated experimentally:

- Create and investigate oat slurry preparation influence on flux recovery and membrane surface properties.
- Investigate the influence of high enzyme concentrations and cleaning sequence on the flux recovery.
- Investigate the influence of pre-filtration after oat slurry preparation on the flux recovery.
- Investigate the influence of cleaning time on the flux recovery.

7 Materials

Different materials were needed for the plate-and-frame UF described in this report. These include oat slurry that would be used as a feed, PES membranes, cleaning agents such as enzymes to create the enzymatic cleaning mix and chemicals to compare enzymatic cleaning efficiency, and also to thoroughly clean the filtration system after each enzymatic cleaning cycle, and plate and frame module.

7.1 Oat slurry preparation

To ensure that the oat slurry feed would not have an effect, the same protocol would be used to create the oat slurry. The oat slurries consist of oat flour, water and inactivated amylase (α-amylase and β-glucosidase). Hydrolyzed oat slurry contains both soluble and insoluble fibers, proteins, fats and oils, and starches. The procedure from Norwood, Eric M was followed to prepare oat slurry.

7.2 PES membrane filters

Polyethersulfone (PES) is a thermoplastic, transparent polymer with chemical structure similar to polysulfone. PES offer high temperature resistant until 200^{o}C. in this UF membrane filtration set-up PES membrane filters were put inside plate-and-frame modules to filter oat slurry. The membrane is chemically resistant over a pH range of 1 – 14. The hydrophobic membrane has high flow rate and a low non-specific protein adsorption.

7.3 Cleaning agents

Both chemical and enzymatic cleaning agents were used. Mainly, enzymatic cleaning agents were used to clean the fouled membrane, whereas harsh chemical cleaning agents were used to re-set the plate-and-frame module, in order to ensure that the maximum initial water flux can be obtained. Although the alkaline chemical cleaning agent RO Dan 144 (Novadan, Kolding) was used to establish a baseline for flux recovery. This baseline will be used to compare chemical cleaning efficiency to enzymatic cleaning.

In the below table (Table 2) a list of applied cleaning agents and their operating conditions are described.

Table 2) an overview of the cleaning agent used in the experiment with their operating conditions

Manufacture	**Product name**	**Cleaning agent**	**Operating conditions**
Novozymes	Lipex^{R} Evity 200L	Lipase (enzyme)	pH: 5-6 Temp: 20 – 60^{o}C Dosage: 0.1- 0.2%
Novozymes	Celluclean 5000L	Cellulase (enzyme)	pH: 5-6 Temp: 20 – 60^{o}C Dosage: 0.1- 0.2%
Novozymes	Amplify 100L	Amylase (enzyme)	pH: 5.5-7.5 Temp: 10 – 50^{o}C Dosage: 0.1- 0.2%
Novadan	RO Dan 300E	Protease (enzyme)	pH: 10-10.8 Temp: 30 – 50^{o}C Dosage: 0.1- 1%

			Contact time: 10 min – 6 hours
Novadan	RO Dan 144	Alkaline cleaner	pH: 12-13 Temp: 30 – 80^{o}C Dosage: 0.1- 0.2% Contact time: 10-120 min

7.4 Plate-and-frame module

To determine, the degree of recovery Alfa laval's plate-and-frame module (Labstak^{TM} M10) and LabUnit M10 systems were deployed. This module consists of a set of two PES flat sheet membranes that are placed in a sandwich-like fashion, with their feed sides facing each other. In each feed and permeate compartment, a suitable spacer is placed. A plate-and-frame stack is built up by the number of membrane sets needed for a given membrane area equipped with sealing rings and two end plates. The equipped membrane module is then mounted to the filtration system (LabUnit M10) where it comprises, beside the module, a cross-flow pump, a heat exchanger, valve and pressure gauges. two containers can be equipped, one to run the feed and cleaning solution, and one to run backflush.

8 Experimental procedure

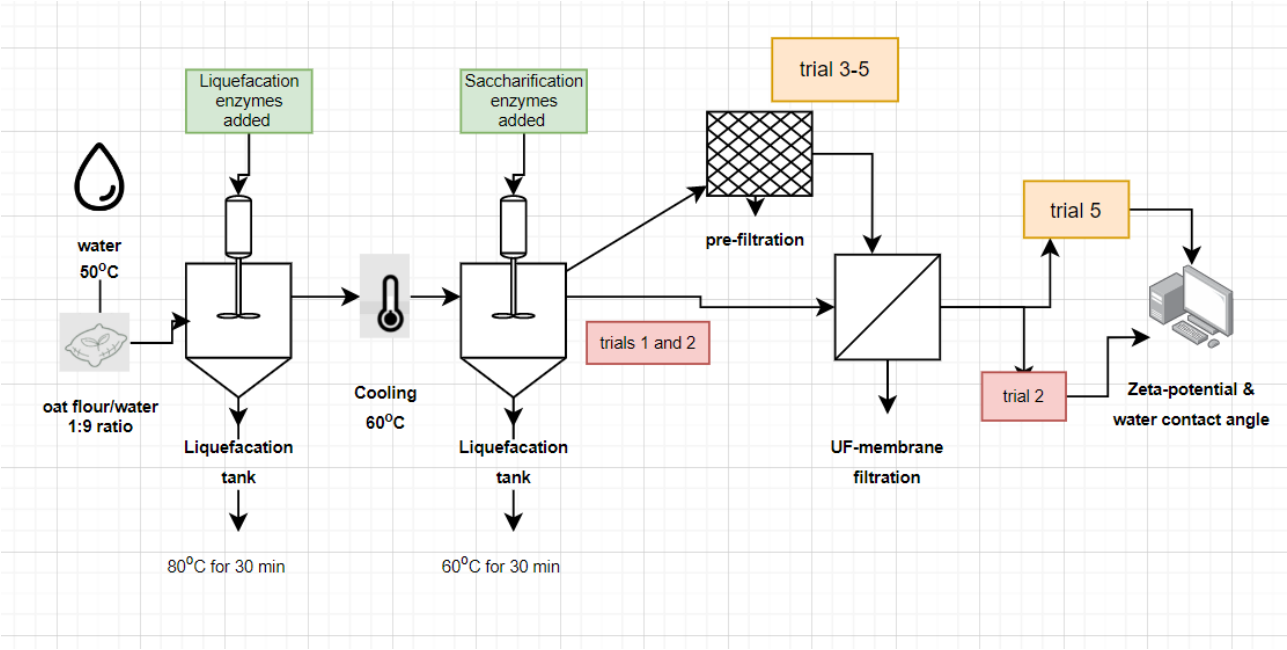

Figure 12: Flowchart over the whole process. the green boxes indicates the liquefacation and saccharification steps. The pink Boxes indicate the trials without pre-filtration and the orange boxes indicate the trials that underwent pre-filtration.

