Membrane filtration for the recovery of zinc chloride from wastewater from a recycling process for cellulose textiles

by

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Preface

This bachelor thesis was conducted at the Department of Chemical Engineering at Lund University.

Firstly, I would like to acknowledge Mats for being my supervisor and providing me with this thesis. For always taking time to bounce ideas, and your valuable feedback. Thank you.

I would like to thank Gregor and Edvin, for showing such incredible enthusiasm over this project, your investment helped me stay positive, regardless of difficulties and obscure results.

And to Ola for being my examiner, and for always checking in on me during long days in the apparatus hall. Thank you.

Finally, I would like to thank my family and friends for always supporting me.

Ebba Andersson, January 2022, Lund

Abstract

Today, textile consumption in the world is high. Each year, textiles are bought and thrown away far more than the world's resources allow. In an attempt to find a sustainable way to reuse textiles, Department of Chemical Engineering at Lund University has started a research project to investigate the possibilities of reusing textile fibers. By breaking down textiles into fibers, it is possible to reuse the same textile fiber for new textiles. This decomposition of textile fiber can be done with e.g., zinc chloride.

The purpose of this project is to investigate the possibilities for purifying the wastewater from this novel recycling process, with the aim to discharge it into a municipal wastewater treatment plant, while at the same time recover the zinc chloride so that it can be reused for the process.

Purifying the wastewater from the recycling process is of the utmost importance, as zinc chloride is environmentally unfriendly and hazardous to health and must not be allowed to be released into municipal wastewater treatment plants. Zinc chloride is also a finite resource and reusing it in the same process is beneficial for both the environment and the economy of the recycling process. Keeping the process economy in mind is important, thus, an inexpensive recycling process is the aim.

In this project, the basic idea was that the waste stream would be purified in two steps by means of membrane filtration. First microfiltration was used to separate residual cellulose from the wastewater. In a second step, nanofiltration was conducted to recover the zinc chloride. A number of micro- and nanofiltration membranes were tested at different pressures, to identify suitable operation conditions for the recovery process.

It was possible to recover both cellulose and zinc chloride from the wastewater, but not to the desired purities. Only a small amount of cellulose and zinc chloride was recovered, but the process holds the potential to remove all impurities under the right operation conditions.

Keywords: textile recycling, membrane filtration, microfiltration, nanofiltration, zinc chloride

Sammanfattning

Textilkonsumtionen i världen idag är hög, varje år köpts och slängs textilier långt mer än vad världens resurser tillåter. I ett försök att hitta ett hållbart sätt att återanvända textilierna har institutionen för kemiteknik vid Lunds universitet påbörjat ett forskningsprojekt för att undersöka möjligheterna till att återanvända textilfibrerna från grunden; genom att bryta ner textilierna till fiber ska det gå att återanvända samma textilfiber till nya textilier i en ny återvinningsprocess. Denna nedbrytning av textilfiber görs med zinkklorid.

Syftet med detta projekt är att studera möjligheterna till att rena de avfallsströmmar som bildas i den nya återvinningsprocessen, för att avfallsvattnet ska kunna släppas ut i naturen och för att zinkkloriden som avskiljs ska kunna återanvändas.

Att rena avfallsvattnet från återvinningsprocessen är av högsta vikt, då zinkklorid är miljö och hälsofarligt och inte får lov att släppas ut i naturen. Zinkklorid är även en ändlig resurs och att återanvända den i samma process är gynnsamt för såväl miljön som återvinningsprocessens ekonomi. Att ha process ekonomi i åtanke är viktigt, då en dyr återvinningsprocess inte kommer få något genomslag på marknaden.

I detta projekt var grundtanken att avfallsströmmen skulle renas i två steg med hjälp av membranfiltrering. Först mikrofiltrering för att filtrera bort resterna av cellulosa från vattnet, därefter nanofiltrering för att separera zinkklorid och vatten från varandra. Ett flertal membran av såväl mikro- som nanokaraktär testades vid olika tryck, för att få en uppfattning om vilka förhållanden som krävdes för filtreringen.

Resultaten visade att det går att avskilja såväl cellulosa som zinkklorid i lösningen, dock inte till den renhet som önskats. Resultatet blev i stället att en mindre mängd cellulosa och zinkklorid avskildes, men med potential för att under rätt förhållanden kunna avskilja alla orenheter.

Nyckelord: textilåtervinning, membranfiltrering, mikrofiltrering, nanofiltrering, zinkklorid

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1 Introduction

Over the last 25 years, the amount of clothes purchased per person in the EU has increased by 40%. An average European use roughly 26 kg of textiles each year, but only keeps 15 kg of them for the next year to come. Eleven kg of textiles per person and year in Europe are being discarded, and due to inadequate technology, almost none is recycled [1].

Apart from the consumption of textiles, the garment itself is not environmentally friendly. The textile industry uses 2 700 liters of water to produce a single t-shirt, the same amount of water that would be sufficient for one person's hydration needs for 2.5 years. Apart from that, the textile industry stands for 10 % of the global greenhouse gas emissions [1].

Recent reports show that only 12 % of the textiles ends up being recycled globally. The question is: why is recycling of textiles so rare? One big obstacle for recycling is the complexity of the garments. A garment can be made of cotton, polyester, elastane, linen, and several other kinds of textile fibers, as well as combinations of them all. Furthermore, a piece of cotton clothing is rarely made of 100 % cotton; buttons and zips are objects used in clothing [2]. Because of this, new technologies are required to solve the challenges of textile recycling. Those technologies need to be efficient and simple so that they allow a reuse of garments that are not suitable for the secondhand market.

To find a solution to the recycling problem, a research project at the Department of Chemical Engineering at Lund University has been started to develop a new recycling process for textiles [3] [4]. The idea is to create a process that dissolves the textiles to textile fibers; creating the possibility to create completely new textiles, instead of a reuse of old textiles. This dissolvement is performed using zinc chloride. In the project presented in this report, the wastewater produced by the process was investigated. Ideally, it will be possible to recover the zinc chloride for reuse in the process; thus, the possibilities for separation of wastewater and zinc chloride were investigated. The separation was to be made with membrane filtration in three steps: coarse, micro, and nano.

1.1 Aim

The aim of this bachelor thesis is to evaluate the possibilities of recovery of the zinc chloride used in a textile recycling process, by extracting it from the wastewater produced in the process. This is done by evaluating different membrane filtration processes, and the impact the pore size has on the removal rate of cellulose, and zinc chloride.

The goal was to remove cellulose and zinc chloride from the wastewater in two steps – first, microfiltration was conducted to remove remaining cellulose fibers from the wastewater, thereafter nanofiltration was applied to recover the zinc chloride. Ideally, this will make the wastewater be pure enough to be released into communal wastewater treatment plants.

This study should be seen as a screening for the possibility to use membrane filtration in the process presented. To obtain exact results of which membranes, pressures and flows that should be used, further analyzes must be made. Because of this, few to none replicates of each tested membrane were be made.

2 Background

2.1 Cellulose textiles

Cellulose textiles are textiles made from natural fibers, such as cotton, jute, and hemp. These fibers have been used for thousands of years by humans, as the fibers easily can be extracted from plants [5]. All plants produce cellulose, but only a few are cultivated for their fibers. Cotton, with its high percentage of cellulose, is dominating for this application. The fiber length and length uniformity of cotton gives it the ultimate spinning properties required to spin the textile fibers into yarn [6].

Nevertheless, like so many other natural resources cotton needs a place to grow and be cultivated. Because of this, it is important to utilize the product to its fullest, to use the cotton fibers over again. Using the cotton only once is wasteful, as the fibers are still usable.

2.2 Zinc chloride

Zinc chloride ($ZnCl_2$) is a highly soluble compound that can be solved in water, alcohols, amines, and acetone among others. With water it forms hydrates with 1 – 4 mol, giving it a strongly hydroscopic ability. When combined with ammonia in a solvent, zinc chloride forms complexes with the ammonia [7]. Zinc chloride has a high viscosity when melted, and in gas phase, the molecule is linear [8].

When solved in water, the solution does not only consist of zinc and chloride ions, but but the solution also contains zinc chloride bound to the water [9]. This considered, it is very hard to predict the properties of the solution.

The applications of zinc chloride are many. It can be used as a catalyst and dehydrating agent [10], but also in textile processing. Concentrated zinc chloride dissolves starch, silk, and cellulose. This property has been utilized in the recycling process that creates the wastewater used in this study.

2.3 Membrane filtration

Membrane filtration is a separation technique that is designed for the separation of molecular mixtures. The technique is applied in chemical industries such as food and pharmaceutical industries. Two of the most common applications of membrane filtration is to produce potable water from seawater, and to clean industrial effluents [11].

Membranes consist of a semipermeable barrier, separating two phases from each other by controlling the movement of molecules across the barrier. The feed is separated into retentate and permeate; where compounds retained by the membrane accumulate in the retentate, while compounds that pass through the membrane are collected in the permeate [12].

