

# Fouling and Cleaning During Treatment of Thermomechanical Pulp Mill Process Water

by

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# Preface

This master thesis is the final piece in my education, Master of Science in Chemical Engineering. The work has been performed at the Department of Chemical Engineering at Lund University during January 2015 to June 2015. I would like to start by thanking everyone at the department for the friendly and supportive environment.

My supervisors Ann-Sofi Jönsson and Johan Thuvander deserve many thanks for all the help and guidance they have given me throughout the thesis. Thank you for always being positive and for all the valuable aspects on my work, both experimentally and while I wrote my report.

Finally, I would like to thank my family and friends for the support and encouragement throughout my master thesis.

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# Abstract

One of many possible applications for membranes in industries is to separate valuable products from wastewater. However, usage of membranes inevitably leads to fouling. Fouling means that the treated solution affects the membrane and causes a permanent decrease of the permeate flux. That means that the membrane requires cleaning so that the flux can be restored and the full potential of the membrane can be utilized. Membrane cleaning can be performed by different methods, one of them being chemical cleaning. This master thesis aims to investigate which parameters that affect how the fouling takes place, as well as which parameters that affects the chemical cleaning of the fouled membranes.

The experimental work has been performed by treating an ultrafiltration membrane with process water from a thermomechanical pulp mill. The experimental work consisted of two main parts, the fouling experiments and the cleaning experiments. The fouling experiments investigated the fouling influence of temperature, duration and concentration of the treated solution. The results from the experiments showed that the fouling is influenced by the temperature and that more severe fouling is achieved at higher temperatures. The cleaning experiments showed that the efficiency of a cleaning method is dependent on both the cleaning agent concentration and the cleaning time. Two cleaning agents, Ultrasil 10 and sodium hypochlorite, were used in the cleaning experiments.

A conclusion that can be drawn from this work is that it would be interesting to investigate if the fouling in membrane plants could be reduced by using lower temperatures industrially. Less fouling would lead to a reduced need for chemical cleaning, which probably would increase the membrane lifetime as chemical cleaning often is the most damaging procedure that a membrane is subjected to. A lower temperature could lead to financial savings both by an increase of the membrane lifetime, but also as the operating time between the required cleaning can increase. However, a lower filtration temperature is negative from an economical perspective as the flux is lower at lower temperatures and the production will thus be more time consuming. A way of overcoming the reduced production pace could be to increase the membrane area.



# Sammanfattning

Membran kan bland annat användas för att separera värdefulla produkter från utsläppsvatten i industrier. När membran används är det dock oundvikligt att fouling sker. Fouling innebär att membranet smutsas ned, vilket orsakar en permanent minskning av permeatfluxet. Det leder till att membranen måste rengöras för att fluxet ska kunna återställas och membranets fulla potential ska kunna utnyttjas. Rengöringen kan ske genom flera olika metoder, varav en av dessa är kemisk rengöring. Genom det här examensarbetet undersöks det vilka parametrar som påverkar hur foulingen sker samt vilka parametrar som påverkar den kemiska rengöringen av de nedsmutsade membranerna.

Det experimentella arbetet har genomförts genom att ett ultrafiltreringsmembran har smutsats ned med processvatten från ett termomekaniskt massabruk. Det experimentella arbetet bestod av två huvudsakliga delar, nedsmutsningsförsöken och rengöringsförsöken. I nedsmutsningsförsöken undersöktes hur temperaturen, försökstiden samt koncentrationen på filtreringslösningen påverkade foulingen. Resultatet av nedsmutsningsförsöken visade att nedsmutsningen är temperaturberoende och att svårare fouling sker vid högre temperaturer. Från rengöringsförsöken kunde det fastställas att hur effektiv en rengöringsmetod är, beror av både koncentrationen rengöringsmedel och rengöringstiden. Två olika rengöringsmedel, Ultrasil 10 och natriumhypoklorit, användes i rengöringsförsöken.

En slutsats som kan dras från det här arbetet är att det skulle vara intressant att undersöka om foulingen i membranläggningar skulle kunna minskas genom att utnyttja lägre temperaturer industriellt. Minskad fouling skulle leda till ett minskat behov av kemisk rengöring, vilket troligtvis skulle öka membranens livstid då kemisk rengöring ofta är det mest skadliga ett membran utsätts för. En lägre temperatur skulle kunna leda till ekonomiska besparingar både genom en ökning av membranens livstid, men även genom att drifttiden mellan de nödvändiga rengöringstillfällena kan öka. En lägre filtreringstemperatur är dock negativt ur en ekonomisk synvinkel då filtreringen sker långsammare vid lägre temperaturer och produktionen således kommer att ta längre tid. Detta skulle dock kunna åtgärdas genom att använda en större membranarea.





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# 1 Introduction

When membranes are used in any application, it is inevitable that fouling will occur. Fouling leads to a decrease in the permeate flux. It is caused by the main fouling mechanisms cake layer formation, pore blocking and adsorption (Shi et al. 2014; Maartens et al. 2002). Another phenomena that also has a negative effect on the permeate flux is concentration polarisation.

There are some actions that can be used to reduce fouling. Pre-treatment of the feed stream, improvement of the membrane's anti-fouling properties and optimisation of the operational conditions are examples of preventions that can be made (Shi et al. 2014). However, it is not possible to completely avoid fouling so even if preventions are made, there will still be a need for membrane cleaning.

The fact that fouling is inevitable makes efficient membrane cleaning a prerequisite in membrane plants. The severity of the fouling and how it will occur is strongly dependent on both which membrane that is used, as well as the solution that is treated and what components that it contains (Puro et al. 2010). The content of the process water can show a great variation depending on, for example, what starting material that is used, which process technology that is applied and what products that are produced. The many possible variations complicate membrane cleaning as it makes it difficult to predict how fouling will occur, and as a consequence what cleaning properties that are suitable for a specific process water (Pokhrel & Viraraghavan 2004; Puro et al. 2010). As mentioned, it is not only the process water that affects the fouling; the membrane itself is also of importance. The membrane module and material affect how the fouling will occur, and it also affect what cleaning conditions that can be used without damaging the membrane, and how effective the cleaning agent and the cleaning conditions will be (Regula et al. 2014).

Studies on fouling and membrane cleaning are generally focussed on either fouling or cleaning, but the two processes have been proved to be closely connected and dependent of each other, when membrane fouling and cleaning were evaluated over a number of operational cycles (Weis & Bird 2001). The five main operating parameters that influence chemical cleaning are what cleaning agent that is used and in what concentration, the temperature, the cross-flow velocity and the cleaning time (Shorrock & Bird 1998; Väisänen et al. 2002).

To be able to efficiently clean the membrane is, of course, interesting from an economical perspective as well. Cleaning affects the membrane lifetime and hence the cost of a membrane process and should therefore not be performed more often than necessary. The cleaning conditions are usually harsher than normal operating conditions, and hence the chemical cleaning reduces the membrane lifetime more as compared to normal operating conditions. Furthermore, energy is required for heating rinsing water and cleaning solutions and the cleaning agents induce an extra cost. Cleaning will also cause an interruption in the operation of the plant. Development of membrane cleaning is also interesting from an economical and environmental perspective as usage of membranes in pulp mills can make it possible to separate high-value added products from what today is wastewater.

## **1.1 Aim**

The aim of this master thesis was to study fouling and cleaning of an ultrafiltration membrane when treating process water from a thermomechanical pulp mill. Influence of concentration and temperature of the process water on membrane fouling, and concentration of the cleaning agent, and duration of the cleaning operation on recovery of pure water flux, was investigated.

## **1.2 Implementation**

The development of new cleaning methods today is normally a matter of trial-and-error (Wallberg et al. 2001). This way of tackling the problem was also used in this investigation. The experimental work was divided into two parts: 1) developing a method to produce reproducible, irreversible fouling that requires chemical cleaning and 2) evaluation of different cleaning schemes.

The fouling experiments were focused on finding a repeatable and not too time consuming method, rather than finding a method that resembles the conditions to be in a full-scale, industrial membrane plant. The cleaning experiments were designed to investigate how the cleaning agent concentration and the cleaning time affect flux recovery. An alkaline cleaning agent was used in most experiments, but cleaning with sodium hypochlorite was also investigated.

All experiments were performed on hydrophilised polysulphone (PS) ultrafiltration membranes (Alfa Laval UFX5 pHt) with a 5 kDa cut-off.

## **1.3 Limitations**

The study is only focused on cleaning of one type of polymeric ultrafiltration membrane and only fouling of one process water was studied. In order to further investigate fouling and cleaning of membranes in other applications as, for example, in biorefineries, more membrane types and different process water should be used in new experiments.

## 2 Fouling

Permeate flux reduction in membrane filtration can be due to either concentration polarisation or fouling. It occurs when molecules in the feed solution affects the membrane by forming a deposit on either the membrane surface or inside the porous structure. The three main fouling mechanisms are adsorption, pore blocking and cake formation.

Fouling can be divided into reversible and irreversible fouling. There are discussions on the distinction between the two, but one definition is that the separation between the two types is how easily the fouling is rinsed away. Reversible fouling is defined as fouling that is removed by rinsing with purified water at zero transmembrane pressure. A fouling mechanism that often is of reversible form is cake formation. Irreversible fouling on the other hand is fouling that cannot be removed by rinsing and requires chemical cleaning. Fouling by adsorption and pore blocking are often of irreversible form. When the distinction is defined like this, the rinsing condition is essentially what defines what is termed as reversible and irreversible fouling respectively. By using this definition it is impossible to determine what mechanisms that caused the reversible fouling, and even if the flux decline that was restored after rinsing was caused by fouling or if it was caused by the temporarily mass transfer resistance from concentration polarisation (Shorrocks & Bird 1998; Maartens et al. 2002; Shi et al. 2014).

Apart from the division into reversible and irreversible fouling, fouling is further divided into external and internal fouling. External fouling is fouling caused by solutes large enough to be held back by the membrane and takes place on the surface of the membrane, such as cake formation and pore blocking. Internal fouling on the other hand are caused by solutes small enough to enter the porous structure of the membrane, such as adsorption (Shi et al. 2014).

### 2.1 Fouling Mechanisms

Adsorption is an internal fouling mechanism caused by interactions between solutes and the membrane leading to the solutes being adsorbed in the pores. If adsorption will occur depends on what functional groups that are available for interaction between the solutes and the membrane surface, but it is common that adsorption occurs when filtrating solutions containing small hydrophobic molecules, and it is often an irreversible form of fouling. Adsorption occurs spontaneously and usually very quickly when the solutes come into contact with the membrane. The fouling can cause an alteration in the charge and hydrophobicity of the membrane, which might cause more fouling. It is a fouling mechanism that requires cleaning chemicals, since desorption is thermodynamically unfavourable (Shi et al. 2014).

Pore blocking is a form of external fouling that is caused by solutes large enough to be held back by the membrane. It usually occurs quickly, when there are only little deposits on the surface and the solutes can be in direct interaction with the pores. The result when a pore is blocked is often that the flux in the surrounding open pores increases. The fact that the flux increases, may lead to an increase of the internal fouling in the pores that are not blocked (Shi et al. 2014).

Cake formation is also an external fouling mechanism caused by solutes building up layers on the surface of the membrane. The layer formed on the surface is often called a fouling cake, and the additional resistance that the fouling cake causes is called cake resistance. In some cases, depending on what solutes that are present, a formed fouling cake can act as a pre-filter that protects the surface from further fouling (Shi et al. 2014). The morphology of the fouling cake will decide the magnitude of the flux decline, and the interaction between the cake layer and the membrane will determine whether the fouling is reversible or irreversible. In cases where the cake formation is of a reversible form, it will still cause a high concentration of solutes at the membrane surface, which will increase the probability of irreversible fouling (Shorrock & Bird 1998).

Concentration polarisation is not a fouling mechanism. It is a temporary mass transfer resistance caused by formation of a concentration gradient at the membrane surface, caused by accumulation of solutes and particles large enough to be held back by the membrane. Due to the semi-permeable properties of the membrane, it is inevitable that concentration polarisation will occur (Shi et al. 2014). The effect of concentration polarisation is a decline in product flux, but after the membrane is rinsed, the accumulated solutes are washed away and the product flux will be as high as the initial value (Maartens et al. 2002). Although concentration polarisation on its own is not considered as a type of fouling, the high concentration of solutes at the membrane surface can cause fouling, namely cake formation (Wallberg et al. 2001; Shorrock & Bird 1998).

## **2.2 Foulants**

The properties of process water from different biorefineries can vary greatly. This makes it difficult to predict how the fouling will occur for a certain process water. In general, the components in the effluent streams from pulp mills originates from either the wood or chemicals used in the process at the mill. The content of the effluent streams are thus varying depending on what kind of wood that the mill uses, what process that is used, as well as what chemicals that are used in the process, if chemicals are used. This means that there are many potential foulants in the process water, as the effluent streams from a pulp mill may contain the following components in various extents: suspended fibres, lignins, hemicelluloses, extractives such as resin and fatty acid micelles, lignans, sugars (mono-, oligo- and polysaccharides) and other carbohydrates, as well as residual cooking chemicals (Puro et al. 2002; Carlsson et al. 1998; Puro et al. 2010).

