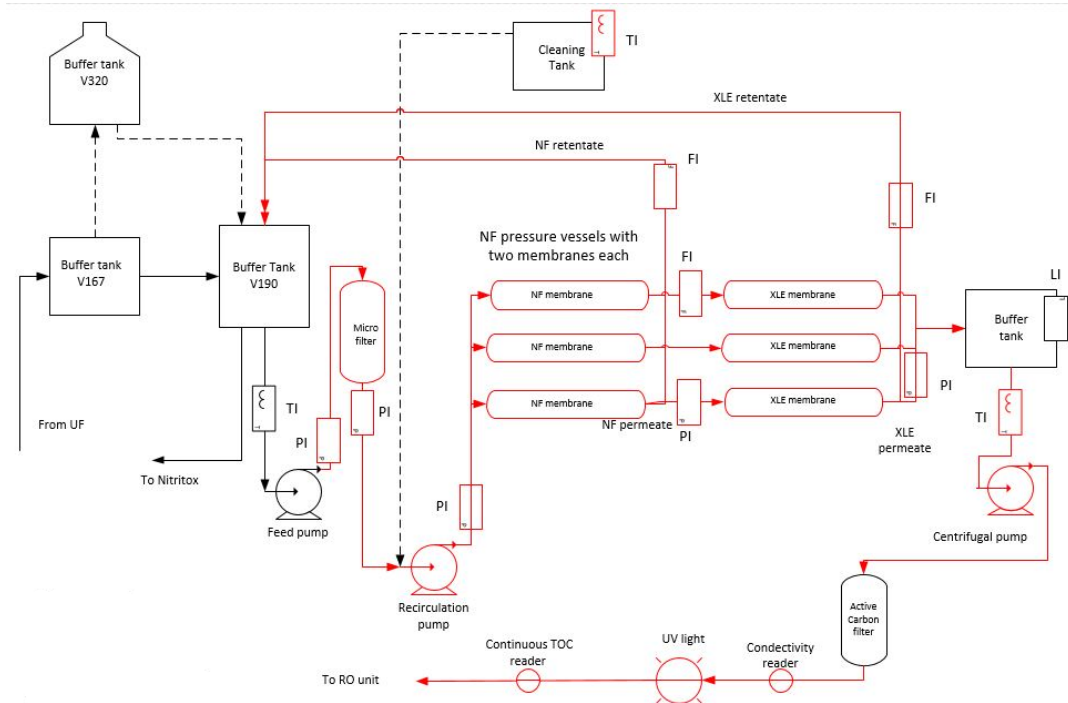


Wastewater Treatment with Nanofiltration in Pilot-scale



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Wastewater Treatment with Nanofiltration in Pilot-scale

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Picture in the front page is the flowsheet of the NF system which is created by Safa & Jane

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Preface

This master thesis is the final product of the master's degree education, which is the last part of studying Chemical Engineering study at the Faculty of Engineering, Lund's University. All of the work presented henceforth was conducted at Dow Chemical site in Landskrona and at the Lund's University.

We would want to thank several persons that have contributed academically, practically and that have supported us through the completion of the master thesis. We would firstly want to thank our supervisor, Martin Kronwall at Dow who have been an exceptional supervisor. All the support, valuable input and time you have been providing us throughout this six months have been very helpful and inspiring. Your hardworking attitude has inspired and excited us for our first employments in the chemical field.

We would also thank all the workers at Dow that have been helping us with this master thesis. Especially thank to Jochen Henkel from Dow Water and Process Solutions who provided us with insightful advices and help with design software ROSA.

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Lastly, we would want to thank our families and friends for being supportive and helpful during our time studying in LTH.

Abstract

During the spring semester 2018, an investigation about supplementary cleaning of the waste water at Dow Chemical site in Landskrona was done. Different water-based binders from acrylic monomers are produced by Dow and large amounts of water is used for such processes. The wastewater, that is treated currently by ultrafiltration (UF), contains different chemical residues such as surfactants, residual monomers and polymers. The UF content also varies from batch to batch because of different products being produced at Dow Landskrona. From UF, permeate and concentrate are produced. The concentrate is collected and sold as a product known as (TN-1), while the permeate should be approved before sending it to the municipal wastewater plant (WWTP). From both economic and environmental perspectives, the UF permeate should be filtered further by nanofiltration (NF) to produce sufficient clean water to be reused.

In this study, a pilot plant with NF90-4040 membrane from Dow Filmtec was used to investigate the nanofiltration. The UF permeate from Dow was filtered further to produce NF permeate and concentrate. The operating pressure was 5 and 10 bars and the temperature varied from 33 to 38°C, while pH was in the range of 8 and 10. The conductivity and pH was measured for UF permeate, NF permeate and concentrate at Dow. The flux with different volume reduction (VR) was also measured. Bacterial growth analysis was performed in Dow, while total organic carbon (TOC) and molecular mass analysis for the NF permeate and concentrate were performed in Lund university.

After 12 batches performed at Dow, the conductivity and TOC values in the NF permeate were still higher than in the city water. Therefore, RO membrane is recommended to be used as a second stage after NF to reduce the conductivity and TOC. A screening of flat sheet membranes was performed at Lund university with three different RO membranes. XLE and SW30-HR from Dow Filmtec and RO98 pHt from Alfa Laval. The XLE membrane was chosen further because of good retention. The NF permeate had also a smell issue which also had been solved by trying different methods. Active carbon column was the suitable one which already exists in Dow.

For the full scale, six NF and three XLE membranes were determined to handle the wastewater. The full-scale should be able to handle even the worst-case scenario at Dow. NF membranes are effective to produce clean water and the pure water flux (PWF) was obtained after each chemical cleaning. Yet another RO membrane stage is required to meet the water specifications used in the process, especially when the UF permeate is considered as a worst-case. A cost estimation was also conducted for full scale in Dow Landskrona. The investment cost was estimated to be 1.9 million SEK and the operating cost at 200 000 SEK per year. During the payback period, the cost of treated wastewater costs 28 SEK/m³ and after the payback period the cost of the treated wastewater is reduced to 11 SEK/m³.

Chemical precipitation was also tested as an alternative method for the NF concentrate treatment. Jar tests were performed to conclude which chemicals to be used. The test has showed that it is possible to precipitate the surfactants and to be removed from the NF concentrate. Further studies need to be done for larger amounts to decide whether this method is suitable or not.

Keywords: wastewater; nanofiltration; ultrafiltration; chemical precipitation; pilot-scale.

Sammanfattning

Under vårterminen 2018 gjordes en undersökning om tilläggsrening av avloppsvattnet vid Dow i Landskrona. Olika vattenbaserade bindemedel från akrylmonomerer framställs av Dow och stora mängder vatten används för en sådan process. Avloppsvattnet, som nu behandlas genom ultrafiltrering (UF), innehåller olika kemiska rester, såsom ytaktiva ämnen, kvarvarande monomerer och polymerer. Innehållet i UF permeatet varierar också från sats till sats på grund av olika produktionsscheman på Dow Landskrona. Från UF produceras permeat och koncentrat. Koncentratet samlas in och säljs som en produkt som kallas TN-1, medan permeatet bör godkännas innan det skickas till kommunalt avloppsvattenverk. Ur både ekonomiska och miljömässiga skäl bör UF-permeatet filtreras vidare genom nanofiltrering (NF) för att producera tillräckligt rent vatten för att återanvändas.

I denna studie utfördes experimenten i pilotskala med NF90-4040 membran från Dow Filmtec för att undersöka nanofiltreringen. UF-permeatet från Dow filtrerades ytterligare genom NF för att producera ett renare permeat. Driftstrycket var 5 och 10 bar och temperaturen varierade från 33 till 38°C, medan pH var i intervallet 8 och 10. Konduktivitet och pH-värdet mättes för UF-permeat, NF-permeat och koncentrerat vid Dow. Flödet med olika volymreduktion (VR) mättes också. Bakteriell tillväxtanalys utfördes i Dow, medan total organisk kol (TOC) och molekylmassanalys för NF-permeatet och koncentratet utfördes i Lunds universitet.

Efter 12 experiment utförda på Dow Chemical site i Landskrona, visade det sig att konduktivitets- och TOC-värdena i NF-permeatet fortfarande var högre än stadsvattnets. Därför rekommenderas RO-membran att användas som ett andra steg efter NF för att ytterligare minska konduktiviteten och TOC. En screening av platta membraner utfördes i Lunds universitet med tre olika RO-membraner. XLE och SW30-HR från Dow Filmtec och RO98 pHt från Alfa Laval. XLE-membranet valdes på grund av god retention. NF-permeatet hade en avvikande doft som löstes genom att prova olika metoder. Aktiv kol var den lämpliga metoden och finns redan i Dow.

För fullskala bestämdes sex NF och tre XLE membran för att hantera avloppsvattnet. Fullskalan ska kunna hantera även värsta scenariot hos Dow. NF-membraner är effektiva för att producera rent vatten och det rena vattenflödet (PWF) erhöles efter varje kemisk rengöring. Ytterligare ett RO-membranstadium krävs för att uppfylla de kraven på vattnet som skall användas i processen. En kostnadsberäkning genomfördes också för fullskala på Dow i Landskrona. Investeringskostnaden beräknades till 1.9 miljoner kr och driftkostnaden kostar 200 000 kr per år. Under återbetalningstiden kostar det behandlade avloppsvattnet 28 kr/m³ och efter återbetalningstiden kostar det istället 11 kr/m³.

Kemisk fällning testades också som en lämplig metod för NF-koncentratbehandlingen. Experiment utfördes för att avgöra vilka kemikalier som ska användas. Testet har visat att det är möjligt att fälla ut de ytaktiva ämnena och att avlägsnas det från NF-koncentratet. Ytterligare studier måste göras för större mängder prover för att bestämma om denna metod är lämplig eller inte.

Nyckelord: avloppsvatten; nanofiltrering ; ultrafiltrering ; kemisk fällning; pilotskala .

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1. Introduction

Dow chemical plant in Landskrona-Sweden produces water-based binders from acrylic monomers which are used mainly in the paint industry. Large amounts of water is required for such a process and city water is used as the fresh water source. The fresh water is deionized by passing through an ion exchanger before use in the process to decrease the conductivity. Chemical residuals end up in the drain such as polymers, metal ions, surfactants, and residual of monomers.

Nowadays, an ultrafiltration unit (UF) is used for wastewater treatment in the plant. The permeate should meet the specification of municipal wastewater treatment plant (WWT) before discharging it to the municipal wastewater network. Based on previous research *Nanofiltration of ultrafiltration permeate from chemical wastewater* done last year in Dow chemical by Martin Gunnarsson, a nanofiltration set up in lab scale was investigated in order to treat the permeate further so that it could be reused in the process again. This will reduce the amounts of fresh water used and the wastewater discharged to WWT plant. It's also a beneficial solution for other plants where fresh water is considered as a major cost.

Gunnarsson recommended NF90, XLE and AP as membranes that have the capability to produce a permeate that can be reused in the membrane. Several of his experiments were on flat sheet membranes and he performed one spiral wound membrane experiment on NF90 which could reach an 85% volume reduction [1].

1.1 Aim

The aim of this master thesis is to apply nanofiltration experiments in pilot scale instead of lab scale and to investigate the functionality of the membrane with large amount of permeate. To be able to reuse the treated wastewater, the treated wastewater has to reach some quality demands. Therefore, the water will be analysed to secure its quality. Also, it is important to resolve the problems that showed up in the previous experiments such as fouling. After each filtration, chemical cleaning will be performed to clean the membrane and the goal is to find a suitable cleaning sequence and chemical that is efficient. A full scale will be performed and a complete cost estimation for the nanofiltration implementation will be calculated.

1.2 Background

The beginning of the of the master thesis, a literature study was completed to gain a deeper understanding of membrane separation and the quality demands of the treated water for recirculation in the processes. The theory that will be presented are about some fundamentals of pressure driven membranes, membrane fouling and chemical cleaning. Chemical precipitation for surfactant removal and hydrogen sulphide occurrences in water will also be presented.

1.2.1 Quality Demand of the Water and Quality of UF Permeate

The water treated by ultrafiltration and nanofiltration has to achieve some requirements before it is allowed to be reused in the process. The nanofiltration permeate has to be free from bacteria, surfactants and have a conductivity ≤ 0.02 mS/cm [2].

The surfactants have to be completely absent from the water due to its tendency of causing foams. The treated wastewater needs to be free from surfactants before being reused in the processes.

Metals for instance as zinc are poisonous and cannot be released to the environment. Conductivity is a measurement of the water's ability to conduct electricity, therefore conductivity is an indication of the level of ions in the water. If the conductivity of the nanofiltration permeate is higher than 0.02 mS/cm, an ion exchanger or reverse osmosis (RO) could be used to remove the remaining ions.

Total organic carbon (TOC) measures the level of organic molecules in the water. A TOC analysis can measure both the present organic carbon and the inorganic carbon (IC). The concentration of TOC should be the same as the city water, which is 3 mg/l. The chemical oxygen demand (COD) indicates the amount of oxidizable organic material in the water. A high concentration of COD is harmful for the aquatic life form and the acceptable COD concentration is 1.2 mg O₂/l [2].

The quality of UF permeate can vary a lot due to different products are being made in the factory. The variation of chemicals and also different doses of alkali being used in the UF cleaning can affect the initial TOC and conductivity concentration of UF permeate. Therefore, the NF system has to be able to handle the worst case.

1.2.2 Removal of Surfactants by Coagulation and Flocculation

The surfactants in the wastewater at Dow Landskrona are mainly anionic surfactants. Surfactants are widely used in the process industry. It is needed as for instance for synthesizing paints, polymers and cosmetics. The surfactants in industrial wastewater has to be removed and not be released to the nature. Surfactants causes foaming in rivers and the consequences of surfactants is both short-term and long-term changes in the ecosystem. It is harmful to humans, marine life and the vegetation.

One efficient separation method for removing the surfactants from wastewater is called chemical precipitation. The method involves three steps; coagulation, flocculation and sedimentation. The first step uses coagulant chemicals to destabilize particles in the water so they aggregate into precipitates. Metal salts such as aluminum sulfate and ferric chloride are the most common used inorganic metal coagulants. They are highly positive charged ions and when added to water, it neutralizes the suspended particles. The neutralization is necessary due to the fact that anionic surfactants have negative charges and repel each other and consequently remain in suspension. Therefore, by adding proper amount of coagulant, the surfactants will gain a neutral surface charge and clump together into small flocs.

Flocculation means that the destabilized particles will aggregate into larger masses due to the addition of flocculant aid which are organic polymers and collision by mixing. Larger masses simplify the removal of the particles from the wastewater. The coagulation process typically occurs in less than 10 seconds while flocculation requires 20 to 45 minutes. During sedimentation, the precipitate will sink down to the bottom and the precipitate-free liquid above is called the supernatant.

Typical dosages of aluminum sulfate and ferric chloride are 10 to 150 mg/L and 5 to 150 mg/L. The dosages depend of the raw-water quality [3].