Overall, five trials were conducted throughout three oat slurry batches (Figure 12). The first trial established a baseline for chemical cleaning. The second trial investigated the influence of high enzyme concentration and high cleaning time. Third trial investigated the influence of order of sequence, with lesser enzyme concentration and cleaning time. The fourth and fifth trials were investigating the influence of pre-treatment, with same conditions of experiment three, while experiments five had a slightly higher cleaning time (Table 3).

Table 3) Cleaning conditions of the five trials

Trial	**Cleaning time (min)**	**pH**	**Concentration % (w/w)**	**Temperature (°C)**	**cycles**	**sequence**
1	30	neutral	0.8	30	1	Alkaline
2	60	5.8	0.9	30	1	Acidic
3	2x 30	5.8 then 10.1	0.6 then 0.2	25 then 30	2	Acidic → basic
4 (pre-filtration)	2x 30	5.8 then 10.1	0.6 then 0.2	25 then 30	2	Acidic → basic
5 (pre-filtration)	2x 15 + 1x10	10.1 then 5.8 then 10.1	0.2 then 0.6 then 0.2	30 then 25 then 25	3	Acidic → basic → acidic

For all the experiments a plate-and-frame membrane module with two sets of PES membrane filters mounted to a M10 filtration system from alfalaval was used(Figure 13)and (Figure 14). The TMP was set to 2.5 bar and for each cleaning step 5 litters of cleaning solution was used. The procedure was the same for all the experiments. first, the plate-and-frame module would be dissembled, and four virgin PES membranes would be assembled accordingly. Thereafter, the plate-and-frame module would be mounted to the M10 filtration system. One of the containers, would be filled with Demi-water (DM) at 25^{o}C ± 2. Then the power supply would be turned on to rinse the membrane for glycerol and also to ensure that no leakage or drop of pressure are observed, simultaneously, the pressure will be set to 2.5 bar. After a short rinsing the power supply will be turned off again, and a 5 liter of 0.2% Ro dan 18 to ensure that the glycerol is removed. The 5 liter solution is added to the other container and the temperature is adjusted to 25-30^{o}C. the filtration system is again turned on. the retentate and permeate hoses are put in the container to ensure circulation, as soon as the RO dan 18 has been observed in the retentate hose. RO dan 18 gets to circulate for 15 minutes before returning the retentate and permeate hoses to their original place and switching to the other container containing DW. The filtration system is rinsed thoroughly to ensure no cleaning residues are retained in the system or pipes. Finally, the initial PWF is measured, by first adjusting the retentate flow by increasing or decreasing flow at 2.5 bar until a flux of 1 L/m are obtained. Then the permeate flow is measured, be weighting the mass of the water that comes through the permeate after 30 seconds. Two replicas are measured for each PWF. After fouling and cleaning, the same method is used to measure the final PWF. The initial and final fluxes can then be used to calculate the flux recovery.