Compared to other separation processes, membrane filtration is easier electrifiable, more energy efficient, yields higher quality of products and is simpler to operate. However, membranes can be frail and can require excessive pretreatment [11].

2.3.1 Dead-end and crossflow filtration

The two filtration methods used in this research are dead-end filtration and crossflow filtration. Dead-end filtration is perpendicular filtration, where the compounds are separated from the liquid by forcing the liquid through a membrane. When all, or some, of the liquid has gone through the membrane, the batch can be refilled [13]. Crossflow filtration is tangential filtration where the flow reaches the filter surface at high speed from the side, as can be seen in Figure 2.1, only letting a slight flow of liquid pass through the membrane [14].

With crossflow filtration, the buildup of residues in filter cakes tends to be smaller than for dead-end filtration, as the continuous flow across the membrane hinders a filter cake from settling [15]. Nevertheless, the filter cake in dead-end filtration can be avoided with the help of continuous stirring of the sample in the modulus, as applied in the case of this trial.

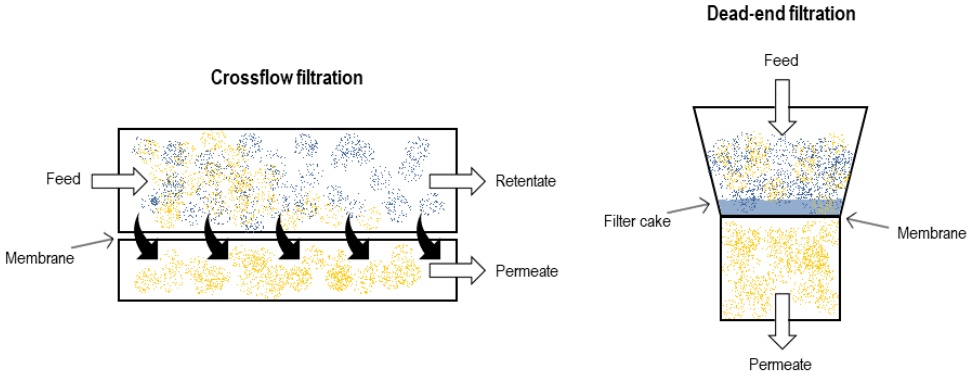

Figure 2.1. Schematic figures of crossflow and dead-end filtration.

2.3.2 Fouling of membranes

When filtrating different types of solutions, fouling is to be expected. There are three main ways for a compound to foul a membrane: by blocking the pores; by creating build up in the pores (adsorptive fouling); or by creating a filter cake. Fouling causes reduction of the flow and, if not treated, total stop of flow.

Larger compounds, those too large to enter the pores, are kept back in the retentate of the filtration. When running a dead-end filtration, these particles tend to sediment to the bottom of the filtration device, creating a cake effect. The cake layer causes particles to form a hindering layer in front of the membrane, blocking the feed from going through the membrane, thereby reducing the permeate flow. Dead-end filtrations tend to use stirring to create a flow in the device, to hinder the sedimentation from happening. Cake effects can also occur with crossflow-filtration; however, the cake will only lower the flux, not stopping it all together [16].

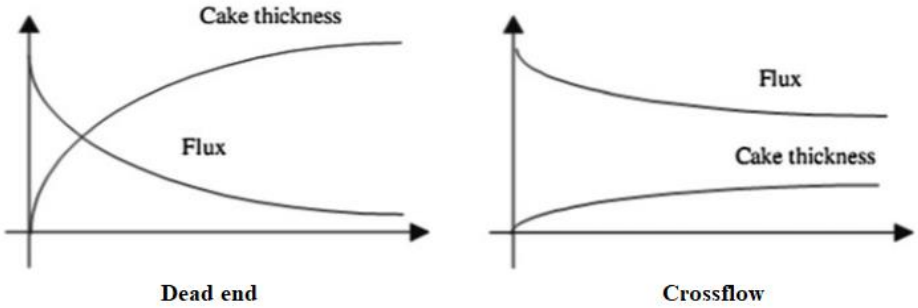

Figure 2.2. Schematic of how cake thickness affects the permeate flow over time for dead end and crossflow filtration [16].

2.4 Types of membrane filtration

Membrane filtration can be performed with numerous parameters. By using different pore size, transmembrane pressure and permeate flow, compounds of different sizes and with different characteristics will be held back.

Membrane filtration is separated into categories based of the applied cut-off size on the particles held back, the particles that stays in the retentate. These categories and specific parameters for these categories of membranes can be seen in Table 2.1.

Table 2.1. Parameters typical for crossflow filtration [14]

	Cut-off size	Transmembrane pressure	Permeate flow
Microfiltration	> 100 nm	0.2 – 5 bar	50 – 1000 L m^{-2} h^{-1}
Ultrafiltration	10 – 100 nm	2 – 10 bar	< 100 L m^{-2} h^{-1}
Nanofiltration	> 1 nm	5 – 30 bar	< 100 L m^{-2} h^{-1}

In this study, all the filtration techniques in Table 2.1 will be applied, as well as coarse filtration.

Coarse filtration is filtration used to remove large, visibly compounds and dirt. The filtration can be compared to a strainer, as the pores in coarse filtration are visible large and the held-back material only consists of the particles it collected. In this report, coarse filtration with pore sizes up to 500 µm will be used.

Microfiltration is filtration used to remove particles and microorganisms from a liquid sample. The particles removed are commonly suspended solids and bacteria. In microfiltration, the larger particles are swept away, and smaller particles accumulate on the membrane surface as a filter cake [14].

In ultrafiltration, the cut-off size is reduced further from the microfiltration, which allows for restraining viruses from going through the membrane. In contrary to microfiltration, for ultrafiltration it is the larger particles that are collected in the retentate [14].

The finer filter type, nanofiltration, can (apart from suspended solids, bacteria, and viruses) retain multivalent ions from passing through the membrane. These membranes have a small pore size; and can cut of molar masses of 200-600 g/mol [14].

3 Material and Methods

3.1 The wastewater

In this study, the textiles used to create the wastewater were white cotton, as the removal of dyes and pigments are more complex and in this stage of the trial, a simplification of the textiles needed to be done.

The wastewater contained water, cellulose residues, and zinc chloride; all combined in a heterogeneous mix. Cellulose was not dissolved in the wastewater, creating the heterogenous state of the mixture. With zinc chloride, it is not known if the molecule dissolves in the water or if it stays together. Due to this unclarity, it is hard to predict how the wastewater will react when introduced to other compounds.

3.2 The Albi module

For the dead-end filtrations, the pressurized batch module named Albi was used. The Albi module can hold a volume of 380 ml, it can also be pressurized and heated. The module is equipped with a magnetic stirring module to create a flow in the module, this to reduce the fouling of the membrane.

Figure 3.1. The Albi module during pressurized trials.

3.3 Membrane conditioning

To begin any measurements, the membrane must be conditioned. The conditioning was carried out with Ultrasil 10, a cleaning agent targeting the protective layer of the membrane. Ultrasil 10 is a sodium based alkaline EDTA with a basic pH [17].

The membrane was carefully cut out from the membrane sheet, in a shape suitable for the filtration used. When cutting the membrane, one should be careful not to scratch the surface of the membrane on any side. A scratch on the surface might lead to additional larger holes in the membrane, causing higher flux, no holdback, and incorrect measurements.

Before starting the cleaning with Ultrasil 10, the module required to be heated to a temperature of 50 °C. To do this, the module was filled with deionized water, as heating without any liquid will cause the membrane to crumple.

When the module was heated, the deionized water was replaced with Ultrasil 10 in a 0.5 w/w% mixture. The mixture was made with Ultrasil 10 powder and warm deionized water. The Albi module was filled with the cleaning agent for around 1 hour, to allow for heating to the temperature of 50°C. After 1 hour, the cleaning agent was be filtrated out at 2 bars. Note that the filter can be as shocked with pressure changes as it can be chocked with temperature changes, so the pressure should not be increased with more than 0.2 bar per minute.

When the retentate had reached a volume reduction of around 80%, the cleaning agent was removed from the module and two batches of deionized water was filtered. Between every batch, the retentate was washed out so no build-up of Ultrasil 10 was created. When filtering with deionized water, the temperature should gradually go towards room temperature, as the measurements of the sample will be carried out at room temperature (19-20 °C). This was done to simulate the work conditions most applicable in an up-scaling.

3.4 Filtration

Ideally, for this process the filtration will be carried out in two steps. First, the remaining cellulose fibers will be cut off to purify the wastewater to only water and zinc chloride. In the second step, the zinc chloride will be recovered from the water, creating two pure streams.

However, because of the extent of large compounds in the wastewater, a coarse filtration was also preformed, to remove visually detectable compounds from the wastewater, see Figure 3.2. All filtrations were set in room temperature.