Several studies that are focussed on determining the foulants from ultrafiltration of process water from pulp and paper mills can be found. As an example, the same research group has made two studies for determining fouling from extractives on ultrafiltration membranes. In the first study (Puro et al. 2002), the filtration was made with ground wood mill process water, and in the second study (Puro et al. 2011) it was two different process water from a chemithermomechanical (CTMP) pulp mill, one from a softwood pulping process, and the other from a combined softwood and hardwood pulping process. The results from both studies were that it was resin and fatty acids that were the major foulants. The latter study showed that resin and fatty acids caused a larger share of the extractive fouling (80%) than its original share

in the extractives (50% and 30%, respectively, for the two CTMP process water). Except from resin and fatty acids, traces of lignans and sterols could also be found among the foulants. The difference between the two studies, are that in the study on ground wood mill process water, all results points towards it being the dissolved and not the colloidal extractives that caused the fouling. This meanwhile all the results in the study on CTMP process water pointed towards that the resin and fatty acids were in colloidal form. The study with the two different process water could observe some differences in the fouling from the different process water, which confirms that how the fouling takes place is dependent on the properties of the process water. Although it is known that the properties of process water from different pulp mills that use different wood types and technologies can vary greatly the results from these two studies had some similarities. Thus, the similarities in the results indicate that the results might be applicable on the study with thermomechanical pulp mill process water used in this work.



## 3 Cleaning

The purpose of membrane cleaning is to restore the flux that has decreased due to the fouling mechanisms presented above. The four possible membrane cleaning procedures are chemical, electrical, mechanical and hydraulic cleaning. This thesis is focussed on chemical cleaning. Chemical cleaning can be performed in various ways, which method that is used is mainly depending on what is suitable for the membrane plant. In this thesis, the chemical cleaning will be performed by adding the chemicals to the feed tank, a method known as cleaning-in-place (CIP).

The chemical cleaning takes place by a heterogeneous reaction between the cleaning chemical and the foulants. The cleaning reaction can be divided into six stages (Lin et al. 2010; Trägårdh 1989):

1. Bulk reactions
2. Transport of cleaning chemicals to the fouled surface
3. Transport of cleaning chemicals into fouled layer
4. Cleaning reactions
5. Transport of cleaning reaction products back to interface
6. Transport of products to bulk solution

### 3.1 Cleaning Agents

The cleaning agent is the chemical that is used for cleaning. It can be a pure chemical or a composed detergent. There are a number of important properties to take into consideration when choosing cleaning agent. The cleaning agent should be able to loosen and dissolve the foulants, avoid and prevent new fouling and preferably be gentle to the membrane surface. It is however not only the foulants that has to be taken into consideration, the membrane material must also be considered. It has been found that some combinations of cleaning agents and membrane materials are not suitable. Besides the above mentioned demands, the cleaning agent must also be chemically stable during cleaning and preferably easy to rinse away after cleaning. Finally, safety concerns and costs are important factors when choosing cleaning agent (Trägårdh 1989; Wallberg et al. 2001).

The cleaning agents can affect fouling on the membrane surface in the three following ways: It can remove the foulants, change the morphology of the foulants or affect the surface chemistry of the deposits so that the hydrophilicity or charge is altered. If an unsuitable cleaning agent is used, it might affect the foulants negatively in some of the ways (Weis et al. 2003).

There are several possible chemicals available as cleaning agents. It is common to divide the cleaning chemicals into the six main categories: acids, alkalis, oxidants, surfactants, chelating agents and enzymes (Shi et al. 2014; Trägårdh 1989). It is said that inorganic foulants can be removed by acidic cleaning agents, while organic foulants can be removed by surfactants, alkaline cleaning agents and oxidising cleaning agents. The oxidising cleaning agents should

however be used carefully, as they might be especially harmful for the membrane (Wallberg et al. 2001).

### **3.1.1 Formulated Cleaning Agents**

There are a number of formulated cleaning agents available, one of them being Ultrasil 10 that is used in the experiments. The formulated cleaning agents are often a mixture of alkalis, phosphates, sequestering agents and wetting agents (Trägårdh 1989). It has been found that the formulated cleaning agents can be superior to chemicals alone over a longer cleaning cycle (Weis & Bird 2001; Weis et al. 2003). This is most likely due to that the formulated cleaning agents contain components that can interact or counteract depending on the fouling problem. The formulated cleaning agents are generally of a universal nature and can thus be used for a wide variety of foulants. However, the same attribute that makes the cleaning agents universal, might be a disadvantage as well. All the chemicals in the formulated cleaning agents are most likely not necessary for all applications, and might instead be damaging the membrane (Weis & Bird 2001).

### **3.1.2 Enzymes**

Enzymes can be used for membranes that cannot withstand high temperature and pH. (Trägårdh 1989). In a study where enzymes were used for cleaning tubular PES membranes after ultrafiltration of pulp and paper effluent, the enzymes were not efficient for the cleaning. Instead it seemed like the enzymes caused additional fouling by adsorption onto the membranes (Maartens et al. 2002). The above mentioned study tried three different enzymes for cleaning and none of them gave a significant increase in pure water flux. There are however many more enzymes that could be used, and that might be efficient cleaning agents for suitable membrane and foulants.

### **3.1.3 Alkaline Cleaning Agents**

Alkali hydroxides, carbonates and phosphates are example of alkali cleaning agents. Some of the alkalis do not have particularly good cleaning abilities themselves, and it is mainly their pH-regulative property that aids the cleaning. Sodium hydroxide can be used for cleaning of membranes fouled by organic and microbial foulants, but it can also be effective to remove inorganic colloids and silicates. It saponifies fat and solubilizes protein to some extent. Sodium hydroxides role as a cleaning agent can be boosted by adding sodium hypochlorite or when combined with surfactants (Trägårdh 1989; Regula et al. 2014).

### **3.1.4 Oxidants**

Hypochlorite is a popular cleaning agent due to its availability, price, and that it is can be used for cleaning membranes fouled by organic matter (Arkhangelsky et al. 2007). Sodium hypochlorite is an oxidising agent that generates active chlorine when used. It can be used combined with other chemicals, such as sodium hydroxide, but it has some cleaning ability itself. The cleaning ability of hypochlorite is thought to be due to enlargement of the pores of the membrane. Chlorine compounds are likely to form radicals that can damage the membrane. While membrane cleaning in general is harmful to the membranes, sodium hypochlorite is considered the most damaging cleaning agent (Trägårdh 1989; Regula et al. 2014).

### **3.1.5 Acids**

When cleaning with acid solutions, it is common that the pure water flux becomes time dependent and decreases over time. One reason for that is that the acid solutions usually make a negatively charged membrane more hydrophobic. This can also be seen when only deionised water is used for cleaning. When the charge of the membrane is removed, the membrane becomes more hydrophobic and thus, the flux declines (Wallberg et al. 2001). Another reason for the decreasing pure water flux is that acidic cleaning agents are good for removing inorganic deposits. That makes it likely that the membrane becomes more porous after acidic cleaning. When the more porous membrane is exposed to pressure during the pure water flux measurements, remaining deposits will become more and more compact with time and as a consequence, the flux will decline (Lindau & Jönsson 1994).

### **3.1.6 Surfactants**

Surfactants can aid the cleaning for other cleaning chemicals. It can improve the wettability and rinsability, and improve the contact between the cleaning chemicals and the deposits. When surfactants are used, a shorter rinsing time can give as efficient cleaning as a longer rinsing time without surfactants. However, some surfactants and membrane materials are not suitable combinations. If so, the surfactants can be absorbed on the membranes and instead of aiding the cleaning, the surfactants will cause a flux decline (Trägårdh 1989).

### **3.1.7 Chelating Agents**

A common component in formulated cleaning agents is the chelating agent ethylene diamine tetra acid (EDTA). The chelating agent plays an important role if there are metal ions among the foulants. Metal ions are able to form complexes with organic, phenolic and acidic compounds. But EDTA is also able to form complexes with the metal ions, so when a cleaning agent with EDTA is used, the EDTA can bind the metal ions. When the positive metal ions forms complexes with the EDTA it will aid the cleaning since it means that the membrane surface can keep its negative charge. It is advantageous to have a negative charge on the membrane from a fouling perspective as it will prevent deposits from further interaction with negatively charged organic groups and thus prevent additional fouling (Weis et al. 2003).

### **3.1.8 Combining Cleaning Agents**

Different cleaning agents are suitable for removal of different foulants. This means that in some cases, it is necessary to combine two different cleaning agents in order to achieve satisfactory cleaning. Cleaning with more than one cleaning agent should be performed in separate cleaning cycles. When a combined cleaning cycle of both an alkali and an acidic cleaning agent is used it is crucial that the rinsing step between the two chemicals is sufficient. If not, remaining chemicals might affect the pH and thus make the following cleaning less efficient (Trägårdh 1989).

Cleaning with acidic cleaning agents has been proved to cause a time-dependent pure water flux, which is not a problem for alkaline cleaning. Experiments with combinations of acidic and alkaline cleaning agents have showed that the time-dependant behaviour is a problem no matter in what order the two cleaning detergents are used. In order to overcome the problem, it seems as it is best to have three cleaning cycles, first an alkaline, followed by a second acid-

ic and finally a third alkaline cleaning cycle. When the cleaning was performed in that order the pure water flux was not time-dependent. The pure water flux after acidic cleaning is time-dependent due to the fact that the acidic cleaning agent removes inorganics and therefore makes the membrane more porous. When an alkaline cleaning agent is used, organics are removed. The removed organics are likely to reveal hidden inorganics beneath the organic deposits. In order to remove as much deposits as possible it is thus better to start the cleaning with an alkaline cleaning agent that will remove organics and reveal inorganics, which the second acidic cleaning agent can remove. Finally in order to get a time-invariant pure water flux, a third cleaning cycle with an alkaline cleaning agent is required (Lindau & Jönsson 1994).

## 4 Cleaning Procedure

The first step when starting to use a new membrane is pre-cleaning. The pre-cleaning is performed in a similar way to the latter cleaning of fouled membranes, but perhaps with a lower cleaning agent concentration. The pre-cleaning usually increases the flux. The purpose of the pre-cleaning is to remove preservatives and chemicals that are left from the membrane preparation. The pre-cleaning will also change the pore surfaces due to adsorption of the cleaning chemicals, which opens the membrane pores (Nyström & Zhu 1997). When the pre-cleaning is finished, the pure water flux is measured. The pure water flux measured after pre-cleaning is often used as a reference for the severity of the membrane fouling and the efficiency of the membrane cleaning.

The cleaning procedure after fouling normally consists of the following three parts; rinsing with purified water, chemical cleaning and finally rinsing with purified water. However, as earlier mentioned, some foulants might need more than one cleaning chemical for satisfactory removal of the fouling. If so, the cleaning chemicals are used in separate cleaning cycles and the cleaning procedure is thus a longer process where the steps above are followed by a second cleaning step and a finishing rinsing step (Trägårdh 1989).

The first step of membrane cleaning is always rinsing. It is an important part of the cleaning as it helps to remove loose particles, which means that the amount of cleaning agent needed can be reduced (Astudillo et al. 2010). The first of the six steps that a cleaning reaction is divided into are bulk reactions, i.e. reactions between foulants in the bulk and cleaning agents. Efficient rinsing can reduce the bulk reactions. The rinsing should continue until there is no detectable sign of foulants or product in the permeate or retentate. When the rinsing is finished, the pure water flux is measured. In some cases, rinsing might be enough to reset the condition of the membrane, i.e. if concentration polarisation or reversible fouling caused the product flux decline. This shows the importance of measuring the pure water flux before cleaning.

When the rinsing is finished, the cleaning continues with a cleaning agent. The cleaning chemicals are dissolved and poured into the feed tank. The cleaning is usually accomplished under recirculating conditions, meaning that both the permeate and the retentate are circulated back to the feed tank (Trägårdh 1989).

Studies have shown that it is important to examine the cleaning over a long cycle of repeated fouling and cleaning. The results shown after only one or a few cleaning cycles are seldom the same as that after several cycles of fouling and cleaning. During the first cleaning cycles, a cleaning chemical can be outstanding compared to another, but when the cleaning cycles continues, the other one can prove to be more effective (Weis & Bird 2001; Weis et al. 2003).

### 4.1 Influence of Operating Parameters

A number of operating parameters influence the membrane performance both during filtration and membrane cleaning. The influencing parameters that will be discussed below are the

transmembrane pressure, the concentration of the chemical or cleaning agent, the cross-flow velocity and the cleaning time. Besides the operating parameters, the influence from the membrane itself is discussed.