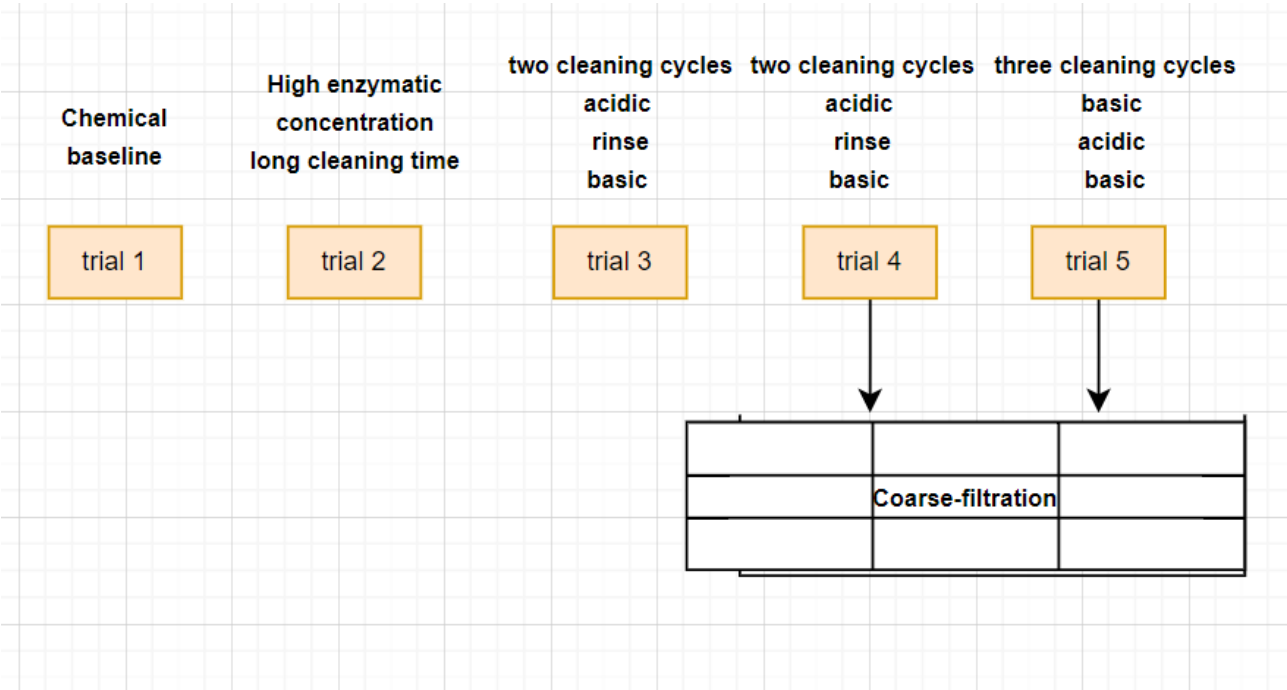

Figure 13) Selected screening of the different trials

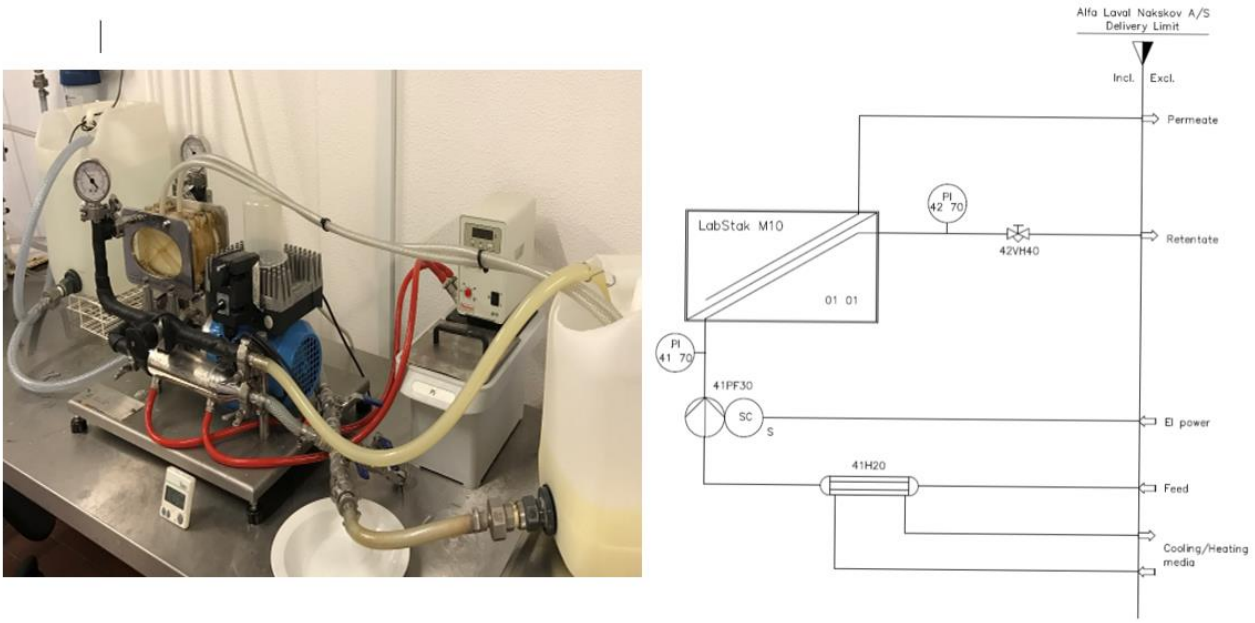

Figure 14) depiction of the UF filtration system used in this report

8.1 Cleaning efficiency baseline

As mentioned earlier, the first experiment was conducted to establish a baseline, by cleaning the fouled membrane module with chemical agent. The oat slurry to foul the membrane was made prior and was stored in 10 liters containers at room temperature. The chemical agent used was an alkaline cleaner RO Dan 144. 5 liters of 0.8% solution of the agent at 30^{o}C was made.

8.1.1 Oat slurry preparation

Oat slurry is made by the mixing of processed oat grain (e.g. oat flour) and water in the present of amylases (α-amylase and β-glucosidase). Oat consists of a food matrix rich in starch, soluble- (β-glucan) and insoluble fibers (lignin, hemicellulose, and cellulose), fats and also contains proteins (globulins, and prolamins) as mentioned in Chapter 2. Efficient hydrolysis is therefore needed, in order to break down the complex oat structure and retrieve the valuable compounds. Efficient hydrolysis steps (gelatinization, liquefication, and saccharification) are needed to release monomeric sugar units. Strong acid hydrolysis is an approach to evaluate the efficiency of enzymatic hydrolysis. the strong acid will break down the complex starch structures and convert branched sugars to monomeric units.

Oat slurry to use as feed in the UF membrane system was produced in a 50-liter reactor. The reactor was equipped with a heater and heating jacket to control the temperature. First 10% w/w of oat flour (bulk) was mixed with 90% w/w at 60^{o}C while stirring (hand-stirring) for 10 minutes until the mixture becomes homogeneous. Then the slurry is heated to 85^{o}C until a gelatinize viscous mixture is observed. Then the mixture is cooled to 80^{o}C and the pH is adjusted to 5.5 and 0.2% w/w alpha-amylase is added and the mixture is incubated for 30 minutes while stirring. The temperature is then further reduced to 60^{o}C where beta-glucosidase is added, and the mixture is incubated for further 30

minutes. The enzymes are then inactivated by heating the slurry to 85ºC for 10 min. lastly, the slurry is cooled, and pH is adjusted to neutral pH.

8.1.2 Membrane fouling

After the assembling of the plate-and-frame module and pre-cleaning of the membrane, 5 litter of the hydrolyzed oat slurry is weighted into a container and mounted onto the filtration system. The timer is set to 1 hour, before the filtration system is turned on. the timer starts as soon as the oat slurry is visible in the retentate. Similar to the pre-cleaning both the permeate and retentate hoses are placed onto the foulant container to ensure recirculation. The TMP is adjusted to 2.5 every time it increases due to concentration buildup. Before the fouling time is up, a cleaning solution is prepared and the rinsing container with 25ºC warm DW is adjusted and filled up.

8.1.3 Membrane cleaning

When the time was up, the circulation is reversed and the rinsing container with DW is then flowing through the membrane via backflush, in the meantime, the foulant container is discharged and rinsed. The pipes and system are also thoroughly rinsed before re-assembling the container and pouring the prepared alkaline solution (5 liter 0.8% RO Dan 114 at 30ºC). before starting the cleaning procedure, initial pH is taken and noted. The cleaning procedure is set to run for 30 min, before the time runs out, final pH measurement is taken to determine the decrease in pH. The flow was reversed, and the cleaning container is subsequently rinsed, and the pipes and systems are rinsed for cleaning agents. The final PWF is measured in similar manner as above and the experiment is ended.

8.2 Influence of high enzyme concentration and cleaning time

The second experiment is the first enzymatic cleaning of fouled membrane. In this experiment the influence of high enzyme concentration and cleaning time on the flux recovery was observed. The oat slurry preparation of the second experiment is almost identical to the first experiment, with one modification, the oat slurry was mixed with an industrial mixer instead of hand stirred. Besides that, the procedure is complete the same. The membrane fouling was also similar, with the only difference of, that the oat slurry in the second experiment was stored in the refrigerator.

8.2.1 Membrane cleaning

For the enzymatic solution mix, 5 liters of 0.3% w/w concentration of each of the following enzymes were prepared: Celluclean 5000L, Amplify, and lipex 200L. the pH was adjusted to 5.8, and the temperature was adjusted to 30ºC, since it was the optimum parameters for the three enzymes. The rest of the procedure is identical to the previous cleaning. The treated membranes were removed from the module and put into sealing plastic and stored in the refrigerator for further membrane analysis. The hydrophobicity and charge of the membrane were analyzed with zeta-potentials and water contact angle analysis. The membranes were dried, by exposing them to the air, and carefully dapping then with a clean tissue.