1.2.3 Occurrence of Hydrogen Sulfide

The occurrence of hydrogen sulfide (H_2S) can be found in water systems. It is a colorless gas and toxic by inhalation which has the characteristic smell of rotten eggs already at low concentrations (0.1 ppm). Besides being poisonous, the gas is also flammable. H_2S at 150 ppm numbs the sense of smell and can cause workers being unaware of the dangerous after a while when they assume the odor has disappeared.

Severe health issues caused by hydrogen sulfides are for instance headaches, eye irritations and also breathing problems. Higher doses (300-500 ppm) of the poisonous gas lead to unconsciousness and even death since H_2S impairs the blood's capacity of transporting oxygen.

The gas is formed when bacteria decompose organic matter under anaerobic conditions in places as swamps or sewers. H_2S also arises when elemental sulphur comes in contact with organic matter at high temperatures [4].

The NF permeate has no color, but in some occasions, it has a smell. The smell is probably coming from volatile organic compounds (VOC) and sulphur compounds dissolved in water such as H_2S because it smells sometimes like egg. A further study to investigate the smell source is recommended because the sulphur compounds are poisonous and to decide the proper method to remove it. H_2S removal methods will be discussed in later section of this report.

1.2.4 Fundamentals of Pressure Driven Membranes

Membrane processes are well used in the separation technology. There are several pressure-driven membranes applied in industries, they are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The concept of membrane processes can be described as membrane being a conventional filter with very fine pores to separate particles. The advantage of membrane processes over distillation and adsorption is no need of chemical, biological or thermal change of the involved components being separated since membrane separation is based on a physical mechanism. Therefore, membrane separation is an especially attractive method in food industry where the products are temperature and solvent sensitive.

In a membrane process, the feed stream will be split into two streams with different compositions. One of the streams is the retentate (also called concentrate or reject) which is the stream that has been retained by the membrane. It consists of the material that have been rejected by the membrane but also of material that hasn't been given the opportunity to pass through the membrane yet. Therefore, for reaching higher quality, the retentate stream can be mixed with the feed stream. The reduction of volume of the feed and retentate is called for volume reduction (VR). The other stream is called the permeate stream, it consists less molecules or particles than the membrane pores. The permeate stream can be named for the product stream too.

Pressure-driven membranes can be operated in two modes: dead-end and cross-flow operations. In the dead-end mode, the feed enters the membrane module vertically while in cross-flow mode, the feed flows tangentially to the membrane surface. The advantage of cross-flow mode is that the tangential flow shear away the accumulated rejected species at the membrane and it limits the fouling rate [5].

The driving force in the pressure-driven membrane processes is the pressure between the feed and the permeate and is referred to as the transmembrane pressure (TMP). The productivity of the membrane separation is by measuring the permeate flux. It indicates the rate of mass

transport across the membrane. The permeate flux is directly proportional to the TMP and inversely proportional to the viscosity (μ) as shown in equation (1). The viscosity is controlled by the feed concentration and temperature. Therefore, for a higher permeate flux, the temperature and TMP can be increased and the feed concentration should be decreased.

$$PWF = \frac{TMP}{\mu R_m} \quad (1)$$

Where: R_m is the filtration resistance of the membrane.

1.2.4.1 Nanofiltration

Nanofiltration (NF) is one of the four major pressure driven membrane filtration methods. It has features that are intermediate between reverse osmosis (RO) and ultrafiltration (UF). Nanofiltration membrane has the pore sizes of 0.5-10 nm, 100-500 Da and the transmembrane pressure (TMP) which is 10-30 bar [5].

Nanofiltration has two kinds of separation mechanisms. The first one is called the sieving mechanism which is when uncharged solution is being transported by convection due to pressure difference and also by a concentration gradient across the membrane. Uncharged compounds larger than the membrane's pore dimension will be retained while smaller compounds will be transported through the membrane. The retention of uncharged compounds is caused by the sieving mechanism.

The other mechanism is caused by electrostatic interaction between the charged components and the membrane. The NF membrane has a negative charged surface due to functional groups and therefore an electrostatic repulsion force occurs between the membrane's surface and the charged compounds. Nanofiltration can reject charged compounds much smaller than the membrane's pore due to this mechanism.

The zeta potential is known as electro kinetic potential, measured in millivolts (mV), it measures the potential difference across the phase boundaries between solid and liquids. A study has found that with increased pH, the zeta potential becomes more negatively charged and when the pH decreases the zeta potential becomes more positive. The salt rejection increases with higher pH and negative zeta potential while at lower pH, the electrostatic repulsion became weaker which resulted in a reduced rejection efficiency. To increase the filtration efficiency, the pH of the feed can therefore be adjusted to change the charge of the membrane and even some of the molecules [6].

Nanofiltration is widely applied in water treatment and is often a sufficient method for producing clean drinking water but microfiltration (MF) or ultrafiltration (UF) is often used as prefiltration before NF. Nanofiltration has the capability to remove multivalent ions, sugars, peptides, amino acids and organic acids. Aside from application in water treatment, nanofiltration is also applied in the food industry, textile industry, pulp and paper and in the field of metal and mining [7].

1.2.4.2 Reverse Osmosis Membrane

Reverse osmosis (RO) membranes are used in processes such as water reuse, high purity water treatment and specific contaminant removal. RO is efficient at removing numerous inorganic contaminants as antimony, arsenic nitrate and radionuclides. It has also shown the ability of removing synthetic organics such as pesticides. It is less common to use RO for specific contaminants removal due to other more cost-effective alternatives. RO are most widely used

in water treatment. The alternative processes for the purpose of water recycling and high-purity process water are ion exchanger and distillation [3].

RO membranes have similar characteristics to NF membranes. Both of them are pressure driven and efficient in water purification processes. Of all categories of membranes, RO membranes have the smallest pores and its ion rejection capability is higher than NF's. Another characteristic of RO that's similar to NF membranes is the negative charge at the membrane's surface due to ionized functional groups.

Pretreatment of the wastewater before RO is important. Due to the very fine pores of RO membranes, larger particles can easily accelerate the fouling. The sources of fouling and scaling are precipitation of salts, oxidation of metals and also biological substances. The cleaning agents for RO membranes are also alkaline and acidic chemicals as for NF membranes.

1.2.5 Membrane Material

Membrane materials are divided into two classes; polymeric and ceramic membranes. Polymeric membranes are far cheaper than ceramic membranes due to a simpler manufacturing. They are widely used in the industry and are available in different pore sizes. The disadvantages of polymeric membranes are its limitation on several operating conditions as pH, temperature and pressure.

Inorganic membranes are known for high mechanical strength, and chemical and thermal stability. The lifetime of an inorganic membrane is longer than a polymeric membrane and another advantage of inorganic membranes is the wider range of pH, temperature and pressure. However, inorganic membranes are brittle and therefore sensitive to dropping and excessive vibration.

The market today is greatly dominated by polymeric membranes but the demand for nonpolymeric materials is increasing steadily due to their better performance and longer lifetime [5].

The NF90 membrane that will be used in the experiments is a polymeric membrane made of polyamide thin-film composite. Usually, nanofiltration membranes are made of several layers of materials. It is normally three to four layers. One of the layers are called as a support layer, its purpose is to give strength to the membrane and it is often made of a fiber network. The second layer of the membrane can also have a supporting function and are either a microfiltration or an ultrafiltration membrane. The top layer gives the special functional properties of a nanofiltration membrane. The top layer of a NF90 membrane is made of polyamide [7].

1.2.6 Membrane Modules

The membrane module describes the membrane's arrangement inside the device in order to separate the feed stream into a permeate and retentate streams. Nowadays, there are different types of membrane modules that have been used commonly in industry. These modules are designed to match special characteristics on filtration areas, energy consumption, hydrodynamic conditions, etc.

Based on previous research, the most suitable membrane module in this application was spiral-wound module [1]. This type consists of two membrane sheets which are separated by a mesh-

like spacer and the membrane active sides are facing away. Three edges of the two membrane sheets are attached together, while the fourth one is open to a perforated centre tube for removal of permeate. Two additional mesh-like spacers are placed as a feed channel spaces on the other two sides of “the envelope”. The mesh-like spacers have a thickness range from 0.56 to 3 mm. These sheets are rolled in a spiral configuration around the perforated centre tube. The spiral module is appropriate for turbulent flow region due to presence feed spacers. The pressure drop in this type is relatively high since additional drag are generated by the feed spacers. The ratio between surface area to volume ratio is rather high for spiral module as well, but its capital cost is the lowest compared to the other different types of membrane modules. The mesh-like spacers can be easily blocked by suspended particles in the incoming stream and can block the feed channel partially. To avoid such a problem, pre-treatment for the feed stream is required in the spiral-wound module to minimize the content of suspended particles [5].

1.2.7 Membrane Fouling

In the usage of membrane separation, fouling is almost inevitable. Fouling occurs due to deposition of suspended or dissolved substances onto the external surface of the membrane. The fouling can be either biofouling (caused by living organisms) or be organic/inorganic fouling (caused by organic/inorganic compounds). The consequence of fouling is a reduction in the active area of the membrane which results in reduction in flux. There are several parameters that influence the rate of fouling. For instance, the pore size distribution, material of the membrane and the hydrodynamic of the membrane module.

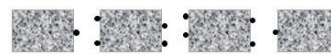
In porous membranes, four kinds of fouling mechanisms exist, they are illustrated in figure 1. They are:

- a. Complete pore blocking
- b. Internal pore blocking
- c. Partial pore blocking
- d. Cake filtration

(A) Complete pore blocking



(B) Internal pore blocking



(C) Partial pore blocking



(D) Cake filtration

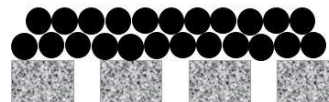


Figure 1. The four different fouling mechanisms of porous membranes redrawn by writer from inspiration [5].

The complete pore blocking occurs when the particles in the feed are larger than the pore size. If the particles are much smaller than the pore size, an internal pore blocking can happen. The small particles enter the pores and get adsorbed or deposited into the pores. In partial pore blocking, particles seal the pores over time but might not block the pore completely. The last fouling mechanism is called cake filtration, it means that a layer of cake built by particles have been formed above the membrane surface [5].

1.2.7.1 Fouling Control

Fouling is an issue which has to be controlled for the cause of minimizing the cost of cleaning and also to reduce the downtime of the process. Current cleaning in place methods (CIP) requires large amounts of water and consumptions of chemicals used in caustic- and acid wash. By being able to control the fouling rate to an acceptable rate, savings can also be made in energy consumptions and in the purchase of membranes.

There are different approaches to control the fouling rate. The approaches can be applied separately or in combination. In this master thesis, four approaches will be mentioned shortly:

1. Physical cleaning
2. Flux control
3. Chemical cleaning
4. Feed pretreatment

Back flushing is physical cleaning and it is carried out by reversing the permeate flow through the membrane. It removes the foulant on the feed side and reestablish the flux rate to a higher rate. To be able to conduct back flushing, the membrane module needs to have a high-pressure resistance. If the back flushing is performed during a short period of time and with high frequency then it is called pulsing. Flux control means finding the critical flux which is defined as a level of flux where the fouling is minimal.

The chemical cleaning includes the selection of suitable chemical agents and also determining the cleaning procedure. This approach of removing the foulant depends largely of experience and cannot be easily predicted. In feed treatment, pH and salt concentration can be adjusted to reduce the fouling tendency [5].

1.2.8 Membrane Cleaning

As mentioned in the previous section Fouling Control, there are several approaches for controlling the fouling rate. One of the methods is cleaning the membrane with chemical agents which will be described more next.

1.2.8.1 Chemical Cleaning

In chemical cleaning, a chemical solvent is circulated in the system at a specific pH, temperature and circulation time. The transmembrane pressure should be low during the cleaning. The common chemicals used in the industry for membrane cleaning are acids, bases and surfactants. The chemicals break down the structure of the foulant from the membrane.

Both alkaline and acidic chemicals are commonly used in membrane cleaning. The most common chemicals applied in the industry except alkaline and acidic chemicals also includes the usage of enzymes and surfactants. The cleaning ability of alkaline chemicals is the saponification of fat and lipids. Acidic chemicals are effective in the removal of metal oxides and inorganic deposits [5].

The chemicals that probably will be used as the chemical agents in this master thesis are: Ultrasil 10, hydrochloric acid pH 2 and citric acid pH 4. Ultrasil 10 is a highly corrosive detergent which consists of EDTA, phosphate and anionic surfactants. EDTA is a metal chelating agent and widely used to remove limescale. It has a hexadentate ligand which has the ability to bind minerals and metals. Anionic surfactants ionize when added to the water and get a negative charge which binds to particles that are positive charged.

Citric acid has a milder property compared to hydrochloric and can therefore be more easily be rinsed.

1.2.8.2 Design of Cleaning Sequence

There are many variations of cleaning sequences, but a standard cleaning, shown in figure 2, starts with prerinse and thereafter detergent wash, post rinse, acidic rinse and ends with a final rinse.

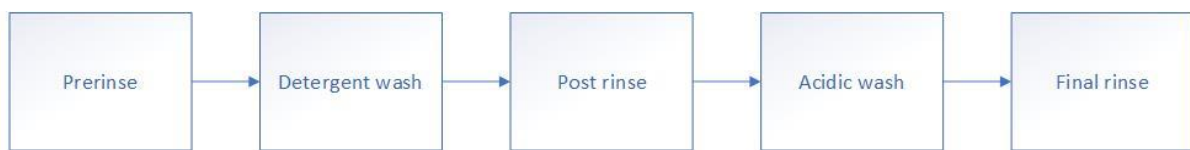


Figure 2: The standard cleaning sequence.

1.2.8.3 Cleaning Efficiency

The cleaning efficiency will be determined by the pure water flux (PWF) recovery. The flux recovery is estimated by taking the water flux after cleaning divided by the initial pure water flux [4]. The PWF can be measured after the final rinse.

$$\text{Flux recovery} = \frac{J_{wc}}{J_{wi}} \cdot 100\% \quad (2)$$

1.2.8.4 Factors Affecting the Cleaning Efficiency

There are several factors that affect the cleaning efficiency. One of them is water rinsing. It is an effective method of removing loosely bound deposits on the membrane and the pre-water rinsing should be performed at the same temperature as the cleaning. The duration of the water rinsing is usually between 5 to 20 minutes, but it highly depends on the size of the membrane.

A higher temperature both increases the cleaning efficiency due to a faster reaction kinetics and increases the mass transport which also leads to a more effective cleaning. However, a higher temperature can increase the fouling for some components as fats. Awareness of the membrane's maximum operating temperature has to be considered too during cleaning. Multiple cleaning cycles may be needed before the flux stabilize [5].

2 Material and method

The pilot-scale equipment with a NF membrane will first be presented and later the lab-scale set-up used for experimenting the RO membranes. Each equipment is illustrated with a simplified flow scheme. The methods conducted for analyzing the NF permeate and reject will also be presented. The NF's permeate and reject goes through several analysis and the analysis are TOC, size-exclusion chromatography (SEC), biochemical oxygen demand (BOD), NitriTox, water hardness and bacterial growth.