#### **4.1.1 Transmembrane Pressure**

In order to achieve an efficient cleaning, the transmembrane pressure should be kept as low as possible, preferably zero, but at least lower than the pressure during fouling. Zero transmembrane pressure will lead to the highest flux recovery after a fixed cleaning time. The reason for this is that when the pressure is decreased, the foulants are no longer forced into the pores, and will thus easier be removed. (Väisänen et al. 2002; Bartlett et al. 1995; Weis & Bird 2001).

#### **4.1.2 Concentration**

It is difficult to find information of how the cleaning agent concentration influences the cleaning efficiency. However, the membrane manufacturer normally specifies what concentration intervals that are recommended to use (Regula et al. 2014). Cleaning with higher concentrations might lead to a shorter membrane lifetime. Using higher concentrations than necessary is also disadvantageous from an economical perspective as it leads to higher costs.

#### **4.1.3 Temperature**

Many of the cleaning agents that are used for cleaning are powders that are dissolved in water. The dissolution is better at higher temperatures, and for that reason it is assumed that the cleaning agents are more efficient at higher temperatures. It is thus claimed that the temperature used for cleaning should be at least moderately high (Nyström & Zhu 1997). But it is, of course, not only the cleaning chemicals that dissolve better at higher temperatures; an increased cleaning temperature is likely to increase the solubility of organic foulants as well. That makes it likely that the cleaning can be performed faster at higher temperatures (Wallberg et al. 2001).

When the cleaning temperature is chosen, the specifications of the membrane must also be considered. The membrane manufacturers are usually specifying the recommended operating limits for the membrane, which should be followed during cleaning as well. In the same way, the formulated cleaning agent may also have a recommended temperature interval in which it should be used.

#### **4.1.4 Cross-Flow Velocity**

Better cleaning conditions are thought to be achieved at higher cross-flow velocities than those used at normal operation. The reason for that is that higher velocities provides a shear force that can help carrying away reversible foulants (Shorrock & Bird 1998; Shi et al. 2014; Weis & Bird 2001).

#### **4.1.5 Cleaning Time**

Cleaning times found in literature show a wide variety and is, of course, dependent on the type of fouling and its severity, as well as the cleaning agent and the concentration of it. However, cleaning times found in literature suggests that the first rinsing step with purified water

should be performed for 10-20 min. The cleaning step where the detergent is active lasts for 20-40 min, and the final rinsing step, which is performed with the purpose of removing remaining cleaning agent, can be performed for an additional 10-20 min. Another option is to perform the rinsing steps until there are no detectable signs of the solution or the detergents left in the system or until a stable pure water flux can be measured (Wallberg et al. 2001; Väisänen et al. 2002; Weis et al. 2003; Weis & Bird 2001).

From an economical perspective it is important to use the optimal cleaning time. When a short and a long cleaning time is equally effective, the shorter time should be chosen, since membrane cleaning reduces both the operation time and the membrane lifetime (Maartens et al. 2002; Levitsky et al. 2012).

#### **4.1.6 The Membrane**

The properties of the membrane influence the fouling. The three major properties of the membrane that affects the fouling are the charge, morphology and hydrophilicity. Pulp and paper mill process water are usually containing both positively and negatively charged compounds. Using a membrane with a weak charge can thus reduce the fouling. Membranes with higher cut-off values are more sensitive to fouling compared to tighter membranes, and membranes with rougher surfaces are fouled faster than membranes with smoother surfaces. It is also thought that hydrophilic membranes can diminish fouling problems (Puro et al. 2010).

The cleaning chemicals can affect the membrane by a change in the surface charge. An altered surface charge can lead to a change in the fouling mechanism (Weis & Bird 2001). While it is found that the cleaning chemicals affect the membrane, it is suggested that the importance of the membrane material considering membrane cleaning decreases over time. When membrane cleaning is evaluated over a short term, the membrane material, its porosity and surface roughness have a large impact on membrane cleaning. However, over the long-term, the membrane surface becomes irreversibly fouled, and the cleaning will mainly be dominated by interactions between the cleaning agent and the foulant (Weis et al. 2003).

## **4.2 Measuring Cleaning Efficiency**

There is no standard method for measuring the cleaning efficiency of membranes. However, a common method is to evaluate the cleaning efficiency by comparison of the pure water flux of a new membrane and that of the same membrane when it has been fouled and then cleaned. When the flux is used for measuring the cleaning efficiency it is essentially the fouling resistance that is used for evaluation. An increasing fouling resistance means a decreasing permeate flux, and membrane cleaning can be viewed as reduction of fouling resistance (Shorrock & Bird 1998). When the pure water flux declines after filtration of a solution, the only possible explanation is irreversible fouling (Maartens et al. 2002).

The efficiency based on the pure water flux can be determined as flux recovery, defined as the ratio between the flux after cleaning and the flux of the pristine membrane (Väisänen et al. 2002). It is also common to measure the pure water flux of the fouled membrane before cleaning. That measurement will give information of how fouled the membrane actually was, and if

the pure water flux is restored, it will show that the fouling most likely was in a reversible form.

There is however some drawbacks with measuring the cleaning efficiency from the pure water flux. The first drawback with the method is that the flux measurements are dependent on transmembrane pressure, temperature and cross-flow velocity. This means that meanwhile the method gives a good evaluation of the cleaning of the membrane at the specific conditions, it can be difficult to use for predicting the membrane behaviour at different conditions (Astudillo et al. 2010; Trägårdh 1989). Secondly the pure water flux is not a constant value even at constant conditions; it changes over time due to changes in the charge on the membrane surface. Nor is the pure water flux a reliable indicator of how the product flux will be as a good pure water flux not necessarily means a good operational flux. In addition it does not give any indication of how quickly the membranes will become fouled by the process solution. In order to know if the cleaning really was satisfactory, it is better to measure the product flux in the following run (Trägårdh 1989; Wallberg et al. 2001).

But on the other hand, it is not suitable to measure the cleaning efficiency only from the product flux. The product flux can be measured in order to see when the fouling occurs, seen as a decline in the product flux over time. The flux decline means that fouling takes place, but it does not give any information of what kind of fouling that has occurred. If, for example, the product flux decline is due to concentration polarisation or reversible fouling, the product flux should be as high as the initial value after rinsing with purified water. By only measuring the product flux it will be difficult to decide when the fouling is reversible, and when it is irreversible and cleaning detergents are needed. In order to know, the pure water flux should also be measured as that will indicate whether the fouling was removed by rinsing or if chemical cleaning is required. Measuring the product flux is however a good supplemental method as it can tell when it is necessary to clean the membrane (Maartens et al. 2002).

Apart from determining the cleaning efficiency from the pure water flux, it can also be interesting to evaluate how the fouling and cleaning has affected the membrane. This can be performed by surface characterisation methods such as Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM) and atomic force microscopy (AFM). However, the surface characterisation methods are generally destructive and are generally not used in industrial applications (Väisänen et al. 2002; Regula et al. 2014).



# 5 Material and Methods

## 5.1 Material

### 5.1.1 Process Water

The solution used for fouling the membranes in the experiments was process water from a thermomechanical pulp mill. The process water was pre-filtrated with a 75  $\mu\text{m}$  filter sieve before the experiments in order to remove fibres and other large particles. The lignin content in the process water varied between 0.98-1.09 g/l.

The process water was usually used in its initial state, but two experiments with concentrated process water were performed. For these experiments, the process water was concentrated by evaporation. The concentration began with filtration of the process water with a 75  $\mu\text{m}$  filter sieve. The first evaporation was performed with 10 kg of process water that was concentrated to the volume reduction 0.8, achieving 2 l of concentrated process water for the fouling experiment. The second evaporation was performed in three steps, starting with 10 kg of filtrated process water. After partial evaporation of the process water, 5 kg of filtrated process water was added at two occasions, giving the total mass 20 kg. The second evaporation proceeded until the process water was concentrated to a volume reduction of 0.95, with 1 l of concentrated process water for the fouling experiment.

The process water was normally stored in a cold room, but some of it was stored in a freezer. There is only a limited time that the process water can be stored in a cold room before it starts to degrade. When it was noticed that the degradation had occurred, process water that had been frozen was used for the experiments before new process water was delivered.

### 5.1.2 Membrane

The membrane used in the experiments is a hydrophilic polymeric flat-sheet ultrafiltration membrane from Alfa Laval (UFX5 pHt) with a 5 kDa cut-off. The membrane is based on a polypropylene support material and has a surface of permanently hydrophilic polysulphone. The recommended operational limits for the membrane are shown in Table 5.1.

*Table 5.1. Recommended operational limits for the Alfa Laval membrane UFX5 pHt (Alfa Laval n.d.).*

<b>Parameter</b>	<b>Limits</b>
<b>Temperature (<math>^{\circ}\text{C}</math>)</b>	0-75
<b>NaOH (%)</b>	0.1-0.5
<b>Na-EDTA (%)</b>	0.1-0.5
<b>Chlorine (ppm) at 50<math>^{\circ}\text{C}</math>, pH 10</b>	< 200

### 5.1.3 Cleaning Chemicals

The experimental work was mainly focused on cleaning with the alkaline cleaning agent Ultrasil 10 from Ecolab. Ultrasil 10 is a strongly alkaline powder that can remove fat, protein and forage residues and is suitable for ultrafiltration plants with alkali resistant membranes.

The cleaning agent consists of 15-30% ethylene diamine tetra acetate (EDTA), 5-15% phosphates, 10-20% NaOH, <5% anionic surfactants (Ecolab 2005).

Apart from cleaning with Ultrasil 10, an experiment with an alkaline sodium hypochlorite was performed. The sodium hypochlorite solutions were based on “Klorin original”, Colgate-Palmolive, containing 2.7 wt.% sodium hypochlorite. The hypochlorite solution was dissolved in a 0.1 wt.% NaOH solution (pH 10) when the cleaning experiment was performed.

## 5.2 Experimental Setup

The experiments were performed with a flat-sheet membrane module with a membrane area of 1960 mm<sup>2</sup>. A schematic of the experimental setup is shown in Figure 5.1. The pump was connected to a frequency converter, which is used to control the cross-flow velocity. The cross-flow was measured using a rotameter, and pressure gauges measured inlet and outlet pressure of the membrane module. The pressure is regulated by a valve situated on the retentate pipe.

The heating equipment is not shown in Figure 5.1, as two different heating equipments were used in this work. In the first, low-heat equipment, heating was mainly achieved by a heating coil surrounding the pipe between the tank and the pump. In the second, high-heat equipment, an immersion heater inside the tank was the main heating equipment. In both equipments, a heating jacket on the outside of the tank was used as an additional heating source, mainly during the initial heating. The heating jacket was usually not used after the desired temperature was reached and a constant temperature was to be kept. The high-heat equipment gave a much faster heating of the solution. However, using the immersion heater made it necessary to use a larger feed volume in the experiments.

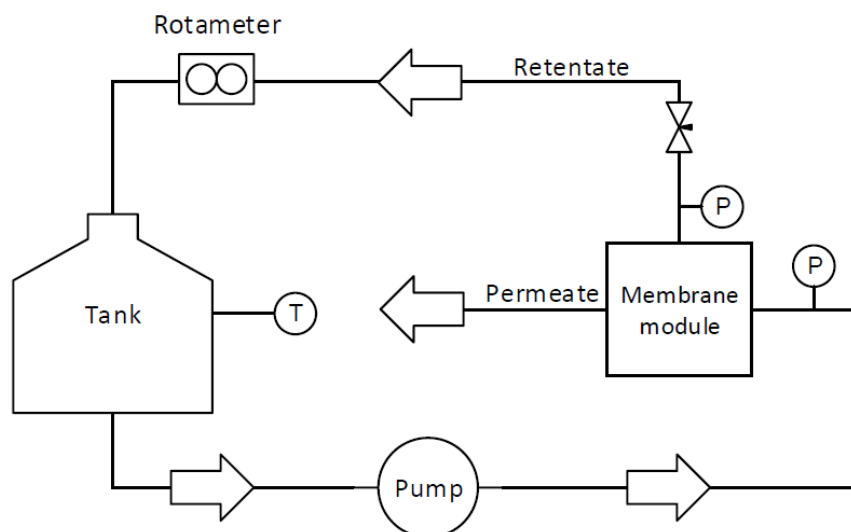


Figure 5.1. Schematic of the experimental setup. *T* stands for temperature sensor, *P* stands for pressure sensor.

## 5.3 Experimental Procedure

### 5.3.1 Fouling

Several fouling experiments were performed at different conditions before an efficient fouling method was found. The influence of temperature, duration and concentration was investigated by varying the parameters in the experiments. The cross-flow was 0.46 l/min in all experiments. Table 5.2 shows the conditions at which each of the fouling experiments were performed. Fouling experiment A-F was performed with the purpose of investigating membrane fouling and to find a suitable fouling method for the cleaning experiments. The following fouling experiments, G-H, was performed to verify the results from the previous experiments. The subsequent cleaning experiments were performed using the conditions from fouling experiment F.