8.3 Influence of multiple cleaning cycle and sequence order

The third trial was investigating the influence of addition of cleaning cycle and sequence order. The oat slurry preparation was identical to the second trial slurry preparation. In this cleaning trial two enzymatic cleaning steps were carried out. In the first sequence 5 liters 0.2% w/w each of the acidic enzymes (Lipex, Celluclean, and amplify) followed by a rinsing step, then followed by the second enzyme solution; 5 liters of 0.2% w/w RO Dan 300E. The acidic enzyme mix were prepared at the same conditions (25^{o}C, 5.8 pH, for 30 min). The basic enzyme was prepared at 30^{o}C, and the pH was adjusted to 10-10.8. the cleaning time was also set to 30 min.

8.4 Influence of pre-filtration

The fourth and fifth trials were investigating the influence of pre-filtration. The preparation of oat slurry for forth and fifth trial were similar to the second and third trials, but in the last two trials. The oat slurries underwent coarse filtration, with a kitchen sieve. The filtered masses were discharged, and the filtered oat slurries were then poured into containers and stored inside refrigerator until use. For the fourth trials the cleaning fouling- and cleaning conditions were identical the third trial. The only difference is that fourth trial has undergone pre-filtration.

8.5 Influence of pre-filtration and sequence order

as mentioned above, the slurry preparation was identical to the fourth trial, however the cleaning protocol was modified slightly. the order of cleaning sequence was changed, so the alkali enzyme solution was initiated first, followed by rinsing step, then followed by the acidic enzyme mix solution and then finished with a short alkali step. the overall cleaning time ended being 1 hour and 15 minutes. After measuring final PWF the membranes were removed from the modules and sealed into plastic bags and stored inside the refrigerator for the analysis of zeta-potential and water contact angle.

8.6 Fouling analysis

For the second and fifth trials, the membranes were analyzed for impact of fouling. New (virgin) membrane and membranes that had underwent cleaning after fouling were sealed in plastic bags and analyzed for surface charge and hydrophobicity. The glycerol coated virgin membrane was first soaked in a container containing 0.8% RO Dan 144 solution for 15 min. it was then dried gently with tissues, till it was not moisture anymore. The fouled membranes were similarly also dried in the air and gently dapped with tissues.

8.6.1 water contact angle

Water contact angle measures the hydrophobicity or hydrophilicity of a membrane surface. Drop shape analyzer DSA100 from Krüss was used. A small rectangular sample was cut from the membrane. It was then placed onto the machine were a needle containing water droplets. The droplets would drop on the surface and the values of the contact angles of the drop would be measured. A mean of all the measured values would be taken for each sample.

8.6.2 Zeta-potential

An electrokinetic analyzer from Anton Paar was used to measure the zeta-potential. The software used was SurPASS™. The instruction guide from Anton Paar was followed to assemble the membranes into the device. The zeta-potential at 6, 8, and 10 were measured for each membrane.

9 Results

9.1 Influence of oat slurry preparation on flux recovery

Efficient oat slurry preparation is important, since efficient preparation will break down larger molecules into smaller molecules, hence reduce the molecular weight of the slurry, through hydrolysis process. UF is defined by their molecular weight cut-off (MWCO) as explained in chapter 3. Effective enzymatic hydrolysis can thus have an impact on the final flux recovery. Less macromolecules will form fouling inside- and on the surface of the membrane, leading to less foulants that need to be removed. Figure 15 and Figure 16 show the DSM's results of liquefication and saccharification of oat slurry, respectively. These results can be used as a mean to evaluate how much starch molecules that have been converted into monomeric- or branched sugar units. In this project 2000 ppm of α-amylase was used in the liquefication step for around 45 min at 70ºC. for the saccharification step 2000 ppm of β-glucosidase at 50ºC for 45 min. This mean, with consideration of different enzyme products with different performance and activity, that around 5% (W) of sugar units could be released.

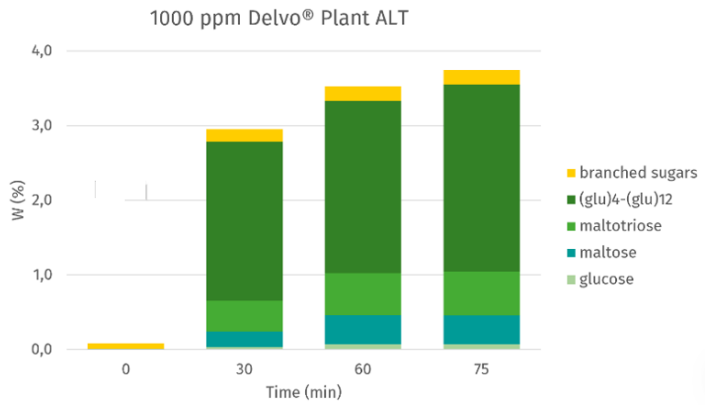

Figure 15) sugar content of liquefied oat slurry with alpha-amylase (Delvo Plant ALT)

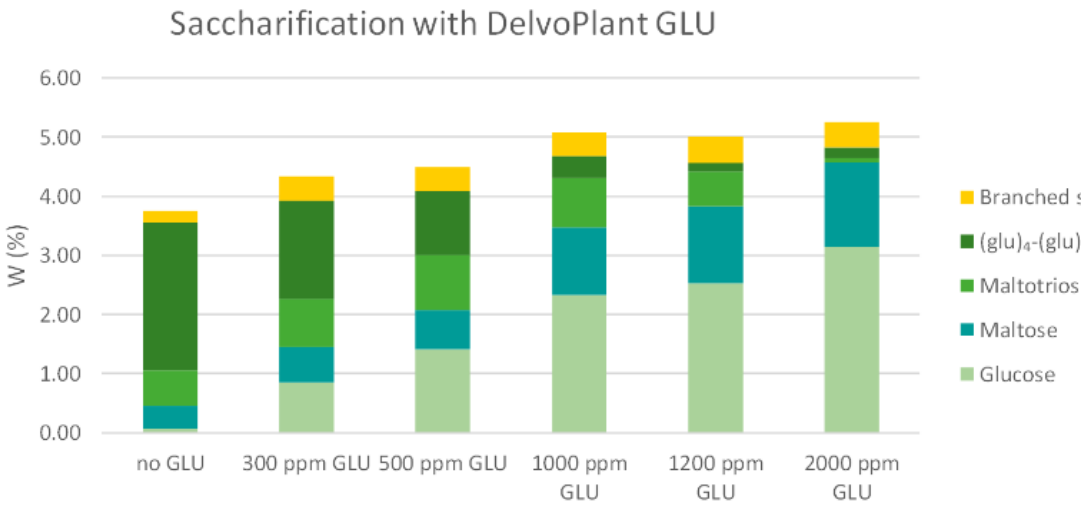

Figure 16) Effect on beta-glucosidase (GLU) concentrations on the formation of monomeric sugars in saccharification of oat slurry

During the storage of the prepared first batch oat slurry, which has been stored at room temperature, that is began to smell and change color to a darker tone compared to the lighter tone of the newly prepared slurry.