Five methods were performed to remove the smell from NF permeate. The methods will be described in this section.

2.1 Pilot-Scale Experiment

The pilot-scale equipment was placed in the ultrafiltration section in Dow, Landskrona as shown in figure 3 below. The system consists of two tanks with a volume of 1000 liter. The first tank is filled with UF permeate, while the second one is used for collecting the NF permeate. The temperature of the UF permeate is preferably remaining constant by using a fan heater and insulation around the UF permeate tank. However it was difficult to keep it constant through the process. By using a centrifugal feed pump, the UF permeate is pumped into the system. The feed pump can deliver higher pressure, but the system is designed to deal with a maximum pressure of 10 bar. The UF permeate flows through a micro-filter with a pore size of 5 μm to guarantee that there are no large particles passing through the membrane. Two pressure gauges are placed before and after the micro-filter.



Figure 3 Photo of the experimental setup for pilot scale

The UF permeate is pumped into the pressure vessel by using a recirculation pump, which delivers a 5 bar higher pressure than the feed pump. The pressure can be adjusted in this pump to reach the desired pressure and a pressure gauge is located after the recirculation pump. The UF permeate flows through the pressure vessel that contains the spiral-wound membrane, in which the filtration process occurs. The two outlet streams, i.e., the NF permeate and retentate are passing through two flowmeters. There is also a pressure gauge placed after the pressure vessel to measure the pressure drop through the pressure vessel. The NF retentate is recirculated to the UF permeate tank to concentrate it further. While the NF permeate is collected in the NF permeate tank as shown in figure 4 below. At each decided volume reduction (VR), a sample from both NF permeate and retentate is taken to measure different parameters.

For chemical cleaning, the same system is used. The UF permeate tank will be filled with the cleaning chemicals. The only change in the system is that both NF permeate and retentate flows will be gathered in the UF permeate tank. The cleaning solution of 500 L will be recirculated for an hour. Later, a 500 L of DI water will be used to wash the system and remove the cleaning chemicals in order to use the system for the next batch.

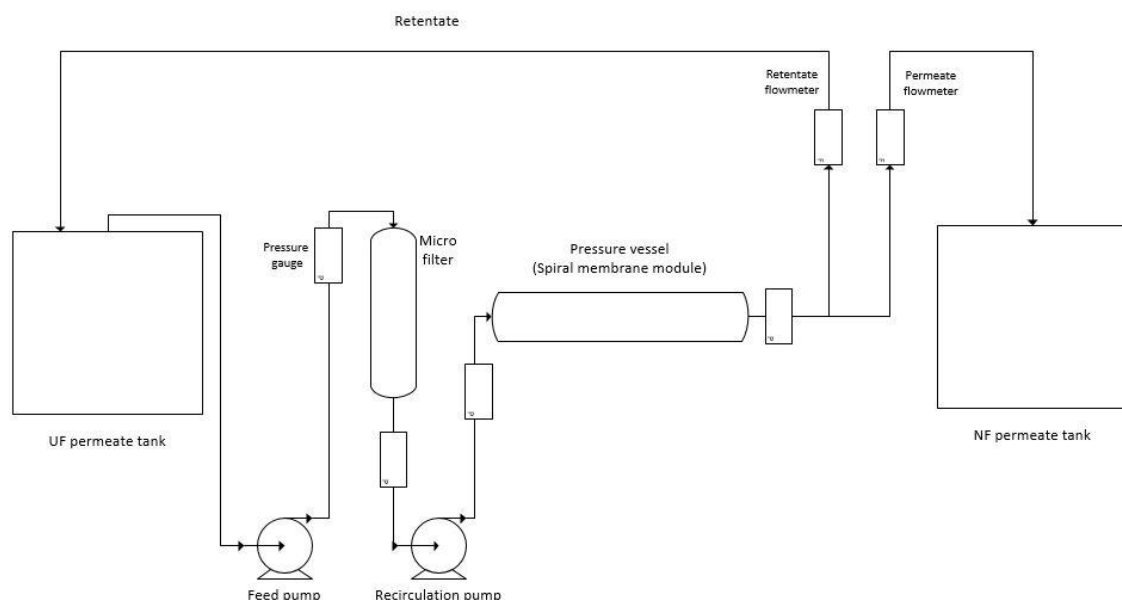


Figure 4 A scheme of the pilot-scale system

2.1.1 Alkali Cleaning and DI-water Flush

Chemical cleaning was conducted after each NF trial with the available alkali chemical at Dow which is a solution of 85% potassium hydroxide (KOH) and 15% EDTA. Both of them have the concentration of 46 mol/dm^3 . This chemical is already being used in the chemical cleaning for UF.

The chemical cleaning occurs at the temperature range $38\text{-}40^\circ\text{C}$ and circulates around the NF system in approximately 40-60 minutes. The pH was adjusted to be 11 at every cleaning but sometimes lower or little higher than pH 11 occurred.

The NF system was flushed with DI water with the temperature 38-40°C after every alkali cleaning session. The DI water flushing is in progress for 20 minutes and the pure water flux (PWF) was measured after the flushing. The initial pure water flux was measured to be 43.1 L/m²h.

2.1.2 NF90-4040

The NF90 membrane is of polyamide thin-film composite and the active membrane surface is 7.6 m². This membrane was recommended by Gunnarson due to good TOC and conductivity retention [1]. It has a high productivity performance in removing salts, nitrate, iron and organic compounds. The stabilized sodium chloride rejection is more than 97.0%. The membrane has several operating limits and they are presented in the list below [8]:

- Maximum Operating Temperature: 45°C
- Maximum Operating Pressure: 41 bars
- Maximum Feed Flow Rate: 3.6 m³/h

The pH range and temperature limits during cleaning is presented in the table 1:

Table 1: pH range of the NF90 membrane in different temperatures.

	Max Temp 45°C	Max Temp 35°C	Max Temp 25°C
pH range	1-10.5	1-12	1-13

The membrane module is stored with a liquid preservative solution consisting of bisulfite and citric acid. Bisulfite is a reducing agent and functions as a biocide, controlling the microbial growth while citric acid act as a buffer. At the initial membrane installation, the membrane should be washed thoroughly with DI-water to wash away the preservative solution [9].

2.2 Flat Sheet Analysis

To decrease the TOC in the NF permeate further, RO membrane unit is recommended after the NF. A lab-scale experiment is performed in Lund university with three different RO membranes to enhance the NF permeate quality. An experimental set-up at the Chemical Engineering Department, Lund University, which has three flat sheet modules in parallel is used to perform the screening test as shown in figure 5. The cross-sectional area of each membrane is 19.6 cm² which is used to calculate the flux. In addition to the three parallel flat sheet modules, the equipment consists of a tank that occupies 12 L with an immersed heater/cooler to heat/cool the NF permeate to the desired temperature and the current temperature is shown by a thermometer. The pressure can be adjusted by the pump and the valve shown in the figure and it can be read by two pressure gauges before and after the three modules. The flow, pressure, temperature and cross-flow velocity (CFV) can be recorded by using LabView 6.0 software (National Instruments Co., TX, USA) that is installed in the lab's PC. The flux (kg/m².hr) of each RO membrane is calculated by weighing the gathered water through the membrane area per hour. The CVF can be regulated by a frequency converter that is connected to the pump. The transmembrane pressure (TMP) can be calculated and recorded in the same software, which represent the mean value of the pressure gauges before and after the three modules.

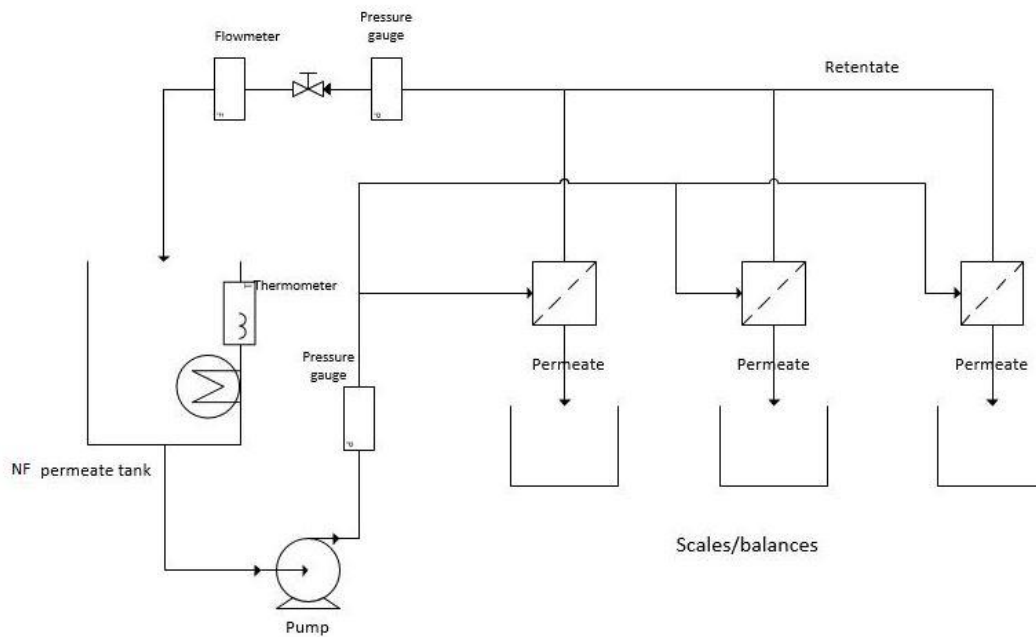


Figure 5 The flow scheme for the fat sheet membrane modules.

To start the experiment, the tank is filled with deionized water to clean the equipment. The temperature and the TMP are adjusted to 38°C and 5 bars respectively, while the CFV is adjusted to 0.5 m/s. The cleaning detergent (KOH and EDTA) is mixed with small amount of deionized water. The cleaning detergent is added slowly to guarantee a homogenous cleaning solution in the tank and to avoid high pulses of concentrated cleaning detergent that can harm the membrane. When the cleaning solution is well mixed with a pH of 11, it will be recirculated at 38°C for an hour. The pH value is chosen according to the temperature interval for each membrane. Figure 6 shows the equipment used in LTH.



Figure 6 Photo of the equipment used in LTH to perform RO experiment.

After the cleaning procedure is completed, the system is flushed with deionized water to remove the cleaning solution and to measure the pure water flux (PWF). The deionized water is drained and replaced by 12 L of NF permeate. The temperature and CFV are adjusted to 38°C and 0.5 m/s respectively, while the TMP is adjusted stepwise to 5,8 and 10 bars. The reason behind these chosen parameters is to check if the same NF parameters are applicable for RO membrane as well and give good results. This means that no need for heat exchanger nor buffer tank is needed between NF and RO units.

At each a pressure adjustment, both the permeate and the retentate are recirculated to the feed tank unit reaching steady state. Later, the flux is recorded by weighing the permeate at each time interval. Samples for each module at different pressure are withdrawn for further analysis. At the end of the filtration, the system is emptied and flushed with deionized water and PWF is measured before the chemical cleaning. The same procedure for chemical cleaning is used and the cleaning detergent is lately replaced by deionized water to measure the PWF. The reason behind measuring PWF before and after the NF filtration is to make sure that the cleaning detergent is efficient and to examine the fouling in the membrane.

2.2.1 RO Membranes

Three different types of RO membranes were tested in the flat sheet experiments. They are XLE and SW30-HR from Dow Filmtec and RO98 pHt from Alfa Laval.

XLE and SW30-HR are both sold as spiral-wound elements with polyamide thin-film composite membrane. The maximum operating temperature is 45 °C for both products while the maximum operating pressure is 69 bars for SW30-HR and 41 bars for XLE. The typical stabilized sodium chloride rejection for SW30-HR is 99.7% and 99.0% for XLE [10,11].

The RO98 pHt membrane has a sodium chloride rejection of $\geq 98\%$. The support material is polypropylene and the product type is thin-film composite membrane. Typical operating pressure for the membrane is 15-42 bar and it's tolerant to high temperature, the maximum operating temperature is 60 °C [12].

2.3 TOC

The TOC was analyzed at Lund's University with a total organic carbon analyzer TOC-5050 made by Shimadzu. The TOC analyzer is based on a 680°C combustion catalytic oxidation, in which a sufficient amount of the injected sample is heated until the water is totally evaporated. The total carbon (TC) will be measured by a sensor. The inorganic carbon (IC) is measured by mixing the carbon in the sample with phosphoric acid, so it will react with the acid. The TOC value is later measured by subtracting the IC from TC. The results will be shown later in the screen of the device as well as a printed paper roll [13].

2.4 SEC

Size-exclusion chromatography (SEC) was performed at Lund's University. SEC is a separation method based on how the molecules in the solution are separated according to their molecular weight. The column used in SEC is filled with materials containing many pores. The molecules in the solution of various sizes flow through the column, the smaller molecules penetrate the pores while the larger molecules will elute from the column faster due to not entering the pores [14].

With SEC, information of how much a sample contain of respective molecular weight can be obtained. Samples of UF permeate and NF permeate was analyzed with SEC for the purpose of identifying the molecular weight retained by the NF membrane.

2.5 BOD

Biochemical oxygen demand (BOD) measures the amount of dissolved oxygen consumed by aerobic biological organisms when decomposing organic matter in water at a certain temperature and over a specific time period. BOD is an important water quality parameter; a high BOD means that the oxygen will quickly be depleted in the water and the consequences are stressed aquatic organisms that will suffocate and die. The BOD analysis of the NF permeates and reject was sent to be performed by Synlab.

2.6 NitriTox

NitriTox is a toxicity analyzer. In the municipal water treatment, there is a biological waste water treatment called nitrification that uses some certain bacteria to oxidize ammonium to nitrate. The bacteria are highly sensitive to toxicity; therefore, toxicity is the main disturbance in the nitrification process. A failure in the nitrification process leads to increased discharge of ammonium into rivers, causing damages to the environment [15].

At Dow in Landskrona, the UF reject has to first pass the Nitritox before being released to the municipal water treatment. If the reject doesn't pass the Nitritox, it will be collected in a buffer tank for more treatments to lower the toxicity.

2.7 Hardness

Hardness in water depends on high mineral content. Multivalent cations, especially magnesium (Mg^{2+}) and calcium (Ca^{2+}) are the two minerals responsible for the hardness in water. Some common mineral forms of calcium are calcite ($CaCO_3$), anhydrite ($CaSO_4$) and fluorite (CaF_2).

Magnesium and calcium salts do easily precipitate and react with soap to form a foam that is hard to remove. The precipitate and the foam interfere with many processes in various industries. Hardness of water is represented as the sum of the concentration (mol/L) of calcium and magnesium [3]:

$$Hardness, \frac{eq}{L} = 2[Ca^{2+}] + 2[Mg^{2+}] \quad (2)$$

Another concern of hardness is scale formation. The scale formation plugs pipes which decreases the heat transfer coefficients. The accumulation of inorganic precipitates causes scales on membrane surface. To clean the membrane from scale formation, acidic chemicals need to be utilized.

