Lappeenranta – Lahti University of Technology LUT

School of Engineering Science

Master's Programme in Chemical Engineering

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SEPARATION METHODS FOR INDUSTRIAL WASTEWATERS CONTAINING ACID AND METAL SALTS

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Erotusmenetelmät happoa ja metallisuoloja sisältäville teollisuuden jätevesille

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Vesi kasvattaa jatkuvasti arvoaan sen kysynnän kasvaessa ja tarjonnan väistämättä vähentyessä maapallolla. Entistä tehokkaampia, helppokäyttöisempiä ja halvempia erotustekniikoita tarvitaan, jotta vedenkäsittely saataisiin mahdollisimman korkealle tasolle, mahdollisimman laajalla alueella. Tässä työssä keskityttiin erityisesti suuria volyymeita käyttävien teollisuudenalojen suolapitoisten ja happamien jätevesien erityisominaisuuksiin ja niiden vaikutuksiin jätevedenkäsittelyssä.

Tutkimuksen tavoitteena oli kartoittaa erilaisia mahdollisia tekniikoita teollisen mittakaavan jäteveden käsittelylle, joista membraanierotus vaikutti erityisen lupaavalta. Työssä käsiteltiin tarkemmin eri membraanierotustekniikoiden periaatteita, eroavaisuuksia sekä erotusmekanismeja. Nanosuodatus valikoitui lupaavimmaksi tekniikaksi ja siinä käytettyjä kalvoja ja niiden rakennetta sekä erotukseen vaikuttavia ilmiöitä käsiteltiin tarkemmin.

Kokeellisessa osassa erilaisten nanosuodatuskalvojen tehokkuutta tutkittiin useilla erillisillä liuoksilla, jotka mallinsivat tutkittujen teollisuusalojen jätevesiä. Lopuksi membraaneja karakterisointiin niiden ominaisuuksien, kulumisen ja mahdollisen ”fouling” asteen määrittämiseksi.

Työn positiiviset tulokset osoittavat erityisesti kaksiarvoisen metalli-ionin erottelun olevan erittäin tehokasta sekä ionien erottelutehokkuuden kasvun happopitoisessa liuoksessa. Kaikki kalvot myös kestivät lyhytaikaisen käytön erittäin happamissa olosuhteissa.

ABSTRACT

Lappeenranta – Lahti University of Technology LUT
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Separation methods for industrial wastewaters containing acid and metal salts

Master’s thesis

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72 pages, 45 figures, 9 tables, and 4 appendix

Examiners: Prof. Mika Mänttäri, M.Sc. Sakari Modig

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Water is continuously growing in value due to increased usage and decreasing supplies. More effective, simple, and economical separation methods are needed to increase wastewater treatment efficiency around the world. Focus on this study was high volume industrial wastewaters with properties such as high acidity and salinity.

The goal for this study was to map out different separation techniques for industrial scale wastewater treatment, from which membrane separation showed most potential. A closer look at different membrane separation process principles, separation mechanisms and differences between them was made. Nanofiltration had the most potential based on the research, therefore membranes and membrane systems currently used as well as separation mechanisms were studied more closely.

In the experimental part filtrations with different nanofiltration membranes were done to define their separation performance in laboratory scale tests. Wide variety of different types of solutions were used including real industrial wastewater. Lastly, membrane characterization was done to define differences between membranes that could explain differences between separation efficiency. Characterization was done to used and new membranes in order to study possible changes in membrane properties.

Results from this study were in line with the information found from literature. Multivalent cation rejection was extremely good and addition of acid in the feed solution increased permeate flux and zinc sulphate rejection while decreasing sodium sulfate rejection. All membranes did also sustain this short-term use in highly acidic environment without substantial change in performance.

ABBREVIATIONS AND LIST OF SYMBOLS

Abbreviations

FTIR	Fourier-transform infrared spectrometry
HCl	Hydrochloric acid
ICP	Inductively coupled plasma spectrometer
IEP	Isoelectric point
KCl	Potassium chloride
MWCO	Molecular weight cut off
Na_2SO_4	Sodium sulfate
NF	Nanofiltration
RO	Reverse osmosis
SD	Standard deviation
TFC	Thin film composite membrane
TOC	Total organic carbon
UF	Ultrafiltration
$ZnSO_4$	Zinc sulfate

Symbols

A	Surface area of membrane
A_s	Streaming channel area
C	Concentration

C_F	Concentration in feed
C_P	Concentration in permeate
i	Van´t Hoff factor
I	Current
J	Permeate flux
L_s	Streaming channel length
m_p	Mass of permeate
P	Pressure
R	Ideal gas constant
R_s	Rejection
R_f	Resistance due to fouling layer
R_m	Resistance due to membrane
R_p	Resistance due to polarisation layer
T	Temperature
t_p	Time
Q	Permeate flow
π	Osmotic pressure
ε	Dielectric coefficient
ξ	Zeta potential
θ	Contact angle
μ	Viscosity

CONTENTS

LITERATURE PART

1. Metal salts and acid containing industrial wastewaters

As water is constantly rising in value as a resource, multiple different industries with high water consumption are struggling with issues concerning wastewater treatment. The impact of disposed wastewater is massive for the environment and wastewater recycling and pollution is considered as the most crucial problems of the current century (Choudhary, Peter et al. 2020). Industrial wastewaters are a large concept, since different industries produce wastewaters with different compositions. The focus in this study will be on waters containing metal salts and acids.

Although regulations and treatment methods have improved treatment of wastewaters, limitations in these regulations differ depending on the country and continent. Advances in technology and new technologies are being made but issues such as high cost, low efficiency and sensitivity still limit the treatments (Pooja, Kumar et al. 2021). As water is also constantly rising in value as a resource with the consumption globally rising, multiple different industries with high water consumption are especially struggling with these wastewater treatment issues. Mining, electroplating, and textile manufacturing are great examples of industries where volumes of wastewater are high, and treatment can be difficult due to dissolved materials.

In mining operations different deposits can be targeted in order to extract materials such as metals, coal, or gems. Mining has potential to cause damage to environment and humans in different ways one being the wastewater developed by the process. Large amount of water is used in the process which gets polluted after being in contact with metals and sulphides (Hatar, Rahim et al. 2013). Mining wastewater contains dissolved metal ions, sulphate and it is highly acidic, which makes it toxic to aquatic organisms (Samaei, Gato-Trinidad et al. 2020). Untreated and poorly treated mining wastewater can cause severe issues, such as deformation, reduced reproduction, organ damage, cancer and death to humans and animals (Samaei, Gato-Trinidad et al. 2020, Pooja, Kumar et al. 2021).

Electroplating is electrochemical method used to add a metallic protective or decorative layer to surface of the component. Electroplating is done in a chemical bath by using a current to force metal coating on the object. Metals used to plate with end up in the wastewater after rinsing and from the bath where electroplating was done. Wastewaters from electroplating contain different metals, such as copper, zinc and nickel and have low pH. (Mathew 2008) Electroplating process consumes a lot of water and dissolved metal ions can cause similar effects to humans and animals as ions dissolved in mining wastewater (Pooja, Kumar et al. 2021).

In textile manufacturing polymer of some sort is extruded through a spinneret to produce a filament. Before this process called spinning, the polymer needs to be first converted to semi liquid state and after the extrusion manufactured filaments need to be coagulated in a chemical bath. This requires a lot of chemicals and water to wash the chemicals off later which results in polluted wastewater. The generated wastewater contains toxic wastes such as acids, metal salts, and carbon disulfide. (Woodings, Woodings 2001)

Wastewaters in all of these three different industries contain metals or metal salts and have high acidity and/or low pH. These issues cause the treatment to be costly and often ineffective at removing these toxic substances. Different possible methods for removal of metal salts and acid and their advantages and disadvantages are compared next.

2. Metal salt and acid removal methods

Conventional ways of treating water with dissolved metal substances are membrane separation methods, chemical precipitation, and ion exchange (Borbély, Nagy 2009). Other possible treatments are physical treatments such as cold crystallization and evaporation. Principles, advantages, and disadvantages considering industrial wastewater treatment for these methods are next presented in this chapter.

2.1. Chemical precipitation

Chemical precipitation is a method where dissolved substances are converted to a solid phase with chemical treatment. The conversion of metals is done by adding chemicals to the wastewater. These chemicals react with metal ions present and form insoluble precipitates. Precipitates then form a solid phase which can be removed from the solution via filtration or sedimentation. (Fu, Wang 2011)

Most common precipitation methods are hydroxide precipitation and sulphide precipitation in which either a hydroxide source or a sulphide source is added to the solution. The solubility of metals depends on solution pH value which hydroxide rises to precipitate metals as their respective hydroxides (BrbootI, AbiD et al. 2011). Sulphide on the other hand has high reactivity with heavy metal ions and hence has faster reaction rate (Zainuddin, Mamat et al. 2019). Zainuddin et al. stated in their study that optimal pH for zinc removal is 9 with hydroxide precipitation and 10 with sulphide precipitation.

Chemical precipitation as a method is effective and widely used method. Advantages for it are that it is relatively easy to operate, it has potential to remove most of the metals and operating is also cheap (Kurniawan, Chan et al. 2006). However, precipitation also has multiple drawbacks like large amounts of created slurry which is expensive to dispose and has long term environmental impact (Kurniawan, Chan et al. 2006). The separation of multiple metals simultaneously is difficult due to different preferred pH values between metals, and additionally highly acidic solutions have increased chemical consumption when pH is controlled or solution is neutralised (Zainuddin, Mamat et al. 2019). In sulphide

precipitation dosing and process control can be difficult due to high sensitivity of the process and toxic hydrogen sulphide gas can be released as a side product (Zainuddin, Mamat et al. 2019). Precipitation is also relatively slow process which can be a disadvantage when treating large amounts of wastewater (Kurniawan, Chan et al. 2006).

2.2. Ion exchange

Ion exchange is already being used in example for wastewater treatment in electroplating industry and for water demineralizing. In ion exchange ion present in the solution is exchanged to ion attached to an immobile solid particle with the same charge. The immobile solid particle is often resin made from high molecular weight polyelectrolytes that can exchange some mobile ions for ions in the medium. Each resin has distinct number of mobile ions, which determines the maximum ions exchanged by each unit. This way unwanted substances such as metal ions and acids can be changed to either hydrogen or hydroxyl ions depending on their charge. After the capacity of each resin has been filled resins must be regenerated. Regeneration is a reverse reaction, where cation resin is regenerated with acid and anion resin is regenerated with sodium hydroxide. In regeneration the ions captured from wastewater are released and they can be disposed. (Cheremisinoff 2002)

Ion exchange is a very effective method to remove all unwanted ions from a solution and the treated water has less ions compared to water treated with chemical precipitation (Dąbrowski, Hubicki et al. 2004). Modern ion exchange resins also have possibility to be highly modified which leads to high selectivity in ion removal from the medium (Cheremisinoff 2002). Ion exchange does not require outside electricity or create any sludge unlike chemical precipitation, and it can also be used to remove acid from the wastewater (Abdulgader, Kochkodan et al. 2013).

Drawbacks for ion exchange mostly come from the capacity of ion exchange resins and the volume of water treated being relatively low. Ion exchange has been found effective by Kurniwan et. al. for solutions with metal ion concentrations up to around 100mg/L (Kurniawan, Chan et al. 2006). The cost of running ion exchange system comes from regeneration chemicals. Chemicals used for regeneration and the amount needed depends on used resins and substances removed. For example, cation resins are used for metal ion

removal. These resins require large amounts of strong regeneration chemicals, which can make ion exchange expensive to run with wastewaters that have high concentration of dissolved substance (Cheremisinoff 2002).

2.3. Cold crystallization and evaporation

Cold crystallization is a method for wastewater treatment where the solubility of an unwanted solute is reduced by lowering the temperature. This method is simply based on the effect temperature has to solubility. When temperature is lowered enough solute crystallizes and can be easily filtered out.

Other similar method for crystallization is eutectic freeze crystallization. The principle of lowering solution temperature is similar, but in freeze crystallization ice crystals are slowly formed, which makes the solute more concentrated in remaining water. Ice crystals, containing theoretically pure water, can be removed and eventually the unwanted solute crystallizes out at eutectic temperature. (Lewis, Nathoo et al. 2010)

Evaporation works in similar way, but instead of lowering the temperature the goal is to reach boiling point of the solvent. As the solvent evaporates the solute gets more and more concentrated in the remaining solution and eventually crystallizes out. Evaporation can be carried out until no solvent is left and only the impurities remain as solid materials.

As these crystallization methods can be extremely efficient and reach theoretically 100% purity, they are also expensive. Cold crystallization requires least energy, but it cannot reach high removal rates for the solutes. Both freezing and vaporizing solvent requires large amounts of energy and especially when dealing with large amounts of wastewater the electricity costs become too high for these methods to be reasonable as the main treatment method.

2.4. Membrane separation

Membrane separation methods have risen in popularity due to their good qualities like ambient operating temperature and high customisation for desired substances (Porter 1990). Membranes have been used on an industrial scale already for few decades and significant development both in membranes and in the separation processes have been made. Because of their high customisation, different types of membrane separation are being used in sea water treatment to drinking water, industrial wastewater cleaning, valuable material recovery, macromolecule separation, and smaller functions in medical field (Porter 1990, Juang, Shiau 2000, Cheremisinoff 2002, Charcosset 2012).

Membrane separation is based on the membranes ability to permeate one component easier than other because of differences in physical and chemical properties between the membrane and the components transporting (Mulder 1996). A driving force results this component transport through the membrane, which in the case of all processes discussed in this work is difference in pressure (Mulder 1996). Membrane density varies between filtration methods with ultrafiltration and microfiltration having the lowest density membranes and reverse osmosis having most dense ones (Mulder 1996). When membrane density increases in order to separate smaller molecular weight components the hydrodynamic resistance increases as well and higher driving forces are needed (Mulder 1996).

Membrane filtration can be done as dead-end or cross-flow filtration. In dead-end filtration the feed is directed straight to the membrane which causes the issue of cake formation. Cross-flow filtration decreases cake formation significantly by directing the feed tangentially across the membrane. This retentate flow can then be cycled back to the feed. Tsibranska et. al found that in batch mode operation cross-flow system had better rejection rates than dead-end. (Tsibranska, Tylkowski 2013, Cheremisinoff 2002) Both systems are presented in figure 1.