Table 5.2. Summary of the fouling experiments. TMP denotes transmembrane pressure, V the initial feed volume, VR the volume reduction in the experiment and  $V_p$  the permeate volume per membrane area.

Fouling Experiment	T (°C)	TMP (bar)	V (l)	VR	$V_p$ (l/m <sup>2</sup> )	Time (h)	Solution
<b>Low-heat eq.</b>							
A	30	2.5	2	0.22	224.5	15	Process water
B	30	2.5	5	0.16	419.4	41	Process water
C	50	2.5	2	0.27	278.1	17	Process water
D	45	2	2	0.33	341.3	23	Conc. process water*
E	45	2	1	0	-	22	Conc. process water**
<b>High-heat eq.</b>							
F	75	2	4	0.15	314.6	16	Process water (frozen)
G	30	2	4	0.11	216.7	16	Process water (frozen)
H	75	2	4	0	-	16	Deionised water
I	50	2.5	3.5	0.15	258.4	17	Process water (frozen)

\* Feed concentrated by evaporation to VR 0.8

\*\* Feed concentrated by evaporation to VR 0.95

All experiments are performed with a pristine membrane. When the new membrane was mounted in the module, the first step of each experiment is pre-cleaning. The membrane was cleaned with a 0.25 wt.% Ultrasil 10 solution, and the cross-flow 1.86 l/min at 50°C for one hour. After cleaning the membrane was thoroughly rinsed with deionised water, and the pure water flux,  $J_0$ , was measured.

Although the experiments were performed at different conditions, the method that was used was the same in most experiments. The pump was started and water that remained in the system from the pure water flux measurement was displaced. After this, the solution was recirculated in the system at a low cross-flow (0.46 l/min) and transmembrane pressure (0.1 bar) while it was heated to the wanted temperature.

When the desired temperature was reached, a parametric study was performed. In the parametric study, flux was measured at constant cross-flow velocity and increasing transmem-

brane pressure in the interval 0.5-3.0 bar. Flux was measured during 5-10 minutes at each pressure stage. When the flux no longer increased with pressure, the rest of the fouling experiment was performed at this pressure, 15-41 h. During the experiment, the process water was concentrated by recycling retentate to the feed tank and withdrawing the permeate. This procedure was not used in experiment E, where no volume reduction was achieved as both retentate and permeate were recycled to the feed tank.

When the filtration of the process water was finished, the system was rinsed with deionised water. In experiments performed at temperatures  $> 45^{\circ}\text{C}$ , rinsing started with  $50^{\circ}\text{C}$  water and then gradually colder water, ending rinsing at  $20^{\circ}\text{C}$ . In experiments performed at  $30^{\circ}\text{C}$  rinsing was only performed with  $20^{\circ}\text{C}$  water. Rinsing was performed until it seemed to be only pure water in the system. The pure water flux,  $J_f$ , was measured.

### 5.3.2 Cleaning

Five cleaning schedules were evaluated (see Table 5.3). Cleaning agent, concentration and cleaning time varied meanwhile temperature ( $50^{\circ}\text{C}$ ), transmembrane pressure (1 bar) and cross-flow (1.86 l/min) were similar in all cleaning experiments. The concentration of the cleaning solution was increased stepwise during sequential cleaning of the membrane in method II and V. The cleaning time was increased sequentially in method III and IV.

Table 5.3 Cleaning methods used in the experiments.

Cleaning method	Cleaning agent	Concentration	Cleaning time (h)
<b>I</b>	Ultrasil 10	0.25 wt.%	1
<b>II</b>	Ultrasil 10	0.5-2.5 wt.%	1
<b>III</b>	Ultrasil 10	2.5 wt.%	1- 2
<b>IV</b>	Ultrasil 10	0.5 wt.%	1-18
<b>V</b>	Sodium hypochlorite*	200-400 ppm	1

\* In a 0.1 wt.% NaOH solution (pH 10)

Membrane and equipment were thoroughly rinsed with deionised water after cleaning. Permeate was continuously discharged during rinsing in contrast to the cleaning operation when both retentate and permeate were recycled to the feed tank. Rinsing started with water at  $50^{\circ}\text{C}$ . The temperature of the rinsing water was gradually lowered until the rinsing was finished with water at  $20^{\circ}\text{C}$ . The rinsing was performed at 0.5 bar and 1.16 l/min and continued until there were no detectable signs of detergents in the system. The pure water flux,  $J_c$ , was measured.

The cleaning agent Ultrasil 10 contains NaOH and EDTA, two of the chemicals with a maximal recommended concentration set by the membrane manufacturer. Table 5.4 shows the Ultrasil concentrations used when cleaning and its corresponding NaOH and EDTA concentrations.

Table 5.4. Ultrasil 10 concentrations used in cleaning method II and the corresponding concentrations of NaOH and EDTA.

Ultrasil 10	NaOH	EDTA
0.5	0.1	0.15
1.0	0.2	0.3
1.5	0.3	0.45
2.0	0.4	0.6
2.5	0.5	0.75

### 5.3.3 Measurement of Pure Water Flux

The pure water flux is measured at least three times in each experiment; after pre-cleaning, after fouling and after each cleaning. All measurements of the pure water flux were performed with 30°C deionised water at a cross-flow of 1.16 l/min at four transmembrane pressures (0.5, 1.0, 1.5, 2.0 bar). Flux was measured for 10 minutes at each pressure.

Measurements of the pure water flux were used to determine the cleaning efficiency, denoted as fouling ratio and flux recovery, defined below.

$$Fouling\ ratio = 1 - \frac{J_f}{J_0}$$

$$Flux\ recovery = \frac{J_c}{J_0}$$

The fouling ratio and flux recovery are calculated for the four measurements at different pressures, and the average of the four values for each experiment is presented in this study.

## 5.4 Analysis

During the experiments, samples of the feed, permeate and retentate were withdrawn. The feed sample was taken when the wanted temperature was reached, before the parametric study was started. The permeate and retentate samples were taken at the end of the experiments. These samples were analysed as described below.

### 5.4.1 Acid hydrolysis

In order to measure the content of sugar in the samples and the share of acid-insoluble and acid-soluble lignin, the samples are subjected to acid hydrolysis. The acid hydrolysis was performed by adding 72% sulphuric acid to the samples. The hydrolysis was then performed in an autoclave.

### 5.4.2 Lignin

The total amount of lignin in the samples was measured by measuring the ultraviolet (UV) absorbance at 280 nm with a spectrophotometer. The feed samples were filtrated before the measurement in order to remove possible remaining fibres. The extinction coefficient 17.8 l/g cm was used.

After the acid hydrolysis, the amount of the acid insoluble lignin and the acid soluble lignin can be determined. During the acid hydrolysis, the acid insoluble lignin is precipitated. The samples from the acid hydrolysis were filtrated in order to separate the two types of lignin. The acid insoluble lignin will be captured in the filter crucible. The filter crucible was dried in an oven at 105°C overnight before the amount of lignin can be determined by mass.

The acid soluble lignin was determined from the filtrate of the above mentioned filtration. The content was determined by measuring the UV-absorbance at 320 nm with a spectrophotometer. The extinction coefficient 30 l/g cm was used.

#### **5.4.3 Hemicelluloses**

The filtrate from the acid hydrolysis was also used for determining the sugar content in the samples. Before the analysis, the samples were filtrated with a 0.2 µm filter. The samples were analysed by high-performance liquid chromatography (HPLC) in order to find the concentration of monomeric sugars in the samples. The concentration of hemicelluloses in the samples was determined from the amount of monomeric sugars after anhydro corrections of 0.88 for the pentoses and 0.90 for the hexoses.

#### **5.4.4 Size distribution**

The size distribution of the samples is determined by size-exclusion chromatography (SEC). Both the feed and the permeate samples are filtrated (0.2 µm) before the analysis. The instrument has two detectors, a refractive index (RI) detector and a UV detector. The RI detector is a universal detector that detects everything with a refractive index different from the solvent. In this analysis it is used for detection of sugars. The UV detector uses the wavelength 280 nm and was used for detecting lignin compounds.

# 6 Results and Discussion

## 6.1 Fouling Experiments

The first part of the experimental work was the fouling experiments. Figure 6.1 shows the results from fouling experiment A-F. As can be seen in the figure, all experiments did cause fouling as the fouling ratio is lower than one. However, experiment F stands out as it is the experiment with the most severe fouling ratio and the only experiment with a flux recovery lower than one. The conclusion is thus that it was possible to restore flux when the temperature during treatment of the process water was  $\leq 50^{\circ}\text{C}$ , irrespective of the concentration of the process water.

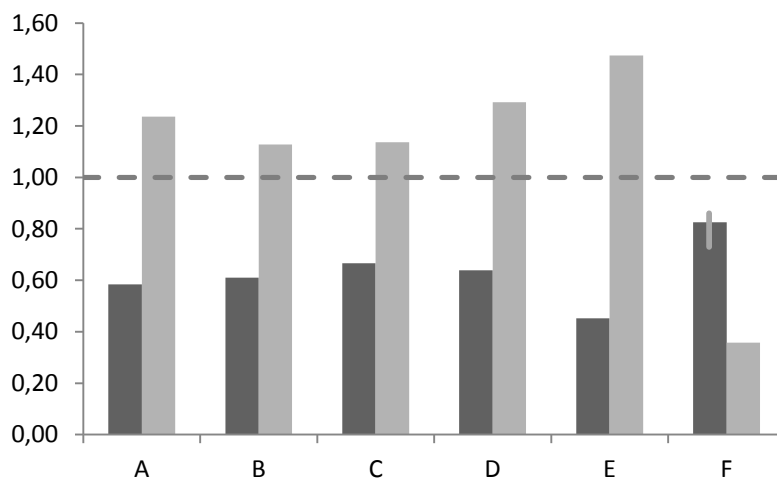


Figure 6.1. Fouling ratios and flux recoveries for fouling experiment A-F, using cleaning method I. The darker staples represent the fouling ratio, and the lighter staples represent the flux recovery.

Since severe fouling was achieved in experiment F, the fouling conditions used in the experiment were repeated for the subsequent cleaning experiments. The fouling ratio for experiment F shown in Figure 6.1 is the average value for all experiments with the same fouling conditions. The grey line in the fouling ratio staple shows the fouling ratio variation for the five experiments (see section 6.4.1 for further information). Experiment F was the only experiments with replicates. The other experiments were not repeated due to time constraints.

### 6.1.1 Influence of Temperature and Concentration

A comparison of the flux recoveries and fouling ratios of experiment A-E in Figure 6.1 shows that the first four experiments were more similar than the fifth. There is one main difference between experiment E and the other experiments - it was the only experiment in which the permeate was not withdrawn. Experiment E was performed with recirculation of both permeate and retentate to the feed tank. The results from experiment E compared to the other experiments shows that this was not a good option when fouling is sought.

There were some unexpected results in the experiments. Experiment D and E was performed with concentrated process water. The recirculation of the permeate in experiment E makes it difficult to compare it with experiment A-D. However, experiment D was performed with conditions similar to experiment A-C. As the process solution was concentrated to a volume reduction of 80% in experiment D it was expected that this experiment would give more fouling than the previous experiments. The results presented in Figure 6.1 shows that so was not the case. The fouling ratio was in the same range as the previous experiments and the flux recovery was higher compared to the previous experiments. Experiment D was performed with a lower transmembrane pressure than the previous experiments, but it was a pressure decided from the parametric study so it should have been high enough. Regardless if the pressure had impacts on the severity of the fouling, it can still be determined that the fouling with a more concentrated process solution was not more severe.

A higher concentration did not seem to be the key in finding a method for achieving severe fouling. The results from experiment A-C gives an idea of how the duration and the temperature affect the fouling. Experiment A and B were performed with the same conditions except for a longer duration in experiment B, and experiment A and C were performed with the same conditions except for a higher temperature in experiment C, and a slightly longer duration time. Figure 6.1 shows that experiment C gave the highest fouling ratio of those three, but the flux recovery for experiment B and C were very similar. What experiment B and C has in common compared to experiment A is that the conditions are altered so that a larger volume will pass through the membrane. A longer duration time naturally gives a larger permeate volume, and a higher temperature gives a higher flux which means that (disregarding possible differences in flux decline) a larger permeate volume is achieved at the same duration time. However, no matter what it was that caused the fouling, it seems that either longer durations or higher temperatures would be the next step to examine.

### **6.1.2 Achieving Severe Fouling**

The previous experiments had suggested that longer durations or higher temperatures should cause more severe fouling. As the fouling method preferably should not be too time consuming, the temperature influence was investigated. In order to investigate the possibility of achieving fouling by higher temperatures, the highest recommended temperature for the membrane (75°C) was used in experiment F.

It is difficult to establish why a high temperature was required for achieving fouling. The solubility might have affected the fouling as it is higher at higher temperatures. There are a larger amount of dissolved extractives than colloidal extractives at higher temperatures. The fact that more severe fouling is achieved might thus be an indication that it is the dissolved and not the colloidal extractives that foul the membranes, as Puro (2002) found in the first study. However, that is only speculations and it is difficult to predict if the fouling is related to the solubility. An explanation is that a higher solubility leads to more foulants available to interact with the pore structure of the membrane.