Hardness control of samples of the NF permeate and reject was performed by Synlab.

2.8 Bacterial growth

The bacterial growth analysis was performed at Dow Landskrona. Dip slides was used for measuring and observing the microbial activity in the UF permeate and the NF permeate. The dip slides have to be incubated at 30°C for seven days.

2.9 Smell removal

In the Dow laboratory, small lab-scale methods were tested such as bubbling with air, heating, vacuum pump, hydrogen peroxide and active carbon.

The first method was simply consisting of a rubber tube with distributed fine pores that was placed in the bottom of a beaker. The air bubbles were rising through the water in order to release the dissolved gases. The second method was heating the NF permeate to its boiling point to release the dissolved gases.

The third method was bubbling the NF permeate with air, then using vacuum pump. The fourth method was mixing hydrogen peroxide with the permeate in order to oxidize the dissolved gases. Lastly, the active carbon was a simple trial, in which the NF permeate was poured through a cone filled with active carbon that was already available in Dow site.

4 Results and discussion

The results of the experiments from the NF pilot plant in both lower and higher pressures will be presented in this chapter. TOC and conductivity values will be presented and discussed.

The TOC and conductivity values from the experiments of RO membranes will also be presented in this chapter and a discussion of which RO membrane is more suitable will be discussed.

The results from different methods for analysing the treated wastewater will be presented but unfortunately, misunderstandings happened and therefore the samples sent for Synlab to analyse never occurred. Results from BOD and hardness analysis are therefore missing.

4.1 NF Trials at 5 bars

From the 2nd of March to the 22nd of March, six batches of UF permeate were filtered at the operating pressure 5 bar. In appendix A, the data of TC, IC, TOC, conductivity and also the retention of both TOC and conductivity are presented. The TOC retention is from the range of 94.7% to 98.91%. The average TOC retention value is 97.41%. The lowest conductivity retention is 89.9% and the highest value is 98.8%. The average conductivity retention is 95.31%. The TC, IC and TOC values for NF reject is also presented at appendix A.

A mistake made from the NF trials in 5 bars was not investigating the conductivity and pH of the NF reject at every VR as performed with the NF permeate. It could be interesting to observe how the conductivity increase at every increased VR and see how the pH varies at the reject stream. At the two last trials at higher pressure, parameters of both NF permeate, and reject were noted.

The figure 7 below is from the fourth batch and shows UF permeate in the middle, NF permeate up to 70% VR on the right and NF concentrate up to 70% VR on the left. This picture shows the results visually and it is obvious that the NF concentrate's color becomes more yellowish at higher VR. While NF permeate has no color after nanofiltration.



Figure 7. The picture shows the nanofiltration results at different VR from the fourth batch. In the middle is the UF permeate, on the right is NF permeate and on the left is NF concentrate.

4.1.1 The influence of concentration on flux

Due to the varying composition in the UF permeate, the initial concentration was different at every trial as presented in figure 8. A higher initial conductivity affects the initial NF permeate flux negatively and affect how far VR it's able to reach at the trial. Permeate flux is directly proportional to TMP and inversely proportional to the viscosity. The viscosity of the permeate is controlled by the feed composition and temperature. So, at lower temperature and higher concentration, the flux will be lower.

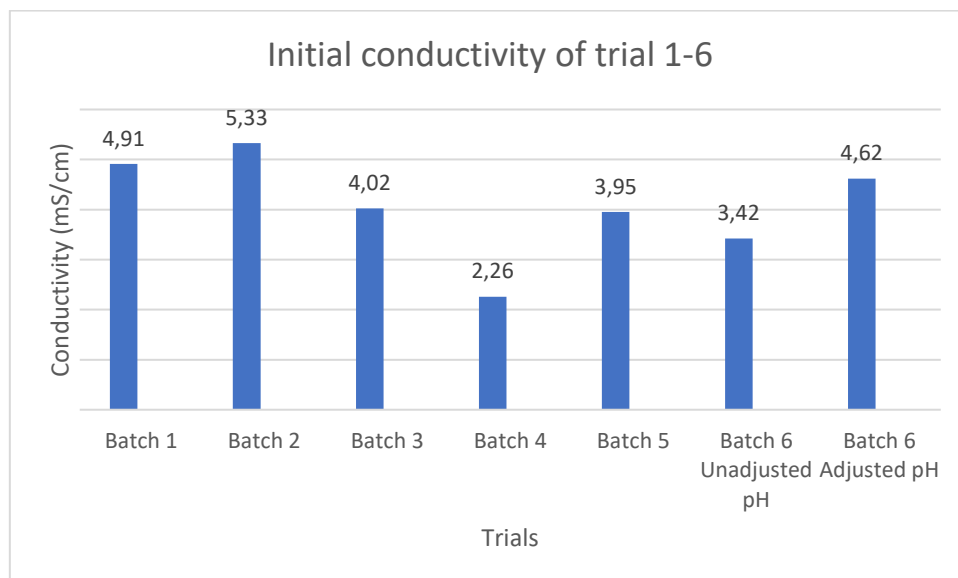


Figure 8. Initial conductivity of trial 1-6.

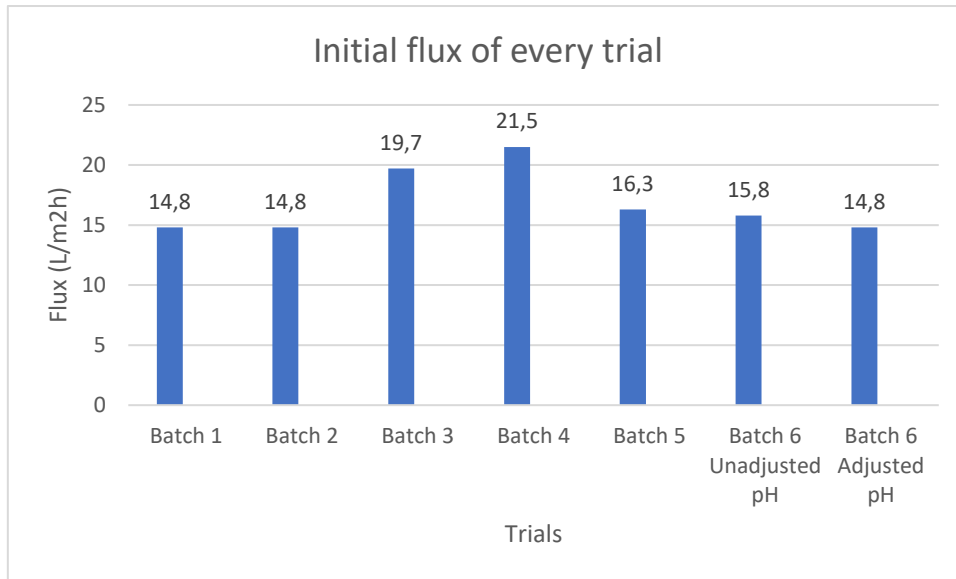


Figure 9. Initial flux of trial 1-6.

The NF permeate initial fluxes are shown in figure 9. For instance, the fourth trial with the lowest initial conductivity at 2.26 mS/cm has the highest initial NF permeate flux at 21.5 L/m²h while the trial one, two and the last trial with higher conductivity have the lowest initial flux at 14.8 L/m²h. At trial four, with higher flux, 70% VR were able to be reached. Figure 10 shows how the flux declines with higher volume reduction.

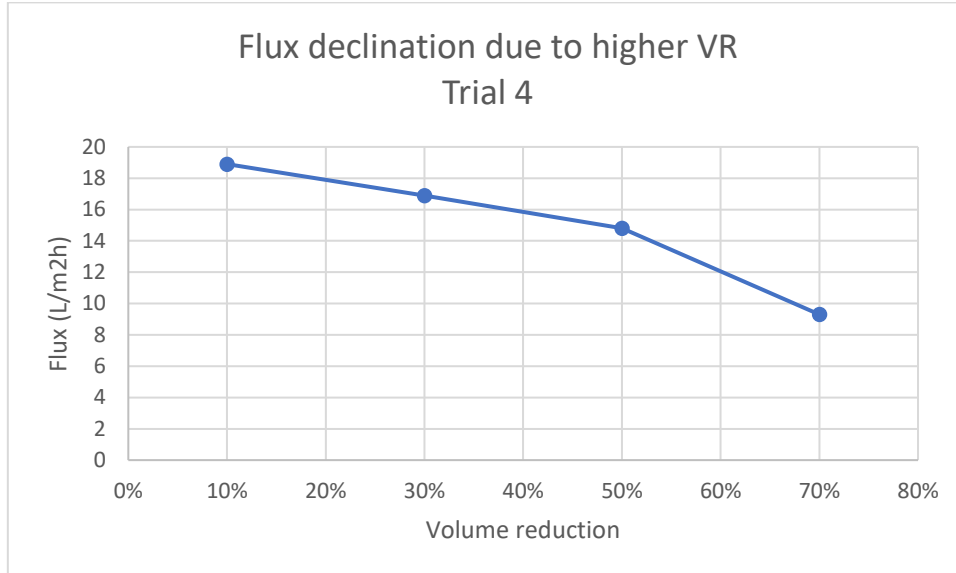


Figure 10. Flux decline due to higher VR.

4.1.2 pH adjustment

In the last trial conducted at 5 bar, pH was adjusted to investigate the TOC rejection performance by pH adjustment. According to theory, an increased pH would have a better effect at separation of negatively charged components that's could have a size smaller than the pores of NF membrane. This due to the mechanism caused by electrostatic interaction between the charged components and the membrane.

For comparison, the same UF permeate was divided into two IBC. The first IBC was unadjusted and had a pH of 8.1 and a conductivity of 3.42 mS/cm. The unadjusted pH batch was filtered first and the experiment was stopped at 20% VR. Alkali cleaning and water flushing happened in-between the unadjusted and adjusted batch. The adjusted batch had a pH of 10 and conductivity increased to 4.62 mS/cm due to the addition of alkali chemical. The adjusted batch was also stopped at 20% VR.

The TOC retention of the adjusted trial was a bit higher (98.91%) than the unadjusted trial (98.88%). However, the conductivity retention was lower for the adjusted batch, it was 95.5% compared to 98.8%.

For a better comparison, more data have to be collected in an experiment for investigating pH adjustment. Due to time limitation, a one-day experiment was conducted for this study which resulted in only one point (20% VR) for evaluation. Advantage of higher pH is the higher TOC rejection but the disadvantage of pH adjustment is the increased workload including such as chemical dosing, extra buffer tank and also pH readjustment of the NF permeate.

4.2 NF trials at higher pressure

NF trials at higher operating pressure, 8-10 bars were also experimented. Data of batches 7-12 from 28th of March to 16th of April are presented in appendix B. The average TOC retention is 96.92% and the average conductivity retention is 97.09%.

The feed pump had to be changed from a centrifugal pump to an available hose pump to reach higher TMP. The disadvantage of a hose pump is the pulsating flow due to rotational motion while a centrifugal pump delivers a smooth consistent flow. Therefore, the TMP was oscillating from 8 to 10 bars.

The relationship between flux and concentration is the same for NF trials operated at higher pressure as for NF trials at 5 bars. Higher concentration gives lower flux. No pH adjustment was performed at higher pressure.

4.2.1 Influence of higher pressure

Higher pressure generates a higher flux, therefore more trials could reach higher VR much faster during the experiments compared to the trials at 5 bars. Trial 7 and 8 had high conductivity, almost 7 mS/cm, but the trials could still proceed due to the higher pressure providing a high flux. Trial 9 reached 80% VR, trial 10 reached 85% VR and trial 11 reached 70% VR. The initial conductivity is shown in figure 11 and the initial flux in figure 12.

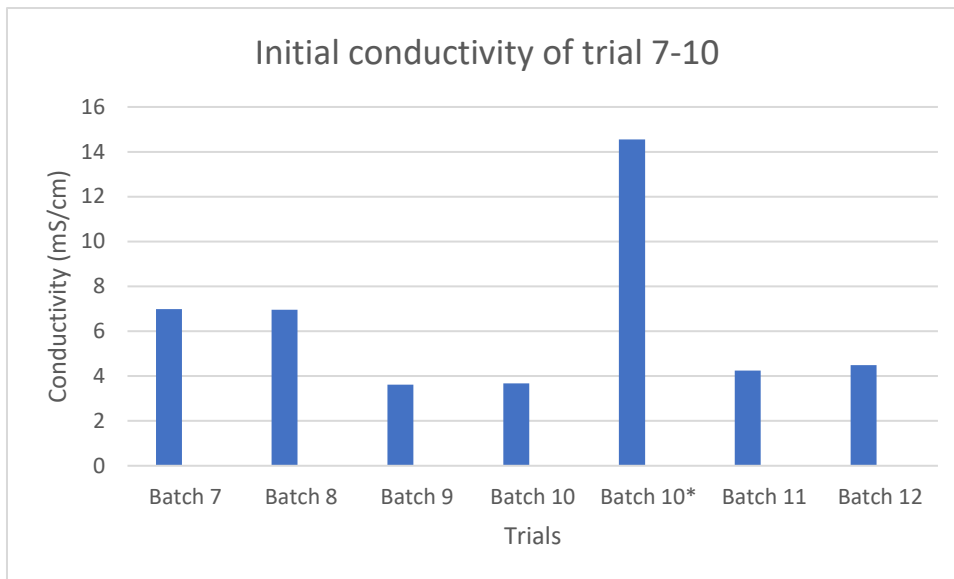


Figure 11. Initial conductivity of trial 7-12.

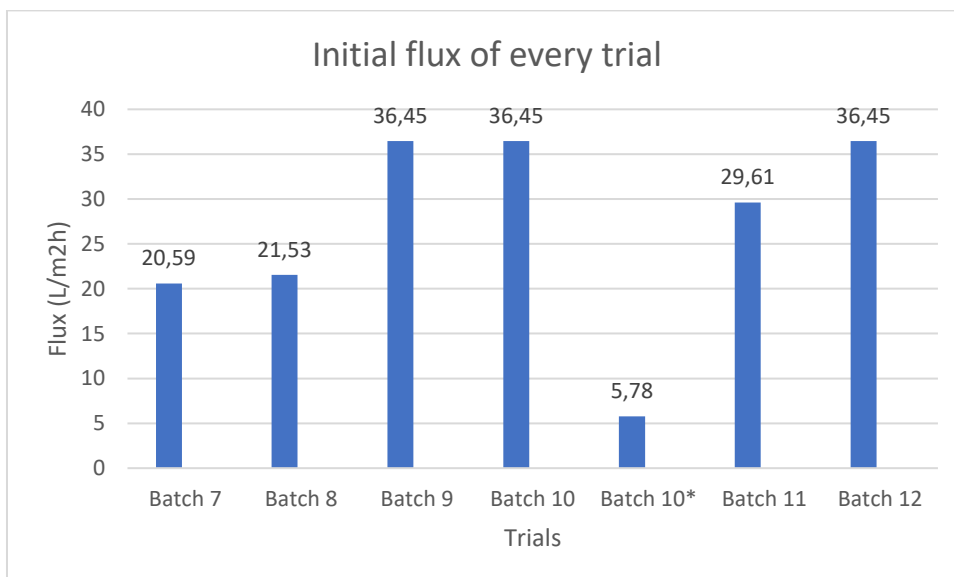


Figure 12. Initial flux of trial 7-12.