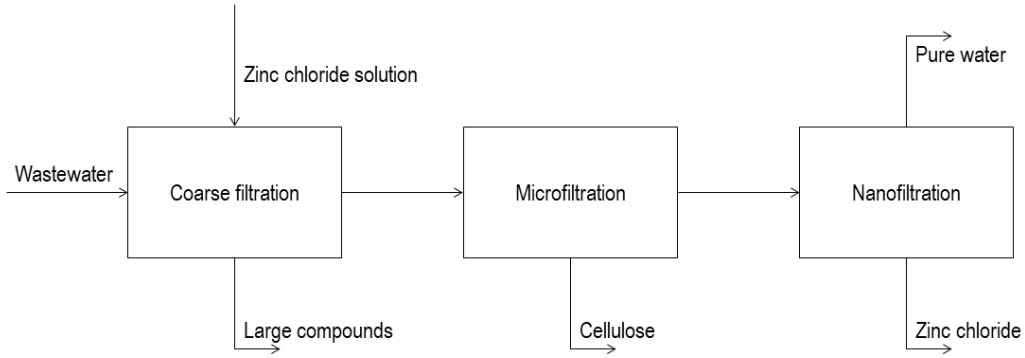

Figure 3.2. The filtration process of the wastewater from the textile recycling process, containing coarse filtration followed by membrane filtrations in two steps; first, microfiltration, followed by nanofiltration.

3.4.1 Coarse filtration

Before the membrane filtration began, a coarse filtration was carried out of roughly 25 liters of the raw material. The filtration was done with four metal strainers, in the following order and with the pore sizes 425 µm, 250 µm, 125 µm, and 60 µm.

This filtration was designed to remove larger pieces of cellulose, as large fragments could be seen in the wastewater. These compounds would most likely foul the finer filters, as the compounds would block larger regions of the membrane area. With this initial removal of cellulose, the fouling that would occur in the microfiltration would be lesser and with smaller, barely visible compounds.

3.4.2 Microfiltration

Three membranes for microfiltration were used in this study. The membranes had the same material and characteristics, but the pore sizes differed.

Table 3.1. Membrane data for the microfilters used in this study [18]. All membranes are commercially produced by Alfa Laval

	Support material	Characteristics	Pore size	Typical operating pressure
MFG1	Polypropylene	Polysulphone	0.1 µm	1-3 bar
MFG2	Polypropylene	Polysulphone	0.2 µm	1-3 bar
MFG5	Polypropylene	Polysulphone	0.5 µm	1-3 bar

For MFG1 and MFG2 filtrations were carried out at 0.3, 0.5, 0.7 and 1.0 bar. For MFG5 the filtration also occurred at 0.3, 0.5 and 0.7 bar – but was cancelled in the 1.0 bar case as the flux in general for MFG5 was too high to work with, referencing ideal permeate flows from Table 2.1.

One batch was made for each pressure. As the membranes are sensitive to pressure changes, the pressure was raised slowly with 0.1 bar/ min. Therefore, it is incorrect to say that all permeate was performed at the same pressure, as the permeate from the pressure increased from

0 to the set pressure is included in the total permeate. The Albi module can hold 380 ml wastewater, meaning that the module is filled up and the filtration is carried out at one pressure until a desired volume reduction is reached. In this study, the given volume reduction was set to around 80%. Unfortunately, the reduction was sometimes hard do manage, as the flow could be irregular and nonpredictable.

The pressures for this filtration series were chosen on the lower side of the spectrum because the permeate flow would become too high for the membrane at higher pressures, increasing the risk of membrane malfunctioning.

3.4.3 Ultrafiltration

One ultrafiltration membrane was tested in this study as a reference to see if the microfiltration was able to successfully remove the cellulose from the wastewater. Significant difference in performance between the two filter types would, if detected, indicate that separation demand a finer membrane.

If the results would have shown that a significantly larger amount of cellulose was held back by the ultrafiltration, in comparison to the microfiltration, more ultrafiltration filters would have been tested.

Table 3.2. Membrane data for the ultrafilter used in this study [19]. The membrane is commercially produced by Alfa Laval

	Support material	Characteristics	MWCO value	Typical operating pressure
GR40PP	Polypropylene	Polysulphone	100 000	1-10 bar

Filtration with GR40PP is carried out at 1.0, 2.0 and 3.0 bar.

3.4.4 Nanofiltration

The nanofiltration were carried out to recover the zinc chloride from the wastewater. Two different membranes were used from two different suppliers. The feed used were wastewater crossflow filtrated with MFG2 at 0.7 bar.

A notable difference with nanofiltration in comparison to microfiltration was that the different pressures the filter was carried out on was applied during the same batch, meaning there was only one retentate per filter, compared to one retentate per filter and pressure during the micro filtration.

Table 3.3. Membrane data for the nanofiltration membranes used in this study [20] [21]

	Support material	Characteristics	Typical operating pressure (bar)
Alfa Laval NF99HF	Polyester	Thin-Film composite	15-42
Dow NF270	Polypiperazine	Thin-Film composite	-

The nanofiltration was carried out at 10 and 11 bar, not performing at higher pressures as the pressurizing equipment did not allow it. For each pressure, around 150 ml permeate were generated before the pressure was increased. Because of this, both pressures were tested on the same batch; therefore, the retentate was a product blend from both pressures, and will not indicate anything about specific pressures, only specific membranes. For both filtrations, the temperature of the feed was set to room temperature.

As the amount of retentate differed between the membranes used, the concentration in the retentate was standardized after measurements using equation 3.1, to enable comparisons between the results. This standardization is not done for the microfiltration retentate as they are all estimated to have been taken at 80%.

$$C_{std} = \frac{C_{measured}}{\left(\frac{380 - V_{retentate}}{380}\right)} \tag{3.1}$$

3.5 In-depth analysis

To evaluate the possibilities for recovery of zinc chloride further, one membrane for microfiltration and one for nanofiltration were chosen for deeper analysis.

3.5.1 Crossflow-microfiltration

For the microfiltration, a crossflow-filtration were set up to estimate the possibility to create a process with less fouling then the dead-end. The process performed at 0.7 bar and room temperature with the MFG2 membrane. The filtrated wastewater, the crossflow permeate, was used with all of the nanofiltration trials.

The crossflow set-up was prepared with the same method as the dead-end filtration; cleaning with Ultrasil 10 and heavily washed afterwards. All analysis methods were used as well.

3.5.2 Nanofiltration at higher pressure

For the nanofiltration, the dead-end filtration with NF99HF were tested at 20 bar in addition to 10 and 11 bar. The procedure was performed at room temperature. Just as with the other membranes for nanofiltration, around 150 ml of permeate were generated and the rest remained as a retentate. As this filtration were only carried out on one pressure instead of two, the concentrations in the retentate were adjusted for the larger volume left in the retentate stage.

Apart from the higher pressure, no differences were made in the preparation and execution of the filtration compared to the lower pressures.

3.6 Analysis of data

To evaluate the filtration technique and parameters used in each experiment, four analysis methods were used. Apart from the analysis methods, the flux of the permeate was also measured during the trials.

3.6.1 Pure water flux

To estimate the amount of fouling of the membranes, a pure water flux (PWF) was measured before and after the filtration. The PWF was carried out with deionized water, meaning that no fouling would occur from it. Hence, the flux from PWF before and after filtration of the wastewater is only affected by the fouling created by the wastewater.

The PWF was measured at three different pressures, which three depends on the type of membrane, see Table 3.4. The pressures were uniquely chosen for each type of membrane, as different sized membranes can handle higher or lower pressures, see Table 2.1.

Table 3.4. Pressures used to create a pure water flux-series, to evaluate the amount of fouling after filtrations

	Pressure (bar)		
Microfiltration	0.5	1.0	1.5
Ultrafiltration	2.0	2.5	3.0
Nanofiltration	5.0	7.0	10.0

At each pressure, the flux and the mass reductions were measured for 5 minutes. Then, the pressure was raised. Note that if the module were to run filtrate all of the deionized water, the module needed to be refilled before the measurements could continue. If the flow through the membrane on a specific temperature was so high that the module was emptied earlier than 5 minutes, the time it took to empty the module were used for measurements instead.

The measurements of the PWF were carried out at in the same manners before and after the filtration of the textile wastewater. The fluxes could then be compared, as the pressure independent constant that can be calculated from the linear regression between the repeated measuring points. The slope of the linear regression is equivalent to the permeability. The permeability before and after was later compared and a permeability decrease was calculated.

3.6.2 Titration with EDTA

The concentration of zinc chloride in the solution was determined by a titration using EDTA. For the titration, the samples were diluted 1:1 000, as the amount of zinc would be very high (thereby needing excessive amounts of EDTA to detect) otherwise.

The concentration of zinc ions in the solution can be determined with EDTA as the molecules of the indicator and the EDTA interact with the zinc chloride, as can be seen in the following reaction formula.