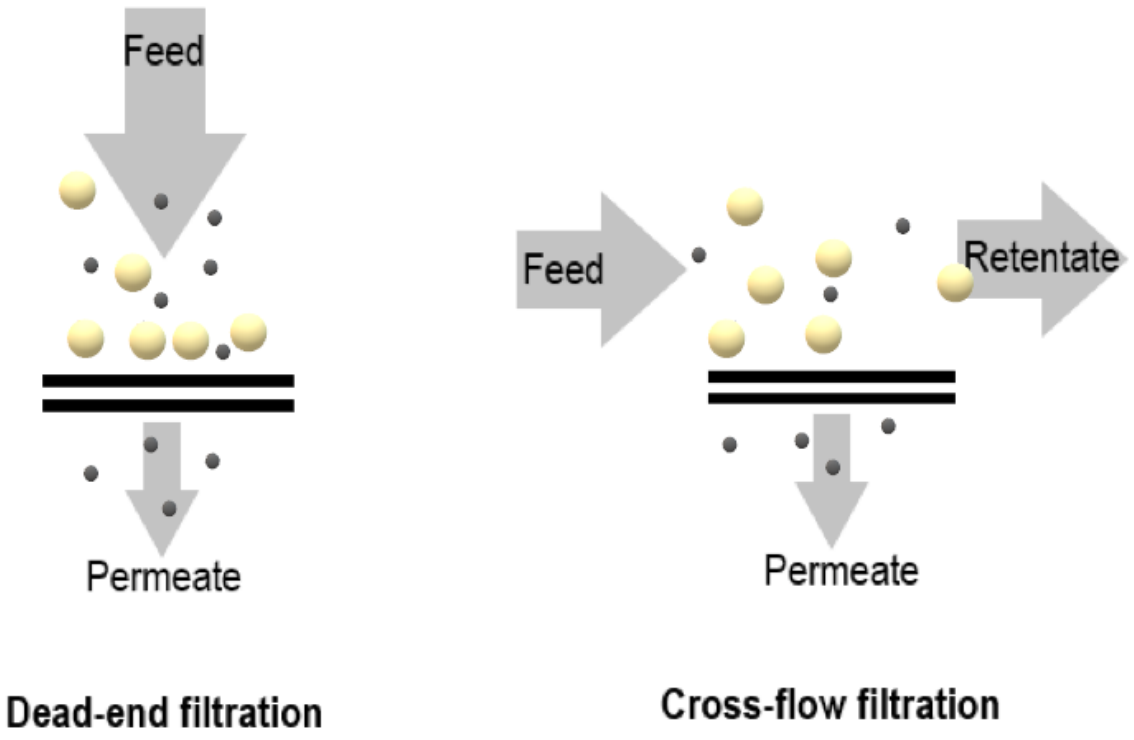

Figure 1. Dead-end and cross-flow filtration methods. (Tsibranska, Tylkowski 2013)

Out of all discussed separation methods membranes seem to have the most potential for metal ion removal, and they are already widely used in water and wastewater treatment (Cheremisinoff 2002). Membrane separation is effective, highly customizable, relatively low cost and easy to operate. Different membrane separation methods are next studied closer individually.

3. Types of membrane separation

Membrane separation can be divided into different membrane processes based on the membrane and driving force they use. Electrodialysis, microfiltration, ultrafiltration, nanofiltration and reverse osmosis are five processes that are commonly used in water treatment (Cheremisinoff 2002). In this study ultrafiltration, nanofiltration and reverse osmosis were chosen to be more closely studied to determine the best one for task in question. Characteristics and principles for these three membrane processes are next discussed more in detail individually.

3.1. Ultrafiltration

Ultrafiltration (UF) membranes are the least dense out of the selected membrane separation methods in this study. Because of lower density and larger pore size, targets for ultrafiltration are suspended materials and macromolecules. Largest industrial uses for ultrafiltration are paint recovery from water-soluble coat bases in electrocoating industry, protein recovery from cheese whey in food industry and concentration of waste-oil emulsion in machine manufacturing and maintaining industry (Cheremisinoff 2002). Ultrafiltration is a versatile membrane process which works best in solutions where entrained solids or dissolved ions are not present.

Lower density ultrafiltration membranes enable separation at lower pressures because they have lower membrane resistance compared to nanofiltration and reverse osmosis membranes (Cheremisinoff 2002). Ultrafiltration works in the same principle as normal filtration and the separation is roughly determined by the membranes pore size. When the feed solution is pressured, water and small molecules, such as salts pass through the membrane due to pressure difference between solutions on different sides of the membrane. Big advantages versus normal filtration come from the possibility to run cross-flow filtration to avoid membrane clogging with continuous retentate removal (Cheremisinoff 2002). These advantages make ultrafiltration membrane process superior to normal filtration in variety of analytical and industrial processes. Example of a cross-flow ultrafiltration system is presented in figure 2.

3.1.1. Rejection and permeate flux in ultrafiltration

Membranes with molecular weight cut off (MWCO) of 1000 to 100 000 Daltons and pore sizes of approximately 0.02 micrometres to 0.2 micrometres are considered ultrafiltration membranes (Wagner 2001). MWCO is the lowest molecular weight of particle that said membrane can separate with 90% rejection. In ultrafiltration the rejection is mostly determined by molecular weight. Molecules larger than the pore size of membrane are rejected by the membrane surface. Simultaneously particles which are smaller in size have pass through the membrane and are possibly captured by inertial impaction. Increasing flow rate decreases the rejection by inertial impaction. Beside flow rate, retention efficiency of ultrafiltration depends on particle size, concentration, pore size and pore length (Cheremisinoff 2002). The shape and flexibility of molecules is also good to take into consideration. More rigid molecules have higher rejection than flexible ones and temperature can increase the flexibility of molecules leading to decrease in molecular weight cut-off.

Flux is the volumetric flow rate trough a given area, in this case membranes surface area. Permeate flux for ultrafiltration membrane can be modelled as resistance series model. This model can be used to estimate flux through the membrane by determining resistances hindering the permeate flux (Grandison, Lewis 1996). Because ultrafiltration is considered as a sieving process, and ultrafiltration membranes have low fixed charge which has no impact on separation of metal ions, these mechanisms are much simpler than in nanofiltration process or reverse osmosis process. Flux estimation equation is presented in equation 1.

$$J = \frac{\Delta P}{\mu\left(R_m + R_f + R_p\right)} \tag{1}$$

Where	J	Permeate flux, kg/(m^2*h)
	P	Pressure, psi
	μ	Solvent viscosity, Pa*s
	Rm	Resistance due to membrane
	R_f	Resistance due fouling layer
	R_p	Resistance due to polarisation layer.

Membrane resistance can be measured by using pure water to determine how much resistance used or new membrane has. Fouling layer is layer which cumulates on the surface of used membrane due to fouling of particles this can take longer time and is harder to determine. Polymerization layer resistance is caused by the polymerization layer. This mechanism occurs when molecules are rejected by the top layer of a membrane. Rejection results into increase of said molecule close to membrane surface which makes permeance more difficult. This mechanism can be seen begin within first few minutes of filtration as a decrease in flux. Concentration increase in the feed solution will also decrease the flux. Thus the effect of fouling, polarisation and concentration increase to changes in flux can be hard to estimate individually. This makes theoretical estimation of flux difficult. (Grandison, Lewis 1996)

3.1.2. Possible use of ultrafiltration in this study

Because ultrafiltration membranes have no rejection of dissolved ions the ultrafiltration process needs to be combined with other unit operations if removal of ions is needed (Cheremisinoff 2002). It is economically advantageous to use ultrafiltration over tighter

membrane processes when larger contaminants such as organic molecules need to be removed due to lower processing pressure. Ultrafiltration could be in example paired with reverse osmosis in a wastewater treatment sequence, where ultrafiltration is first used to remove organic matter and large molecules from the solution and the permeate is fed to reverse osmosis system which then removes dissolved ions.

With solutions that are covered in this study, ultrafiltration process could be used as a pre-treatment to remove large and insoluble molecules before nanofiltration process or reverse osmosis process.

3.2. Reverse osmosis

Reverse osmosis (RO) is a pressure driven process in the same way as ultrafiltration. Unlike ultrafiltration reverse osmosis membranes are semipermeable and pore-less, and they are used to target especially dissolved contaminants. Larger molecules and insoluble matter can also be separated but it can quickly result in membrane fouling and higher operating costs than necessary (Bergman 2007).

Reverse osmosis is widely used in water purification and common applications are in example seawater desalination, generation of ultrapure water for industrial use, generation of high purity water for food industry and contaminant recovery from industrial waste water (Kucera 2015). Reverse osmosis membranes offer the finest filtration available, and they can be used to generate contaminant free water or to concentrate contaminants to feed water. Concentrating contaminants, also known as dewatering, has been found to be efficient treatment for high salinity wastewaters by Kim et al. (Kim, Kim et al. 2018).

In reverse osmosis high pressure exceeding the physical resistance and osmotic pressure is applied to the feed side to force water through the membrane surface. The physical resistance required depends on the membrane properties such as thickness and material. Osmotic pressure on the other hand depends on used solution and can be calculated with equation 2. (Bergman 2007)

$$\pi = icRT \tag{2}$$

Where	π	Osmotic pressure, bar
	i	Van ‘t Hoff factor
	c	Concentration, mol/l
	R	Ideal gas constant, J/(K*mol)
	T	Temperature, K.

Osmotic pressure is the pressure created by osmosis. Osmosis is the phenomenon of spontaneous solvent diffusion through semipermeable membrane while preventing the passage of solutes (Shon 2015). Osmosis naturally occurs from less concentrated solution to more concentrated. To force osmosis in the wrong way and get water through the membrane surface hydraulic pressure applied needs to overcome the physical resistance and osmotic pressure. At this point dissolved solids are largely rejected and passing dissolved solids have smaller rate of mass transfer than water in the membrane which results in smaller slower pass-through speed (Bergman 2007). Water passing through the membrane thus contains fewer dissolved solids than the water entering the system. Principle of reverse osmosis is presented in figure 3.

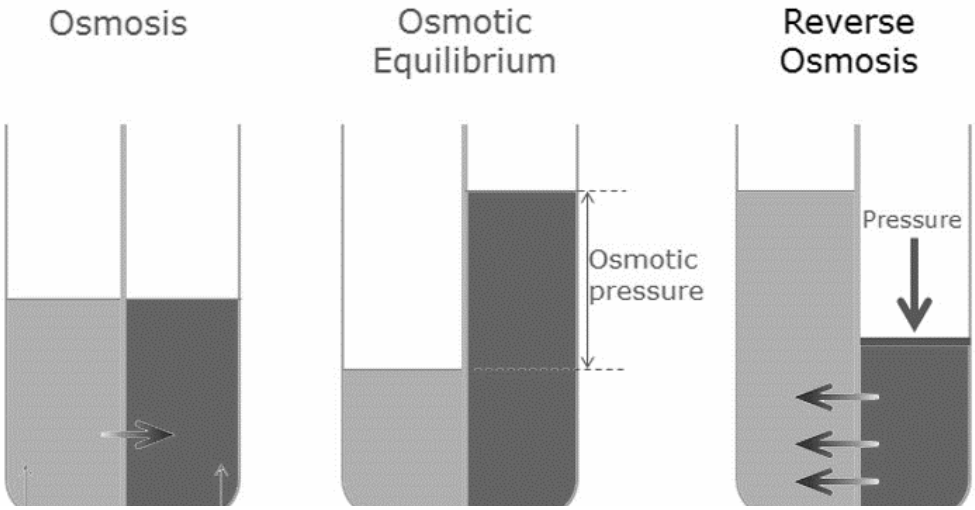

Figure 2. Principle of osmosis, osmotic equilibrium, and reverse osmosis (UNESCO, WWAP 2014)

3.2.1. Rejection and permeate flux in reverse osmosis

With reverse osmosis suspended solids which are usually considered as particles larger than 0.5 micron mean diameter are rejected 100% because they cannot pass through the membrane. MWCO for reverse osmosis membranes is around 100 Daltons. Their rejection rates depend nearly linearly on applied hydraulic pressure because it affects the water permeation. For this reason, when pressure is lowered rejection rates get considerably lower and highest possible hydraulic pressure should be applied for best solute rejection. (Cheremisinoff 2002)

Size and shape are the main rejection mechanisms for uncharged molecules. Rejection of contaminants is also highly affected by ionic charge of a component. These mechanisms affecting charged molecule rejection are more complicated and the rejection efficiency depends often on multiple mechanisms. These mechanisms are studied more closely in chapter 5, but simplified effects of characteristics are next listed shortly. Generally, rejection of multivalent ions is higher than rejection of mono-valent ions. This is because reverse osmosis membranes have fixed charge which causes good multivalent ion rejection. As mono-valent ions have lower charge their rejection efficiency is lower as well (Pérez-González, Ibáñez et al. 2015). Other characteristics affecting contaminant rejection besides molecular weight and ionic charge are polarity, degree of hydration and degree of molecular branching (Kucera 2015). Increase in polarity and hydration degree generally decrease rejection but increase in molecular branching increases rejection and for example isopropanol is rejected better than propanol (Kucera 2015). Feed solutions pH value can change the surface charge of used membrane as well as the charge of the solutes, which can cause increase or decrease in rejection (Van der Bruggen, Bart, Geens 2008).

These properties of reverse osmosis membranes can give preliminary indications on rejection efficiency of specific substances before practical testing.

Permeate flux for reverse osmosis membranes can be estimated with extension of equation 1 where pressure term is modified to take osmotic pressure into account. Permeate flux equation is presented below:

$$J = \frac{\Delta P - \Delta\pi}{\mu\left(R_m + R_f + R_p\right)} \tag{3}$$

Where π Osmotic pressure, psi.

As with ultrafiltration exact numerical values for resisting forces are difficult to estimate or to even define from test results. The rejection of charged molecules also makes flux estimations for reverse osmosis membranes even more complexed.