This could indicate that microorganisms were formed and producing biproducts, such as lactic acids and alcohols. The production of organic products could lead to fouling, which can interact with the PES membrane and increase its surface charge and decrease its hydrophobicity. The formation of microorganisms can lead to biofouling, where biofilm and other byproducts can be formed on the membrane surface. This could lead to quicker blockage of the membrane, and even harder cleaning of the membrane.

Oat drink does not contain high amount of proteins, compared to cow milk, nevertheless, protein denaturation still pose threat to UF filtration. Protein denaturation is the process, where proteins evolve from their native state to a less-ordered state. The denatured protein can block the pores, since it becomes wider and can interact and bind with other molecules. furthermore, a denatured protein exposes its buried hydrophobic residues, which can react with the PES membrane and reduce its permeability.

9.2 Influence of cleaning parameters

In this section the results of the effect of the cleaning parameters; cleaning time, enzyme concentrations, cleaning cycles, cleaning sequences, have on the flux recovery will be explained. Pure water flux recovery is the percentage of the initial water flux of a clean membrane that can be recovered after fouling and subsequently cleaning. The PWF can be calculated as:

$$Flux\ recovery = \frac{J_{wc}}{J_{wi}} \cdot 100\%$$

Where J_{wc} is the water flux after cleaning, and J_{wi} is the initial water flux. Figure 17 shows the five trials flux recovery. This result clearly shows that the chemical cleaning agent had the best flux recovery with 21.65% of the initial flux recovered. The best enzymatic cleaning trial is the fourth trial, where the oat-slurry had undergone a pre-filtration before UF and had two enzymatic cleaning cycles with a recovered flux of 14%. The lowest flux recovery was observed at the second trial or the first enzymatic cleaning procedure. This trial investigated the influence of enzyme concentrations and cleaning time with a flux recovery of 2.7% of the initial flux.

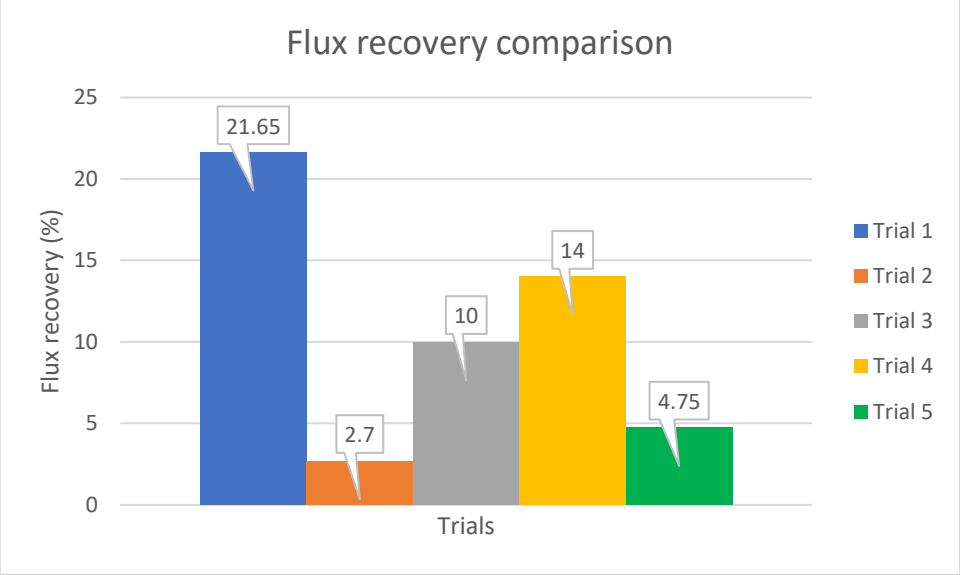

Figure 17: Flux recovery comparison for the different trials

9.2.1 Chemical baseline

The first trial had the highest flux recovery among the five trials. The first trial was made to establish a baseline for what is possible to achieve with chemical cleaning. it was achieved with 0.8% of RO Dan 114, which is an alkaline cleaner at 30°C for 30 min. According to alkaline cleaners can saponify fats, and dissolve proteins to remove organic foulants, such as grease and pectin. Alkaline cleaners can on the other hand produce foulants and damage the membrane, especially if the cleaning agent is a strong one. The report also shows that alkali cleaners have higher cleaning efficiency compared to acidic, metal chelating agents, surfactants and oxidants, where alkali cleaners had a flux recovery of greater than 70%, while the rest had recovery of less than 55%. This indicates that the oat slurry feed is difficult to clean with only alkaline cleaner in an UF setting. One of the reasons could bet that, the oat slurry contains high amounts of suspended solids, that requires a pre-filtration or MF-setting that can withhold the biggest compounds before it is sent to UF[13]. M reports that the efficiency of chemical cleaning depends on mass transfer of the chemical and foulants to and from the membrane, diffusion to the active species, and the rate of reaction. It could be possible that, the cleaning agent was limited in one or more steps. The limitations can be reduced, by draining and rinsing thoroughly in each cleaning step, to ensure that the detergents in the bulk are not consumed, henceforth the activity of the agent is kept under control. The mass transfer can also be improved by improving the crossflow and hydrodynamics.

The foulants in the oat slurry could be strongly bound to the membrane, which means that the alkaline cleaner is not strong enough to penetrate and break down the foulants. Wetting agents, that has amphillic properties can be used to break down the strong bounds between the foulants an membrane.

9.2.2 Influence of concentration and cleaning time

The second trial was investigating the influence of enzyme concentrations and cleaning time have on the cleaning efficiency. Enzyme concentration of 0.9% of enzyme mix solution is high and might not work as intended. [13]reports that enzymatic cleaners were most effective when operated at certain windows of concentrations and cleaning times. They also state, that higher concentration can lead to further increase in fouling. This explain why the second trial, had the lowest flux recovery among the five trials, with 2.7% revocery. It also had the longest cleaning time of 60 min in recirculation. This could enable the enzymes to attach to the surface of the membrane or inside the pores. M also state, that enzymatic cleaning using lipase-based enzyme for inorganic membrane fouled by whey protein with a short operating time of 20 min, a cleaning efficiency close to 100% was achieved.