A part of how the experiment was implemented that might have affected the fouling is that despite that the experiment was performed at 75°C, the deionised water used for rinsing after



the fouling experiment was only 50°C. The temperature difference can contribute to the severity of the fouling, as there might be foulants present that are sensitive to temperature differences. It is stated by Trägårdh (1989) that it normally is preferred to rinse with water of the same temperature as the filtrated solution. The reason for that is both that the membrane can be sensitive to temperature differences, but it is particularly important if there are solutes present that is likely to form gels at lower temperatures. The rinsing conditions might thus have affected the severity of the fouling.

If the fouling is caused by foulants that are sensitive to temperature differences, the rinsing water might have been affecting the unexpectedly low fouling that was achieved in experiment D and E with the concentrated process water. Experiment D and E were the only experiments in which the rinsing was performed with deionised water at a higher temperature than which the fouling was performed, although the temperature difference was only 5°C.

Furthermore, it is not only the foulants that can be sensitive to temperatures; the membrane might also be affected by it. In order to establish that it was not the temperature used in experiment F, and the temperature difference in the subsequent rinsing that affected the membrane so that severer fouling was achieved, see experiment H.

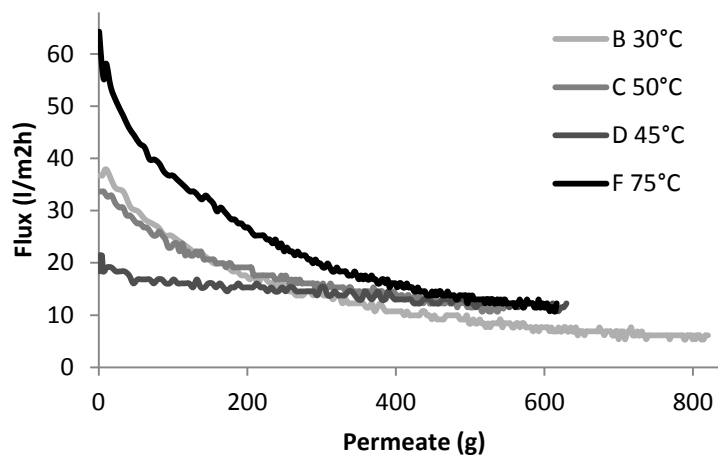


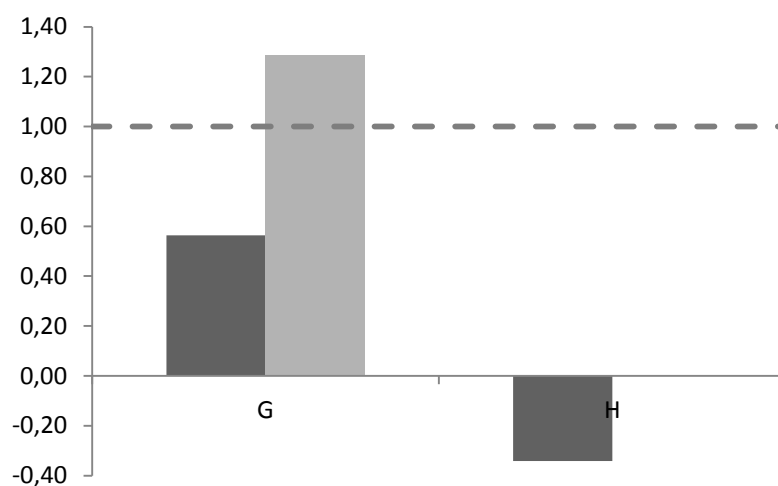
Figure 6.2. Flux measured during fouling experiments B, C, D and F plotted against the amount of filtrated permeate.

The flux was measured during the fouling experiments. Figure 6.2 shows a comparison of the fluxes measured in experiment B, C, D and F. There is no data for experiment E as the permeate was recirculated during the experiment. As Figure 6.2 shows, there is a big variation between the experiments. The order of the flux values at the beginning of the experiments are as expected. The experiment performed at the highest temperature shows the highest flux, and the experiment with the concentrated process water has the lowest flux. The flux is fairly constant throughout experiment D meanwhile the other experiments show a clear flux decline over time. The largest flux decline is observed in experiment F. The larger the flux decline during the experiment is, the larger reduction of the membrane permeability is achieved.

Since experiment F was the experiment with the severest fouling, the observed behaviour confirmed that the large flux decline was due to a large permeability reduction.

### ***Verification of the Fouling Method***

Two experiments were performed to verify that the fouling achieved in experiment F was not caused by any other circumstances than the conditions used in the experiment. The main reasons for the verification were that experiment F was the first experiment performed with the high-heat equipment, frozen process water and that the experiment was performed at the maximal recommended temperature of the membrane. The fouling ratio and the flux recoveries from the verification experiments are shown in Figure 6.3.



*Figure 6.3. Fouling ratio and flux recovery in experiments G and H, using cleaning method I. The darker staples represent the fouling ratio, and the lighter staple represent the flux recovery.*

The first verification experiment was experiment G. It was performed with the same conditions as experiment F (i.e. with frozen process water) except at a lower temperature. As Figure 6.3 shows, the fouling achieved at these conditions was not severe enough not to be removed by the cleaning. The results resemble those from experiment A, which was performed at the same temperature.

The second verification experiment was experiment H. The experiment was performed in order to verify that it was not the high temperature that was too harsh for the membrane and damaged it. Since the experiment was performed with deionised water, it was not cleaned afterwards and there it thus no flux recovery measured. However, as shown in Figure 6.3, the pure water flux measured after the experiment was higher than the initial pure water flux giving a negative  $1 - J_f/J_0$  ratio. The pure water flux measured is actually in the same range as the flux recoveries for the previous experiments A-E. This proves that the fouling observed in experiment F was not caused by damage of the membrane at 75°C.

The fact that a higher pure water flux than the initial is achieved after filtration of warm deionised water as well as after the cleaning in the unsuccessful fouling experiments are an in-

interesting behaviour. These results might be an indication that the pre-cleaning is incomplete, and that the high temperature rinsing and the cleaning, respectively, continues with the purpose of the pre-cleaning and open the pores more, leading to higher flux values.

## 6.2 Cleaning Experiments

All cleaning experiments are performed with membranes fouled according to the conditions used in fouling experiment F, i.e. treating the process water at 75°C. The first two experiments evaluating the influence of the concentration and time were performed with process water that had been frozen. The low-concentration experiment was performed with a mix of process water that had been frozen and process water that had not been frozen, and the hypochlorite experiment was performed with process water that had only been stored in the cold room.

### 6.2.1 Influence of Concentration

The first cleaning experiment was performed in order to investigate how the cleaning agent concentration affects the membrane cleaning. Cleaning method II presented in Table 5.3 was used for this, with concentrations increasing with 0.5 wt.% in each experiment as shown in Table 5.4.

Figure 6.4 shows the flux recoveries achieved after each cleaning cycle in the experiments. None of the flux recovery values are greater than one, meaning that it was not possible to fully restore the initial pure water flux in the experiment. The flux recovery increases after each cleaning cycle, but it cannot be determined from this experiment if the increased restoration is due to the higher concentrations or the repeated cleaning alone.

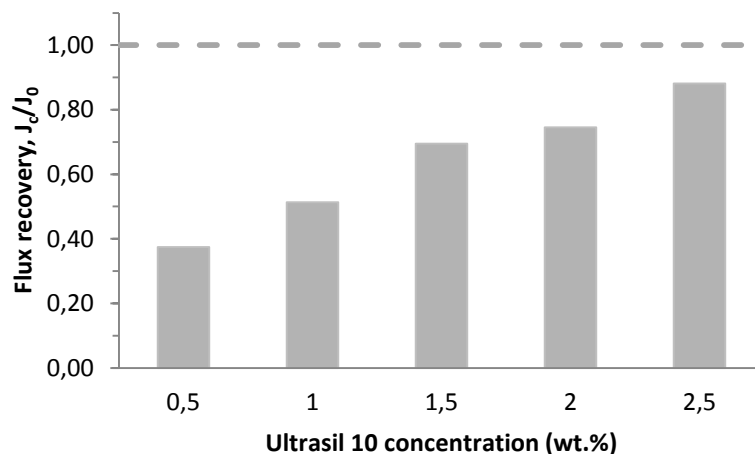


Figure 6.4. Flux recoveries for each cleaning cycle with increasing cleaning agent concentration, using cleaning method II.

The last two cleaning cycles are performed with EDTA concentrations above that recommended by the manufacturer, and when 2.5 wt.% Ultrasil 10 is used, the upper limit of the NaOH recommendation is reached as well. This means that the highest concentrations might be too harmful to use in a longer perspective.

### 6.2.2 Influence of Cleaning Time

The next experiment was an investigation of how the cleaning time affects the efficiency. The investigation was performed with cleaning method III presented in Table 5.3. The concentration, 2.5 wt.% Ultrasil 10, was chosen as it had not been possible to remove the fouling in the previous experiment, so the highest concentration was used to see if it at all was possible to remove the fouling. As mentioned, when this Ultrasil 10 concentration is used, it is above the recommended EDTA concentration and at the upper limit of the recommended NaOH concentration. This means that in the longer run it is not recommended to use as high concentrations in membrane cleaning.

Figure 6.5 shows the results from the investigation. As seen, a full restoration of the initial pure water flux was achieved after the second cleaning cycle.

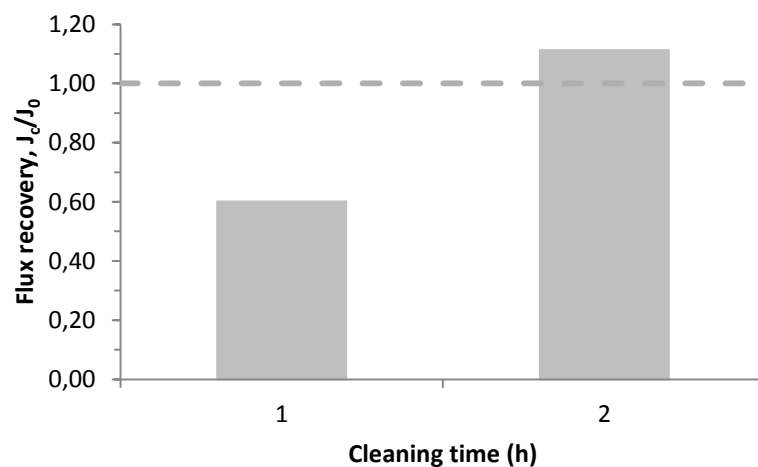


Figure 6.5. Flux recoveries for each cleaning cycle with 2.5 wt.% Ultrasil 10 and increasing cleaning times, using cleaning method III.

An evaluation of the results from the time investigation together with the concentration investigation shows that both the cleaning time and the cleaning agent concentration affects the cleaning. The first cleaning cycles in both experiments are performed at same conditions except for different Ultrasil 10 concentrations. A comparison of the flux recoveries from these cleaning cycles, seen in Figure 6.4 and Figure 6.5 respectively, shows that a much higher restoration was achieved for the higher concentration. The restoration of the first cleaning cycle in the time investigation is even higher than the restoration after two cleaning cycles in the concentration investigation. This establishes that the concentration influences the cleaning efficiency.

The second cleaning in the time investigation was performed during 2 h. After that, the initial pure water flux was restored. A full restoration of the pure water flux was never achieved in the concentration investigation despite several cleaning cycles. This shows that the higher restoration was achieved by the longer cleaning time, and thus the cleaning time also affects the cleaning efficiency.

The fact that a higher concentration gives better cleaning is not so unexpected since a higher concentration means that there are more chemicals available that can remove the foulants. The fact that a longer cleaning time is more efficient might be a bit more unexpected. The two experiments show that the foulants could not be removed by the repeated cleaning cycles, but they were removed after the 2 hour cleaning. The explanation to this must be that the removal is a slow process.

The two experiments have shown that higher concentrations and longer cleaning times gives better cleaning. It is known that chemical cleaning is the most harmful procedure that the membranes are subjected to, and neither high concentrations nor long cleaning times are good for the membranes.

### 6.2.3 Influence of Low-Concentration Cleaning

The previous experiments have shown that both the concentration and the cleaning time affect the cleaning. Once this was established, an experiment with a more reasonable concentration was performed. The chosen concentration was 0.5 wt.%, and the experiment was performed as the time investigation; with constant conditions except from an increasing cleaning time. Figure 6.6 shows the results from the experiments. As shown, it was not possible to clean the membrane with a concentration of 0.5 wt.%. The first three experiments were performed with cleaning times increased by one hour, but the fourth had a much longer cleaning time. The flux recoveries do not indicate that the increasing cleaning times had any direct effect on the cleaning. Each new cleaning cycle did give an increased restoration of the initial pure water flux, but it does not seem like the longer cleaning times gave any higher restorations than the shorter ones. This proves that although a longer cleaning time influences the cleaning, there seems to be a certain amount of cleaning chemicals that is needed in order to be able to clean the membrane.