3.2.2. Possible use of reverse osmosis in this study

Reverse osmosis targets separation of contaminants which this study is also focused on. Effective separation of soluble multivalent ions is one object which reverse osmosis fulfils. Questions about mono-valent ions separation efficiency can be answered with small scale testing of water solutions. Larger molecules present in solution might cause issues due to membrane fouling but proper pretreatment should solve this issue. Since reverse osmosis membranes are tightest membranes, available operating pressures can become remarkably high when using high concentration solutions. This also effects permeate flux negatively which should be kept as high as possible due to large volume of processed water streams. For these reasons slightly loser nanofiltration membranes could be better in this situation. However reverse osmosis is much more fitting to processes this study concentrates than ultrafiltration.

3.3. Nanofiltration

Nanofiltration or NF is as well a pressure driven membrane process. Nanofiltration membranes were originally developed as a variant to reverse osmosis membranes with a goal to lower the needed pressure by decreasing the rejection of smaller, less charged ions (Bergman 2007). Principle of nanofiltration is the same as in reverse osmosis where osmotic

pressure needs to be overcome with hydraulic pressure applied to the feed solution. Tight nanofiltration membranes are similar to reverse osmosis membranes and loose membranes are more like ultrafiltration membranes. Specific features for nanofiltration are high rejection for multivalent ions, high rejection of organic compounds, and low rejection of monovalent ions (Van der Bruggen, Bart, Geens 2008). With these qualities nanofiltration membranes are sort of an intermediate between ultrafiltration and reverse osmosis membranes, which allows to obtain higher permeate fluxes than reverse osmosis and better rejections than ultrafiltration (Gomes, Cavaco et al. 2010).

3.3.1. Rejection and permeate flux in nanofiltration

Nanofiltration membranes have somewhat flickering boundaries with ultrafiltration and reverse osmosis membranes. These membranes have rejection properties more similar to reverse osmosis membranes with high rejection of multivalent ions (>99 %), moderate rejection to mono-valent ions (0-70 %) and high rejection for organic compounds (>90 %) (Van der Bruggen, Bart, Geens 2008). Nanofiltration membranes have similar transport mechanisms with reverse osmosis and nanofiltration membranes, as well as its own characteristics (Van der Bruggen, Bart, Geens 2008). Rejection mechanisms of nanofiltration that are similar to reverse osmosis considering charged particles are discussed in more detail in chapter 5. Mechanisms for uncharged molecules are similar to both ultrafiltration and reverse osmosis membranes (Kucera 2019). Molecular weight cut off for nanofiltration membranes varies greatly. Commercially available nanofiltration membranes MWCO values vary between 100 to 1000-5000 Daltons (Kucera 2019). Similarly to reverse osmosis membranes nanofiltration membranes also have a fixed charge which changes with the feed solutions pH.

Permeate flux for nanofiltration membranes can be estimated similarly with reverse osmosis membranes. Again, estimation is difficult due to multiple different mechanisms and resisting forces overlapping.

3.3.2. Use in this study

Nanofiltration membranes have advantages over reverse osmosis membranes especially in permeate flux values and in needed operating pressure. Lower operating pressure allows higher amounts of permeate and is economically advantageous. Nanofiltration membranes are also better in solutions where larger molecules such as organic matter is present. Based on literature only possible downside in nanofiltration membranes compared to reverse osmosis membranes is lower mono-valent ion rejection. Actual rejection rates for multi- and mono-valent ions as well as organic molecules and acid will be tested for different nanofiltration membranes in the experimental part of this study.

4. Membranes

Nanofiltration and ultrafiltration membranes are usually asymmetric, and the outer layers properties determine filtration characteristics while the membrane support has no effect, unlike reverse osmosis membranes, which are categorised as dense membranes which means that the selective layer has no pores, or no pores that are visible to microscopic observation (Jiang, Na 2017). Cellulose acetate is the original material for UF, NF and RO membranes. It is cheap and hydrophilic, which makes it less prone to fouling. However, cellulose acetate is limited by temperature and pH because they do not work properly and get damaged in highly acidic conditions and in high temperatures (Wagner 2001).

4.1. Thin film composite membranes

Thin film composite membranes (TFC) were made to replace original cellulose acetate membranes. They are widely recognized to be good in water and wastewater treatment as their biggest advantages are high flux and very high salt rejection (Wagner 2001, Luo, Wan 2013). TFC membranes also have good temperature and pH resistance which is important when dealing with solutions that contain acid.

These asymmetric membranes are manufactured by coating the ultrathin selective layer on top of the structural layer with interfacial polymerization. This manufacturing method roots back to 1965 when Morgan introduced it (Morgan 1965). All parts of this thin film composite membranes can be modified to increase their selectivity, permeability and structural strength depending on the use. Other techniques such as photo-grafting, dip-coating, electron beam irradiations and plasma-initiated polymerization are also studied. However, interfacial polymerization is most studied and used out of these. (Lau, Ismail et al. 2012)

Most nanofiltration membranes also acquire electric charge when they are in contact with polar medium, a solvent capable to hydrogen bonding (Drioli, Giorno 2016). During this study, acidic solutions will cause this electric charge to membranes, which can change the membrane selectivity. Figure 4 presents the basic composition of a TFC membrane.

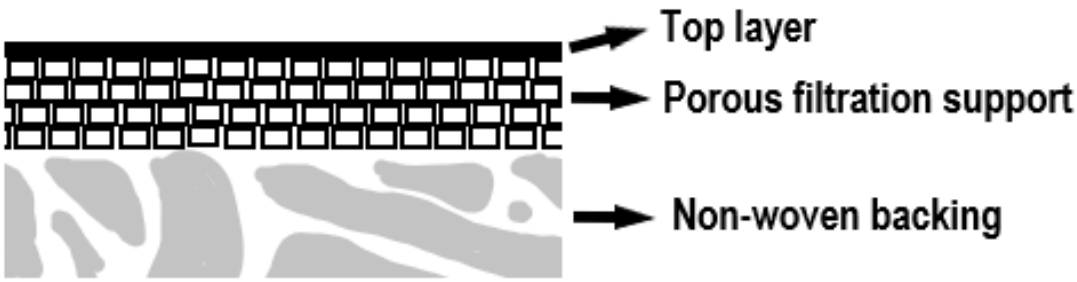

Figure 3. Cross section of thin film composite membrane.

4.2. Membrane module

Membranes can also be designed in different elements. These elements are different configurations of how the membrane can be optimally used in water treating systems. There are multiple different modules such as spiral wound, tubular, plate and frame, ceramic, and hollow fine fiber (Wagner 2001). These modules can also be further modified to fill specified needs. Spiral wound is the most used module, and it can be used in multiple different industries. Spiral wound modules are compact, cheap and special modules can be made to resist high temperatures and extreme pH (Wagner 2001). Design of a spiral wound module is presented in figure 5.

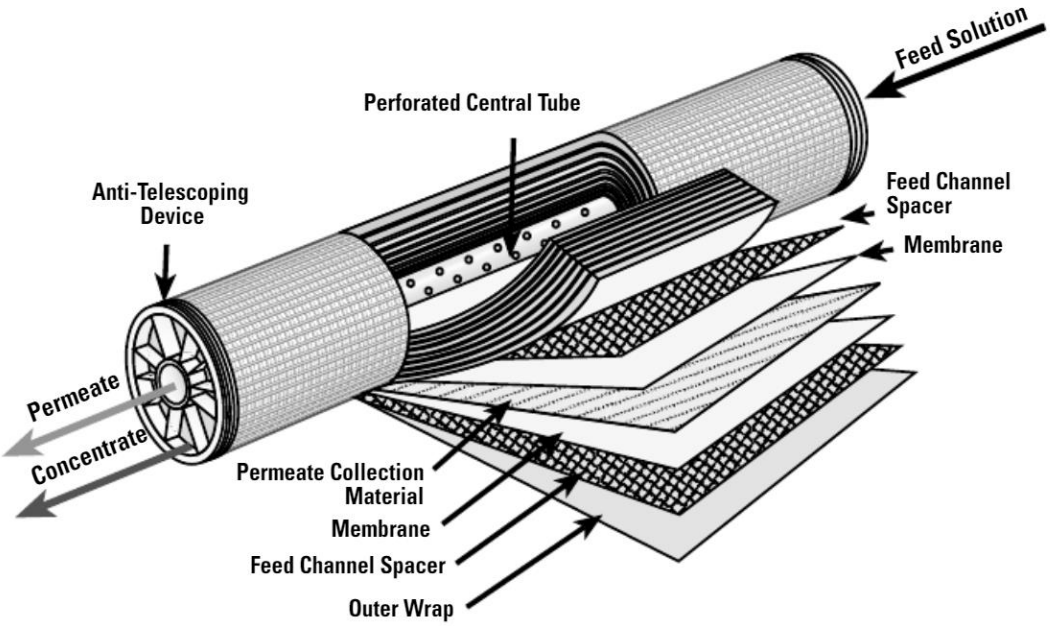

Figure 4. Spiral wound membrane module (Wagner 2001)

4.3. Membrane limitations and fouling

Different things can cause membranes to get damaged or affect negatively to their performance. On top of things discussed earlier such as pH and temperature, pressure can also cause structural damage. All membranes are sensitive to pressure, because after high enough pressure, which varies between membranes, irreversible flattening occurs (Wagner 2001). This flattening is dependent on both temperature and pressure. When this occurs the flux and possibly retention of used membrane changes.

Fouling is another issue, which is caused by particles accumulating on the membrane surface. Fouling causes decrease in flux and can lead to the need of early replacement of membrane. Membrane fouling can be caused by different materials such as microbes, inorganic and organic colloids, organic matter, and precipitated salts (Kucera 2019). Processing conditions also have an impact on fouling speed. Nanofiltration membranes cannot be backwashed, which increases the importance of fouling prevention even more (Kucera 2019). Multiple cleaning techniques for nanofiltration membranes have been developed and choosing the most efficient one depends on the characteristics of used membrane and feed solution (Van der Bruggen, B., Mänttäri et al. 2008). Examples for possible fouling limitation procedures are: pre-filtration with another pressure driven membrane system and usage of cross-flow system.

4.4. Characterisation of used membranes

Membranes have multiple different parameters that impact their separation properties which can be determined with different analytical ways. These analyses were used in this work to define differences in properties between different membranes as well as between used and unused membranes. How these parameters effect separation properties and principle of used analyses is explained in this chapter.

4.4.1. Zeta potential

Surface charge has great influence on membranes permeability and selectivity (Fievet, Szymczyk et al. 2001). Membranes acquire an electric surface charge when they are introduced to an aqueous solution. This surface charge varies in different pH values and reaches zero at isoelectric point (IEP) (Fievet, Szymczyk et al. 2001). IEP is a point where the surface charge of membrane is zero and thus the zeta potential is zero. In pH values above IEP membranes surface charge is negative and positive when pH is below IEP.

Zeta potential can be used as an indicator of membranes surface charge. Zeta potential is a value that describes the electrokinetic potential between solid-liquid interface (Luxbacher 2014). This potential is a difference in charge between bulk fluid (solution) and stationary layer of ions from solution on the membrane surface (Luxbacher 2014). This phenomena is also called double layer.

Zeta potential can not be measured directly but it can be calculated from results of other measurements. One way to calculate zeta potential is streaming potential model which will also be used in this study. Streaming potential is measured by applying hydraulic pressure to an aqueous solution in order to force it through a capillary system or a channel. This creates an electrical response which can be measured as streaming potential or streaming current. Zeta potential can then be calculated from results with equation 4.

$$\xi = \frac{\mathrm{dI}_{str}}{d\Delta_P} \cdot \frac{\eta}{\varepsilon \cdot \varepsilon_0} \cdot \frac{L_s}{A_s} \tag{4}$$

Where, ξ Zeta potential, mV

I Current, A

p Pressure, psi

η Viscosity, Pa*s

ε Dielectric coefficient, F/m

L_s Streaming channel length, m

A_s Streaming channel area, m^2.

4.4.2. Hydrophilicity and hydrophobicity

Hydrophilicity and hydrophobicity define surfaces property of attracting water. Hydrophilic surfaces attract water and hydrophobic surfaces repel it. In membrane separation this property is important because hydrophilic membranes have been found to be less prone to fouling than hydrophobic membranes (Singh 2015). Membranes can be made to be hydrophilic by using hydrophilic polymers such as PVP in the polymer blend or modified to achieve higher hydrophilicity (Singh 2015). It has been found that increase in hydrophilicity via membrane modification has increased membranes water flux and decreased fouling (Liu, Huang et al. 2019, Miao, Wei et al. 2020, Xie, Li et al. 2020). Hydrophilicity or hydrophobicity for a membrane can be defined with a contact angle measurement such as sessile drop method. In this method a droplet is placed on the membrane and a camera captures it. Then a program calculates the internal angle for both sides of the droplet. If contact angle (θ) is under 90° the membrane is hydrophilic, and if over 90° the membrane is hydrophobic. Picture of contact angle measurement is presented in figure 6.

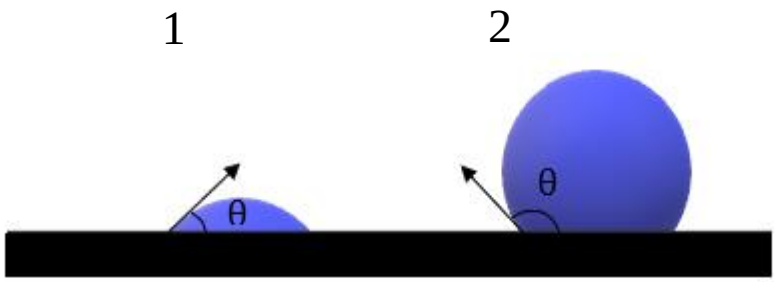

Figure 5. Contact angle measurement. 1 is a hydrophilic membrane and 2 is a hydrophobic membrane.

4.4.3. FTIR

FTIR or Fourier-transform infrared spectrometry is based on molecule vibration. This vibration can be used to characterise functional groups and molecules because they all have different vibration frequencies. This vibration can be seen as absorption of certain wavelength. FTIR device sends light at different wavelengths to the sample and measures the absorption. This way functional groups inside the sample can be identified from the spectra that FTIR device returns. (Topanalytica, Paunikallio)

FTIR spectre can be also used to specify fouling degree of a membrane (Delaunay, Rabiller-Baudry et al. 2008). This can be done by identifying fouling agents from the spectra and comparing it to the spectra of an unused membrane.