Trial 10 had a flux of 5 L/m²h at 80% VR. The trial was ended at 80% VR and chemical cleaning was performed (6th of April), but the IBCs were saved so a continuation of the trial could be conducted on the 9th of April. At the continuation of trial 10, the flux was 3.3 L/m²h at 85% VR. The purpose of the continuation was to investigate how far VR could be reached and also the effect of chemical cleaning in-between filtration.

The chemical cleaning improved the flux for the continuation at first but flux was deteriorated rapidly. It is not profitable to perform a chemical cleaning just to proceed the filtration a little further. For trial 10, 80% VR would have been suitable to end the filtration. The flux decline in trial 10 is shown in figure 13.

In the last experiment performed by Gunnarsson, with a feed of UF permeate with initial conductivity at 2.45 mS/cm was filtered to 85% VR. At 85% VR, the TOC retention was 58.1% [1]. His last experiment is comparable with trial 10, with a relatively low initial conductivity a

high-volume reduction can be achieved. But then again the flux quickly decline with higher feed concentration and also results in a permeate with degraded quality.

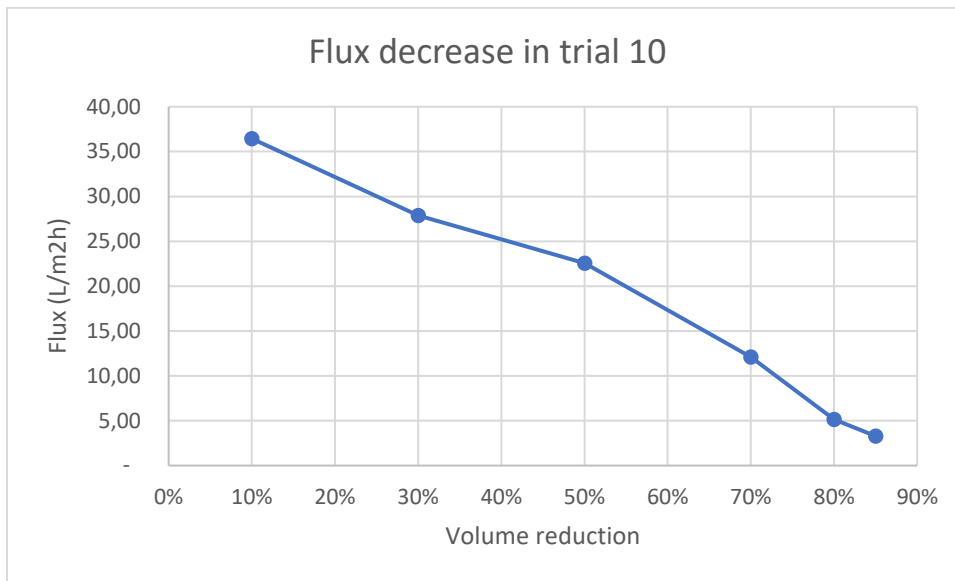


Figure 13. Flux decline in trial 10.

4.3 PWF Recovery

The NF system has undergone 15 cleaning sessions. The PWF after every alkali cleaning were stabilized around the flux of 40 L/m²h as shown in figure 14. The initial PWF was measured to be 43.1 L/m²h. The flux recovery which is the ratio of PWF after cleaning and initial PWF is approximately 93%. This confirms the efficiency of the cleaning procedure and the choice of cleaning solution (described in section 2.1.1).

The flux was 33.8 L/m²h at the date 21st March due to the temperature of DI-water that day was 35 °C, which is 3-5°C lower than the usual flushing temperatures. At 16th April, a small crack occurred on one hose, therefore no chemical cleaning was performed. It resulted to a lower PWF.

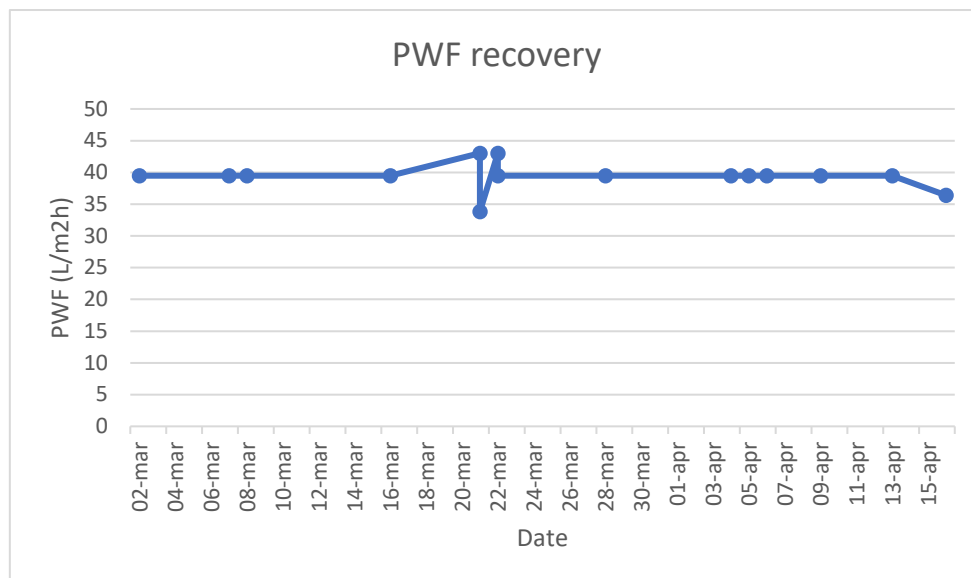


Figure 14. Every PWF recovery from 2nd March to 16th April.

4.5 RO Membrane Results

The PWF of the three tested RO membranes is presented in table 2. XLE has the highest PWF of 0.57 kg/m²h. These PWF were measured at operating conditions 5 bar and 38°C. RO98-HR has 0.30 kg/m²h and SW30-HR has the lowest PWF at 0.004 kg/m²h.

Table 2. PWF for the three RO membranes XLE, SW30-HR and RO98 pHt.

Membrane	PWF (L/m ² h)
XLE	57.50
SW30-HR	0.42
RO98 pHt	29.65

The NF permeate with 80% VR from the trial 10 (6th of April) was collected for the flat sheet experiments. The NF permeate at 80% VR has the pH 7.73, conductivity of 0.46 mS/cm and a TOC concentration at 15.99 mg/L. Three membranes at three different pressures were experimented and the data of conductivity, pH and TOC are presented at table 3. The flux of SW30-HR was very low and no samples could be collected for analysis. Therefore, table 3 only shows data from membrane XLE and RO98 pHt.

From the results, it shows that both XLE and RO98 pHt are suitable membranes for reducing the concentration of TOC and conductivity from the NF permeate. The membranes could at all pressures reduce the TOC levels approximately 50%, while the conductivity reduction is much higher, at around 80-98%. Higher TMP gave better TOC and conductivity retention.

Table 3. Conductivity, pH and TOC is presented for the two RO membranes XLE and RO98 pHt.

Membrane	Conductivity (mS/cm)	pH	TOC (mg/L)
NF Perm 80% VR	0.46	7.73	15.99

5 Bars			
XLE	0.09	7.71	7.62
RO98 pHt	0.06	7.60	7.74
8 Bars			
XLE	0.10	6.66	6.45
RO98 pHt	0.02	6.70	6.94
10 Bars			
XLE	0.05	7.00	6.27
RO98 pHt	0.01	7.02	6.44

XLE membranes had higher fluxes compared to RO98 pHt at all three tested TMP (5, 8 and 10 bar) and it is illustrated in figure 15. The XLE flux at 5, 8 and 10 bars were 53.30, 90.30 and 125.2 L/m²h. Corresponding values for RO98 pHt at the same TMP were 29.10, 51.80 and 62.60 L/m²h.

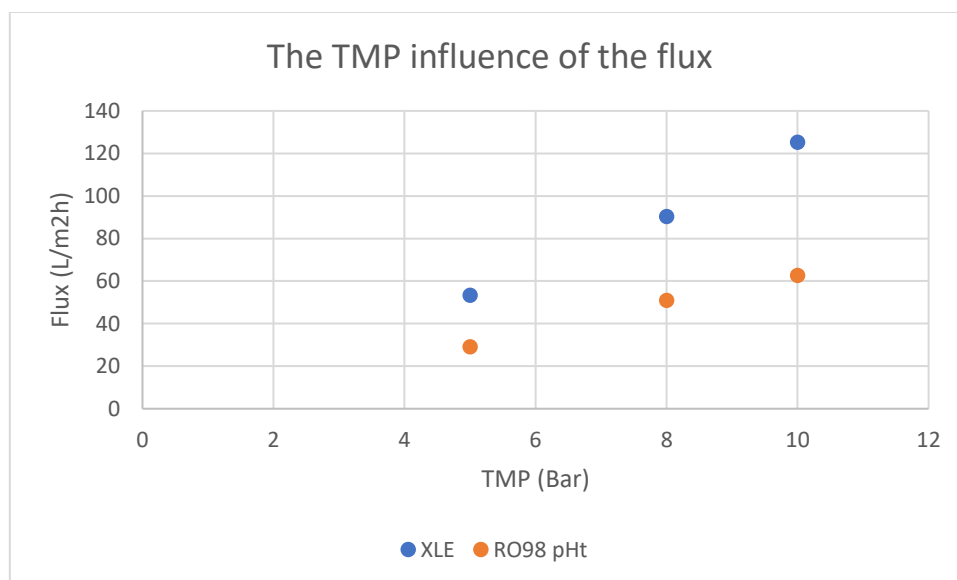


Figure 15. The influence of TMP of the RO membrane's flux.

XLE gives higher flux than RO98 pHt and their capability at reducing TOC and conductivity is almost equal. Therefore, XLE will be recommended before RO98 pHt. Due to the promising results of TOC and conductivity reduction from RO membranes, a two-stage system with both NF and RO membranes and an internal retentate recirculation will be designed at the full-scale system. In appendix C, the values for calculating the fluxes are presented.

4.6 The Smell of NF Permeate

The first method was to use air bubbles in order to release the dissolved gases. This method has an advantage of simplicity. However, it has a disadvantage of longer residence time up to 5 hours. Moreover, it is not economical method when the residence time is so long.

The second method with heating was not efficient because the smell did not disappear and it required more energy to boil such amount of water and then cooling it. The third method with vacuum pump was also not an effective method. The fourth method using hydrogen peroxide in order to oxidize the dissolved gases was also not effective to remove the smell.

Lastly, the active carbon was effective to remove the smell. The smell disappeared completely by repeating the procedure from two to five times. The used active carbon could be used again but it took more times until the smell was disappeared.

Based on these five methods, it seems that the active carbon is the most effective method to remove the smell because it is a safe method and there is already an active carbon column available in Dow site. The carbon waste can also be handled as combustible waste. For future plans, a packed bed column can be designed for only the NF permeate, but it requires a full investigation of which Sulphur compounds are presented in the permeate.

According to Dow Filmtech Membranes Tech Manual, H₂S levels as low as 0.1 mg/L can affect the performance of RO or NF systems negatively. When H₂S are exposed to oxidants such as oxygen in air, precipitation of elemental sulfur or metallic sulfides are formed. These solids will accumulate in channel spacer of the feed/concentrate and results in an operating differential pressure increases and also causes an increase in salt passage and a decrease in flux [16]. Since H₂S is a small, polar and uncharged gas, it permeates both NF and RO membranes and creates a bad odor in the treated water. The removal of the contaminant from permeate is considered as a post-treatment step after NF/RO systems.

4.7 Jar Testing of Removal of Surfactants

Jar tests are performed for the purpose of investigating the different parameters for a good coagulation and flocculation. The parameters studied can be doses of suitable coagulant chemical and flocculation aid, the mixing time, pH and even temperature.

A simple jar testing was conducted for chemical precipitation of the NF reject at 40 % volume reduction from the experiment days 21st of March and 16th of April. On those trials, reject was saved for further treatment. The sample volume required for each jar was 800 ml and the coagulant chemical was 1 mol/L of aluminum sulfate. The flocculation aid was a cationic polymer C-492 with the concentration of 1g/L.

Six trials were done and the two first jar tests had NF reject from the 21st of March. Trial one was diluted with 400 ml deionized water and 5 ml aluminum sulfate and 1 ml of C-492. Flocs were formed almost directly after addition of flocculation aid. During the beginning of the sedimentation, the flocs sank down to the bottom but they floated to the surface after one hour. Trial two was not diluted, the doses of aluminum sulfate and of C-492 was 10 ml respective 3 ml. After one hour of sedimentation, the flocs were both at the surface and at the bottom of the jar.

Trial three to six uses 800 ml undiluted NF reject from the 16th April. The third trial had doses of 5ml aluminum sulfate and 1.5 ml of C-492. Fine threads were formed instead of flocs. In trial four, 10 ml aluminum sulfate and 3 ml C-492 was added. After one hour without mixing, the bottom had one layer of sedimentation. The doses of aluminum sulfate and of C-492 were increased to 15 ml and 4.5 ml at the fifth trial. Bigger flocs than previous trials were formed directly after the C-492 was added and they floated to the surface. In the last trial, 20 ml aluminum sulfate and 6 ml C-492 were added. The flocs formed during the sixth trial are larger than the fifth trial.

TOC levels before and after the chemical precipitation of all six trials is presented in table 4. Figure 16 shows the jar testing.

Table 4. TOC results of the jar testing.

Trial	NF Reject 40% VR	Aluminum sulfate (ml)	C-492 (ml)	TOC before	TOC after (mg/L)	TOC Retention (%)
1	400 ml NF reject (21/3) and 400 ml DI-water	5	1	727.75	411.6	43.44
2	800 ml NF reject (21/3)	10	3	727.75	888.85	-22.14
3	800 ml NF reject (16/4)	5	1.5	680.65	742.15	-9.04
4	800 ml NF reject (16/4)	10	3	680.65	743.6	-9.25
5	800 ml NF reject (16/4)	15	4.5	680.65	734.05	-7.85
6	800 ml NF reject (16/4)	20	6	680.65	716.9	-5.33

The increased TOC values shown at the table 4 after the tests can be due to the added flocculation aid which are polymers. The experiment of coagulation and flocculation may reduce surfactants, but it increases the TOC. Further studies of chemical precipitation have to be conducted to determine whether a chemical precipitation unit at Dow in Landskrona is necessary and its impact of other units as RO unit due to increases TOC.



Figure 26. From left to right is the jar tests for trial 3-6.