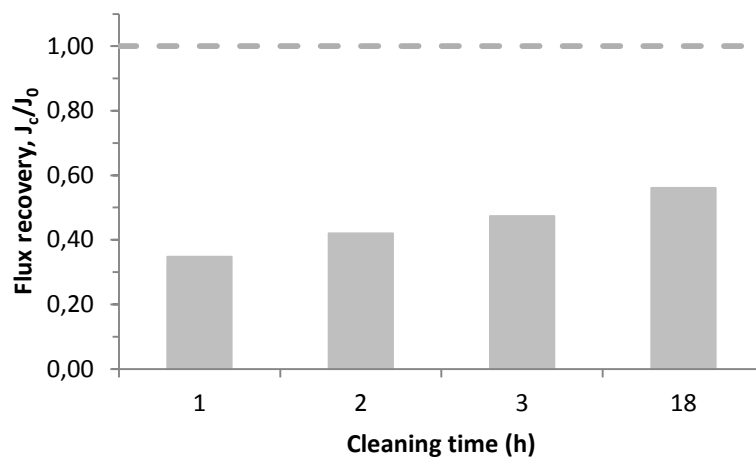


Figure 6.6. Flux recoveries for each cleaning cycle, when cleaning with 0.5 wt.% Ultrasil 10 and increasing cleaning times, using cleaning method IV.

#### 6.2.4 Influence of Hypochlorite Cleaning

Besides from Ultrasil 10, an experiment where sodium hypochlorite was used as a cleaning agent was performed. Hypochlorite is an oxidant that is known to be quite harmful to the membrane. But it is also known to be effective for membrane cleaning, and therefore cleaning with sodium hypochlorite in a sodium hydroxide solution was performed.

Since the purpose of the experiment was to investigate the possibility of cleaning with hypochlorite, the first cleaning cycle was performed with the highest recommended concentration. Figure 6.7 shows the flux recoveries measured in the experiment. The second cleaning gave close to full restoration of the initial pure water flux, but this cleaning cycle was performed with double the recommended concentration so it is questionable if this cleaning is suitable.

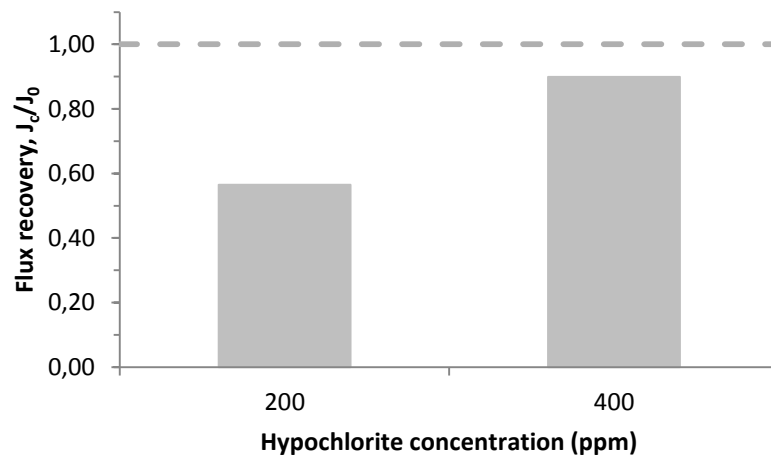


Figure 6.7. Flux recoveries for each cleaning cycle, when cleaning with increasing concentrations of hypochlorite, using cleaning method V, and the cleaning time 1 h.

The flux recoveries obtained can be compared to those achieved when cleaning with Ultrasil 10. The first hypochlorite cleaning cycle was performed with the same conditions as was used in the time investigation except for the different cleaning agents used. The flux recovery for the first cleaning cycles in Figure 6.5 and Figure 6.7 are similar. The second cleaning cycle with double the recommended hypochlorite concentration gave close to full restoration of the initial pure water flux. This flux recovery is similar to the flux recovery achieved in the final cleaning cycle in the concentration investigation shown in Figure 6.4. However, the flux recovery values in the figures are average values of the four measured flux values after each experiment, and the hypochlorite cleaning had a narrower difference between the measured values. The flux recoveries for the 400 ppm cleaning had the span 0.78-1.06 for the four different pressure measurements meanwhile the 2.5 wt.% Ultrasil 10 concentration had the span 0.73-1.12. Both experiments showed a decline of the flux recoveries at higher pressures.

All experiments showed a deviation from the initial pure water flux linearity after fouling and cleaning (see measured pure water fluxes in Appendix A). The deviation was larger in the cleaning experiments with Ultrasil 10 than the hypochlorite experiment. However, the differences in the flux recovery values presented above shows that the deviation could be observed

for the hypochlorite cleaning as well. It is possible that this deviation is caused by a change in the membrane due to the fouling or the cleaning. However, flux values that decreases with higher pressures are often a sign that a filter cake is formed. That might be an indication that the pure water flux is not measured for pure water. Since it is the same equipment that is used throughout all parts of the experiment, it is very difficult to remove everything from it and it is thus possible that the deviation from the initial linearity is caused by remaining cleaning chemicals. The deviation from the initial pure water flux could also be observed for the fouling experiments A-E, in which the flux values after cleaning instead increased with temperature compared to the initial measurement. The increasing values might indicate that the difference is not due to remaining chemicals.

## **6.3 Analysis Results**

Since there were some variations in the results from the different cleaning experiments at different temperatures, samples of feed and permeate were analysed in order to see if the differences in the severity of the fouling could be explained by differences in the permeability of different solutes at different temperatures.

### **6.3.1 Analysis of Feed and Permeate**

Samples of the feed and the permeate from three experiments performed at 30°C, 50°C and 75°C was analysed. The analysed samples were from experiment G (30°C), experiment I (50°C) and the experiment for the influence of the cleaning time (performed with conditions as in experiment F, 75°C). Table 6.1 shows the results from the analyses. The feed samples from the three experiments were found to be quite similar. The feed from the 75°C experiment had slightly lower sugar content than the other two experiments, and the total lignin content and acid insoluble lignin content was higher in the feed from the 30°C experiment compared to the other two. However, overall the feed showed small variations. The process water is delivered from the pulp mill in 10 litre containers, and process water from two different containers were used in the experiment performed at 50°C and 75°C meanwhile the experiment at 30°C was performed with process water from the same container as in the 50°C experiment. The differences in the analysis results of the feed samples show that the feed is not completely homogenous. However, it also shows that the variations between the process water from different containers are not bigger than the process water from the same container. This is pleasing results as it indicates that variations in the results are not likely to be caused by large differences in the feed.

Table 6.1. Characteristics of the process water samples (feed and permeate) from the filtration experiments performed at 30°C, 50°C and 70°C. The difference between the feed and permeate samples from the same experiment is also presented.

	<b>Feed 30°C</b>	<b>Perm 30°C</b>	<b>Δ 30°C</b>	<b>Feed 50°C</b>	<b>Perm 50°C</b>	<b>Δ 50°C</b>	<b>Feed 75°C</b>	<b>Perm 75°C</b>	<b>Δ 75°C</b>
<b>Hemicelluloses (mg/g)</b>	2.55	0.60	24%	2.52	0.61	24%	2.47	0.82	33%
- <b>Arabinose</b>	0.13	0.04	31%	0.13	0.04	31%	0.13	0.04	31%
- <b>Galactose</b>	0.39	0.07	18%	0.39	0.06	15%	0.38	0.08	21%
- <b>Glucose</b>	0.62	0.29	47%	0.61	0.26	43%	0.59	0.32	54%
- <b>Xylose</b>	0.03	0.01	33%	0.03	0.01	33%	0.03	0.01	33%
- <b>Mannose</b>	1.38	0.19	14%	1.36	0.24	18%	1.34	0.36	27%
<b>Total lignin (g/l)</b>	1.08	0.93	86%	1.00	0.90	90%	1.01	0.90	89%
<b>Acid soluble lignin (mg/g)</b>	0.14	0.11	79%	0.14	0.08	57%	0.15	0.11	73%
<b>Acid insoluble lignin (mg/g)</b>	0.46	0.27	59%	0.42	0.27	64%	0.42	0.26	62%

Table 6.1 also shows the differences between the content in the feed sample and the corresponding permeate sample from the same experiment. Regarding the hemicellulose content in the permeate, the experiment performed at 75°C differs from the others. The results show that a larger share of hemicellulose has passed through the membrane in that experiment. It is the mannose, glucose and galactose shares found in the permeate that has increased compared to the experiments at lower temperatures. Concerning the lignin content, the differences between the different experiments were not as big and it does not indicate that there is a difference in the lignin retention between the fouling experiments. There is a difference in the acid soluble lignin content in the permeate sample from the 50°C experiment compared to the other permeate values. However, since all other lignin analysis results are very similar between the permeate samples; this difference is most likely due to an error during the analyses.

The SEC analysis was performed in order to determine the size-distribution of the samples. Figure 6.8 shows the molecular mass distribution of the molecules detected by the RI detector. Figure 6.8a) shows the mass distribution for the feed samples and Figure 6.8b) for the permeate samples. The first peaks in the chromatograms show the presence of salts and monosaccharides. The second peak visible in Figure 6.8a) represents high molecular compounds, such as hemicellulose, and the final small peak is from extractives.



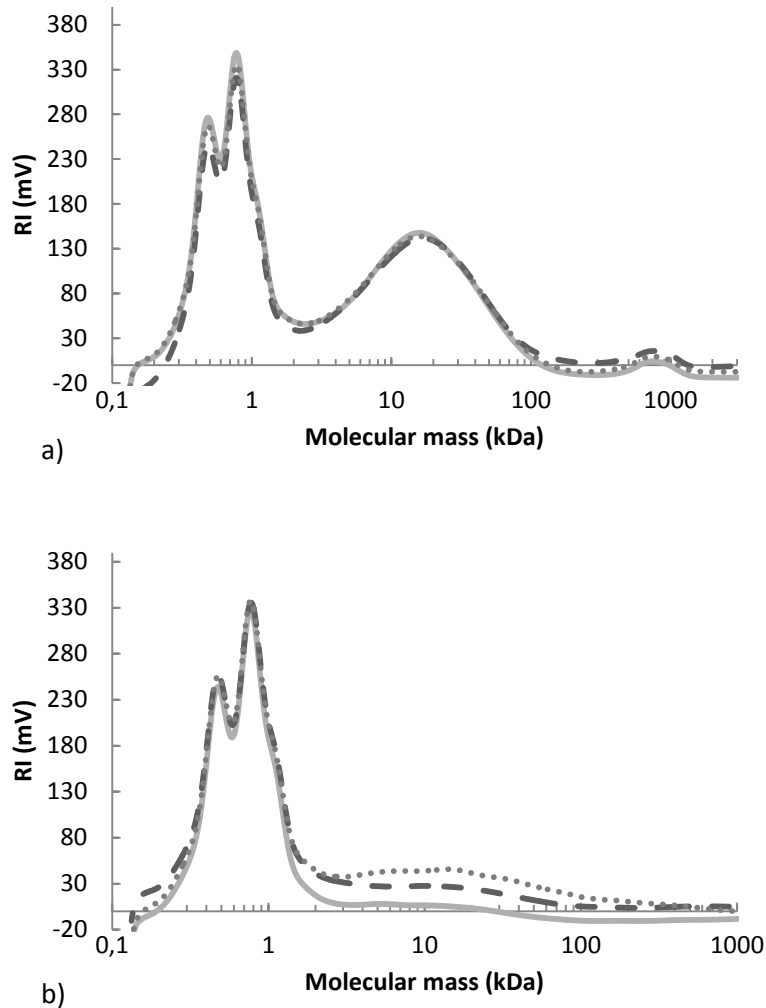


Figure 6.8. Molecular mass distribution of sugars (measured as refractive index) for a) the feed samples and b) the permeate samples. The solid line represents the samples from 30°C, the dashed line from 50°C and the dotted line from 75°C.

The permeate samples is not containing as large molecules as the feed samples due to the filtration. This is confirmed when comparing the peaks in Figure 6.8a) and b). The membrane has separated the small molecules from most of the high molecular compounds and the extractives that were present in the feed samples. The three feed samples show similar contents of the detected molecules. The permeate samples show a bit more variation, namely in the amounts of higher molecular compounds. It is shown that the amount is increasing in the samples with increasing temperatures. There is a possibility that this difference only is due to measurement uncertainties, but the results are somewhat consistent with the temperature increasing hemicellulose content in the permeate samples presented in Table 6.1. The difference between the results is that the difference between 30°C and 50°C were not as big in the HPLC analysis as it seems to be in the SEC analysis. The fact that more of the larger molecules passes through the membrane at higher temperatures might be a result of the higher flux achieved at that temperature, resulting in a higher pressure towards the membrane.