9.2.3 Influence of multiple cleaning cycle and cleaning sequence

The third trial investigated the influence of two enzymatic cleaning cycle and the order of the cleaning sequence. First an acidic enzymatic cleaning step was introduced, followed by an alkaline enzymatic step. The alkaline enzyme solution was a protease with high pH optimum. It was thought that the acidic enzymes consisting of lipase, amylase and cellulase would be broken down by the protease. Thererfore, it was decided to start with the acidic enzyme solution, before cleaning with the basic protease. The cleaning efficiency of 10% recovery, showed a great improvement from the second trial, but not as good as the first trial. It was thought that the oat slurry contained to much colloidal and suspended solids, which quickly would form a cake on top of the membrane and block the pores, or adsorb onto the surface. these sceneries could explain the low cleaning efficiency.

9.2.4 Influence of pre-filtration

The concerns of the latter trial let to the fourth trial, where the slurry underwent a coarse filtration before UF. This coarse filtration improved the cleaning efficiency insignificantly. The PWF recovered was only 14%. This meant that other parameters besides the amount of suspended solids could be improved, since the first trial recovered more flux without any pre-filtration. Therefore, it was believed that basic cleaning will open up the pores and make it easier for suspended solids to pass through, while acidic cleaning agents will close the pores, which could influence the final PWF if not treated with a basic cleaning beforehand.

9.2.5 influence of pre-filtration and cleaning sequence

This led to the fifth and final trial, where a short third enzymatic cleaning cycle were added, and the cleaning sequence of the acidic enzymes and basic enzyme was substituted. The first cycle was a 15 min basic RO Dan 300E with protease, followed by a rinsing and the second enzymatic cleaning of the acidic enzymes for 15 min. The third cycle was a short 10 min RO Dan 300E to re-open the pores, before measuring the final PWF. The flux recovery was measured to be 4.75%, which means that either the cleaning time for each individual step was not enough for the cleaning of oat slurry or that the protease did not pose a significant effect on the foulant and might have denatured the acidic enzymes at the second cycle step. Another explanation could be that the filtration system was not cleaned properly from the previous experiment and might still contain foulants inside the tubes and pipes.

It could also be caused by a pressure drop between the feed side and permeate side. This mean that the membrane from the feed side has been fouled and cannot re-circulate the cleaning solution across the membrane, leading to inefficient cleaning.

9.3 Influence of surface charge and hydrophobicity

The effects of the fouling on the PES membrane were investigated, to reveal whether the fouling or cleaning agents were damaging or modifying the surface charge and hydrophobicity of the membrane. In chapter 5.5 the factors affecting membrane fouling is described. Overall, the surface properties of this PES membrane have a tremendous role in fouling tendency.

9.3.1 Water contact angle

Water contact angle measures the hydrophobicity or hydrophilic of the membrane surface. A water contact angle above 90^{o} indicates that the membrane is hydrophobic, while an angle below 90^{o} indicates that it is hydrophilic. Although According to [15]and [13], PES is still considered to be hydrophobic, where it typically lies between 50^{o} and 80^{o}.

Table 4 and Figure 18 show the water contact angle of virgin, trial 2, and trial 5 PES membranes. the virgin membrane has the highest contact angle, where it then decreases insignificantly. Hydrophobic membranes are desired for their stability and robustness, and for their ability to withstand extreme pH and temperature conditions. However, they are also more prone to fouling, since the surface of the membrane can interact with solutes. This could indicate, even though oat slurry contains proteins and other organic compounds that can interact with the hydrophobic membrane surface, it is not enough to decrease the hydrophobicity of the membrane.

On the other hand, the wet fouled trial-2 and trial-5 membranes were exposed to dry air and dabbing with tissue to remove the wetness. the dried surface could have affected the results. Although, the standard deviation for the two trials are almost identical, which would seem unlikely, that the two different trials would have almost identical contact angle and standard deviation.

Taking into account the low water flux recoveries and the unchanged water contact angles, a hydrophilic membrane can be justified. The robustness of a hydrophobic membrane seems to be irrelevant in the case of oat slurry filtration. Zeta-potential analysis seems to also confirm the thought.

Table 4) water contact angle values for virgin, used trial 2, and trial 5 PES membranes.

	water contact angle (°)
PES, virgin	73.05 ± 9.6
PES, trial 2	70.65 ± 5.9
PES, trial 5	68.9 ± 6

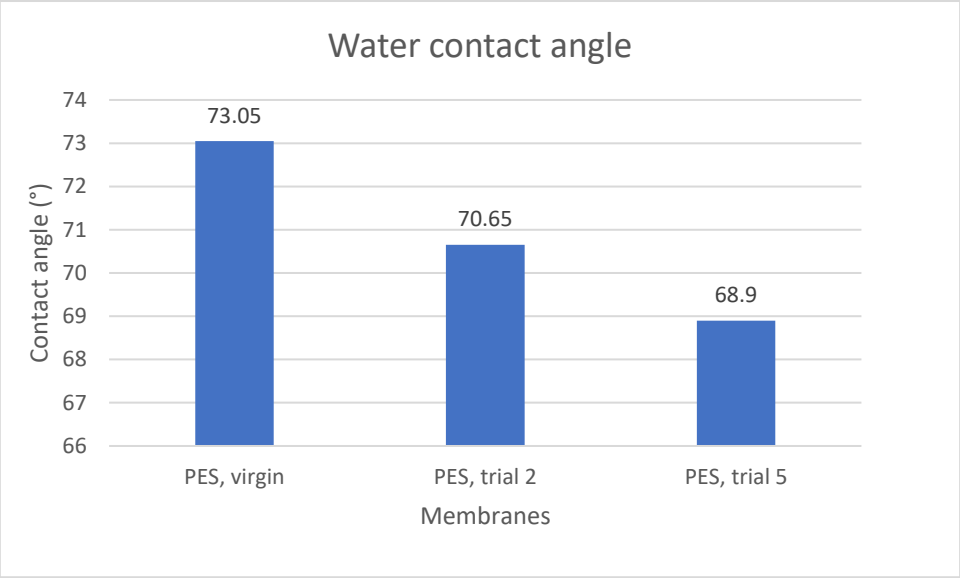

Figure 18) Water contact angle comparison for virgin, Trial 2 and trial 5 PES membranes

9.3.2 Surface zeta-potential

The zeta-potential for virgin, trial 2 and trial 5 PES membranes, at around 6.5, 7,5 and 9.5 are shown in Figure 19 and Table 5. The results show that surface charges decrease a bit from the virgin membrane. This means that negatively charged solutes are repulsed, which means that the PES membranes have high fouling resistances, but it could also mean that the charged molecules are attached to the surface. The oat slurry contains both positively- and negatively charged molecules, such as proteins and fibers, however, the charged of the molecules can be altered and new charged molecules can be formed. As seen in the denaturation of proteins and the enzymatic hydrolysis of starch.