4.8 Results of SEC, Hardness and Bacterial Growth

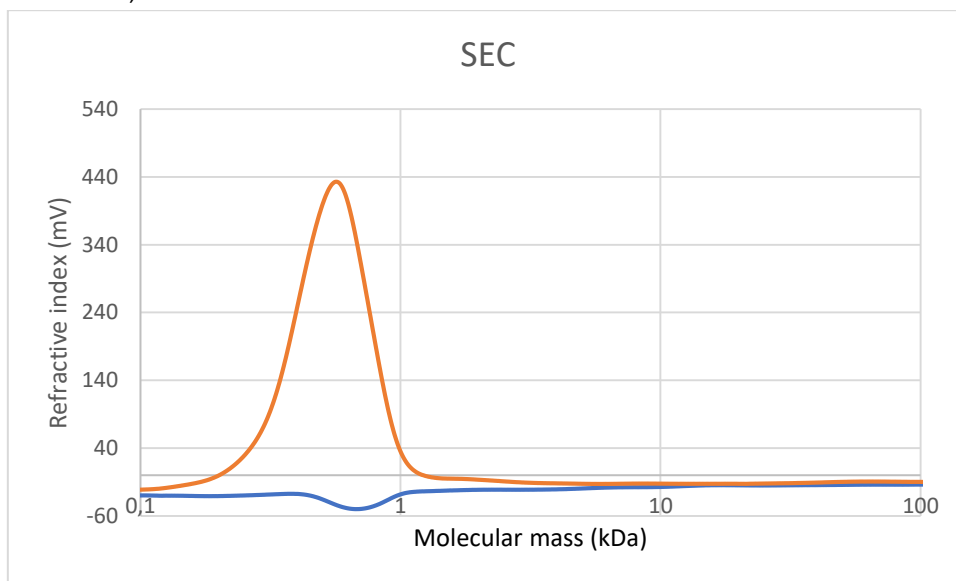


Figure 17. A chromatogram showing the molecular size of the UF feed (orange) and the NF permeate (blue).

Samples from the 2nd of March were used for the SEC analysis. The plot 17 illustrates the molecular sizes from solvent NF Permeate 30% VR (blue) and UF feed (orange).

The dip slides showed a great difference in bacterial growth of the UF permeate and NF permeate as shown in figure 18. The NF membrane should be sufficient in removing bacteria, the bacteria growth in the dip slide may have been caused by external contamination in pilot scale tests.

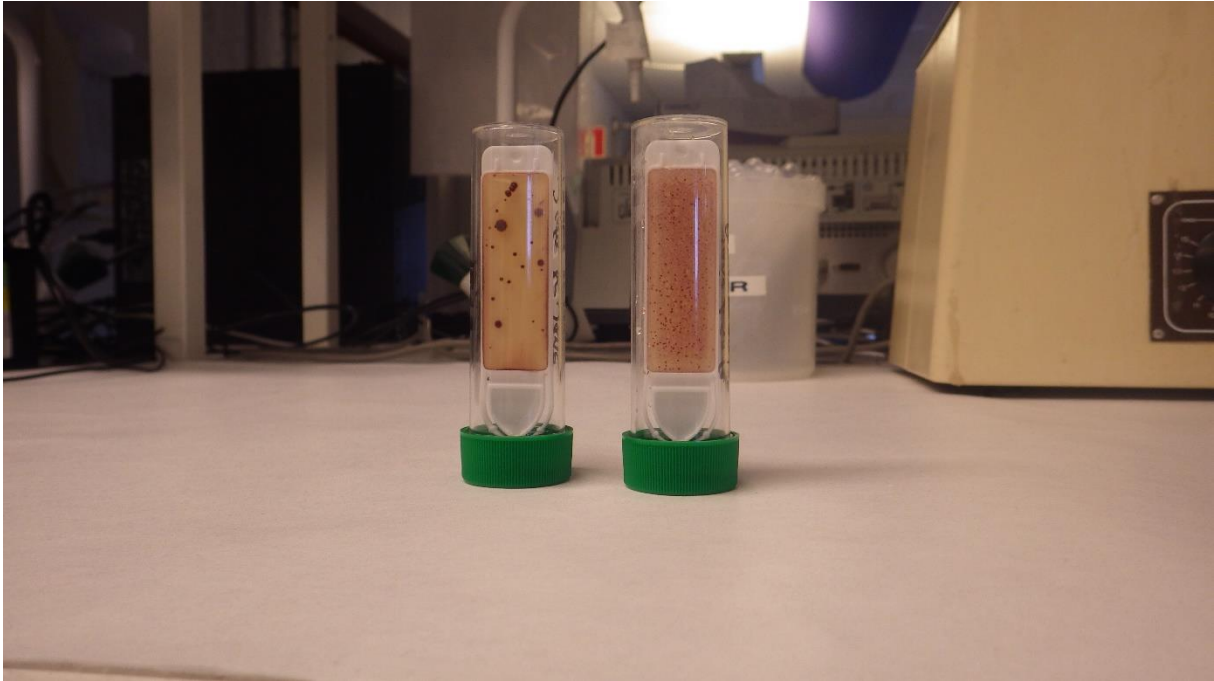


Figure 18. The results of bacterial growth. The left dip slide is for the NF permeate and the right one is for the UF permeate.

4.9 Results of NitriTox and BOD

Three samples of the NF reject have gone through the Nitritox and all three of them passed the Nitritox and are not toxic for the bacteria in nitrification. The samples are: 50% VR from batch 8 (3/4), 80% VR from batch 10 (6/4) and 70% VR from batch 11 (13/4).

5 Design and Cost Estimation

In the full-scale process design, the NF system will be designed as a continuing unit to the already existing UF system. The NF system consists of two passes, first with NF membranes and then with RO membranes to gain higher quality permeate. The cost estimation which includes the investment and operating costs will be presented after the process design.

5.1 Full-Scale Process Design

The current wastewater treatment in Dow, Landskrona is ultrafiltration (UF). After passing through the RO unit/ion exchanger, the free ions are removed, and the conductivity decreased to the desired value. The deionized water is collected in the DI water tank that is used later in the process. After each batch, the reactor, blend tanks and the transfer pipes are cleaned with water. The cleaning water with residues are gathered in the wastewater drainage system (WWDS). The wastewater is then pumped to the tank system that is consisted of three tanks A, B and C which is the biggest and is considered as the feed tank to A and B tanks. The A tank is the feed tank to the UF filtration unit as shown in figure 19 below. When A and B tanks are filled up, the pH is adjusted to a suitable interval between 8 and 9. Either acid or base is added depending on the pH wastewater which is called at that time as white water. The UF can be started after pH adjustment. The UF permeate is withdrawn continuously and the UF retentate is recirculated to the A tank. After each batch, the concentrated retentate is collected in a tank to be charged later into IBCs as a product known as (TN-1). The UF permeate is analysed continuously by the online system, Nitritox to grantee that the stipulated requirement of the municipal WWT plant is reached.

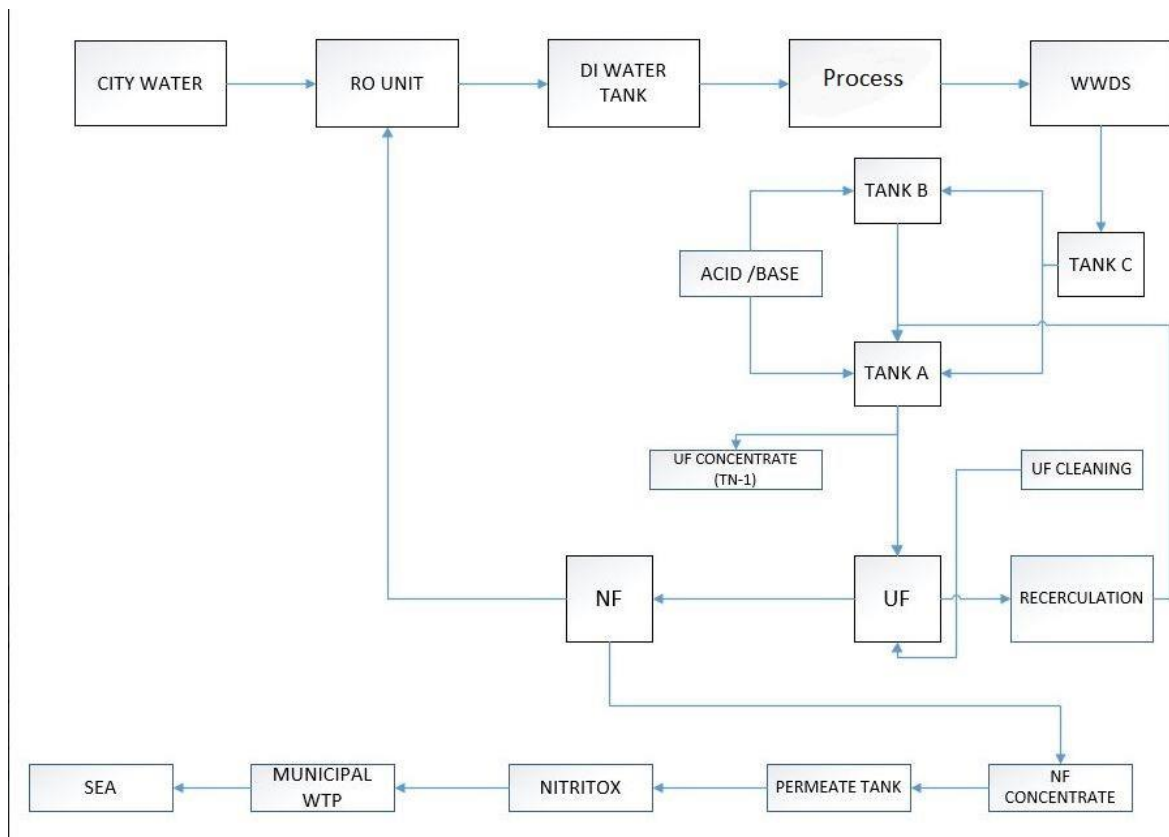


Figure 19 the current and future wastewater treatment plant, combing both UF and NF units

Nowadays, the permeate is pumped to the municipal wastewater network after being approved by the Nitritox analyser. In the future, the UF permeate will be filtered further by nanofiltration unit NF.

In figure 20 below a detailed flowchart for the NF system is shown below. The UF permeate with a flow of 50 m³/day is collected in a buffer tank instead of being pumped to the municipal wastewater network. In Dow Landskrona location, a big tank (V320) that is located outside can be used as a buffer tank or another tank (V190) that is located in the UF section can also be used as a buffer tank. The UF permeate is collected in a small tank (V167) and when it is full, it will be pumped either to V230 or V190 tank with a flow of 6 m³/hr. If the UF has a temperature higher than 45°C, the permeate is preferred to be pumped to V320 to decrease the temperature without installation of a cooler. Otherwise, the NF system tolerates lower temperatures, yet delivering lower fluxes. The NF filtration can be run as a batch or a semi-batch process at a specific volume reduction. In the beginning of the filtration process, V190 tank can be filled from V320 as a first batch and later it can be fed with the continuous UF permeate directly from V167 to get a semi-batch process at a specific volume reduction. Later, the UF permeate is pumped through a micro-filter by a feed pump, frequency-controlled pump, that delivers 1-5 bars. The micro-filter guarantees that no big particles than 5µm are passing to the NF membranes. The pressure is raised to 10 bars by a recirculation pump, frequency-controlled pump, that pumps the UF permeate to the first NF pass that contains six NF-400 membranes. The numbers of membranes are based on the pilot scale experiments. To decrease the conductivity and TOC further, the NF permeate will be passing through a second pass that contains two XLE membranes. The retentate of both NF and XLE membranes will be recirculated to V190 tank.

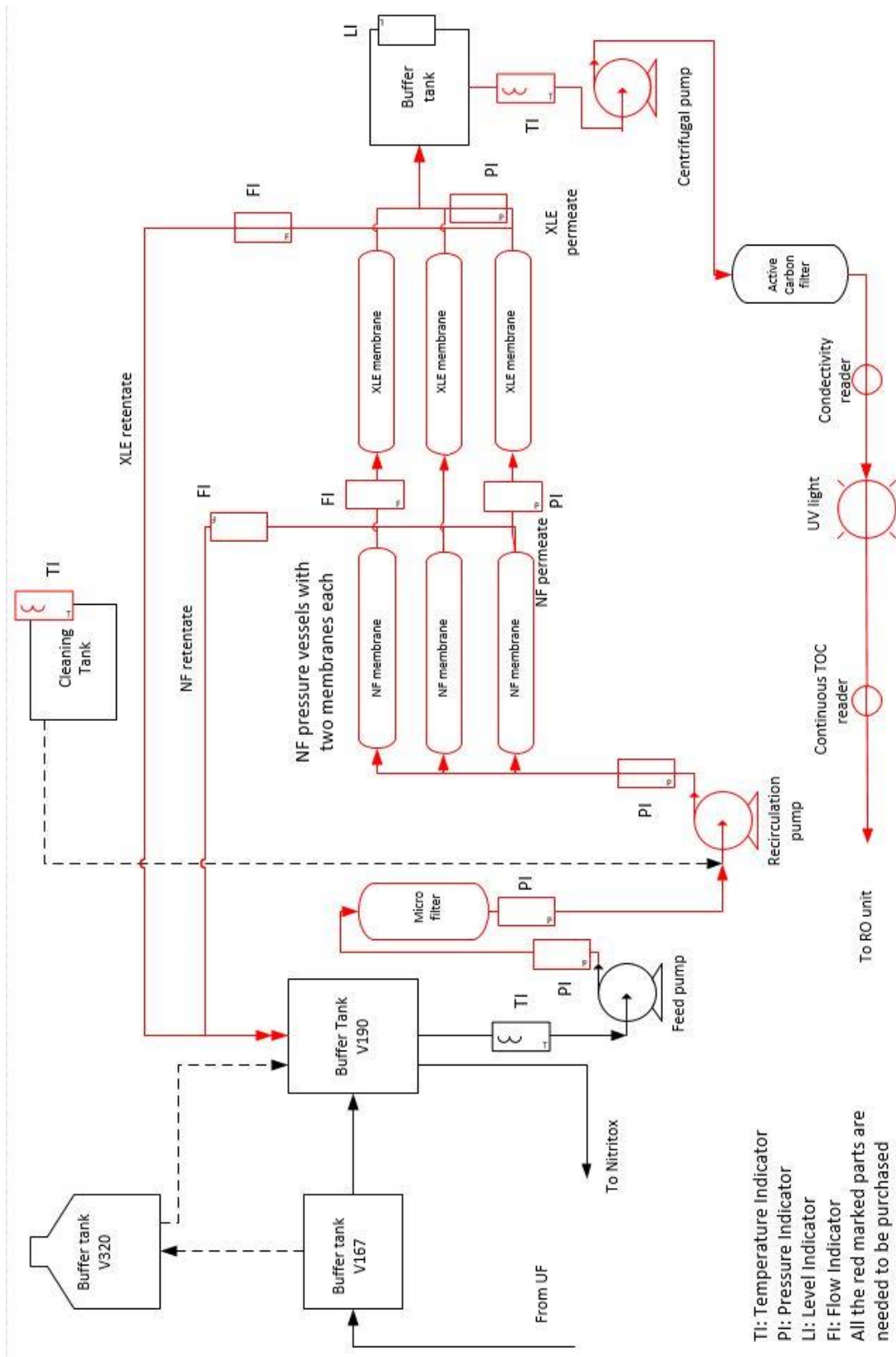


Figure 20 PFD flowchart for the NF system

The XLE permeate will be collected in a buffer tank. A temperature indicator can be installed in this buffer tank to make sure if there is a necessity of energy recovery is required or not. Two level indicators are also required to be installed in this buffer tank. It will be pumped by a

frequency-controlled pump later through active carbon filter to remove the smell before passing through UV light. The UV light gives a bacteria-free water that can be recirculated later to the RO unit. A conductivity and TOC indicators are crucial to guarantee a very good water quality. The recirculation flow to RO unit will be set to 200 L/min. At the end of the nanofiltration process, the last batch in V190 tank will be filtered to a higher volume reduction. The concentrate will be withdrawn and approved by Nitritox before being pumped to the municipal wastewater network. After each nanofiltration process is completed, the membranes will be chemically cleaned and flushed with DI water. The flux of the NF membranes is the determinant parameter in the process. Chemical cleaning should be applied whenever the flux becomes very low. Some batches can be considered as worst case, i.e., have higher TOC and conductivity values. Therefore, it can only be filtered to a lower volume reduction. In figure 20, all the parts that are marked with red colour are needed to be purchased for Dow Landskrona location.