5. Separation mechanisms in nanofiltration

As discussed earlier, nanofiltration rejection and permeate flux is affected by multiple different mechanisms. Mechanisms covered prior such as sieving effect and physical separation with pore sizing consider uncharged molecules. The separation of these molecules is mostly determined by pore size and sieving effect which are simpler than effects affecting charged ions (Nagy 2018). As discussed, earlier nanofiltration membranes have similar separation mechanisms with ultrafiltration and reverse osmosis membranes, which means more mechanisms are influencing nanofiltration membranes separation behaviour. These mechanisms operate simultaneously influencing each other, which can complicate the investigation of these mechanisms and their effect (Zhao, Li 2006). Separation of charged particles is done by mechanisms called Donnan effect and dielectric exclusion. Donnan effect also occurs with porous ultrafiltration membranes and dielectric exclusion occurs with reverse osmosis membranes due to their compact inner structure (Zhao, Li 2006).

5.1. The Donnan effect

When filtering a solution with charged ions, the separation is controlled by effects based on the Donnan effect, due to ions interactions with electric surface charges of the membrane (Gomes, Cavaco et al. 2010). Donnan effect, or Donnan exclusion is a phenomenon occurring when ionic solution is introduced to a charged membrane. The charged membrane attracts ions of the opposite charge and repels ions with the same charge, this is called Donnan potential. Membrane's charge determines the rejection, higher charge equals higher rejection capacity. Donnan potential is highest at low concentration solutions (< 3000 mg/L salt) and concentrations above this reduce the effect which decreases rejection. This decrease can be explained by shielding theory, where increased ion amount increases the number of ions blocking membrane surface. Increasing solution concentration further cancels rejection advantages created by Donnan potential which makes Donnan effect meaningless. (Bartels, Franks et al. 2005, Yaroshchuk 2001) Example of the Donnan effect is presented in figure 7 and example of "shielding" in figure 8.

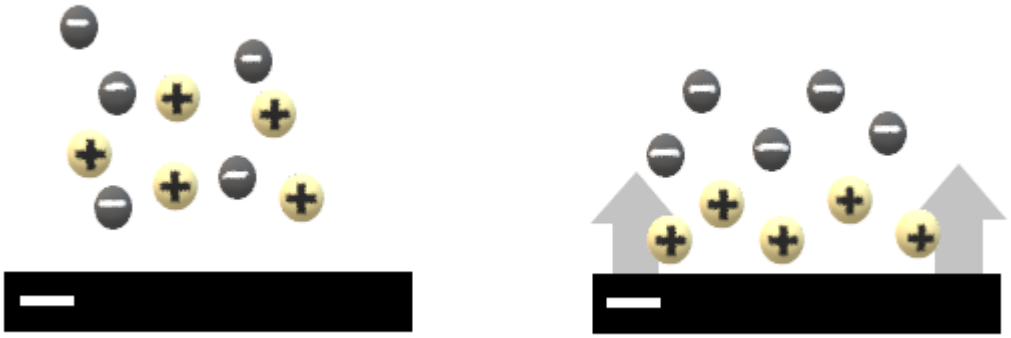

Figure 6. The Donnan effect attracting opposite charge and repelling same charge.

Figure 7. The "shielding" theory decreasing retention with high concentrations.

5.2. Dielectric exclusion

Dielectric exclusion appears in a situation where ion is in higher dielectric constant and induces the charges of same sign as its own. The phenomenon is caused by difference in dielectric constants between the solution and membrane. This creates a repelling force which

affects the ion movement through the membrane. Polarisation charge is dependent on the ion charge and therefore the exclusion energy is dependent on the ion charge. Both cations and anions can be repelled from the pores. (Yaroshchuk 2001)

The membrane surface charge depends on ion concentration and pH of the solution. Most important consideration for ion removal is that membrane charge changes from positive in neutral or alkaline to negative when acidic conditions are introduced (Gomes, Cavaco et al. 2010).

6. Things to consider in experimental part

Multiple technological limitations are possible because solutions are acidic and metal salts used are highly soluble to water. When using nanofiltration and reverse osmosis membranes osmotic pressure limits the range in which filtration can be done (Bergman 2007). Osmotic pressure rises as feeds solute concentration rises and to continue filtration this pressure needs to be overcome. Osmotic pressure also sets the limit on how concentrated solutions we can process from these waste waters. In other words, how much water can be separated from the original solution before osmotic pressure cannot be matched anymore.

Having acid present also creates certain limitations in membrane filtration because it can affect the performance of membranes (Luo, Wan 2013). Acids can also cause corrosion, which leads to issues in performance. In following experimental part membranes were analysed and compared between used (in acidic conditions) and not used ones. This comparison can give us indications if and what effects acidic conditions had on used membranes. However, measurements done were not long enough to see the true extent of effects acid has to membranes in continuously operated system.

Solutions researched in this study have mono- and multivalent ions present. According to literature nanofiltration membranes do not have great rejection efficiency for mono-valent ions. This can become an issue and limit the use of nanofiltration, or it can also be advantageous if multivalent and mono-valent ions need to be separated.

Lastly, organic matter is going to be present in some of the solutions and it can cause fouling as well as the high salinity solutions used. Amount of fouling can be tested after all measurements are done with pure water permeability test, which is done to the membranes before first experiments.

EXPERIMENTAL PART

Aim for this study was to specify permeate flux and Na_2SO_4 & $ZnSO_4$ rejection while using feed solutions with different compositions. Experiments were done to find out how well Na_2SO_4 and $ZnSO_4$ are rejected from solutions that contain Na_2SO_4, Na_2SO_4 and $ZnSO_4$ and how addition of acid to these feed solutions changes the rejection and permeate flux. The goal is to reach rejections of 90 % for both Na_2SO_4 and $ZnSO_4$ with some type of membrane filtration system so that the permeate could be recycled back to the process. Second goal is to see if membranes have high enough permeate flux to make their use feasible in an industrial process. Besides these two main goals, membranes are characterized in order to define if any flattening, fouling or cake formation has occurred during the experiments.

Experiments begun from simpler solutions to better understand the membrane behaviour and got more complexed as more experiments were carried out

7. Filtration equipment

Used filtration equipment was a cross-flow filtration system with four membrane modules side by side. Used system had thermometer to measure temperature from the feed tank and two pressure indicators, one on each side of the module to measure pressure.

Temperature of the solution was controlled with external water circulation heating/cooling unit attached to feed tank and kept in between 29 °C and 31 °C. Flow velocity was controlled with a Hydra Cell G25X pump and pressure could be adjusted by a pressure valve. Pump motor was ABB 7,5 kW electric motor which could produce maximum flowrate of 5,811 m^3/h. Feed flowrate was held at 53 % from maximum constantly to produce flow rate of 3.08 m^3/h which was used throughout the experiments and monitored with a rotameter. Experimental setup is presented in figure 8.

Figure 8. Cross-flow nanofiltration system with four parallel membrane modules.

8. Used membranes

With four modules, four different membranes could be tested at the same time. Each of the modules held 0.022308 m^2 sized membrane sheet. Membranes often have separation characteristics specific for certain industry or application. Wide range of different module types can also be found depending on the use. In this chapter short summary of the nanofiltration membranes chosen to this study is presented. This gives a rough estimate of optimal flow rates, operating conditions and scaling for industrial membrane systems.

NFX, manufactured by Synder Filtration is a nanofiltration membrane with approximated MWCO of 150-300 Da. NFX is a thin film composite polyamide membrane with maximum operating pressure of 600 psi (41 bar) and maximum operating temperature of 50 ˚C. At maximum pressure pH range for this membrane is given to be 3-9.5. (Synder Filtration 2021)

Table 1. Recommended cross flow rate and membrane are for 8-, 6- and 2.5-inch diameter NFX spiral wound membrane modules (Synder Filtration 2021).

Element diameter, inch	**Recommended cross flow rate, m^3/h**	**Membrane area, m^2**
2.5	1.2	3.25
4	2	9.1
8	10	40.8

Filmtec NF 270 manufactured by Dupont is a polypiperazine thin film composite nanofiltration membrane. It is described as a great membrane for TOC removal with medium to high salt passage. No specific MWCO was found for NF 270 membrane. Maximum operating pressure of 600 psi (41 bar) and maximum operating temperature of 45 ˚C. At maximum pressure pH range for this membrane is given to be 3-9.5 for long term and 1-12 for short term use. (Dupont 2021)

Table 2. Recommended cross flow rate and membrane are for 3.9- and 2.4-inch diameter NF 270 spiral wound membrane modules (Dupont 2021)

Element diameter, inch	**Recommended cross flow rate, m^3/h**	**Membrane area, m^2**
2.4	1.4	2.6
3.9	3.6	7.6

Desal-5 DK manufactured by GE-Osmonics (now Suez company) is thin film composite nanofiltration membrane with MWCO of 150-300 Da. Maximum operating pressure of 600 psi (41 bar) and maximum operating temperature of 50 ˚C. At maximum pressure pH range for this membrane is given to be 3-9.5 for long term use.

Table 3. Recommended cross flow rate and membrane are for 7.9-, 3.9- and 2.4-inch diameter DK spiral wound membrane modules

Element diameter, inch	**Recommended cross flow rate, m^3/h**	**Membrane area, m^2**
2.4	-	2.6
3.9	-	7.8
7.9	-	33.8

Desal KH is also manufactured by GE-Osmonics (now Suez company) but has since been either renamed or pulled out of the market. Manufacturer's product information was not available, but Lahti J. et al. stated in their research that it has MWCO of 150-300 Da and pH range of 0 -14 (Lahti, Vazquez et al. 2020). Desal KH can be compared to Duracid series nanofiltration membranes manufactured by Suez, which has extreme pH resistance and MWCO of 150-200. Duracid also has maximum operating pressure of 800 psi (55 bar, 41 bar at maximum temperature) and maximum operating temperature of 70 ˚C. (Lenntech 2021)

For comparison to other membranes presented earlier Duracid membrane properties are presented in table 4.

Table 4. Maximum cross flow rate and membrane are for 7.9-, 3.9- and 2.4-inch diameter NF 270 spiral wound membrane modules (Lenntech 2021).

Element diameter, inch	**Maximum cross flow rate, m^3/h**	**Membrane area, m^2**
2.4	1.6	1.4
3.9	4.1	4.8
7.9	15.9	26.5

All membranes beside Filmtec NF 270 are considered to be tight nanofiltration membranes and their MWCO all the way to the low side of nanofiltration membranes. By product description NF sounds like looser nanofiltration membrane and it is possible that it has low ion rejection. Besides Desal KH the given pH range does not reach low enough for acidic solutions used in this study, which can cause problems at least in long term use.

With four modules, four different membranes could be tested at the same time. Each of the modules held 0.0223 m^2 sized membrane sheet. Before actual filtration, membrane flux was tested to make sure the membranes work properly, and no leaking occurs in the system. This was done by first pressurizing them at 25 bar for 20 minutes and then taking samples of cumulating permeate. This test was done at 10, 15 and 25 bar pressures with pure water.

9. Solutions

Multiple different solutions were used to measure membrane performance. Measuring conditions and solution composition for each experiment are presented in the following chapters.

9.1. Filtration with Na_2SO_4 solutions

First experiments were done using a solution containing Na_2SO_4. Three different Na_2SO_4 solutions were made with different concentrations and experiments were carried out at different pressures. Solutions were made by weighing sodium sulfate and mixing it to water to reach needed concentration. Measured composition of solutions and measuring conditions for these experiments are presented in table 5.

Table 5. Solution composition and measurement conditions for solutions containing Na_2SO_4. All measurements were done at 29 °C temperature

Experiment	**Na_2SO_4 concentration**	**Pressure**	**Time**
1	5.2 %	10 bar	60 min
2	5.2 %	25 bar	60 min
3	5.2 %	30 bar	30 min
4	5.2 %	35 bar	30 min
5	5.2 %	40 bar	30 min
6	10.5 %	30 bar	60 min
7	10.5 %	40 bar	60 min
8	3.7 %	30 bar	15 min
9	3.7 %	40 bar	15 min
10	2.2 %	30 bar	10 min
11	2.2 %	40 bar	10 min

The impact of permeate flowrate and temperature were also tested with Na_2SO_4 solutions. For these experiments used temperature was first changed while using the same solution and in a separate experiment the flowrate was changed while using same solution. This was done to find out if these parameters had impact on permeate flow or rejection efficiency. Solution composition and measuring conditions for these experiments are presented in table 6.

Table 6. Solution composition and measurement conditions for experiments determining the impact of flowrate.

Experiment	**Na_2SO_4 concentration**	**Pressure**	**Temperature**	**Time**	**Flowrate**
12	3.7 %	40 bar	30	15 min	3.0 m^3/h
13	3.7 %	40 bar	30	15 min	2.2 m^3/h
14	3.7 %	40 bar	30	15 min	3.0 m^3/h
15	3.7 %	40 bar	40	15 min	3.0 m^3/h

9.2. Filtration with Na_2SO_4 and $ZnSO_4$ solutions

To study the membrane behaviour with solutions using multiple different metal salts, $ZnSO_4$ was added to the Na_2SO_4 solutions with a ratio of approximately 20 to 15 % $ZnSO_4$ of overall salt. These solutions were made to be close to the original concentrations of Na_2SO_4 solutions for easier comparison of permeate flow and salt rejection. Solutions were made in the same way as Na_2SO_4 solutions. Measured composition and experiment conditions for these experiments are presented in table 7.

Table 7. Solution composition and measurement conditions for solutions containing Na2SO4 and ZnSO4. All measurements were done at 30°C temperature.

Experiment number	**Na_2SO_4 concentration**	**$ZnSO_4$ concentration**	**Pressure**	**Time**
16	4.9	0.6	30 bar	60 min
17	4.9	0.6	40 bar	60 min
18	3.6	0.4	30 bar	20 min
19	3.6	0.4	40 bar	20 min
20	1.5	0.2	30 bar	15 min
21	1.5	0.2	40 bar	15 min

9.3. Filtration with Acidic Na_2SO_4 and $ZnSO_4$ solutions

The addition of acid changes how membranes perform, affecting their selectivity and possibly separation and permeate flux characteristics. After studying the behaviour of used membranes in solutions with multivalent and monovalent metal salts acidic conditions were made by diluting 99 % sulfuric acid into previously noted concentration and adding sodium sulfate and zinc sulfate to reach desired metal salt concentration. Measured Na_2SO_4, $ZnSO_4$ and sulfuric acid concentrations for these feed solutions were determined ICP and are presented in table 8.