The decreases in the surface charges for the fouled trial 2 and trial 5 membranes, may suggest that positively charged compounds might bind to the membrane surface and cause accumulation of fouling. Charged molecules can also lead to aggregation of molecules to form bigger ones, that can block the pore opening. One way to combat aggregation is by adding crossflow or controlling the pH.

Table 5: Zeta-potential for virgin PES membrane

PES, virgin	pH	6.46	7.5	9.23
	Zeta-potential (mV)	-28	-29	-32
PES, trial 2	pH	6.6	7.5	9.46
	Zeta-potential (mV)	-19	-21	-25
PES, trial 5	pH	6.24	7.3	9.42
	Zeta-potential (mV)	-18	-22	-23

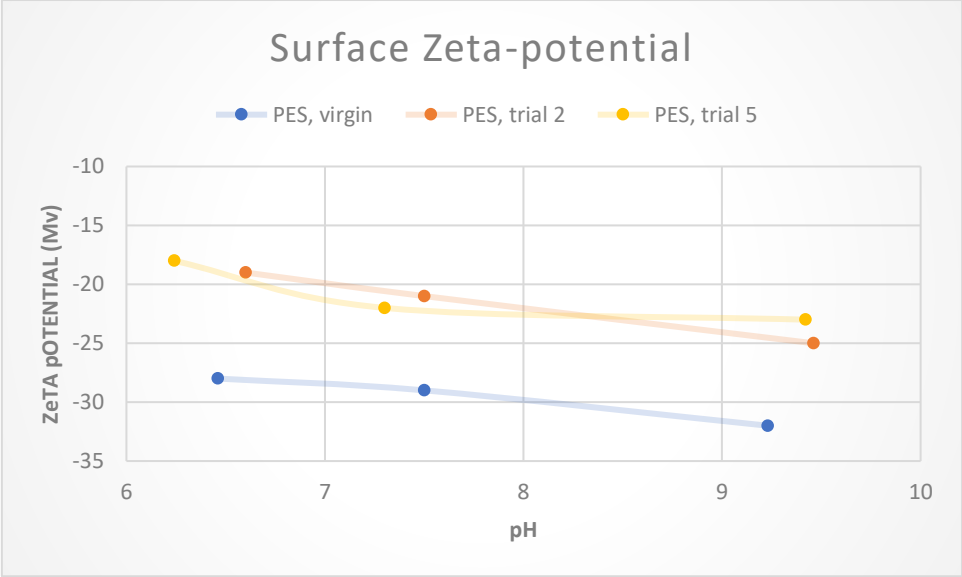

Figure 19) Membrane surface zeta-potential for virgin, trial 2 and trial 5 PES membranes

10 Conclusion

In order to investigate the cleaning efficiency of enzymatic cleaning of fouled UF-PES membrane in a plate-and-frame configuration, different objectives as seen in the problem statement were investigated. Before investigating the cleaning efficiency and flux recovery, oat slurry production was performed. This included, investigating the operating conditions of hydrolysis enzymes, such as enzyme concentrations, operating time, temperature and pH, the selection of an oat material that could enhance solubility of the fibers was also investigated. It was concluded, that processed 8-10% (w/w) of oat flour mixed with 90%(w/w) water and 0.2% (w/w) of the enzymes α-amylase and β-glucosidase, were sufficient to produce oat slurries similar to the ones in the industries.

four operating conditions and one chemical agent as a baseline, which could impact fouling on and inside the membrane were subsequently investigated. The alkaline, chemical agent RO Dan 144 yielded the highest pure water flux recovery at 21.65%, whereas for the enzymatic cleaning the fourth trial that was investigating the influence of pre-filtration of the oat slurry before UF and the influence of two cleaning cycles with acidic enzyme mix cleaning solution followed by a basic enzyme agent, yielded the best PWF recovery of 14%, lower than the chemical baseline, which cleaned oat slurry that has not undergone pre-filtration. The lowest PWF recovery was observed at the second trial, where enzyme concentrations of 0.9% (w/w) and cleaning time of 60 min were investigated for cleaning efficiency. a PWF recovery of 2.7% was measured.

The next objective was investigating the PES membrane's surface properties including charge and hydrophobicity influence on fouling. Membranes from trial 2, and trial 5 as well as a new (virgin) membrane were used to measure both zeta-potential and water contact angle. For the zeta- potential all the membranes showed negative charges. For the virgin membrane the zeta-potential were measured from -28 (mV) to -32 (mV) for pH around 6.5 to 9.5 , For the second and third trials the zeta-potential were ranging from -19 (mV) to -25 (mV) and -18 (mV) to -23 (mV) for around same pH interval as the virgin membrane. The native negative charged on the PES membrane did not change drastically from fouling, which can be concluded that the charged compounds in the slurry did not affect the surface charge significantly.

Similarly, the water contact angle revealed that virgin, trial 2 and trial 5 membranes were all hydrophobic, with water contact angles of 73,05^{o}, 70,65^{o} and 68.9^{o}, respectively. Which mean, that the membranes are more prone to fouling, due to interaction with hydrophobic solutes in the oat slurry and the repulsion of water across the membrane.

In conclusion, the enzymatic cleaning efficiency of UF membrane fouled by oat slurry is not satisfactory. However, it can be improved with screening and optimization of cleaning parameters, including substituting hydrophobic membrane with hydrophilic.

11 Future works

12 Appendix:

12.1 Morphology

The fouling behavior of UF and MF membranes is significantly influenced by the polymer properties, porous structure, and specific surface features of the membranes. The mechanical strength and permeability of the membrane rely on important polymer properties like crystallinity. Achieving a non-fouling or low-fouling membrane entails having a narrower pore size distribution, enhanced hydrophilicity, and larger porosity. However, effectively controlling fouling in UF and MF membranes while increasing porosity poses challenges. The porosity, pore size distribution, and pore tortuosity of the membranes primarily govern fouling and flux in UF and MF processes. UF membranes are predominantly affected by surface coverage, whereas pore blockage dominates in MF membranes due to the interaction between the size of organic matter components and membrane pore size[24].

The smoothness and roughness of UF and MF membrane surfaces also play a role in fouling. Smoother surfaces generally exhibit lower fouling tendencies, likely because rougher surfaces tend to trap foulant particles more easily. Membranes with rougher surfaces are observed to be more susceptible to foulant attachment, resulting in faster fouling rates. Increased roughness provides a larger surface area for foulants to attach, and the ridge-valley structure facilitates foulant accumulation by offering additional adsorption sites. Foulant particles tend to accumulate preferentially in the valleys of rough membranes, leading to valley clogging, which causes more pronounced flux decline compared to smoother membranes[35].