Figure 6.9 shows the molecular mass distribution lignin found by the UV detector. As the molecular mass of the compounds are small enough to pass through the membrane, there is hardly a difference between the feed and permeate samples. This shows that the permeability of lignin is not affected by the temperature.

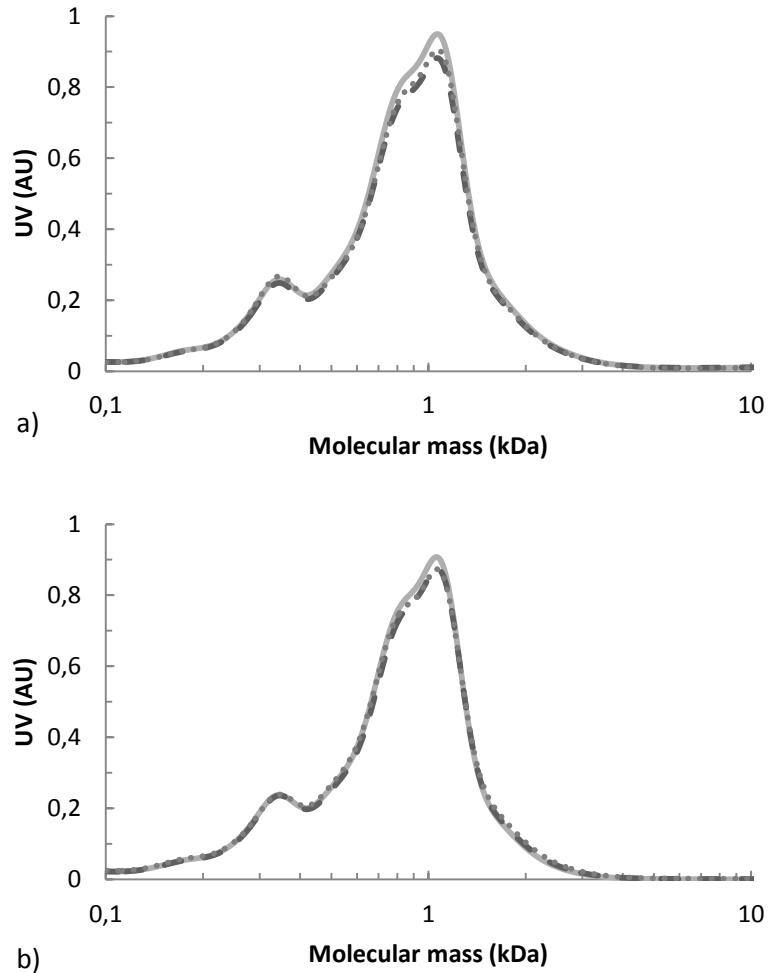


Figure 6.9. Molecular mass distribution of lignin (measured as UV absorbance) for a) the feed samples and b) the permeate samples. The solid line represents the samples from 30°C, the dashed line from 50°C and the dotted line from 75°C.

## 6.4 Additional Experiments

### 6.4.1 Frozen Process Water

Some of the experiments were performed on process water that had been frozen. Previous work with the process water at the Department of Chemical Engineering, Lund University, has shown that the properties of the process water do not change by freezing. In order to confirm that, the fouling ratio for experiments performed with the same conditions were compared.

There were five experiments performed according to the conditions used in fouling experiment F. Three of the experiments were performed with process water that had been frozen,

one of the experiments was performed with a mix of frozen process water and process water only stored in the cold room, and the last one was performed with process water only stored in the cold room. Table 6.2 shows the fouling ratios achieved from these experiments, and the permeate volumes. It can be seen that the fouling ratio for the only experiment performed with non-frozen process water deviates from the other experiments. That indicates that there is a difference between the severity of the fouling achieved from process water that had been frozen compared to non-frozen process water. It also seems that the process water behaves differently during treatment as all experiments are performed with the same conditions and the permeate volume is considerably lower with the non-frozen process water. This contradicts the conclusions drawn from previous work at the department with frozen process water. Instead it seems that the freezing have affected the process water.

The experiment with the deviating fouling ratio was the experiment performed with hypochlorite. The fact that the deviating value was found for the experiment with hypochlorite makes it difficult to determine if the difference in the fouling ratio affected the cleaning efficiency, and might indicate that a replicate of one of the previous cleaning experiments would be necessary to fully determine if there is a difference between the process water that had been frozen and the non-frozen process water.

*Table 6.2. Comparison of the fouling ratio from different experiments performed with frozen and non-frozen process water, respectively, and the same fouling conditions.*

<b>Experiment</b>		<b>Fouling ratio</b>	<b>V<sub>p</sub> (l/m<sup>2</sup>)</b>
<b>Fouling experiment F</b>	Frozen	0.84	314.6
<b>Influence of concentration</b>	Frozen	0.85	300.8
<b>Influence of cleaning time</b>	Frozen	0.85	300.7
<b>Influence of low-concentration cleaning</b>	Mix	0.86	277.4
<b>Influence of hypochlorite cleaning</b>	Non-frozen	0.73	226.8

## 7 Discussion and Conclusions

The aim of the study was to study fouling and cleaning of an ultrafiltration membrane. The fouling experiments showed that it takes high temperatures in order to achieve severe fouling. That is interesting results as it could be an indication that the fouling in membrane applications can be reduced if the filtration is performed at lower temperatures. There is however drawbacks in filtrating at lower temperatures. Since the flux is lower at lower temperatures, the filtration will be more time consuming compared to higher temperatures. The question of what temperature that is optimal to use is thus two-sided, assuming that the fouling can be reduced at lower temperatures. Using a lower temperature might reduce the fouling and the need for chemical cleaning, which will increase the lifetime of the membrane. A reduced need for cleaning also increases the operation time of the membrane plant. This is, of course, good from an economical perspective. On the other hand, a lower temperature leads to a lower production per time unit, which is negative from an economical perspective. But if more fouling is achieved, the need for chemical cleaning will be higher, which probably reduces the membrane lifetime. All this makes the temperature influence on the fouling interesting to further investigate. Perhaps it is more economically efficient to have a lower production if it means that the cleaning can be performed less frequently and the membranes can be used for a longer time. By increasing the membrane area, it would be possible to maintain the production pace despite a lower temperature.

The fouling influence from the duration and the concentration was also evaluated. It was found that a longer duration does give more severe fouling, but not to as large extent as higher temperatures do. The fouling experiments also showed that more concentrated process water does not have a significant effect on the achieved fouling, but that concentration of the solution during the filtration is necessary for achieving severe fouling. These two results somewhat contradicts each other, but it is might be an indication that the fouling is related to the amount of permeate that has passed through the membrane.

The cleaning experiments were mainly performed with the cleaning agent Ultrasil 10, but the possibility to clean the membranes with hypochlorite was also investigated. The cleaning experiments with Ultrasil 10 showed that both the cleaning agent concentration and the cleaning time affect the cleaning, with higher concentrations and longer cleaning times being more effective. It was possible to fully restore the initial pure water flux in an experiment where 2.5 wt.% Ultrasil 10 was used for 2 hours. However, when this concentration was used, the recommended concentration limit of EDTA was exceeded. Cleaning with a lower Ultrasil 10 concentration (0.5 wt.%), with EDTA and NaOH concentrations at the lower span of the recommended interval was not enough to restore the initial pure water flux no matter how long cleaning time that was used. A long cleaning time alone is thus not enough to restore the pure water flux; there is a need for a certain cleaning agent concentration as well.

The hypochlorite cleaning began with a cleaning cycle with the highest recommended concentration. That was not enough to restore the initial pure water flux, so a second cleaning was performed with double the recommended concentration. The second cleaning cycle gave

close to full restoration of the pure water flux. That shows that it is possible to clean the membranes with hypochlorite, but due to the very high concentration it is probably very harmful for the membranes.

## 8 Future Work

Membrane cleaning is a wide area where much more can be investigated. One of the areas that it would be interesting to further investigate is the cleaning efficiency of different cleaning agents. Some examples of what could be investigated are the cleaning efficiency of an acidic cleaning agent and pure sodium hydroxide in comparison to Ultrasil 10. It would also be interesting to examine the cleaning efficiency of cleaning with a combination of cleaning agents.

Apart from a continuous investigation of different cleaning agents it can be studied if it is possible to find an economically optimal combination of a cleaning agent concentration and cleaning time that can remove the foulants. This economical question is difficult as it has to be a balance between the time that the cleaning interrupts the operation and the concentration that is affecting the membrane lifetime. However, it would be interesting to see if it is possible to find the lowest concentration and cleaning time that can be used and still give a full recovery of the pure water flux. It might also be possible to do an evaluation between different cleaning agents regarding the costs for the cleaning agents compared to the efficiency.

Furthermore, it is stated by Weis (2001, 2003) that chemical cleaning must be examined for a longer cycle of fouling and cleaning in order to fully determine the efficiency of a cleaning method. For that reason it would be interesting to perform a longer investigation with successful cleaning methods to see if there is a method that is more efficient than the others over a longer period of time.

Except from the possibilities in further investigating membrane cleaning, it would also be interesting to further investigate how the fouling occurs. The results from the study showed that there is a relation between the temperature and the severity of the fouling. It would be interesting to determine if that is the case and if so, to investigate if there is a critical temperature at which the severity of the fouling increases. Furthermore it would also be interesting to examine the fouled membranes by a surface characterization method to see if it can be determined what it is that fouls the membrane.

Finally, a last example of the future work that would be interesting to perform is to examine fouling and cleaning with process water from other applications. Since it is known that different process water contains different shares of possible foulants, it would be interesting to see if there is a difference between the fouling achieved from the same conditions, and how effective a cleaning procedure is when other foulants are present.

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## Appendix A – Pure Water Flux

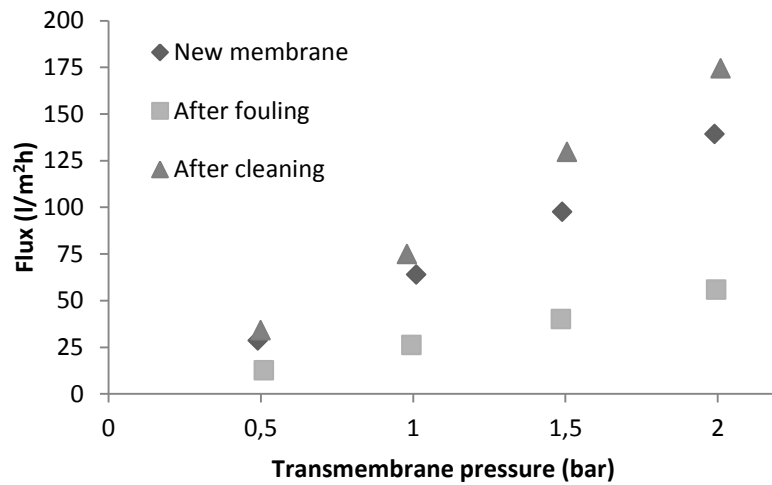


Figure A.1. Pure water flux measurements for fouling experiment A, cleaned with cleaning method I.

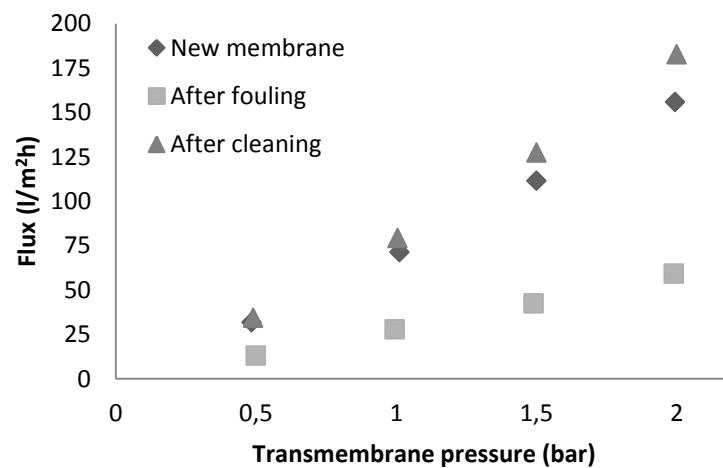


Figure A.2. Pure water flux measurements for fouling experiment B, cleaned with cleaning method I.

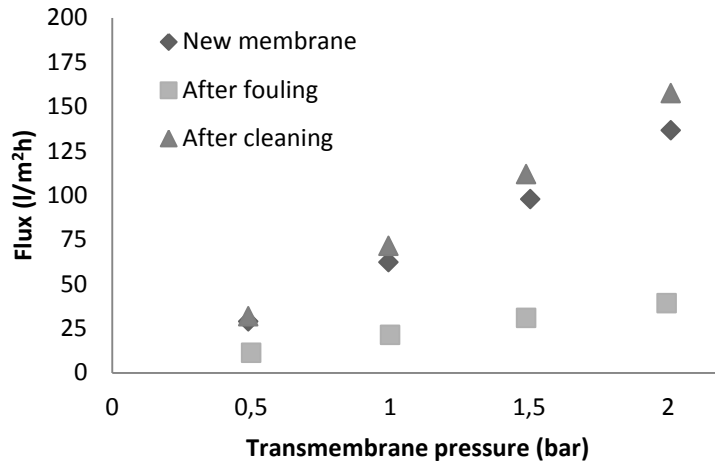


Figure A.3. Pure water flux measurements for fouling experiment C, cleaned with cleaning method I.