Table 8. Solution composition and measurement conditions for solutions containing Na_2SO_4, $ZnSO_4$ and sulfuric acid. All measurements were done at 40 bar pressure and at 30 °C temperature.

Experiment number	**Na_2SO_4 concentration**	**$ZnSO_4$ concentration**	**H_2SO_4 concentration**	**Time**
22	5.4 %	0.5 %	4.8 %	30 min
23	4.7 %	0.5 %	6.9 %	30 min
24	4.8 %	0.6 %	8.9 %	30 min

9.4. Filtration with slightly acidic Na_2SO_4 solutions

As noted in the literature part, addition of acid decreases monovalent ion (Na_2SO_4) rejection. Goal for these measurements was to see if some sulphuric acid concentration where Na_2SO_4 rejection decrease begins can be found. Solutions were made by diluting 99 % sulfuric acid into previously noted concentration and adding sodium sulfate to reach desired metal salt concentration. Measured Na_2SO_4 and sulphuric acid concentrations for made solutions are presented in table 9.

Table 9. Solution composition and measurement conditions for solutions containing Na2SO4 and sulfuric acid. All measurements were done at 40 bar pressure and at 30 ℃ temperature.

Experiment number	**Na_2SO_4 concentration**	**Sulfuric acid concentration**	**Time**
25	3.2 %	0.3%	10 min
26	3.5 %	0.6 %	10 min
27	3.6 %	0.9 %	10 min

9.5. Filtration with real solutions

Besides using solutions with tailored concentrations of sulfuric acid, Na_2SO_4 and $ZnSO_4$ real industrial waters were also experimented with. These industrial waters contained different amounts of sulfuric acid, Na_2SO_4 and $ZnSO_4$ as well as organic molecules. Solution composition and measuring conditions are presented in table 10.

Table 10. Solution composition and measuring conditions for real industrial wastewaters. All measurements were done at 40 bar pressure and at 30 ̊C temperature for 30-minute period.

Sample number	**Na_2SO_4 concentration**	**$ZnSO_4$ concentration**	**H_2SO_4 concentration**	**TOC concentration**
1	5.0 %	0.2 %	0.4 %	1.9
2	4.4 %	0.1 %	0.3 %	1.1
3	7.7 %	0.9 %	4.6 %	6.6

10. Sampling and calculations

Calculation and sampling methods used for permeate flux and salt rejection values are presented in this chapter.

10.1. Permeate flux

Sampling in all experiments was done by taking samples of the permeate flow for a specific time. These samples were then weighted and permeate flow was calculated using equation 5.

$$Q = \frac{m_p}{t_p} \tag{5}$$

Where	m_p	Mass of permeate, kg
	t_p	Time, h
	Q	Permeate flow through membrane, kg/h.

From calculated permeate flow values the permeate flux can be calculated with equation 6.

$$J = \frac{Q}{A} \tag{6}$$

Where	J	Permeate flux, kg/(m^2*h)
	A	Surface area of membrane, m^2.

10.2. Rejection

Rejection for Na_2SO_4 solutions was done with conductivity measurements. First, a calibration line was made by measuring conductivity of solutions with known Na_2SO_4 concentration. Conductivity for permeate samples was then measured and the Na_2SO_4 concentrations of these samples was determined using the calibration line. Rejection of each membrane was then calculated with equation 7.

$$R_s = \frac{C_F - C_p}{C_F} \tag{7}$$

Where R_s Rejection, %

C_F Concentration in feed, g/l

C_P Concentration in permeate, g/l.

Permeate and feed solution compositions when using solutions containing acid, Na_2SO_4 and $ZnSO_4$ were determined with ICP (Inductively coupled plasma spectrometer) analysis done by a third party. Rejection for each membrane was then calculated using equation 7 from obtained results.

The amount of organic matter in samples was measured with total organic carbon (TOC) method by measuring total carbon and redacting total inorganic carbon resulting in TOC also done by a third party.

11. Membrane characterization

These characterization analyses were made to all membranes to further understand what qualities properly working have and on the other hand what those not working as intended have. Comparison between used and new membranes was also made to see how used feed solutions affected the membranes and to see if fouling occurred.

11.1. Zeta potential measurements

Zeta potential was measured from electrokinetic potential using Anton Paar SurPASS system. Measurements were done in room temperature and in pH range of 7 to 3. Zeta potential was calculated by the software. Electrolyte solution used was 1 mM KCl solution and pH was adjusted with HCl. Membranes were cleaned and kept wet for analysis. Measurements were done in surface direction with adjustable gap between membrane samples, which was kept at 120 µm at the start of the analysis. Measurement setup is presented in figure 9

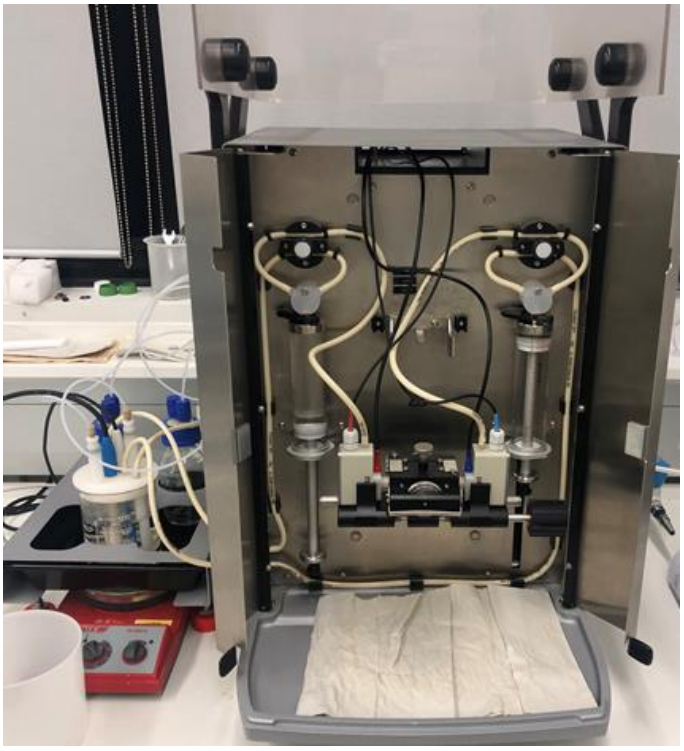

Figure 9. Zeta potential analysis setup Anton Paar SurPASS system.

11.2. Contact angle measurements

Contact angle measurements were done with sessile drop method. Prior to the measurements, all membranes were washed with deionized water and dried in a desiccator for few days to make sure they were completely dry. Sessile drop equipment used was Attension Theta optical tensiometer which is presented in figure 10.

Figure 10. Sessile drop experiment setup.

Measurements were done in room temperature and deionized water was used as the sessile liquid. Contact angle was recorded in order to define hydrophilicity or hydrophobicity for each membrane. Membrane is categorized as hydrophilic if contact angle is under 90° and hydrophobic if contact angle is over 90°. Comparison between used and unused membranes was also done to determine if any changes occurred from acidity or fouling. This measurement was done 10 times for each membrane from which medians were calculated.

11.3. FTIR measurements

FTIR analyses were done for all membranes to determine possible differences in membrane composition and to identify possible fouling agents from the membrane by comparing used and new membranes. Before measurements the membranes were washed with deionized water and dried in desiccator for few days. Measurements were done at room temperature with PerkinElmer Frontier FT-IR-ART spectrometer in wavelength range of 400 to 4000 cm^{-1}.

12. Results and discussion

Permeate fluxes and rejection rates for each substance individually are presented trough-out this study as explained in figure 11. Columns describe permeate flux for each membrane in specific pressure. Numbers above these columns in between brackets describe rejection percentage of a substance. Order for rejection percentage is 1. sodium sulfate 2. zinc sulfate 3. sulfuric acid 4. total organic carbon. Rejection numbers are only presented for substances present in feed solutions and always in this same order.

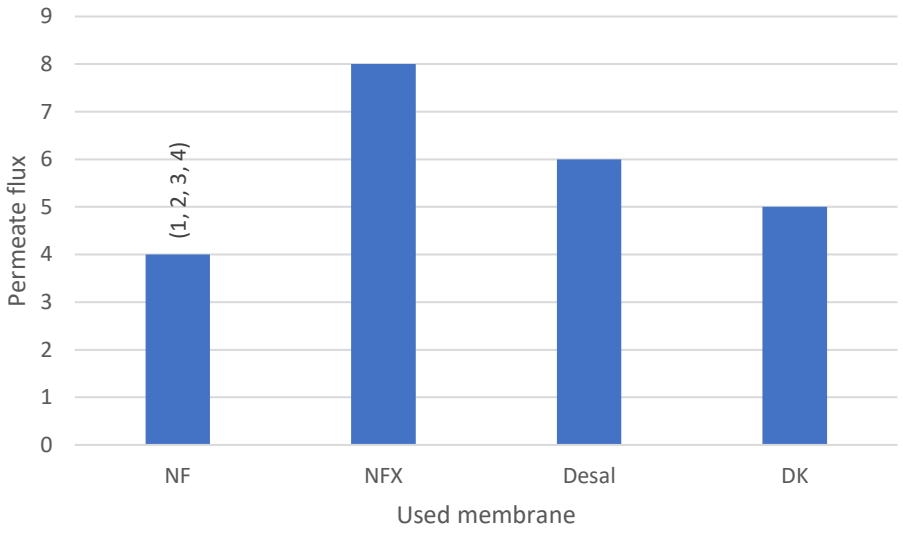

Figure 11. Example figure of permeate flux, Na_2SO_4, $ZnSO_4$, acid and TOC rejection presentation. Numbers above column represent rejection percentage of specific substance in order. 1. Na_2SO_4 2. $ZnSO_4$ 3. sulfuric acid 4. TOC

12.1. Pure water permeability

Pure water permeability for the membranes was done to make sure they were working properly as well as to see if there were any leaks in the experimenting system. Permeate flows through each membrane when using pure water are presented in figure 12.

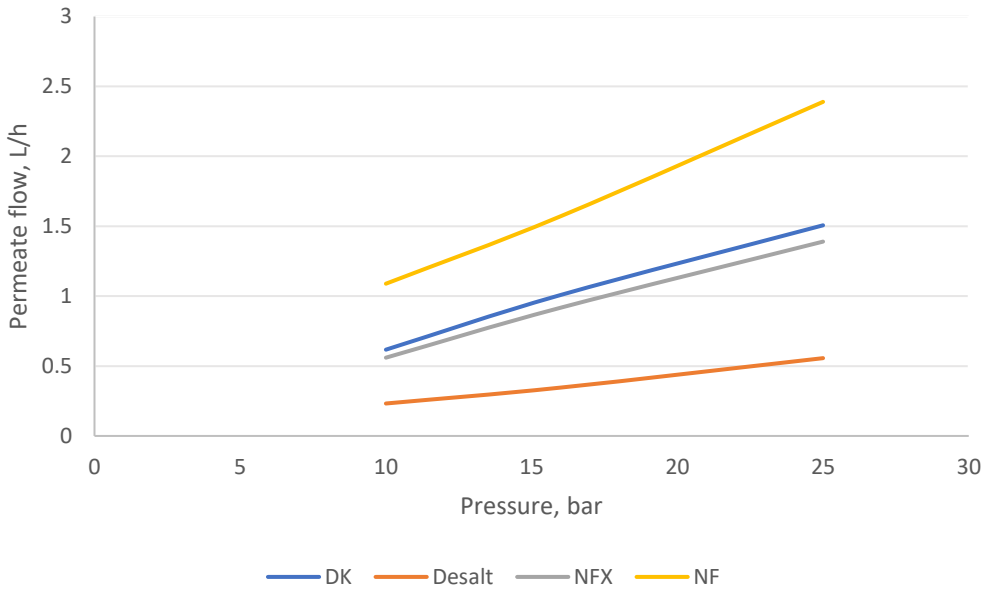

Figure 12. Permeate flow through membrane test with pure water

Permeate flux values in different pressures are then fitted into a figure. A trendline is formed and the average permeability for each membrane can be seen from the slope. These pure water permeability values for each membrane are presented in figure 13.

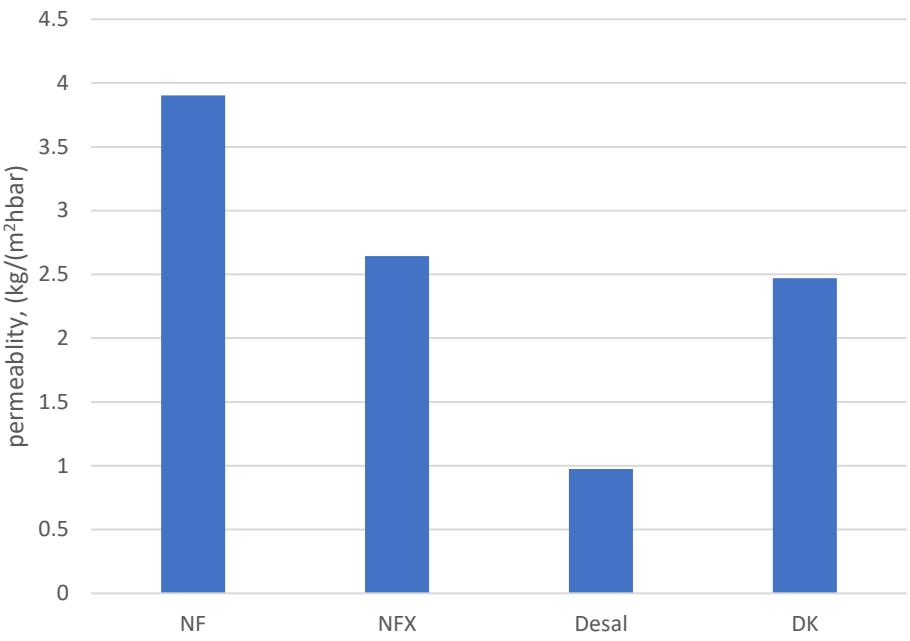

Figure 13. Pure water permeability for each membrane

These pure water permeability values are normal which indicates that the membranes are working as intended and leaking is occurring.