Zn^{2+}	**+**	**HIn^{2-}**	**⇌**	**$ZnIn^{-}$**	**+**	**H^{+}**
Zinc ion (colorless)		*Indicator (blue)*	*pH 10*	*Zinc ion-indicator complex (purple)*		
$ZnIn^{-}$	**+**	**HY^{3-}**	**⇌**	**ZnY^{2-}**	**+**	**HIn^{2-}**
Zinc ion-indicator complex (purple)		*EDTA (colorless)*	*pH 10*	*Zinc ion-EDTA Complex (colorless)*		*Free Indicator (blue)*

(3.2)

The concentration of the samples was later calculated from the amount of EDTA needed for the color change to occur, with the concentration and volume relationship seen below.

$$C_1 \times V_1 = C_2 \times V_2 \tag{3.3}$$

As the concentration of EDTA was known, as well as the volume of the EDTA and the sample, the concentration of the samples could be calculated thereafter.

3.6.3 Total solids- and ash measurements

The total amount of solid in a sample was measured by heating of a known volume of wastewater in two steps. First, the sample was heated to 105 °C to evaporate water for 24 hours. Thereafter, the sample was heated to 575 °C. The results of total solids- and ash-experiments are determined in these two steps: first, after the drying of the sample, a total solid weight is recorded. This weight represents both cellulose and zinc chloride. After ashing, a second weight is recorded, and this weight is that of the inorganic compounds (i.e., zinc chloride) only. With this temperature increase, the cellulose of the sample was burned, and the remainder of the sample ascribed to was zinc chloride. No measurements are made on only the organic compounds (i.e., cellulose), consequently the weight of the organic compounds is calculated as the total mass, minus the inorganic mass.

However, the method was proven not to be as accurate as initially believed, as the water bound to the zinc chloride, the same water that evaporated during the heating. Consequently, a standard curve was made using a known zinc chloride concentration of 65 w/w%. This known solution was then diluted to multiple measuring points, see Figure 3.3.

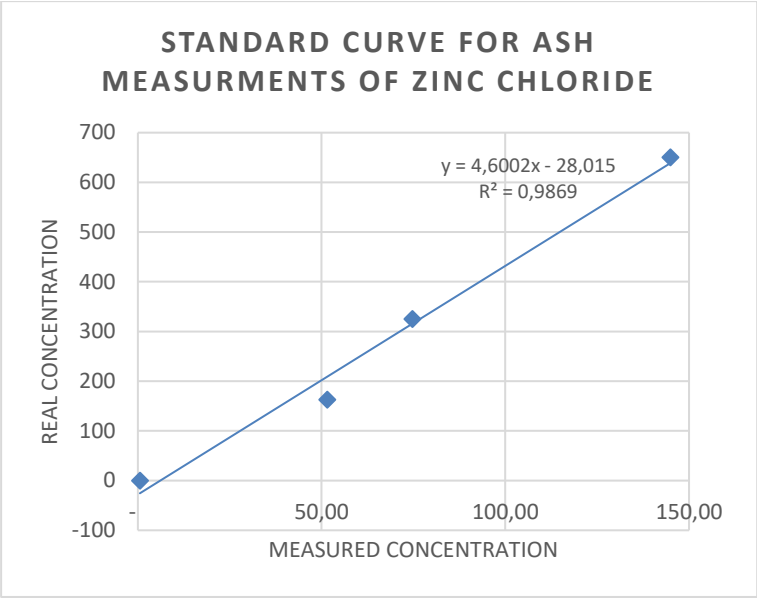

Figure 3.3. The standard curve used to scale the measurements of zinc chloride.

Results from the standard method showed that there was a correlation, but that the values needed to be adjusted according to the regression.

With this, the concentration of cellulose was adjusted from the estimated zinc chloride value. Cellulose content was thus never measured on its own; it is accounted from the zinc chloride measurements.

3.6.4 Particle size

To evaluate the particle sizes in the samples, a spectrometric analysis with Malverns Zeta Sizer was carried out. The instrument calculates the intensity and the size distribution by intensity for each sample, and the samples before and after filtration were compared and evaluated.

The sample was put in a cuvette in the Zeta Sizer and the measurements were carried out with a replication of 3 samples. The samples were at room temperature and well-mixed before use to reduce the risk of sedimentation.

4 Results

4.1 Coarse filtration

When filtrating the wastewater directly from the textile treatment, it was visually detected that larger compounds, such as fibers and dirt were collected in the first two filters, 425 µm and 250 µm. In the denser filters, no particles were visually detected.

4.1.1 Determination of concentration with EDTA-titration

The results from the EDTA-titration to determine the concentration of the wastewater before and after coarse filtration presented in Table 4.1. The results showed that the concentration of zinc chloride was reduced by roughly 9 %.

Table 4.1. The concentration of zinc chloride in the wastewater, before and after coarse filtration

	Concentration $ZnCl_2$ (g/L)
Before coarse filtration	149.9
After coarse filtration	147.2

4.1.2 Total solids- and ash measurements

In the total solids- and ash measurements, the amount of cellulose was estimated to increase after the coarse filtration, as can be seen in Table 4.2. It was also noted that the concentration of zinc chloride was reduced by roughly 8 %, almost the same amount as for the determination of concentration with EDTA, see Table 4.1.

Table 4.2. The concentration of cellulose and zinc chloride in the wastewater, estimated by total solids- and ash measurements

	Cellulose (g/L)	**Zinc Chloride (g/L)**
Before coarse filtration	109.4	46.8
After coarse filtration	101.4	54.6

4.2 Microfiltration

For the microfiltration, the MFG1 and MFG2 filters were performing similar to each other, while MFG5 showed significant difference in results, see Table 4.3.

Table 4.3. The average flux through the membranes at different pressures

	Flux ($Lm^{-2}h^{-1}$)			
	0.3 bar	**0.5 bar**	**0,7 bar**	**1.0 bar**
MFG1	285.6	339.4	469.5	591.1
MFG2	203.5	265.5	316.6	430.5
MFG5	3460.1	3098.8	3087.9	

As can be seen in Table 4.3 the average flux across the membranes is quite similar for MFG1 and MFG2, however for MFG5 the flux was roughly ten times larger. During the filtration, it could be noted that the flux was decreasing over time, as can be seen in Figure 4.1 and 4.2. For each pressure the flux decreased over time, though the flux increased when the pressure increased for MFG1 and MFG2, as can be seen in Figure 4.1 and 4.2. For MFG5 however, the increase of pressure did not result in an increase of flux, but instead a decrease.

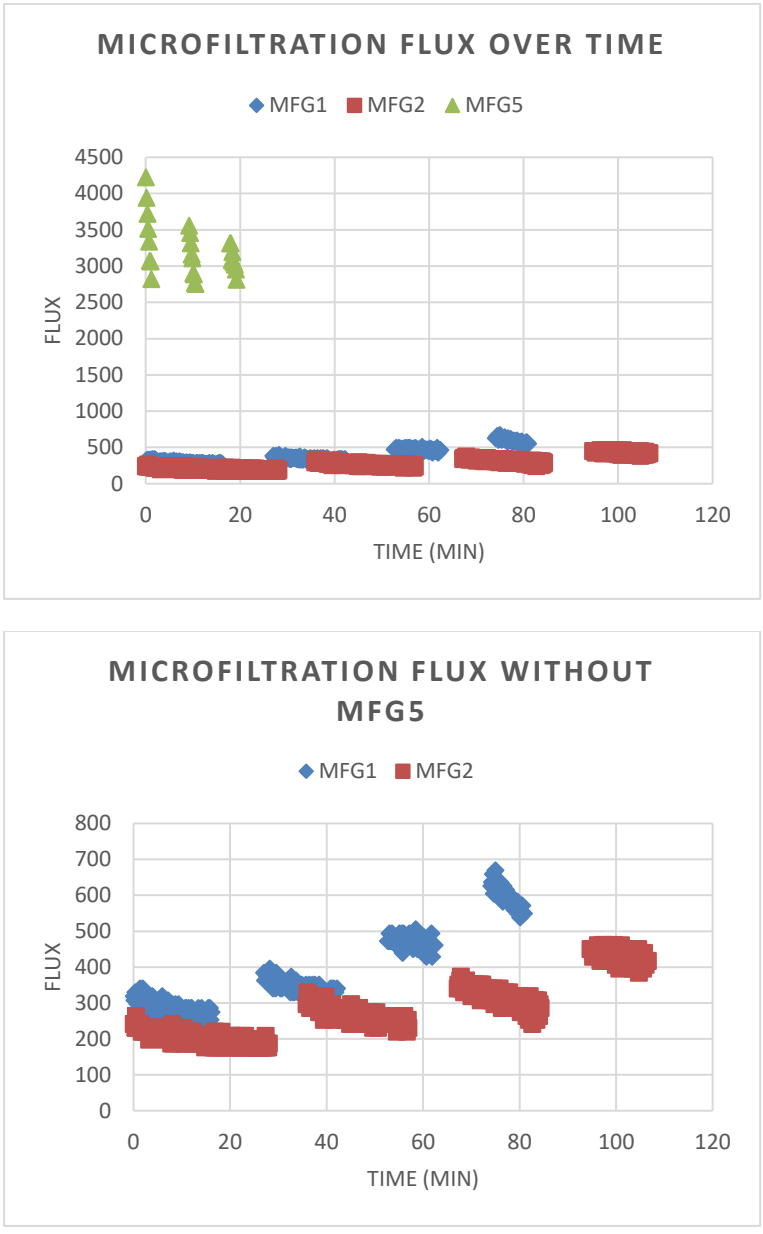

Figure 4.1 and 4.2. The flux for the wastewater for each of the pressures over time, with an enlargement of the profile of MFG1 and MFG2. Each cluster represents one pressure, for MFG1 and MFG2 from left to right 0.3, 0.5, 0.7 and 1.0 bar. For MFG5 from left to right 0.3, 0.5 and 0.7.