12.1.1 Surface properties

Surface charge

The antifouling characteristics of UF and MF membranes are influenced by both the charge on the membrane surface and the charge of the foulant under specific operating conditions. Charged membranes offer advantages such as higher selectivity/retention and reduced fouling. The repulsive forces between the charged membrane surface and the charged foulants in the feed solution prevent fouling deposition on the membrane surface, effectively mitigating fouling. Given the extensive use of MF and UF in water pretreatment and protein separation, significant research is being conducted to develop membrane surfaces that can effectively inhibit protein adsorption. Since most proteins, cells, and colloidal particles (e.g., NOM) carry a negative charge in aqueous solutions, incorporating negatively charged groups on the membrane surface enhances electrostatic repulsion between the membrane and foulants, thereby reducing fouling on the membranes. Achieving high resistance to biofouling caused by both positively and negatively charged foulant molecules involves utilizing neutrally charged surfaces that are highly hydrophilic. Recently, the development of membrane surfaces containing zwitterionic groups (containing both positively and negatively charged groups) has shown greater effectiveness in fouling mitigation. In summary, the optimal approach for fouling mitigation is to select a membrane surface with a charge suitable for the nature of the foulant[24].

Typically, using a membrane with the same electrical charge as the foulants is appropriate. For example, charged membranes have predominantly been developed for separating charged solutes like proteins. The membrane charge should match the charge of the target protein at the chosen pH value to enhance the electrostatic exclusion of the product from the membrane pores.

Hydrophobicity

Typically, commercially available UF and MF membranes are primarily composed of hydrophobic polymers such as PSF, PES, polypropylene (PP), polyethylene, and PVDF. However, hydrophobic membranes are highly prone to fouling, which involves the nonspecific adsorption of solutes onto the membrane surface and within its pores, resulting in a significant decline in flux. It is widely acknowledged that membranes with hydrophilic surfaces exhibit reduced fouling tendencies, and fouling on such membranes is often reversible. As the hydrophilicity of the polymeric material increases, the extent of fouling decreases[13].

It is important to note that many foulant molecules possess hydrophobic properties. Therefore, when the membrane surface is more hydrophobic, hydrophobic foulant molecules have a greater tendency to accumulate on the surface, leading to increased surface contamination. Conversely, when the membrane surface is more hydrophilic, it readily forms a hydrated layer upon contact with the aqueous feed. The formation of this hydrated layer is believed to hinder the adsorption and deposition of hydrophobic foulants on the membrane surface, thereby reducing fouling[13].

12.2 AFM and SEM

The morphological structures of various types of MF and UF membranes exhibit significant variations depending on the application field and the specific production process. AFM and SEM are microscopic techniques used to observe and analyze the structural characteristics of membranes. AFM allows for direct investigation of the adhesion properties of foulants on the membrane surface. It provides information about surface roughness and pore size distribution, which are associated with fouling. Atomic force microscopes operate by utilizing mechanical interactions between a probe and the surface being studied, with the probe scanned parallel to the mean plane (xy) of the surface. The probe tip is attached to the end of a cantilever, as shown in (Figure 20). When the tip makes contact with the surface, the vertical deflection of the cantilever is measured using an optical system that involves bouncing a laser beam off the cantilever onto a dual-element photodiode. The mean plane of the surface can be adjusted by subtracting the surfaces to correct for any imperfections in the selected scan size. This adjustment enables the extraction of roughness parameters, including the membrane's porosity, which is directly associated with fouling[13].

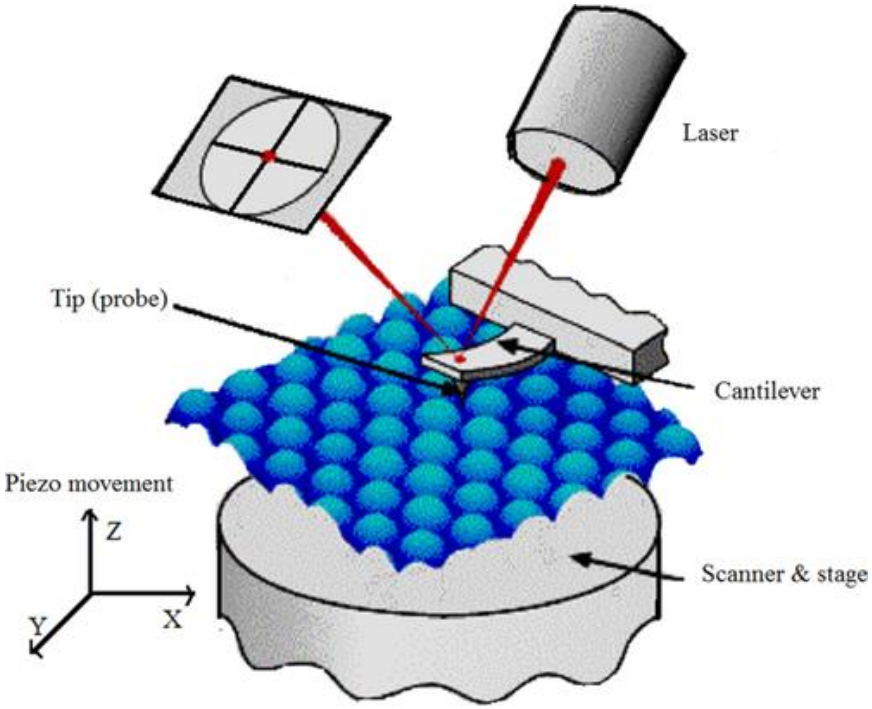

Figure 20) Schematic representation of an atomic force microscope[17]

However, the AFM technique has some limitations. Due to the size of AFM scanning probe tips, there are constraints on the scanning depth, and the AFM may cause distortion of the membrane pore size near the rounded corners at the pore entrance. Additionally, AFM scans a relatively small area at a time, and deriving roughness statistics from such small scan areas may lead to misleading results[40].

While SEM uses electron beams to scan the membrane surface and visualize its structure. The interaction between electrons and atoms in the sample produces various signals that are related to the sample's surface topography and composition, which can be recorded. SEM or field emission SEM can be utilized for image analysis to visualize membrane structures and provide insights into fouling mechanisms, such as pore blockage and surface coverage (gel layer), by employing image processing software to analyze porosity, mean pore radius, and pore size distribution. Image analysis software can be employed to assess porosity, pore size, and fouling mechanisms such as pore blockage and surface coverage[24].

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