12.2. Na_2SO_4 solutions

First tests were done at 10 and 25 bar using 5.2 % Na_2SO_4 solution. Flux was stabilized for 20 minutes after the pressure was changed. Results for these measurements are presented in figure 14.

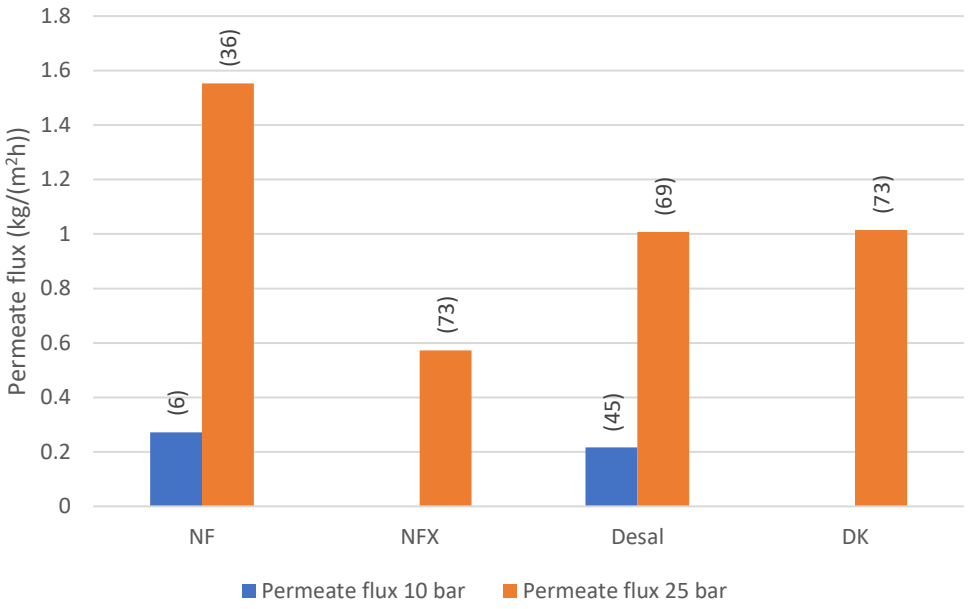

Figure 14. Measured permeate flux and calculated percentage of Na_2SO_4 rejection with 5.2 % feed solution at 10 and 25 bars for all membranes.

As seen in the results all permeate flow amounts and salt rejection rates are low. Due to relatively high Na_2SO_4 concentration in the feed solution this might result from the hydraulic pressure being too low to overcome the osmotic pressure.

In order to solve this problem pressures used in the nanofiltration system were taken up to 30, 35 and 40 bar. Next measurements were done using the same feed solution. Flux was stabilized again for 20 minutes when the pressure was changed. The results for permeate flux and Na_2SO_4 rejection are presented in figure 15.

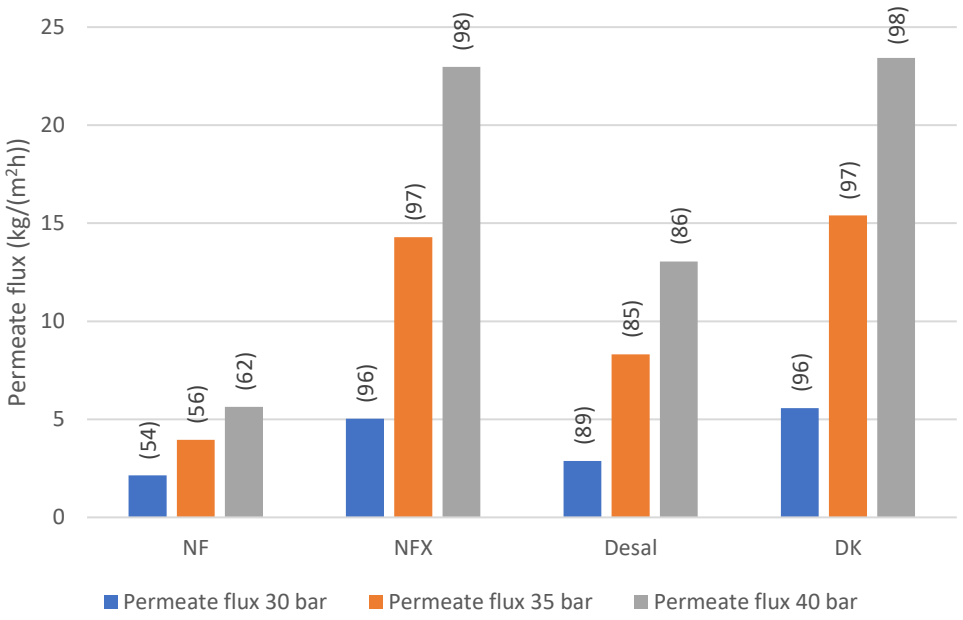

Figure 15. Measured permeate flux and calculated Na_2SO_4 rejection with 5.2 % feed solution at 30, 35 and 40 bar for all used membranes.

Pressure increase resulted the way intended and permeate flux increased while Na_2SO_4 concentration in it decreased. Good results were especially found with NFX and DK membranes.

To find out the behaviour of used membranes in different concentrations 3 new solutions were made using the same salt. Na_2SO_4 concentrations for these solutions came to be 10.59, 3.7 and 2.2 %. Flux was again stabilized for 20 minutes when either the feed solution or pressure was changed. Results of these measurements are presented in figure 16.

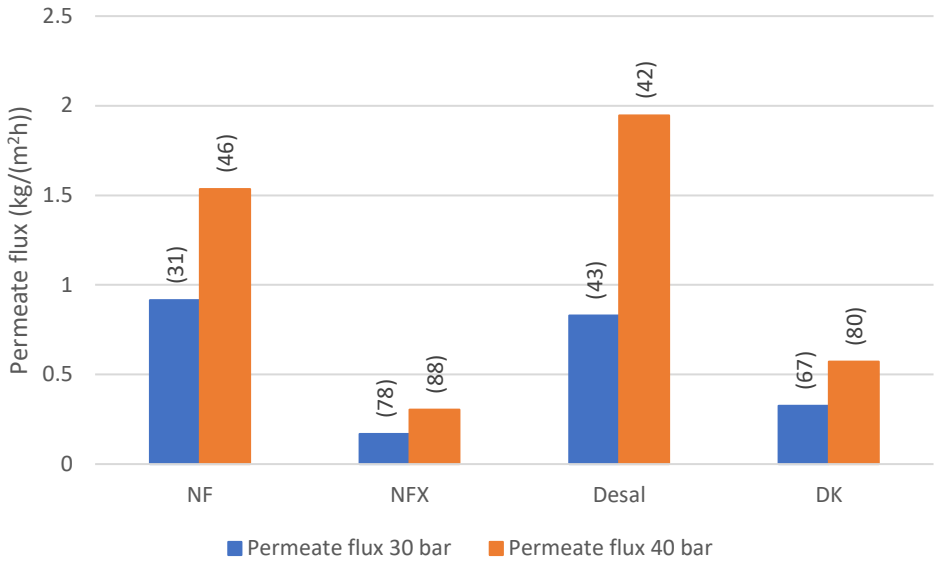

Figure 16. Measured permeate flux and calculated Na_2SO_4 rejection with 10.5 % feed solution at 30 and 40 bars for each membrane.

Next, measurements with the 3.7 % and 2.2 % feed solutions and the results are presented in figures 17 and 18.

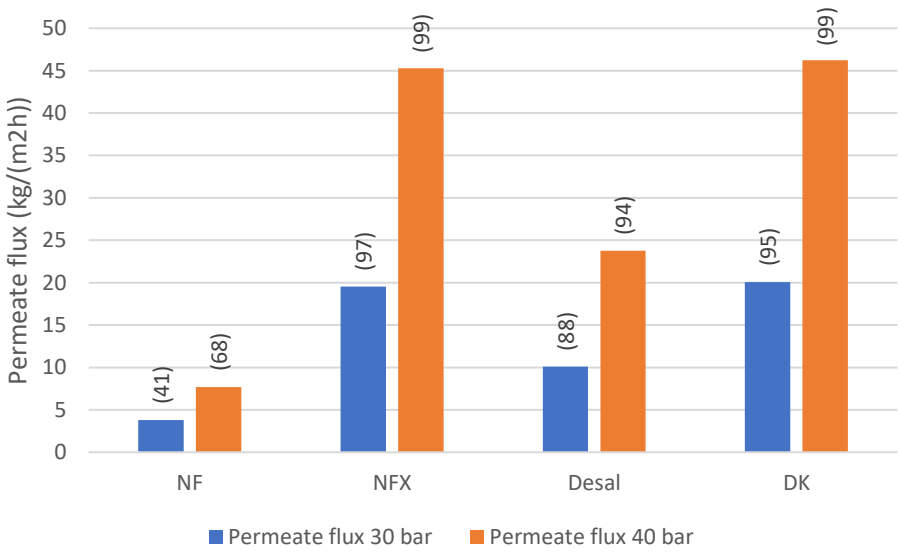

Figure 17. Measured permeate flux and calculated Na_2SO_4 rejection with 3.7 % feed solution at 30 and 40 bars for each membrane.

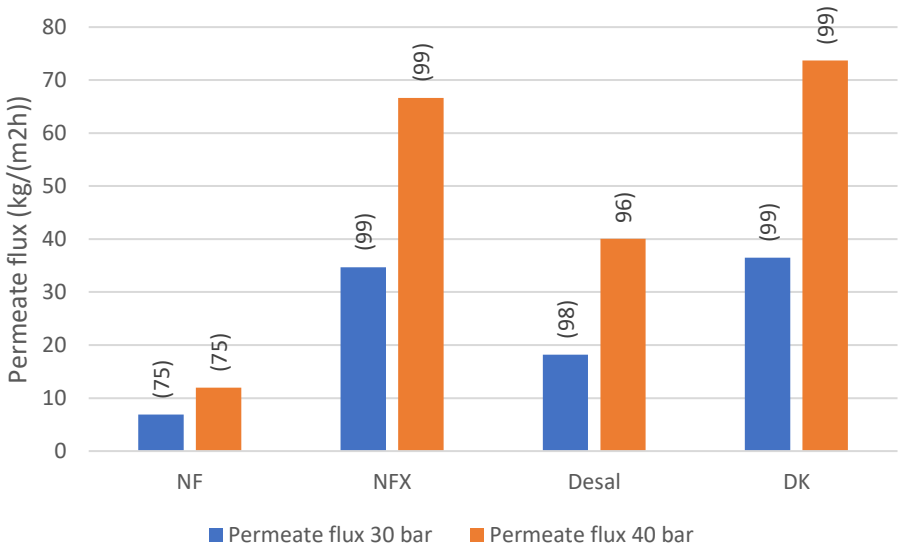

Figure 18. Measured permeate flux and calculated Na_2SO_4 rejection with 2.2 % feed solution at 30 and 40 bars for each membrane.

These results obtained from measurements follow the theory found in literature. Results with low pressures and high concentration Na_2SO_4 solutions were poor most likely because of hydraulic pressure applied did not overcome natural osmotic pressure of the solution. Rising the applied pressure to 40 bar substantially improved both permeate flux through the membrane and Na_2SO_4 rejection. Rejection was constantly over 90 % with NFX and DK membranes while using feed solutions with up to 5.2 % Na_2SO_4 concentration. Desal membrane also had good results with 2.2 % and 3.7 % concentration solutions, which can implicate the need for higher hydraulic pressure compared to NFX and DK membranes. NF membrane did not perform as intended and its permeate flow as well as Na_2SO_4 rejection were noticeably lower than the other three membranes.

12.3. Effect of flowrate and temperature on rejection and permeate flux

Single experiment was also done to see the effect that flowrate has on permeate flux and Na_2SO_4 rejection. To do this, the feed solution containing 3.7 % of Na_2SO_4 was used to do measurements while using 2.2 m^3/h flow rate, which is approximately 30% decrease to 3.08 m^3/h. Results are presented in figure 19.

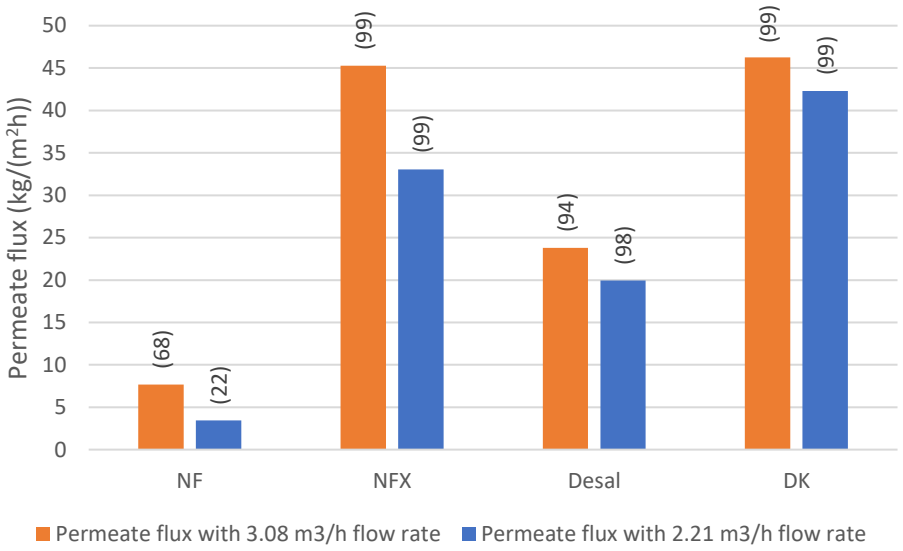

Figure 19. Measured permeate flux and Na_2SO_4 rejection when using a feed solution containing 3.7 % of Na_2SO_4 with varying flow rates.

It can be seen from the results that permeate flux decreased with all membranes when flow rate decreased. NFX had the biggest decrease, but the amounts are similar to all membranes. Only NF had decrease in Na_2SO_4 rejection and Desal even had higher rejection with lower feed rate. This shows that it is very important to keep the same flow rate in order to have results that are comparable.

Permeate flux was also measured in a higher temperature. This was done by using the same solution but changing temperature to 40 °C. This rise of 25 % in temperature did not change permeate flux or rejection at all.