4.2.1 Pure water flux

The permeability of the membranes was measured before and after the filtrations, to estimate how much the membranes had been fouled, presented in Table 4.4.

Table 4.4. The permeability measured with PWF before and after filtration, and the calculated decrease in permeability.

	MFG1	**MFG2**	**MFG5**
Permeability before filtration ($Lm^{-2}h^{-1}$)	255.26	190.08	5558.3
Permeability after filtration ($Lm^{-2}h^{-1}$)	209.27	148.29	5113.9
Decrease in permeability (%)	18.0 %	22.0 %	7.9 %

The permeability decreased the most in MFG2, with as much as 22.0 %, and the least in MFG5, with only 7.9 %.

4.2.2 Determination of concentration with EDTA-titration

An EDTA-titration was made to estimate the concentration of zinc chloride, in the permeate as well as the retentate of the wastewater, see Table 4.5. The same dilution series were used for all varieties of filtration, as the concentrations did not majorly differ between the filtration types.

Table 4.5. Concentration of zinc chloride in the wastewater, before and after microfiltration at different pressures. Calculated from EDTA-titration.

Membrane/Concentration ZnCl2 (g/L) at different pressures				
Before MF	147.2			
	0.3 bar	***0.5 bar***	***0.7 bar***	***1.0 bar***
	Permeate			
MFG1	126.7	143.6	160.4	154.7
MFG2	134.9	140.8	144.5	146.5
MFG5	134.5	146.7	144.5	
	Retentate			
MFG1			152.6	145.4
MFG2			143.6	139.9

Ideally, no zinc chloride would be held back by the microfiltration, however, the results of the EDTA-titration showed that some zinc chloride was held back in the filtration, foremost in the cases of the lower pressures. Realistically, no results should be higher than the concentration from after the coarse filtration, as no concentration of the samples were made. Therefore, the results of the higher pressures with MFG1 are uncertain.

The conclusion is that MFG2 at higher pressures are most suitable to maintain the zinc chloride in the solution, according to the EDTA-method.

4.2.3 Total solids- and ash measurements

To estimate the concentration of cellulose as well as zinc chloride, a total solids- and ash measurement were made, see Table 4.6. Notable is that the concentration of cellulose is calculated from the concentration of zinc chloride, and thus not measured on its own. Consequently, the concentration of cellulose can in some cases show zero, as the calculations show it – however, it is most unlikely that the concentration in fact is zero (as in the case of MFG1 at 1.0 bar).

*Table 4.6. Concentration of cellulose and zinc chloride in the wastewater, before and after microfiltration at different pressures. Calculated from total solids- and ash measurements. *Calculations were made from the zinc chloride value and in this case showed a negative concentration.*

Membrane, pressure (bar)	Cellulose (g/L)	Zinc Chloride (g/L)
Before MF	54.6	101.4
	Permeate	
MFG1 0.3	46.2	104.2
MFG1 0.5	51.3	104.8
MFG1 0.7	49.3	106.1
MFG1 1.0	0*	252.0
	Retentate	
MFG1 0.7	28.8	132.9
MFG1 1.0	6.5	154.6
	Permeate	
MFG2 0.3	55.1	98.2
MFG2 0.5	26.0	129.4
MFG2 0.7	52.4	104.2
MFG2 1.0	61.3	93.6
	Retentate	
MFG2 0.7	48.3	112.6
MFG2 1.0	21.6	138.8
	Permeate	
MFG5 0.3	60.3	90.6
MFG5 0.5	53.2	102.6
MFG5 0.7	40.9	113.4

The total solids- and ash measurements, just as the EDTA-titration, should not show any significant increase in concentration of either cellulose or zinc chloride. Therefore, results showing increase of either zinc chloride or cellulose are uncertain. With that in mind, the best results can be seen with MFG1 at 0.3 bar, as well as MFG2 at 0.5 bar.

4.2.4 Particle size

The particle sizes were measured with a Zeta Sizer. Still, as can be seen in Figure 4.3 and 4.4, the size measurements were showing irregular results, with results showing larger compounds from after the filtration than before. Consequently, these measurements were not considered further, as the results were to irregular to be of significance, see section 0 for further discussion of the matter.

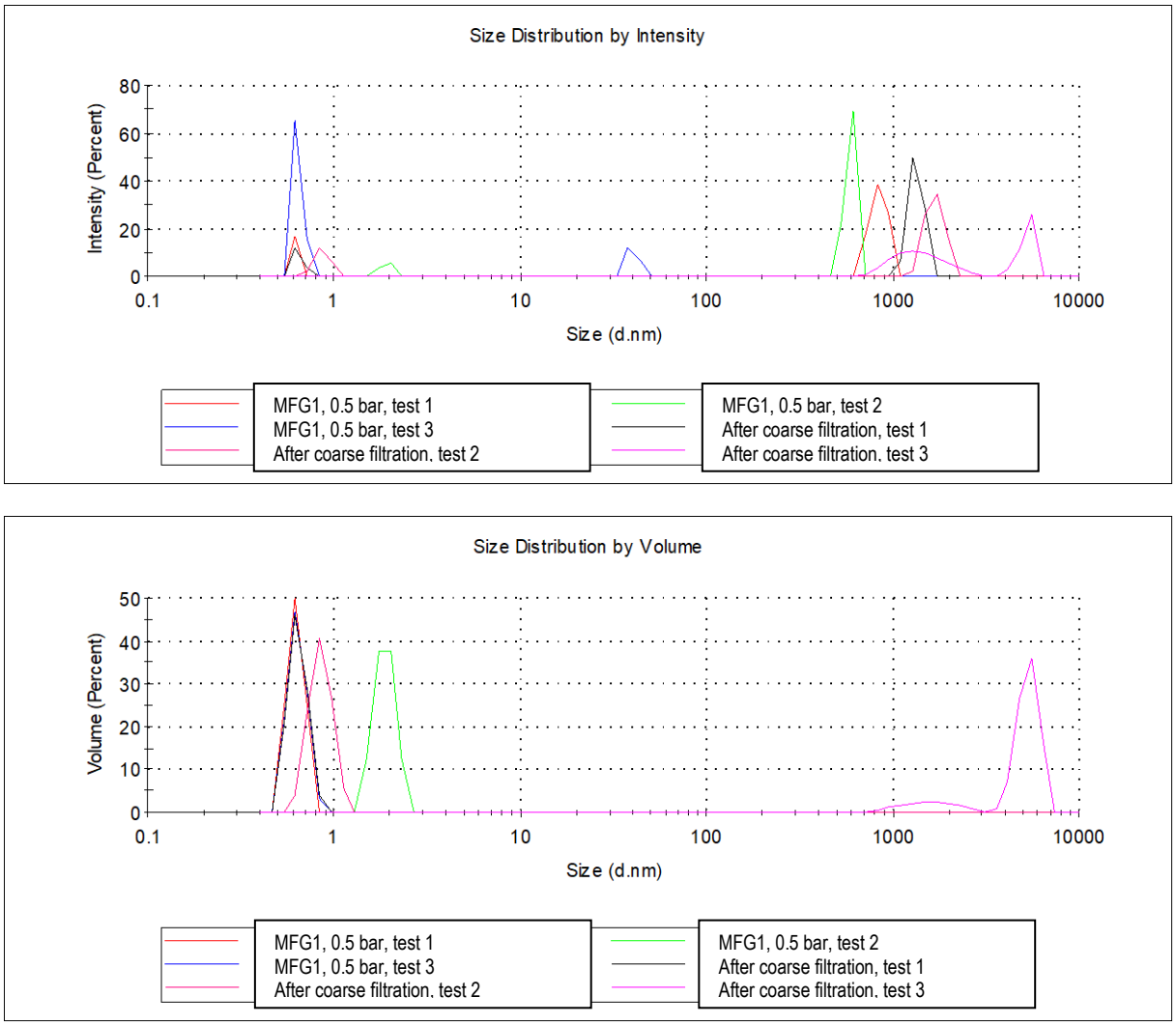

Figure 4.3 and 4.4. Size distribution by intensity and by volume for MFG1 at 0.5 bar, results from the Zeta Sizer.