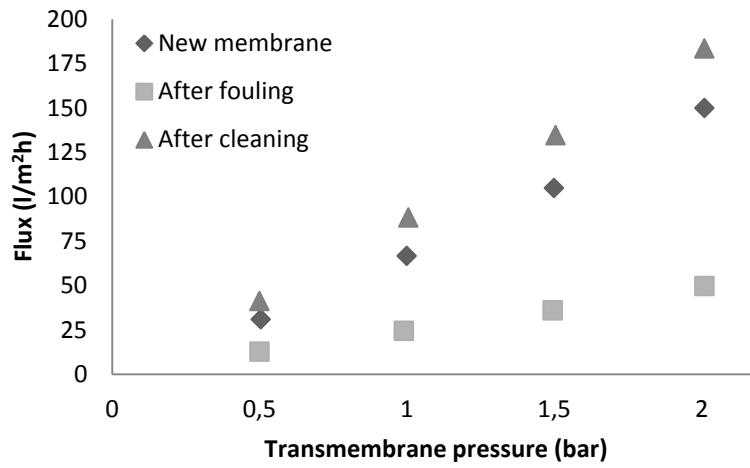


Figure A.4. Pure water flux measurements for fouling experiment D, cleaned with cleaning method I.

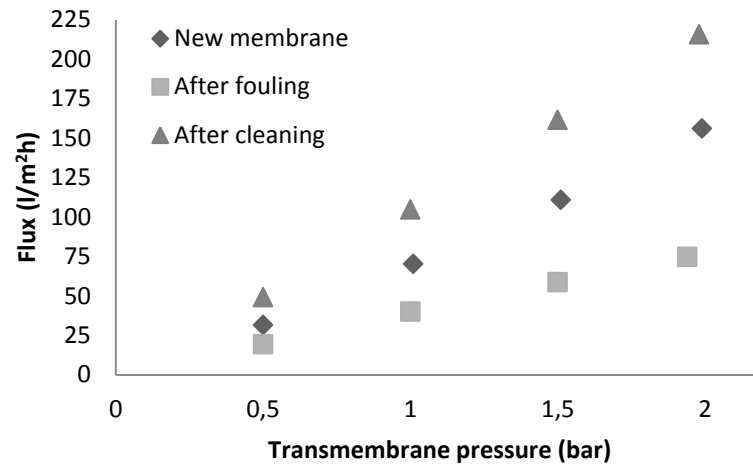


Figure A.5. Pure water flux measurement for fouling experiment E, cleaned with cleaning method I.

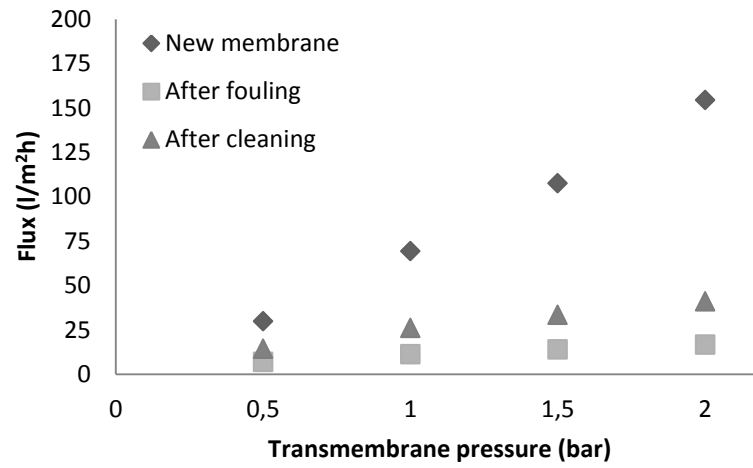


Figure A.6. Pure water flux measurements for fouling experiment F, cleaned with cleaning method I.

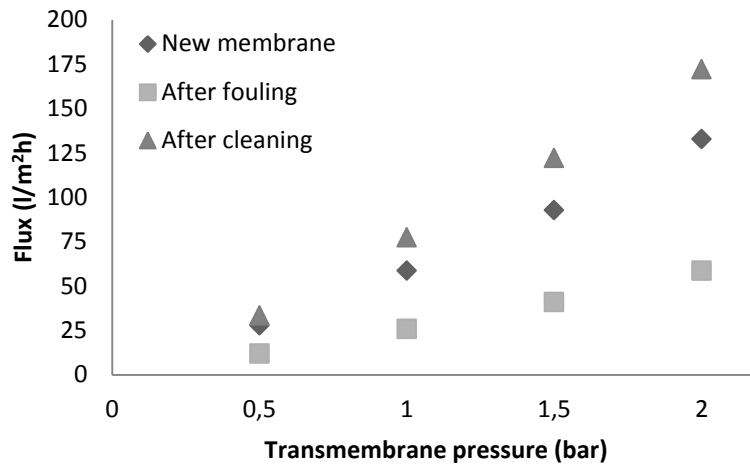


Figure A.7. Pure water flux measurements for fouling experiment G, cleaned with cleaning method I.

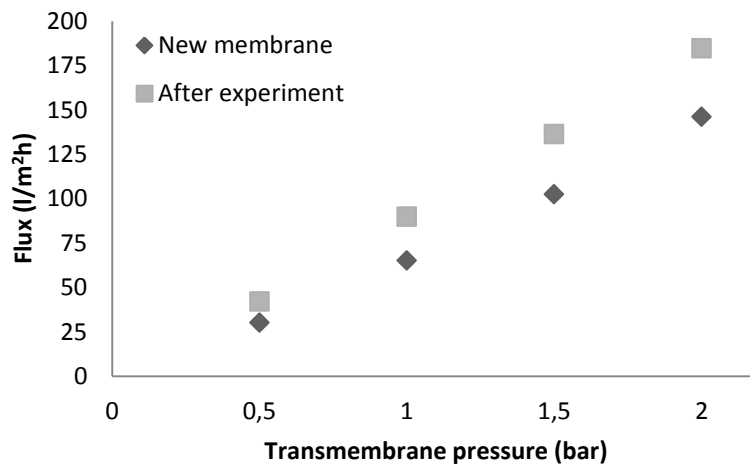


Figure A.8. Pure water flux measurements for fouling experiment H, cleaned with cleaning method I.

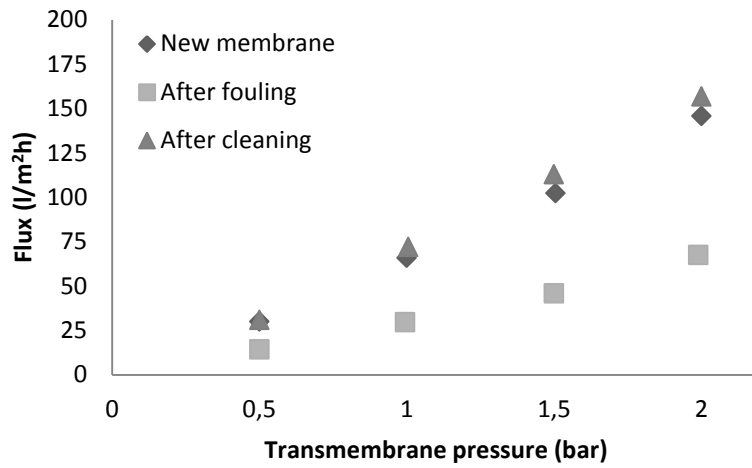


Figure A.9. Pure water flux measurements from fouling experiment I, cleaned with cleaning method I.

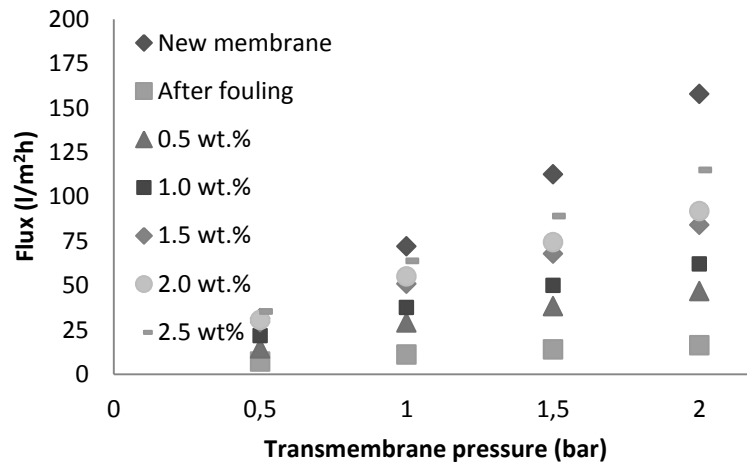


Figure A.10. Pure water flux measurements when investigating the influence of concentration using cleaning method II (fouling according to conditions in experiment F).

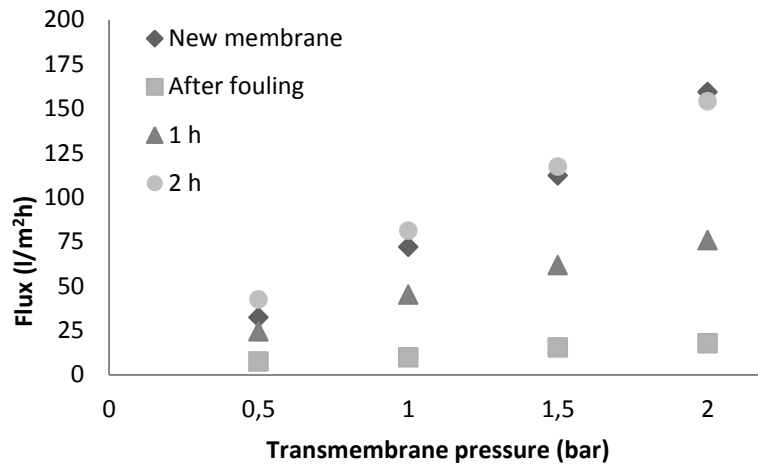


Figure A.11. Pure water flux measurements when investigating the influence of cleaning time using cleaning method III (fouling according to conditions in experiment F).

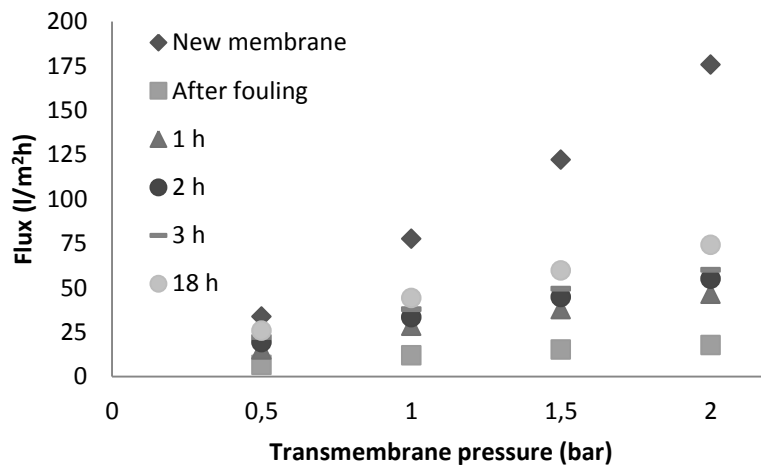
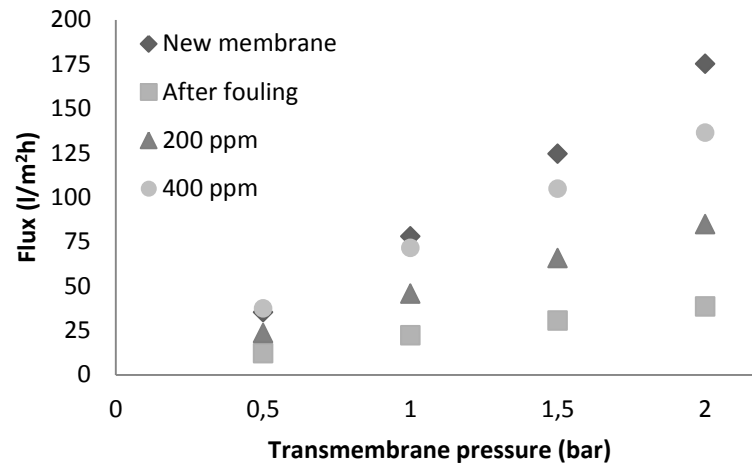


Figure A.12. Pure water flux measurements when investigating the influence of low-concentration cleaning using cleaning method IV (fouling according to conditions in experiment F).



*Figure A.13. Pure water flux measurements when investigating the influence of hypochlorite cleaning using cleaning method V (fouling according to conditions in experiment F).*