12.4. Na_2SO_4 and $ZnSO_4$ solutions

To study the membrane behaviour with solutions using multiple different metal salts, $ZnSO_4$ was added to the Na_2SO_4 solutions with a ratio of approximately 20 to 15 % $ZnSO_4$ of overall salt. These solutions were made to have total salt concentration close to the original concentrations of single metal salt solutions for easier comparison of permeate flow and salt concentration. Flux was again stabilized for 20 minutes when pressure or feed solution was

changed. First measurements were made for the solution with of 5.64 % salt. Measured permeate flow and salt rejection are presented in figure 20.

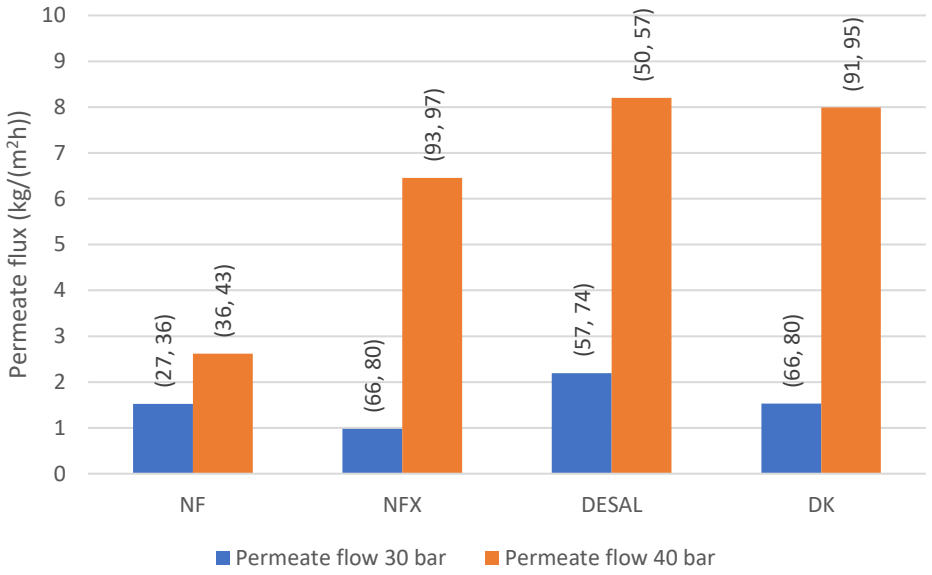

Figure 20. Measured permeate flow and Na_2SO_4 & $ZnSO_4$ rejection with 5.6 % solution at 30 and 40 bar for each membrane.

Same measurements were next done for the 4.0 % solution and lastly for the 1.7 % solution. Results for these measurements are presented in figures 21 and 22.

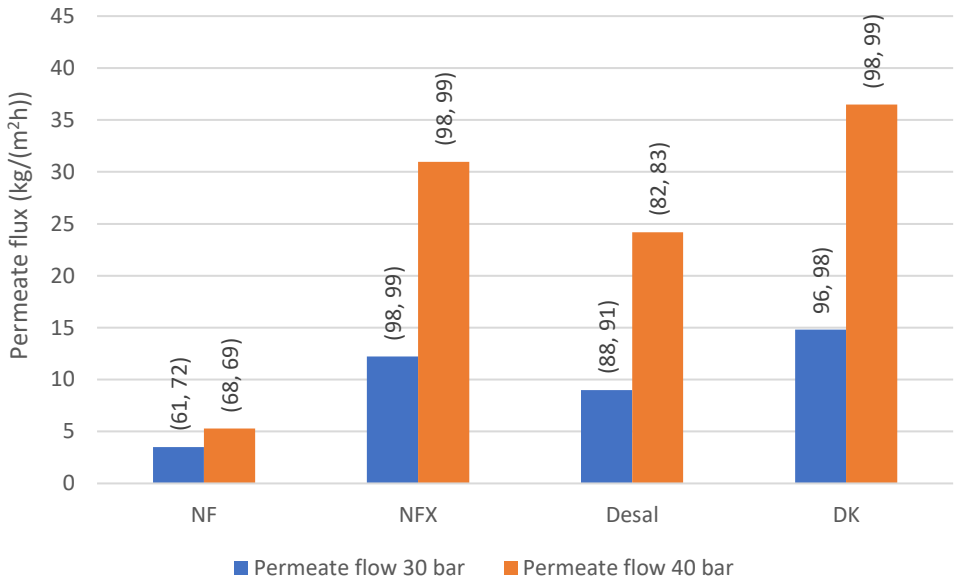

Figure 21. Measured permeate flow and Na_2SO_4 & $ZnSO_4$ rejection with 4.0 % solution at 30 and 40 bar for each membrane.

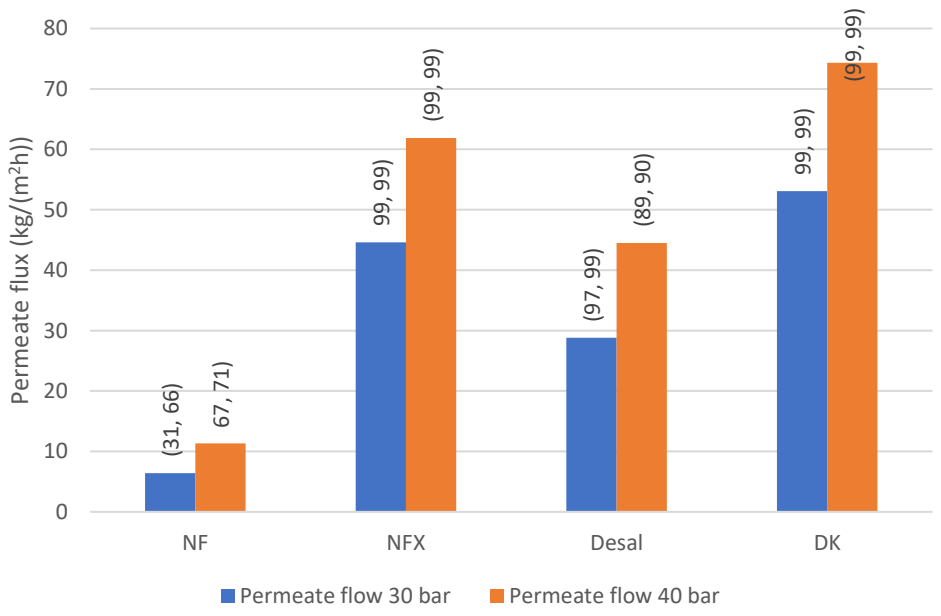

Figure 22. Measured permeate flow and Na_2SO_4 & $ZnSO_4$ rejection percentage with 1.7 % solution at 30 and 40 bar for each membrane.

With two different metal salts in the solution used membranes performed in similar way as with only one salt. Best results were again achieved when the hydraulic pressure was highest compared to osmotic pressure. NFX and DK membranes performed best, having biggest permeate fluxes and best salt rejection. The addition of bivalent metal ion also resulted in some change to natrium rejection. When samples from previously presented measurements were compared to the similar ones with similar feed solution concentrations and same used pressures, it can be seen, that in every sample addition of bivalent ion decreased natrium salt rejection. These decreases are marginal and can also be a result of slightly higher overall metal salt concentration in the solution containing Na_2SO_4 and $ZnSO_4$. Comparison between these results is presented in figure 23 for NFX and DK, and in figure 24 for NF and Desal.

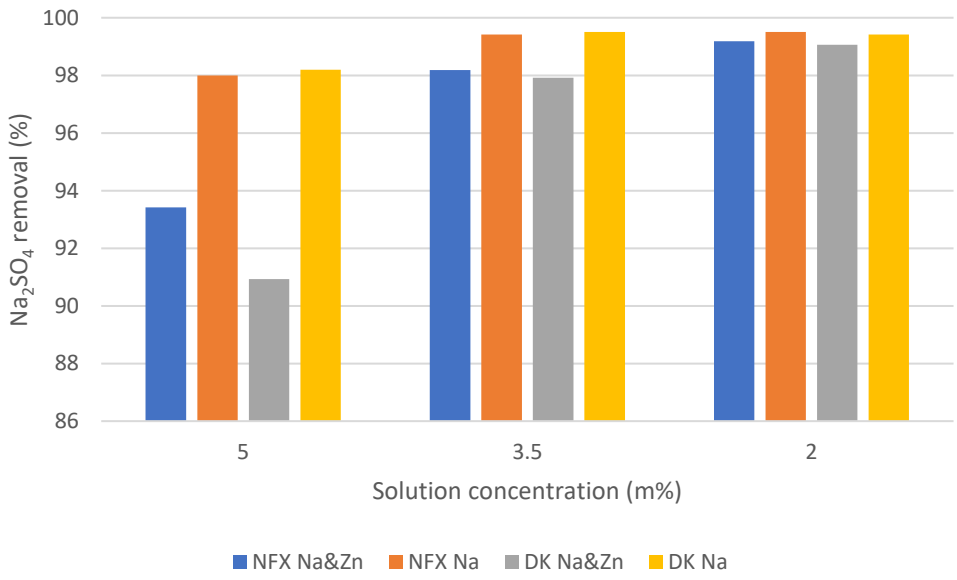

Figure 23. Natrium salt rejection comparison between feed solutions with Na_2SO_4 and solutions with Na_2SO_4 and $ZnSO_4$ using NFX and DK membranes.

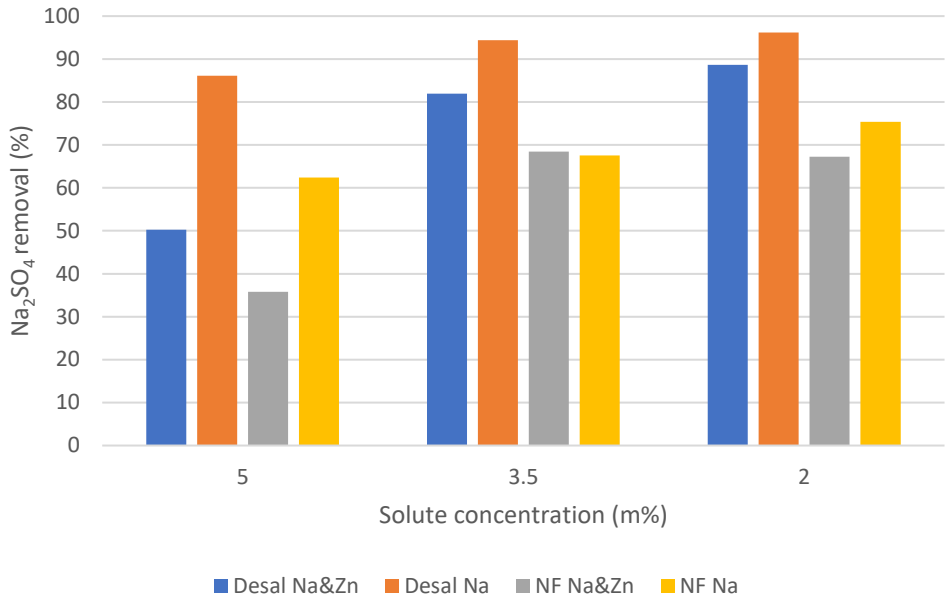

Figure 24. Natrium salt rejection comparison between feed solutions with Na_2SO_4 and solutions with Na_2SO_4 and $ZnSO_4$ using NF and Desal membranes.

12.5. Acidic Na_2SO_4 and $ZnSO_4$ solutions

Results with Na_2SO_4 solutions and with Na_2SO_4 and $ZnSO_4$ solutions consistently showed that better rejection and permeate flux results were obtained when using higher pressure. Because of this only 40 bar pressure was used for the next measurements. In between experiments with different feed solutions the filtration system was neutralised by removing the feed solution and adding pure water. Neutralization was done until feed solution reached pH values over 6.

Permeate fluxes and rejection efficiency for each membrane while using different feed solutions are presented in figure 25.

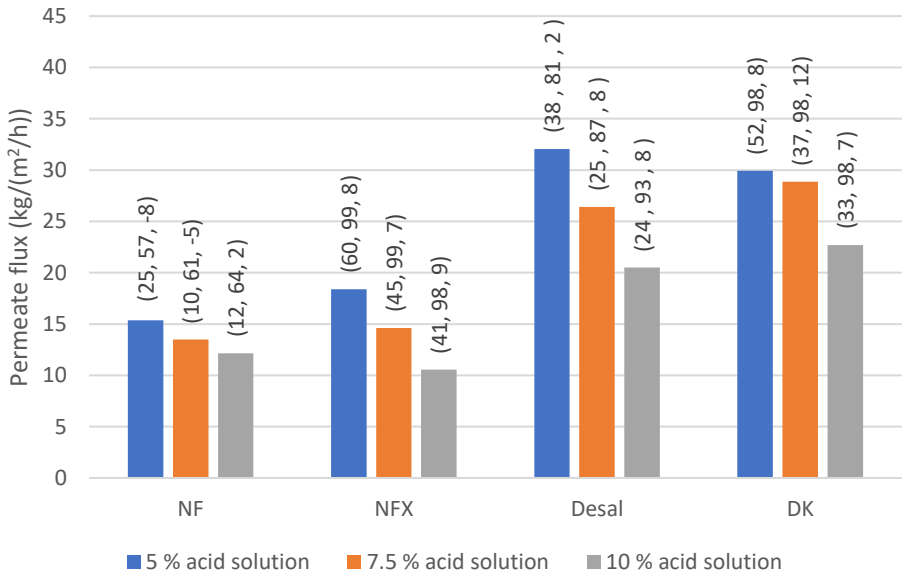

Figure 25. Measured permeate fluxes and Na_2SO_4, $ZnSO_4$ and sulphuric acid rejection at 40 bars for each membrane. Solutions used contained 5% Na_2SO_4 and 0.5% $ZnSO_4$.