Due to the irregularities of the analyze method, this method was not taken in consideration in further analysis for other filtrations.

4.3 Ultrafiltration

For the ultrafiltration, the flux was larger than for the microfiltration, see Figure 4.5. The ultrafiltration flows follow the appearance of MFG1 and MFG2, with a significantly decrease in flux over time, but an increase of flux with the increasing pressure.

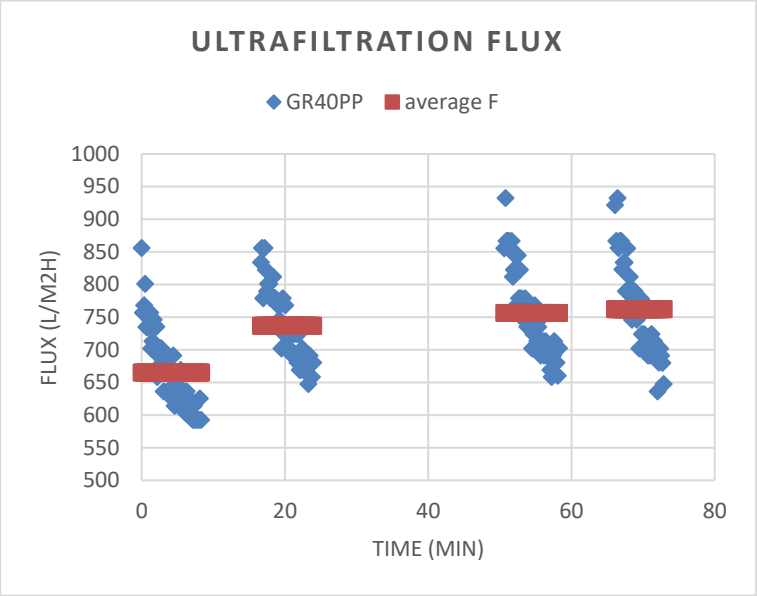

Figure 4.5. The flux for the sample water for each of the four pressures over time, from left to right the clusters represent 1.5 bar, 2.0 bar, 2.5 bar and 3.0 bar.

However, as seen in Table 2.1, the flux for ultrafiltration should not exceed 100 $Lm^{-2}h^{-1}$. As seen in Figure 4.5, none of the analyzed pressures could comply to this limit, as the average fluxes were measured to 650-750 $Lm^{-2}h^{-1}$.

4.3.1 Pure water flux

The PWF was calculated for the ultrafiltration, see Table 4.7.

Table 4.7. The permeability measured with PWF before and after filtration, and the calculated decrease in permeability.

	GR40PP
Permeability before filtration ($Lm^{-2}h^{-1}$)	447.16
Permeability after filtration ($Lm^{-2}h^{-1}$)	358.96
Decrease in permeability (%)	19.7 %

The decrease in permeability lays in the same interval as for the microfiltration. However, the permeability itself is higher than for MFG1 and MFG2.

4.3.2 Determination of concentration with EDTA-titration

An EDTA-titration was made to estimate the concentration of zinc chloride, in the permeate as well as the retentate, see Table 4.8. The same dilution series were used for all varieties of filtration, as the concentrations did not majorly differ between the filtration types.

Table 4.8. Concentration of zinc chloride in the wastewater, before and after ultrafiltration at different pressures. Calculated from EDTA-titration

Membrane/Concentration ZnCl2 (g/L) at different pressures				
Before UF	147.2			
	1.5 bar	***2.0 bar***	***2.5 bar***	***3.0 bar***
GR40PP	132.2	135.6	149.2	143.8

Just as with the PWF, the results of the EDTA-filtration did not significantly differ from the results from the micro filtrations.

4.3.3 Total solids- and ash measurements

To estimate the concentration of cellulose as well as zinc chloride, a total solids- and ash measurement were made, see Table 4.9. Notable is that the concentration of cellulose is calculated from the concentration of zinc chloride, and thus not measured on its own. Consequently, the concentration value of cellulose can in some cases show zero, as the calculations show it – however, it is most unlikely that the concentration in fact is zero (as in the case of 2.0 and 2.5 bar).

*Table 4.9. Concentration of cellulose and zinc chloride in the wastewater, before and after ultrafiltration at different pressures. Calculated from total solids- and ash measurements. *Calculations were made from the zinc chloride value and in this case showed a negative concentration*

Membrane, pressure (bar)	**Cellulose (g/L)**	**Zinc Chloride (g/L)**
Before UF	54.6	101.4
GR40PP 1.5	73.8	78.4
GR40PP 2.0	0*	195.3
GR40PP 2.5	0*	273.5
GR40PP 3.0	13.2	143.4

In these measurements, once again the concentration of zinc chloride in the permeate exceeded the concentration in the retentate in most of the measurements. However, it can be noted that the cellulose to some degrees do stay in the retentate.

4.4 Nanofiltration

After the microfiltration, a nanofiltration was made to extract the zinc chloride from the wastewater stream. The two different membranes used, Dow NF270 and Alfa Laval NF99HF, performed a likewise flow at 10 bar, but at 11 bar, NF270 decreased its flow in comparison to 10 bar, while the flow with NF99HF increased.

Table 4.10. The average flux through the membranes at different pressures

	Flux ($Lm^{-2}h^{-1}$)	
	10 bar	**11 bar**
Dow NF270	22.7	18.7
Alfa Laval NF99HF	29.9	31.0

4.4.1 Pure water flux

The PWF was calculated for nanofiltration membranes, see Table 4.11.

Table 4.11. The permeability measured with PWF before and after filtration, and the calculated decrease in permeability

	Dow NF270	**Alfa Laval NF99HF**
Permeability before filtration ($Lm^{-2}h^{-1}$)	21.22	30.27
Permeability after filtration ($Lm^{-2}h^{-1}$)	14.46	22.45
Decrease in permeability (%)	31.9 %	25.8 %

As can be seen in Table 4.11, the change in permeability was lower in NF99HF. In NF99HF the permeability was also higher in general, leading to a faster process.

4.4.2 Determination of concentration with EDTA-titration

An EDTA-titration was made to estimate the concentration of zinc chloride, in the permeate as well as the retentate, see Table 4.12. The same dilution series were used for all varieties of filtration, as the concentrations did not majorly differ between the filtration types.

Table 4.12. Concentration of zinc chloride in the wastewater, before and after nanofiltration at different pressures. Calculated from EDTA-titration

Membrane/Concentration ZnCl2 (g/L) at different pressures			
After crossflow MF	207.6		
	Permeate, 10 bar	***Permeate, 11 bar***	***Retentate***
Dow NF270	103.8	141.7	312.4
Alfa Laval NF99HF	116.3	97.2	423.2

The concentration of zinc chloride in the permeate should be lower than the feed, and the concentration in the retentate should be as high as possible. Note that the retentate is derived from both experiments, 10 bar and 11 bar.

From Table 4.12 it can be seen that the most beneficial membrane according to the EDTA-titration is NF99HF at 11 bar, as this is the membrane and pressure where the permeates concentration is at its lowest, and the retentates concentration is at its highest.

4.4.3 Total solids- and ash measurements

To estimate the concentration of cellulose as well as zinc chloride, a total solids- and ash measurement were made, see Table 4.13. Notable is that the concentration of cellulose is calculated from the concentration of zinc chloride, and thus not measured on its own. Ideally, if the microfiltration had worked perfectly, the amount of cellulose would be close to zero. For the nanofiltration, the amount of zinc chloride should be lowered from before to after the filtration.

Table 4.13. Concentration of cellulose and zinc chloride in the wastewater, before and after nanofiltration at different pressures. Calculated from total solids- and ash measurements.

Membrane, pressure (bar)	Cellulose (g/L)	Zinc Chloride (g/L)
After crossflow MF	42.1	118.5
Dow NF270, 10	23.6	112.5
Dow NF270, 11	21.7	127.5
Dow NF270, retentate	66.6	239.9
Alfa Laval NF99HF, 10	10.1	116.7
Alfa Laval NF99HF, 11	7.9	130.7
Alfa Laval NF99HF, retentate	25.6	397.9

As can be seen, the amount of zinc chloride has only been lowered in two cases – with both membranes at 10 bar. In the retentate, where the concentration of zinc chloride should increase, the largest increase was made with NF99HF.

4.5 In-depth analysis

The results of the in-depth analyzes of crossflow-filtration with MFG2, and nanofiltration with NF99HF at a higher pressure.

4.5.1 Crossflow-microfiltration

For the crossflow-filtration, both methods for determination of concentration were used, as well as the pure water flux-measurements, see Table 4.14.