The presented full-scale process is different to Gunnarsson's in the amount of NF membranes. The number of NF membranes are doubled in this design and another different is the addition of XLE membranes as the second pass.

5.2 Cost estimation

A rough cost estimation of the full-scale NF system will be presented at this section. The equipment needed for implementing the full-scale system are red marked in figure 20. Equipment that need to be purchased and the cost of it is presented in table 5. The already existing units in Landskrona was not being accounted into the cost estimation.

The cost estimation is based on semi-batch operation at 30% VR and then a batch operation until 80% VR is reached. Design software ROSA 9.1 was used for calculating system water production, system recovery and the operating cost. Costs were given by Dow and one source taken from online. The cost estimation was also helped by values from an article provided by Johan Thuvander [17].

System recovery is the difference between feed flow and reject and divided by the feed flow [4]. A higher system recovery means more wastewater being filtered, that is more product.

$$\text{System Recovery (\%)} = \frac{\text{Feed flow} - \text{Reject flow}}{\text{Feed flow}} \cdot 100 \quad (2)$$

Dow produces approximately 50m³ wastewater each day and the UF feed flow entering the NF system is 6m³/h. The system designed consists of two passes, that's an arrangement of elements where the permeate from pass 1 (NF) becomes the feed of pass 2 (RO). Multi-passes arrangements give higher permeate quality while multi-stages which is reject from stage 1 becomes feed in stage 2 gives higher recovery. The designed system was operated with a TMP of 10 bar and permeate temperature of 38°C. The total dissolved solids (TDS) were estimated with ROSA to be 1400 mg/L. The average flux of the NF membranes was 21.5 L/m²h while the average flux of the XLE membranes was 35.1 L/m²h. The final permeate flow which is the system water production was calculated to 4.30 m³/h.

There were difficulties in creating a system with recirculation stream in ROSA, therefore a system without recirculation was created with a system recovery of 80%. With recirculation the system recovery will decrease and also the system water production would be higher than 4.80 m³/h. A high system recovery can exceed the element recovery and result in more membrane

replacements per year. Another way of decreasing the system recovery is by increasing the elements per pressure vessel. In the cost estimation, two NF membranes are designed to be in each pressure vessel.

Table 5. The cost of the equipment for the NF system.

Equipment needed for the NF system	Cost (Inclusive installation cost)
5 pcs of pressure vessels	Installation and the cost of the equipment is 1.4 million SEK.
6 pcs of NF90-400 membranes distributed among 3 parallel pressure vessels	
3 pcs of XLE-400 membranes distributed among 3 parallel vessels	
1 pc of microfilter 5 µm including vessel	
1 pc of conductivity reader	20,000 SEK
1 pc vertical multistage pump (150 m ³ /h)	100,000 SEK
1 pc centrifugal pump (6 m ³ /h)	50,000 SEK
UV lights	11,000 SEK [16]
TOC reader	170,000 SEK
5 pcs of pressure transmitter and indicators	125,000 SEK
3 pcs of flow transmitter and indicators	75,000 SEK
2 pcs of temperature transmitter and indicators	20,000 SEK
Total purchased cost	1.9 Million SEK

5.2.1 Investment cost

The investment cost includes the cost of the membranes and the other equipment needed in the NF system.

The active area of one NF90-400 membrane is 37.2 m² and the active area of XLE-400 is 40.9 m². The total membrane area is 350 m². The membrane cost per m² is 980 SEK [18]. Therefore, the estimated membrane cost for the NF system is 340 000 SEK. Installation cost is approximately four times the membrane cost and it's 1.4 million SEK. The total investment cost including the purchased cost for membranes, UV lights, pumps, TOC detector, the transmitters and indicators for flow, pressure and temperature and the basic installation cost is in total 1.9 million SEK. The investment cost estimated in Gunnarsson's master thesis was approximately 900,000 SEK less and the reason to the indifference is the increased amount of NF membranes in this presented full-scale process design and the addition of the XLE membranes.

5.2.2 Operating cost

The operating costs consists of replacement costs, cleaning and electricity.

The cleaning cost is 500 SEK/m² per year [18]. So, the yearly cleaning cost for the NF system is 175 000 SEK. The cleaning routine occurs twice per week, so the cleaning cost will be decreased to 50% to 85 000 SEK/year.

The electricity price is stated as 0.55öre/kWh (\$0.11/kWh). From the ROSA simulation, the electricity expenses NPV (net present value) is 10 000 SEK but will be decreased by 50% to 5000 SEK/year due to the system operating hours are not in use all year.

Replacement rate for both NF and RO was estimated to be once per 7 years by ROSA. This rate is highly affected by the feedwater data which is unknown due to the absent results of the hardness analysis. The TDS values filled in could be underestimated and therefore the membrane lifetime was estimated to be 12 months with full-time use. The replacement of the membranes can be operated during winter months when it's less demand of the products being made in Landskrona. The cost of replacement per element is 10 000 SEK. The total cost for membrane replacement per year is 90 000 SEK.

Total operating cost per year is the sum of membrane replacement cost, energy expenses and the cleaning cost and it's 180 000 SEK. Maintenance is included into the operating cost and it accounts for 10% of the operating cost. The total operating cost including maintenance is 200 000 SEK. This is presented in table 6.

Table 6. Presentation of the operating costs.

Membrane replacements costs NPV (SEK)	Energy expense NPV (SEK)	Cleaning cost NPV (SEK)	Total operating cost including maintenance (SEK)
90 000	5 000	85 000	200 000

5.2.3 Current costs

Dow Sweden has to pay a fee to the municipal wastewater treatment plant (WWTP) for exceeding the BOD threshold and the limit of the concentration is 260 mg/L BOD₇. The cost of the fee is 12 kr/kg BOD₇. Even though the amount of volume reject being treated by WWTP will be reduced by NF to 20-30%, but the concentration of BOD₇ will be higher, so the cost will remain. An alternative to avoid the fee cost is by treating the BOD₇ in the industrial wastewater before transferring it to the WWTP. One method to reduce the concentration of BOD₇ is through chemical oxidation by adding hydrogen peroxide. The cost of the hydrogen peroxide and the cost of maintaining the BOD₇ treatment has to be lower than the fee cost at the WWTP to be economical.

Dow Landskrona buys city water for 5.63 SEK/m³. The cost of UF permeate handling 5.63 SEK/m³ and this cost will not remain after NF system is implemented. However, the NF reject handling will cost the same but due to recirculation in NF system, the NF reject volume will be less than the UF permeate. The current cost per m³ of both incoming city water and outgoing UF permeate cost is 11.30 SEK/m³.

5.2.4 Annuity Calculation

The investment cost for the NF system is estimated to be divided into 10 depreciation years. The payment will be made at equal intervals. The annuity cost is included as a yearly expense. The annuity is calculated by multiply the investment cost, to the factor f_A as shown in the equation below.

$$f_A = \frac{X}{1-(1+X)^{-N}} \quad (3)$$

In the equation above, X is the interest rate and N is the economic life expectancy. N in this case is three years and the interest rate are 10%. The f_A was calculated to be 16.3 %. The investment cost for the entire upgrade was 1.9 Million SEK. Annuity cost for the investment cost is therefore 310 000 SEK per year [19].

5.2.5 Cost of the treated wastewater

The depreciation time of the NF plant was set to 10 years with a 10% interest rate. The amount of water recirculated back to the process by NF system is estimated to 4.80 m³/h, which is 80% recovery of the UF feed of 6m³/h.

The cost of the water the first 10 years is 28 SEK/m³ which cost 500% more than the city water at 5.63 SEK/m³. After 10 years when the investment cost is payed off, the cost of water will be 11 SEK/m³. The cost is higher than the city water cost. The calculation is presented as appendix D.

However, the cost of outgoing permeate will be reduced with the NF system. For instance, if 75% of the recovered water will be reused in the system, then only 25% reject needs to be treated by the WWTP.

As mentioned before, the current cost of city water and UF permeate handling is 11.30 SEK/m³.

The first ten years, 1 m³ UF permeate will approximately return 0.75 m³ recirculated water which costs 21 SEK while the 0.25 m³ NF permeate handling costs 1.40 SEK. Dow may need to purchase 25% city water rather than 100% city water to fulfill the need of water in the process. 0.25 m³ city water costs 1.40 SEK. The total cost for 1 m³ water and the handling of 0.25 m³ NF permeate is 23.8 SEK. The requirement of 1 m³ water in the first 10 years costs 12.5 SEK more than the current cost of 11.30 SEK.

After the investment cost is payed, 1 m³ UF permeate will approximately return 0.75 m³ recirculated water which now costs 8.25 SEK and the 0.25 m³ NF permeate handling costs 1.40 SEK. With the addition of 0.25 m³ purchased city water with the cost of 1.40 SEK, the total cost for 1 m³ water and the handling of 0.25 m³ NF permeate is 11.05 SEK. After the payback time, the cost of 1 m³ water, which is 75% recirculated and 25 % purchased, is 0.25 SEK cheaper than the current cost of 11.30 SEK.

To further reduce the cost of treated wastewater, the operating conditions can be optimized so that the operating cost will be reduced. Such optimization can be for instance finding more effective cleaning solutions and reduce the fouling rate so that the membrane's lifetime will be extended. Heat integration in the NF system can be applied to reduce the energy expenses.

6 Conclusion

The NF90-4040 in pilot scale operated at 10 bars gave a permeate with an average TOC retention at 96.92% and an average conductivity retention at 97.09%. A NF system alone is not sufficient at reducing the TOC level to 3 mg/L and a conductivity concentration at 0.02 mS/cm as demanded for wastewater reuse in the process. Flat sheet experiments with XLE shown promising TOC and conductivity values. Therefore, a multi-pass system with NF90-400 in pass 1 and XLE-400 in pass 2 is the recommended design. Permeate from pass 1 becomes the feed in pass 2 creating higher permeate quality.

The cleaning sequence with potassium hydroxide as the alkali solution conducted in the pilot experiments were successful in restoring the same stable PWF after every cleaning.

Operating pressure at 10 bars and 38°C gave a high flux and filtration maintained in a good runtime until 80% VR at an initial conductivity of 3-4 mS/cm.

As mentioned before, it's a rough cost estimation. Our knowledge of designing NF system is limited and the costs from Dow could have been overestimated. The investment cost of the NF system is 1.9 million SEK and the yearly operating cost is 200 000 SEK. The membrane replacement expense was estimated once a year and this resulted in a high operating cost. The replacement rate can be reduced to each every 18 months instead. The first 10 years, the cost of the treated wastewater is 28 SEK/m³, which is 500% more expensive than purchasing city water (5.63 SEK/m³). After the payback period, the cost of treated wastewater will be reduced to 11 SEK/m³.

However, the cost of the outgoing permeate to the WWTP will be reduced with the NF system. The current cost of city water and UF permeate handling is 11.30 SEK/m³. During the first 10 years, the cost of the water (75% recirculated and 25% city water) and the NF reject handling costs 21 SEK. The same cost will be reduced to 11.05 SEK after the payback time which is 0.25 SEK cheaper than the current cost. This rough cost estimation confirms that an implementation of NF system into the facility can be economical to Dow.

7 Future Work

The master thesis has proved that NF and RO have the potential to reduce the concentration of TOC and conductivity of the wastewater to the same level as city water, but it's essential to investigate if the treated water can be reused in the process before building the full-scale NF system. Therefore, the future studies should be about testing to produce Dow's products with the treated wastewater in lab scale. In lab scale, both pure treated wastewater and diluted treated wastewater with DI water can be experimented to produce products.

The handling of NF reject has to be studied further. More jar tests of coagulation and flocculation can be tested with more varying parameters as mixing time, temperature, pH and doses of chemicals.