Table 4.14. Results for crossflow filtration and dead-end filtration, with MFG2 at 0.7 bar and room temperature

	Before MF	Crossflow MF	Dead-end MF
Average flux ($Lm^{-2}h^{-1}$)		101.6	316.6
Decrease in permeability (%)		7.5%	22.0 %
		EDTA-titration	
C zinc chloride permeate (g/L)	147.2	207.6	144.5
C zinc chloride retentate (g/L)		144.5	143.6
		Total solid and ash measurements	
C cellulose permeate (g/L)	54.6	42.1	52.4
C cellulose retentate (g/L)		13.0	28.8
C zinc chloride permeate (g/L)	101.4	118.5	104.2
C zinc chloride retentate (g/L)		120.4	132.9

For the crossflow filtration, the decrease in permeability were only measured to 7.5 %, only a third of the decrease for dead-end filtration.

4.5.2 Nanofiltration at higher pressure

For the nanofiltration at 20 bar, both methods for determination of concentration were used, as well as the pure water flux-measurements, see Table 4.15.

*Table 4.15. Results for nanofiltration with NF99HF at 20 and 10 bar, and room temperature. *Calculations were made from the zinc chloride value and in this case showed a negative concentration*

	Before NF	NF99HF 20 bar	NF99HF 11 bar
Average flux ($Lm^{-2}h^{-1}$)		28.3	31.0
Decrease in permeability (%)		6.2%	25.8 %
		EDTA-titration	
C zinc chloride permeate (g/L)	207.6	119.9	97.2
C zinc chloride retentate (g/L)		381.6	423.2
		Total solid and ash measurements	
C cellulose permeate (g/L)	42.1	26.4	7.9
C cellulose retentate (g/L)		0*	25.6
C zinc chloride permeate (g/L)	118.5	102.4	130.7
C zinc chloride retentate (g/L)		394.8	397.9

The results from the analysis of the nanofiltration at 20 bar compared to 11 bar indicated that the only improvement for the higher pressure were the lower permeability decrease. Apart from that, the results were mainly in favor for the lower pressure, as both the concentrations of zinc chloride (according to EDTA-titration) and the concentration of cellulose (according to total solids- and ash) where better at 11 bar compared to 20.

5 Discussion

5.1 Coarse filtration

When applying the coarse filtration to a larger scale process, one could argue that only filtration at 425 µm and 250 µm was necessary. This because no fouling was detected at denser filters, and therefore the use of them could possibly be a waste of filtration.

However, measurements of the water were only carried out before and after all four of the filters. To ensure the uselessness of the 125 µm and 60 µm filter, it is encouraged in future studies to analyze the wastewater in between every coarse filter, and thereafter perform a more detailed analysis of the matter.

Both methods for measurements of concentration detected a 10 % decrease of zinc chloride concentration. Most likely this decrease is due to the larger compounds that were separated from the wastewater. These compounds were most likely cellulose, but the cellulose may have bound some zinc chloride to itself, therefore reducing the amount of zinc chloride after the filtration.

The total solids- and ash measurements showed an increase of cellulose in the wastewater after the coarse filtration. The most probable reason for this is that the measurements have a large standard deviation and hence the difference was not detectable, more about this in section 5.4.1.

5.2 Removal of cellulose

From the general analysis it can be derived that microfiltration is sufficient to remove some cellulose from the wastewater, see Table 5.1. The permeate flow of ultrafiltration is too high as the flow should be under 100 $Lm^{-2}h^{-1}$ (see Table 2.1), ruling out the ultrafiltration as a suitable method. This together with the results in concentration from ultrafiltration, that do not differ significantly from the microfiltration, concludes that microfiltration will be adequate to remove the cellulose.

*Table 5.1. Overall results for removal of cellulose with the help of micro- and ultrafiltration. The numbers in the parenthesis are the pressures used for the specific result. *Calculations were made from the zinc chloride value and in this case showed a negative concentration*

	Before MF	**MFG1**	**MFG2**	**MFG5**	**GR40PP**
Average flux ($Lm^{-2}h^{-1}$)		591.1 (1.0)	430.5 (1.0)	3460.1 (0.3)	762.5
Decrease in permeability (%)		18.0 %	22.0 %	7.9 %	19.7%
	EDTA-titration				
C zinc chloride permeate (g/L)	147.2	160.4 (0.7)	146.5 (1.0)	146.7 (0.7)	149.2 (2.5)
C zinc chloride retentate (g/L)		152.6 (0.7)	143.6 (0.7)		
	Total solids- and ash measurements				
C cellulose permeate (g/L)	54.6	0* (1.0)	26.0 (0.5)	40.9 (0.7)	0** (2.5)
C cellulose retentate (g/L)		48.8 (0.7)	28.8 (0.7)		
C zinc chloride permeate (g/L)	101.4	252.0 (1.0)	129.4 (0.5)	113.4 (0.7)	273.5 (2.5)
C zinc chloride retentate (g/L)		112.6 (0.7)	132.9 (0.7)		

To conclude which of the microfiltration membranes and pressure used that had the best results, all analyses must be taken in consideration. There was no method clearly superior to another, but with the elevated permeate flow of MFG5, this membrane was phased out quickly.

For MFG1, the results in many regards were irregular, and in some cases (as in the case of total solids- and ash analysis) uncanny, resulting in an uncertainty in the results. Therefore, the results of MFG2 were to be considered the best among the selected membranes.

However, it is important to note that MFG2 did only remove 15 % of the cellulose from the wastewater. Consequently, the technique must be improved and further analyzed before any real conclusions can be drawn.

During the crossflow analysis of MFG2 the permeability reduced to almost a third of the permeability reduction with dead end filtration. With that, the need for cleaning of the filter can

be reduced more and still result in a highly functioning process. The crossflow filtration also showed a larger decrease of cellulose in the permeate, however, it was only a 7 % decrease compared to the dead-end filtrations 1 % decrease. With this in mind, it is hard to proclaim one method more suitable than the other, as none is sufficiently good. However, it is safe to say that the crossflow filtration needs to be further analyzed, as the results indicated that the method was more sufficient than the dead-end filtration.

5.3 Partition of zinc chloride and water

For the partition of zinc chloride and water, both membranes used performed well, however, for the nanofiltration it was clear that NF99HF tend to have better results, see Table 5.2.

*Table 5.2. Overall results for partition of zinc chloride and water with the help of nanofiltration. The numbers in the parenthesis are the pressures used for the specific result. *Calculations were made from the zinc chloride value and in this case showed a negative concentration*

	Before NF	**Dow NF270**	**Alfa Laval NF99HF**
Average flux ($Lm^{-2}h^{-1}$)		22.7 (10)	31.0 (11)
Decrease in permeability (%)		31.9 %	25.8 %
	EDTA-titration		
C zinc chloride permeate (g/L)	207.6	103.8 (10)	97.2 (11)
C zinc chloride retentate (g/L)		312.4	423.2
	Total solids- and ash measurements		
C cellulose permeate (g/L)	42.1	21.7 (11)	7.9 (11)
C cellulose retentate (g/L)		66.6	25.6
C zinc chloride permeate (g/L)	118.5	112.5 (10)	116.7 (10)
C zinc chloride retentate (g/L)		239.9	397.9

For the removal of zinc chloride in the permeate the titration and total solids- and ash measurements showed different results; where titration favored NF99HF and total solids- and ash measurements favored NF270. The amount of cellulose in the wastewater did reduce during the nanofiltration, however, still not to the level aspired (close to zero).

As for the concentration of zinc chloride in the retentate, both methods showed a higher concentration with NF99HF, but the results themself differed a lot. But all things considered, NF99HF were chosen to be examined in more detail.

NF99HF was thus tested at 20 bar as well and compared to the results at 11 bar some differences could be detected. Most notably was the permeability decrease, as was only measured to 6.2 % compared to 25.8 % at 11 bar. Nevertheless, the concentration measurements did differ in their results. The EDTA-titration showed a favor for the lower pressure, as according to these measurements a larger amount of zinc chloride was held back at 11 bar compared to 20 bar.

The total solids- and ash measurements on the other hand favored the higher pressure, as these measurements showed a larger hold back as these conditions. The total solids- and ash measurements also showed a greater hold back of cellulose at the lower pressure. All this considered, it is hard to state that a higher pressure necessarily is a better, as the determination of concentration with EDTA was proven to be more sufficient (see section 5.4.1 below). Therefore, it can be stated that without further studies, it is difficult to determine the pest pressure. On the other hand, what can be stated is that nanofiltration works to separate zinc chloride and water to some extent, and with further analysis, most likely a method for zinc chloride recovery can be found.

5.4 Analysis of data

5.4.1 Concentration measurements

Both the titration with EDTA and the total solids- and ash measurements calculate the concentrations in the samples. To evaluate the accuracy of the methods, both were tested with a standard solution, see Table 5.3.

Table 5.3. Difference from setpoint for measurements of concentration with EDTA-titration and total solids- and ash measurements.

	Accuracy	Standard deviation
Titration with EDTA	0.967	0.00856
Total solids- and ash measurements	1.04	0.196

The results showed that both methods are accurate, however the total solids- and ash measurements had a larger standard deviation. This means that titration with EDTA is giving a more accurate results with smaller error, but that the results for total solids- and ash measurements have a higher risk of being incorrect.

Taken this in consideration, when results from the two methods are conflicting, the results from the EDTA-titration should carry more weight.

The high accuracy and the small standard deviation of titration with EDTA also indicate that all measurements of a sample should be approximately indistinguishable, however, they are. When calculating the deviation of the measured concentrations, the EDTA results have an average deviation of 0.137, 16 times larger than the standard deviation of the standard solution. Given as no alternations were being made to the method of measuring the concentration, it can be argued that the concentration does differ in the samples.

This can be explained by the heterogeneous nature of the samples, as the cellulose in the samples is bound to the zinc chloride, creating a higher concentration of zinc chloride in the presence of cellulose compared to where cellulose is not present.

5.4.2 Calculations of cellulose concentration

When calculating the concentrations using total solids- and ash measurements, a standard curve was used to determine the concentration of zinc chloride as it was detected that the measurements themselves measured to low of a value, see section 3.6.3. The zinc chloride concentrations are thus a product of an upscaled value, and with that, the cellulose results were calculated from these zinc chloride results.

The conclusion of this is that all calculations of a cellulose concentration are indirect values, and if the concentration of zinc chloride is measured incorrect, so will the cellulose concentration be. This is detected in some of the results, as in some cases, the cellulose concentration appeared to be negative, something that is not possible.

5.4.3 The equilibrium during EDTA-titration

During titration with EDTA, the change of color from purple to blue was detected visibly. However, this was proven to be difficult as the color change oscillated between the two colors.

This change is believed to be traced back to the additive of ammonia to the sample, as ammonia is used to raise the pH to 10 (enabling the reaction with EDTA). Ammonia and zinc chloride are reacting on its own as well as with the EDTA, creating zinc hydroxide [22]. The equilibrium between zinc chloride and zinc hydroxide is believed to be the reason for the oscillating color change, as the equilibrium enables zinc hydroxide to react back to zinc chloride, therefore changing back the color from blue to purple, even after an initial color change.

Apart from reacting with the zinc chloride, the ammonia also formed clouds in the samples when it was added to undiluted, micro filtrated wastewater, see Figure 5.1. These clouds are believed to be a reaction of the cellulose in the wastewater and the ammonia, however, the composition of them is not known.

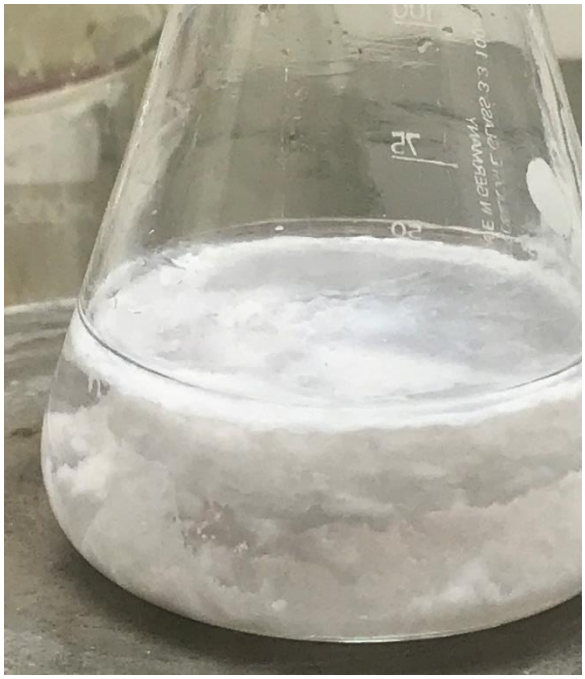

Figure 5.1. Clouds formed in the micro filtrated wastewater after addition of ammonia.

5.4.4 The dismissal of particle size measurements

Even though particle size measurements were made for all samples of this trials, non are shown in this report. This is due to the irregularities of the results. When analyzing the results of the particle size measurements, it was noted no correlations or resemblance was established between samples of seemingly equal character. The results appeared to be randomized, as results from the same vial could show no signs of particles in one measurement, but particles of all sizes in the next.

However, due to the data conducted with the EDTA measurements (section 5.4.1), it can be argued that these results may not be false. The titration indicate that the heterogeneous nature of the samples interferes with the measured results, and with that in mind, it would not be surprising if the results of the particle size also were irregular. Thus, the results would still be as hard to interpret, as no clear distinctions could be made in the results from before and after filtration, and therefore it would still be difficult to draw any conclusions from the trials.

Apart from the irregularities in the results from the Zeta Sizer, the method itself possibly had been insufficient for measuring the particles. The Zeta sizer mathematically converts all particles to spheres in its calculations, and as cellulose is a large, non-spherical molecule, the estimation incorrect.

5.5 Inconsistence in measurements

5.5.1 Replicates of samples

Due to the limited time of the project, as well as the time requirements for conditioning of the membranes and thereafter filtration through them, all samples could not be replicated several times. Many filters were only tested once at each pressure, as the time was not sufficient to do multiple replicates of each pressure. Because of this, the results in the study should be seen as an indicator for how to move forward in future studies.

5.5.2 Room temperature

All filtrations were carried out in room temperature, to simulate conditions most likely to occur in practical application of the method. However, the room temperature was not consistent as the outdoor temperature affected it. With the gradually decreasing temperature outdoor, the temperature in the apparatus hall also decreased. This was seen as the temperature in the room was measured during each trial; however, the temperature drop was never more than 1-2 °C.

The temperature of the room, and thus the temperature of the sample, can affect the permeate flux negative, as a decrease in temperature can cause a decrease in flux. However, as no replicates were made of the trials, this cannot be proven, only assumed. Trials that occurred during colder days (i.e., NF99HF at 20 bar compared to 11) could be affected by the lowered room temperature, and that would also explain the lowered permeate flow for these trials. However, it is uncertain how much of a difference the room temperature would actually do.

5.5.3 Volume reduction

When performing the microfiltration, the volume reduction was set to be 80 %. However, it was proven difficult to control the permeate flow and thus the reduction could differ in the span of 70-90 %.

The same problem was faced with the nanofiltration. With the nanofiltration, 150 ml were set to permeate for each pressure; however, the membranes sensitivity for pressure changes (when resetting the pressure back to 0) resulted in a larger amount of permeate collected. Consequently, the amount of retentate differed as well.

This inconsistent reduction resulted in a difference in concentrations, that were hard to calculate. As the retentate concentration of held back material increased with the increase of reduction, an inconsistent volume reduction resulted in that the results could not be compared.

For the microfiltration, where the retentate was not analyzed in large quantities, this was neglected and seen as a natural difference in results. But for the nanofiltration, where the concentration of zinc chloride in the retentate were significant, an estimated value was calculated to create comparable results. This meant that NF270, that initially had a larger concentration of zinc chloride in its retentate, but also a higher volume reduction compared to NF99HF, had a smaller concentration compared to NF99HF, when the reduction was considered.

5.5.4 Unattainable results

For the concentration measurements, some of the results were contra intuitively and unreasonable, as the concentration for the permeate could be noticeable higher than the concentration in the feed (see the EDTA-measurements for MFG1). The reason for these irrational results might be the wastewaters heterogenous nature, however this is not confirmed. Therefore, the concentration results should be considered with care and only be seen as indicators for how the membrane in question performs, not as indisputable facts.

6 Conclusions

To purify the wastewater from the textile recycling process, three filtrations must be made. First, coarse filtration; to remove larger fragments of cellulose. Secondly, microfiltration; to remove all excessive cellulose from the water stream. Third and lastly, nanofiltration; to separate the zinc chloride and the water from each other.

The result from this study indicate that purification of the wastewater stream is possible, and that the zinc chloride and the water can be separated, however, the study presented in this paper does not show a complete purification or separation. In the future, more membranes must be tested to find a filtration more compatible with the process. Furthermore, the pressures used for the separate filtrations must be optimized.

6.1 Further work

A number of further analyses could be made to this subject. First and foremost, this analysis was a screening, designed to control the possibilities of filtration. Now when it is known that membrane filtration of the wastewater is possible, testing must be made to control which membranes, pressures and flows that should be used, and replicates of the trials must be made.

Additionally, the clouds formed when adding ammonia to the micro filtrated wastewater should be analyzed, as these clouds appeared unexpected and could not be explained.

7 List of Abbreviations

EDTA	Ethylenediaminetetraacetic acid
HIn^{2-}	Indicator
HY^{3-}	Ethylenediaminetetraacetic acid
H^{+}	Hydrogen ion
MF	Microfiltration
NF	Nanofiltration
NF270	Dow NF270
NF99HF	Alfa Laval NF99HF
PWF	Pure water flux
UF	Ultrafiltration
$ZnCl_2$	Zinc Chloride
$ZnIn^{-}$	Zinc ion-indicator complex
ZnY^{2-}	Zinc ion-EDTA complex
Zn^{2+}	Zinc ion

8 Reference List

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