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9 Appendices

9.1 Appendix A: Data of batch 1-6, operating pressure at 5 bars.

Date	Sample	TC (mg/l)	IC (mg/l)	TOC (TC-IC) (mg/l)	TOC retention (%)	Conductivity (mS/cm)	Conductivity Retention (%)
Batch 1							
2/3	UF Start	959.5	204.9	754.6		4.91	
2/3	NF 30% VR	34.82	12.65	22.17	97.1	0.24	95.1
Batch 2							
5/3	UF Start	998.2	204	794.2		5.33	
5/3	NF 10% VR	24.97	7.308	17.66	97.8	0.21	96.1
5/3	NF 20% VR	27.54	8.809	18.73	97.6	0.24	95.5
5/3	NF 30% VR	31.02	10.13	20.89	97.4	0.17	96.8
Batch 3							
8/3	UF Start	740.8	149.85	590.95		4.02	
8/3	NF 10% VR	14.34	4.627	9.713	98.4	0.12	97.0
8/3	NF 20% VR	21.45	7.370	14.08	97.6	0.13	96.8
8/3	NF 30% VR	23.40	8.511	14.88	97.5	0.16	96.0
8/3	NF 40% VR	29.04	11.47	17.57	97.0	0.19	95.3
8/3	NF 50% VR	32.20	12.38	19.82	96.6	0.22	94.5
Batch 4							
15/3	UF start	518.2	70.55	447.65		2.26	
15/3	NF 10%	12.84	3.926	8.914	98.0	0.07	96.9
15/3	NF 30%	15.24	5.183	10.05	97.8	0.09	96.0
15/3	NF 50%	15.28	5.891	9.389	97.9	0.11	95.1
15/3	NF 70%	24.49	11.64	12.85	97.1	0.20	91.2
Batch 5							
20/3	UF start	416.7	118.55	298.15		3.95	
20/3	NF 10%	16.68	5.647	11.03	96.3	0.17	95.7
20/3	NF 25%	34.05	18.14	15.91	94.7	0.40	89.9
Batch 6							
21/3	NF 40%	20.95	11.53	9.420	96.8	0.24	93.9
22/3	UF start unadjusted pH	658.1	107.75	550.35		3.42	
22/3	NF 20% Unadjusted pH	9.911	3.745	6.166	98.88	0.04	98.8
22/3	UF start adjusted pH to 10	694.3	146.05	548.25		4.62	

22/3	NF 20% Adjusted pH	10.21	4.210	6.000	98.91	0.23	95.0
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Date	Sample	TC (mg/l)	IC (mg/l)	TOC (TC-IC) (mg/l)
2/3	NF reject 30% VR	1490	316.3	1173.7
5/3	NF reject 10% VR	1098	224.85	873.15
5/3	NF reject 20% VR	918.9	196.2	722.7
5/3	NF reject 30% VR	1418	289.75	1128.25
8/3	NF reject 10% VR	738.8	126.05	612.75
8/3	NF reject 20% VR	1006	205.5	800.5
8/3	NF reject 30% VR	1183	241.05	941.95
8/3	NF reject 40% VR	1373	287.3	1085.7
8/3	NF reject 50% VR	1661	336.1	1324.9
15/3	NF reject 10%	579.0	85.75	493.25
15/3	NF reject 30%	865.0	122.95	742.05
15/3	NF reject 50%	1126	154.15	971.85
15/3	NF reject 70%	1652	223.85	1428.15
20/3	NF reject 10%	1073	299.95	773.05
20/3	NF reject 25%	961.6	277.95	683.65
21/3	NF reject 40%	1451	404.25	1046.75
22/3	NF reject 20% unadjusted pH	960.5	152.4	808.1
22/3	NF reject 20% adjusted pH to 10	1100	229.5	870.5

2/3 Batch 1					
	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate	8.5	35	4.91	112.5	Yes

NF permeate VR 10%	-	-	-	-	-
NF permeate VR 20%	-	-	-	-	-
NF permeate VR 30%	-	25	0.24	60	No

2/3 Alkali cleaning			
	pH	Temperature	Duration (h)
Before	12	35	1
After	12.1	-	
DI water flush			
		Temperature	Duration
PWF	300 L/h	38	

5/3 Batch 2					
	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate	8.80	38	5.33	112.5	Yes
NF permeate VR 10%	8.00	-	0.21	85.7	No
NF permeate VR 20%	-	-	0.24	66.7	No
NF permeate VR 30%	9.46 (Jane tog det för snabbt?)	-	0.17	54.5	No

5/3 Alkali cleaning			
	pH	Temperature	Duration
Before	11.5	33	
After	-	-	
Flush with DI water at 35 for 5 minutes			
7/3 DI water flush			
	Flow (L/hr)	Temperature	Duration
PWF	300	38	20 min

8/3 Batch 3					
	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate	8.58	38	4.02	150	Yes

NF permeate VR 10%	7.80	36	0.12	133.3	No
NF permeate VR 20%	7.90	35	0.13	120	No
NF permeate VR 30%	7.91	35	0.16	97.3	No
NF permeate VR 40%	7.91	34	0.19	80	No
NF permeate VR 50%	8.2	32	0.22	61.02	No

8/3 Alkali cleaning			
	pH	Temperature	Duration
Before	11.56	35	15:50-16:30
After	11.70	-	
DI water flush			
	Flow (L/hr)	Temperature	Duration
PWF	300	38	16:35-16:57

15/3 Batch 4					
	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate	7.95	35	2.26	163.6	Yes
NF permeate VR 10%	8.41	34	0.07	144	No
NF permeate VR 30%	8.62	33	0.09	128.6	No
NF permeate VR 50%	8.11	32	0.11	112.5	No
NF permeate VR 70%	-	31	0.20	70.6	No

15/3 Alkali cleaning			
	pH	Temperature	Duration
Before	11.20	35	1 h
After	-	-	
16/3 DI water flush			
	Flow (L/hr)	Temperature	Duration
PWF	300	38	10:11-10:31

19/3 -20/3 Batch 5					
	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate 19/3	-	-	3.26	-	Yes
UF Permeate 20/3	8.46	33	3.95	124	Yes
NF permeate VR 10% 20/3	9.25	31	0.17	100	No
NF permeate VR 25% 20/3	8.44	27	0.40	33	No

20/3 Alkali cleaning			
	pH	Temperature	Duration
Before	11.00	35	1 h
After	-	-	
21/3 DI water flush			
	Flow (L/hr)	Temperature	Duration
PWF	327	40	20 minutes

21/3 Continuation of Batch 5					
	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate 40%	-	29	0.24	63.2	Yes

21/3 Alkali cleaning			
	pH	Temperature	Duration
Before	11.00	35	1 h
After	-	-	
21/3 DI water flush			
	Flow (L/hr)	Temperature	Duration
PWF	257	35	20 minutes

21/3 Batch 6					
	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate	8.66	-	2.42	-	Yes

22/3 Batch 6					
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	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate	8.10	31	3.42	120	Yes
NF permeate VR 20%	9.30	29	0.04	103	No

22/3 Alkali cleaning					
	pH	Temperature	Duration		
Before	10.70	40	30 min		
After	-	-			
DI water flush					
	Flow (L/hr)	Temperature	Duration		
PWF	327	40	20 minutes		
22/3 Batch 6 (Adjusted pH)					
	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate	10	31	4.62	112.5	Yes
NF permeate VR 20%	11.35	29	0.23	92	No

22/3 Alkali cleaning			
	pH	Temperature	Duration
Before	10.55	40	30 min
After	-	-	
DI water flush			
	Flow (L/hr)	Temperature	Duration
PWF	300	38	10 min

9.2 Appendix B: Data of batch 7-12, operating pressure from 8-10 bar.

Date	Sample	TC (mg/l)	IC (mg/l)	TOC (TC-IC) (mg/l)	TOC retention (%)	Conductivity (mS/cm)	Conductivity retention (%)
Batch 7							
28/3	UF start	1029	127.4	901.6		6.98	
28/3	NF 10%	16.43	4.076	12.354	98.63	0.08	98.85
28/3	NF 30%	18.7	6.292	12.408	98.62	0.12	98.28
28/3	NF 40%	21.52	7.534	13.986	98.45	0.17	97.56
Batch 8							
3/4	UF start	1219	311.4	907.6		6.96	
3/4	NF 10%	19.99	6.162	13.828	98.48	0.18	97.41
3/4	NF 30%	25.97	8.388	17.582	98.06	0.20	97.13
3/4	NF 50%	34.16	13.65	20.51	97.74	0.29	95.83
Batch 9							
5/4	UF start	430.2	62.75	367.45		3.62	

5/4	NF 10%	16.59	2.65	13.94	96.21	0.02	99.45
5/4	NF 30%	16.39	3.501	12.889	96.49	0.04	98.90
5/4	NF 50%	18.55	4.929	13.621	96.29	0.05	98.62
5/4	NF 70%	28.79	9.042	19.748	94.63	0.07	98.07
5/4	NF 80%	55.41	23.31	32.1	91.26	0.38	89.50
Batch 10							
6/4	UF start	536.9	73.35	463.55		3.68	
6/4	NF 10%	14.29	3.233	11.057	97.61	0.08	97.83
6/4	NF 30%	16.06	4.333	11.727	97.47	0.09	97.47
6/4	NF 50%	19.19	6.158	13.032	97.19	0.13	97.19
6/4	NF 70%	29.57	11.57	18	96.12	0.18	96.12
6/4	NF 80%	53.35	22.95	30.4	93.44	0.46	93.44
Continuation of Batch 10							
9/4	UF start	2759	413.05	2345.95		14.55	
9/4	NF start	114.8	47.02	67.78		0.11	
9/4	NF 85%	145.6	86.8	58.8	87.32	0.52	96.43
Batch 11							
13/4	UF start	734.4	157.95	576.45		4.24	
13/4	NF 10%	14.34	4.471	9.869	98.29	0.08	98.11
13/4	NF 30%	17.93	5.758	12.172	97.89	0.15	97.89
13/4	NF 50%	22.94	8.79	14.15	97.55	0.17	97.55
13/4	NF 70%	40.04	18.76	21.28	96.31	0.38	96.31
Batch 12							
16/4	UF start	415.3	77.9	337.4		4.49	
16/4	NF 10%	13.85	5	8.85	97.38	0.10	97.77
16/4	NF 30%	14.90	6.396	8.504	97.48	0.12	97.33

28/3 Batch 7					
	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate	8.37	35	6.98	-	Yes
NF permeate Initial	-	-	-	156.5	No
NF permeate VR 10%	9.24	31	0.08	156.5	No
NF permeate VR 30%	8.87	29	0.12	94.7	No
NF permeate VR 40%	9.10	29	0.17	85.7	No

28/3 Alkali cleaning			
Pressure (bar)	pH	Temperature	Duration

5	10.55	40	40 min
DI water flush			
	Flow (L/hr)	Temperature	Duration
PWF	300	38	20 min

3/4 Batch 8					
	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate	8.65	38	6.96	-	Yes
NF permeate Initial	-	-	-	163.6	No
NF permeate VR 10%	9.45	34	0.18	144	No
NF permeate VR 30%	9.05	33	0.20	109.1	No
NF permeate VR 50%	9.22	31	0.29	65.5	No
Notes: Passed the NitriTox					

3/4 Alkali cleaning			
Pressure (bar)	pH	Temperature	Duration
5	11.0	38	40 min
4/4 DI water flush			
	Flow (L/hr)	Temperature	Duration
PWF	300	38	20 min

5/4 Batch 9					
	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate	8.14	40	3.62	-	Yes
NF permeate Initial	-	-	-	277	No
NF permeate VR 10%	9.75	36	0.02	277	No

NF permeate VR 30%	9.79	36	0.04	240	No
NF permeate VR 50%	9.32	35	0.05	180	No
NF permeate VR 70%	9.30	34	0.07	105.8	No
NF permeate VR 80%	8.70	30	0.38	36	No

5/4 Alkali cleaning			
Pressure (bar)	pH	Temperature	Duration
5	11.30	40	40 min
5/4 DI water flush			
PWF	Flow (L/hr)	Temperature	Duration
	300	40	20 min

6/4 Batch 10					
	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate	8.11	36	3.68	-	Yes
NF permeate Initial	-	-	-	277	No
NF permeate VR 10%	9.19	34	0.08	277	No
NF permeate VR 30%	8.19	34	0.09	212	No
NF permeate VR 50%	8.01	34	0.13	171.4	No
NF permeate VR 70%	7.78	33	0.18	92	No

NF permeate VR 80% Notes: Passed the NitriTox	7.73	31	0.46	39	No
NF permeate VR 85%	-	-	0.60	25	No

6/4 Alkali cleaning			
Pressure (bar)	pH	Temperature	Duration
5	10.90	41	45 min
6/4 DI water flush			
	Flow (L/hr)	Temperature	Duration
PWF	300	40	20 min

9/4 Continuation of Batch 10					
	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate	10.00	31	14.55	-	Yes
NF permeate Initial	-	-	0.11	43.9	No
40 minutes after start Notes: A little yellow tone of the NF permeate	9.65	-	0.50	24	No
1 h 50 minutes after start Notes: A little yellow tone of the NF permeate	-	-	0.52	12	No

9/4 Alkali cleaning			
Pressure (bar)	pH	Temperature	Duration
5	11.80	40	40 min
DI water flush			

	Flow (L/hr)	Temperature	Duration
PWF	300	39	25 min

13/4 Batch 11					
	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate	8.73	38	4.24	-	Yes
NF permeate Initial	-	-	-	225	No
NF permeate 10% VR	10.10	34	0.08	225	No
NF reject 10% VR	8.69	34	5.93	1200	Yes
NF permeate 30% VR	9.80	33	0.15	189.5	No
NF reject 30% VR	8.63	34	7.05	1800	Yes
NF permeate 50% VR	9.61	33	0.17	144	No
NF reject 50% VR	8.56	34	9.04	1200	Yes
NF permeate 70% VR	9.21	31	0.38	61.02	No
NF reject 80% VR	8.56	33	12.44	1800	Yes

13/4 Alkali cleaning			
Pressure (bar)	pH	Temperature	Duration
8-10	11.00	40	40 min
DI water flush			
	§§§	Temperature	Duration
PWF	300	39	20 min

16/4 Batch 12

The hose from the pressure side got a small crack. Therefore, the experiment had to be cancelled directly.

	pH	Temperature (°C)	Conductivity (mS/cm)	Flow (L/hr)	Foam
UF Permeate	8.78	40	4.49	-	Yes
NF permeate Initial	-	-	-	277	No
NF reject Initial	-	-	-	120	Yes
NF permeate 10% VR	10.03	37	0.10	277	No
NF reject 10% VR	8.70	38	5.53	1200	Yes
NF permeate 30% VR	9.83	38	0.12	225	No
NF reject 30% VR	8.54	37	6.35	1200	Yes

16/4 DI water flush (No alkali cleaning before due to hose crack)			
	Flow (L/h)	Temperature	Duration
PWF	276.9	40	20 min

9.3 Appendix C: Flux measurement in the RO flat sheet experiments

5 bars			
Time	Weight of Module 1 (XLE) (g)	Weight of Module 2 (SW30-HR) (g)	Weight of Module 3 (RO98 pHt) (g)
0	26.8	25.4	27.1
5	35.6	25.4	31.9
10	44.0	25.5	36.5
15	52.7	25.5	41.3
20	61.6	25.5	46.1
25	70.4	70.4	50.9

8 bars			
Time	Weight of Module 1 (XLE) (g)	Weight of Module 2 (SW30-HR) (g)	Weight of Module 3 (RO98 pHt) (g)
0	26.7	25.8	27.0
5	41.6	25.8	34.6
10	57.2	25.9	42.6
15	72.5	26.0	50.9

20	89.3	26.2	59.2
25	100.62	26.3	67.7

10 bars			
Time	Weight of Module 1 (XLE) (g)	Weight of Module 2 (SW30-HR) (g)	Weight of Module 3 (RO98 pHt) (g)
0	22.6	26.7	27.6
5	42.9	26.7	37.3
10	63.4	26.9	47.2
15	83.3	27.1	57.4
20	103.8	27.3	67.6
25	124.7	27.6	78.2

9.4 Appendix D: Cost Estimation

Investment cost = 1.9 Million SEK

Depreciation investment expense = 310 000 SEK

Operating cost = 200 000 $\frac{SEK}{Year}$

Amount of recirculated water = 50m³ · 365 days = $\frac{18250m^3}{year}$

Cost of treated waste water the first 10 years = $\frac{3.1 \cdot 10^5 + 2.0 \cdot 10^5}{18250} = \frac{28 SEK}{m^3}$

Cost of treated waste water after 10 years = $\frac{2.0 \cdot 10^5}{18250} = \frac{11 SEK}{m^3}$