In figure 26 the permeate flux of each membrane was compared to permeate flux of said membrane when using similar solution which had no acid. All solutions contained approximately 5 % Na_2SO_4 and 0.5 % $ZnSO_4$

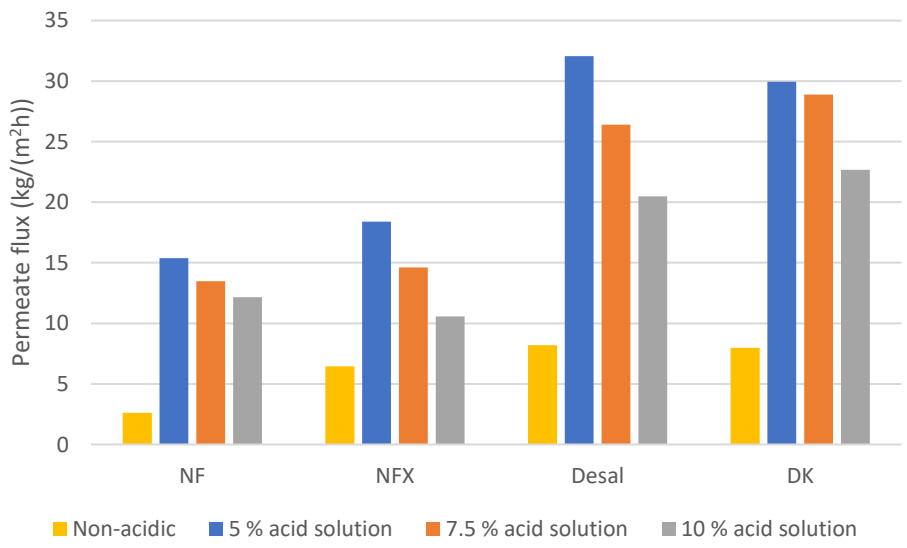

Figure 26. Measured permeate fluxes with feed solutions containing no-acid, 5 % acid, 7.5 % acid and 10% acid. All solutions contained approximately 5 % Na_2SO_4 and 0.5 % $ZnSO_4$.

Permeate flow of all four membranes increased considerably with the addition of acids seen in figure 26. This positive change can be explained with the decreased osmotic pressure difference between feed and permeate which is caused by the lower rejection of Na_2SO_4. Membranes charge also changes when introduced to low pH, which can also cause this change. The addition of sulfuric acid to feed solution also noticeably changed the behaviour of used membranes. As discussed in literature membrane selectivity changes to preferring multivalent ion removal. This can be seen in the decrease of natrium removal percentages as well as in the slight increase in zinc removal percentages. These results were expected to occur when high concentration of acid is present. Acid removal was one question that was asked before experimental part begun. As seen in the figure 25, none of the used membranes substantially removed acid, and in some cases sulfuric acid even concentrated into the permeate.

Highest rejection was again obtained when using NFX and DK membranes. These membranes had close to 100% $ZnSO_4$ rejection in all acid concentrations and the increase was small because removal was close to 100% in non-acidic solutions as well. Desal membrane reached over 90% $ZnSO_4$ removal as the acid concentration increased. NF membrane seemed to not work too well in these conditions either, although it had increased $ZnSO_4$ rejection, Na_2SO_4 rejection dropped down even further, and rejection was again lowest out of all four membranes.

Performance of the membranes in acidic and non-acidic feed solution is next shortly compared in figures 27 and 28.

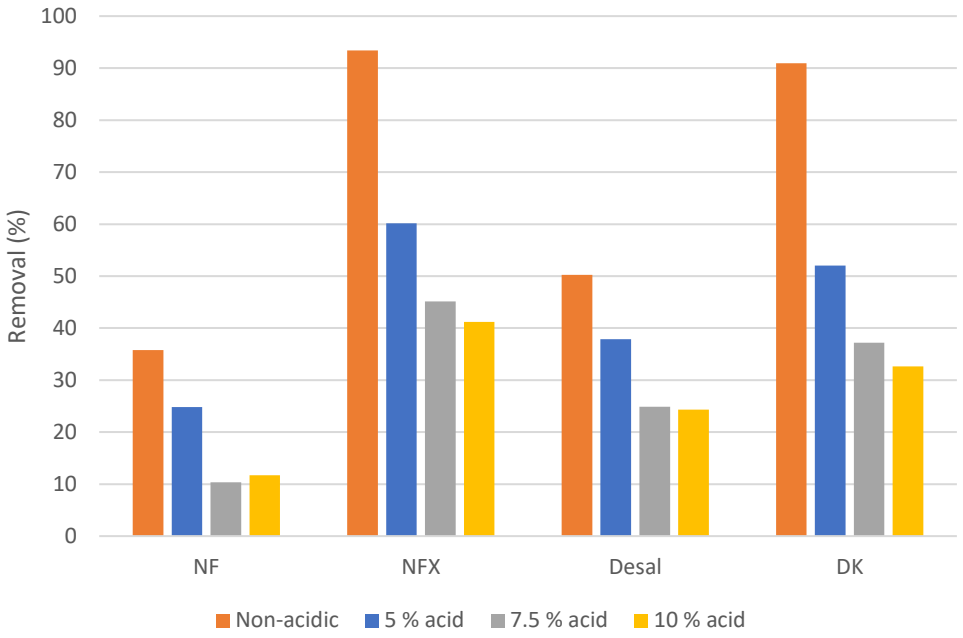

Figure 27. Na_2SO_2 rejection in acidic and non-acidic feed solutions containing 5 % Na_2SO_4 and 0.5 % $ZnSO_4$ with each membrane.

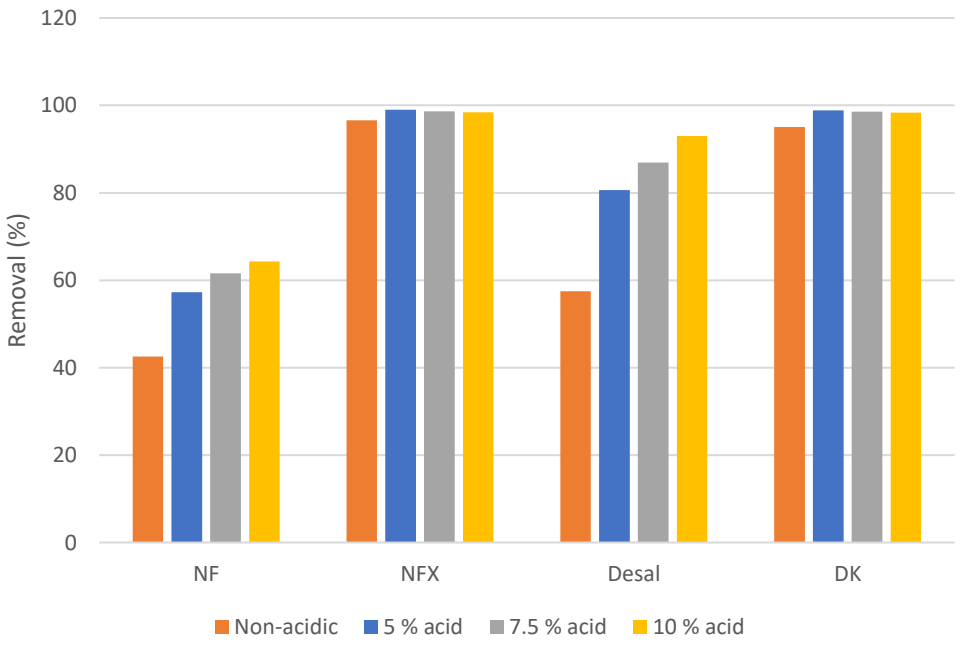

Figure 28. $ZnSO_4$ rejection in acidic and non-acidic feed solutions containing 5 % Na_2SO_4 and 0.5 % $ZnSO_4$ with each membrane.

12.6. Slightly acidic Na_2SO_4 solutions

As noticed before the addition of acid decreases Na_2SO_4 rejection. Because all solutions where this was noticed contained high amounts of acid one series of low acidity solutions was done. Goal for these measurements was to see if some sulphuric acid concentration where Na_2SO_4 rejection decrease begins can be found. Experiment system was again neutralized when feed solution was changed, and flux was stabilized for 20 minutes. Results for these experiments are presented in figure 29.

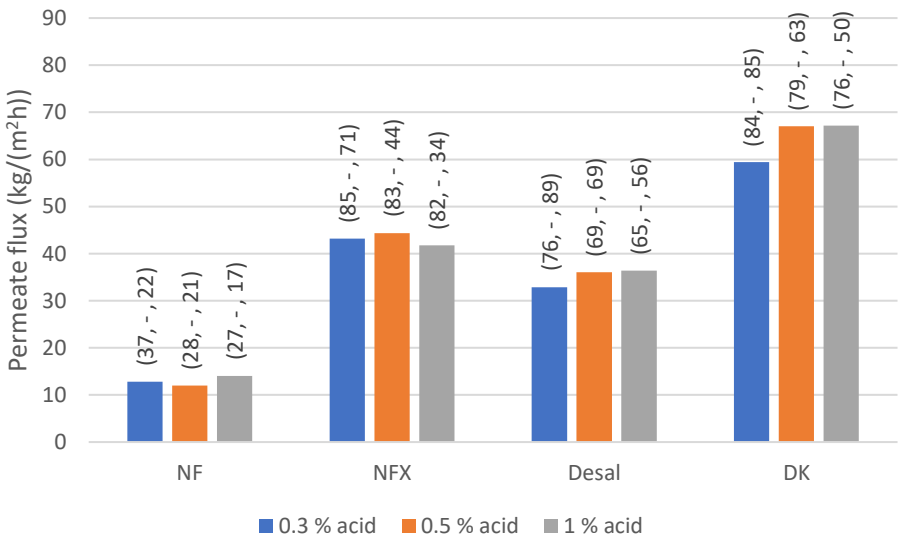

Figure 29. Permeate flux and Na_2SO_4 and sulphuric acid rejection in slightly acidic solutions.

As seen from the figure 29 the increase in acid in such low concentrations had no clear impact on permeate flux. Sulphuric acid removal was surprisingly high at low feed concentrations but quickly decreased as the feed concentration of sulphuric acid increased. These results do indicate that acid removal with NFX, Desal and DK membranes could be possible with low sulphuric acid feed concentrations.

The rejection of Na_2SO_4 steadily decreased as acid concentration increased. Based on these results it can be said that even small amounts of acid in used solution decreases the Na_2SO_4 removal efficiency of these membranes. Comparison between results from non-acidic feed

solution Na_2SO_4 removal percentage and results of this measurement series are presented in figure 30.

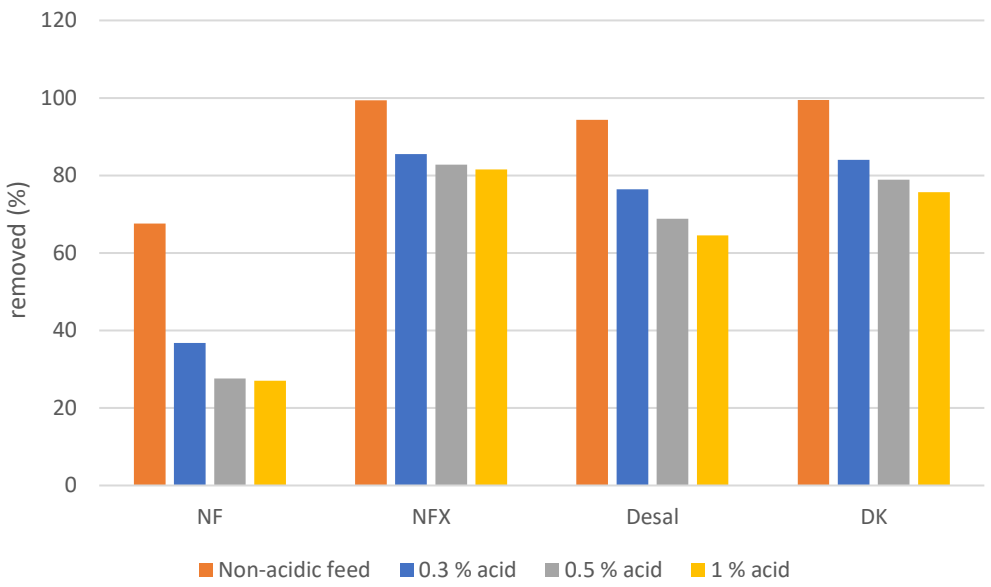

Figure 30. Comparison of Na_2SO_4 rejection between feed solutions containing no acid, 0.3 % acid, 0.5 % acid, and 1 % acid.

12.7. Real solutions

After membrane performance was studied in solutions with tailored Na_2SO_4, $ZnSO_4$ and sulphuric acid compositions in different filtration conditions real industrial wastewaters were also tested. Samples 1 and 2 had similar composition with low acid concentration and relatively low metal salt concentrations. Results for the measurements are presented in figures 31 and 32.

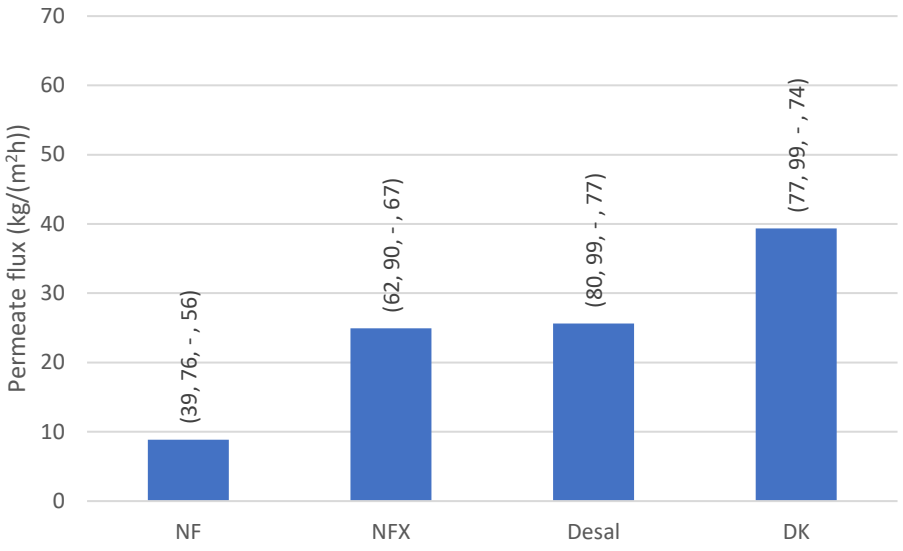

Figure 31. Sample 1 measured permeate fluxes and Na_2SO_4, $ZnSO_4$ and TOC rejection at 40 bars for each membrane.

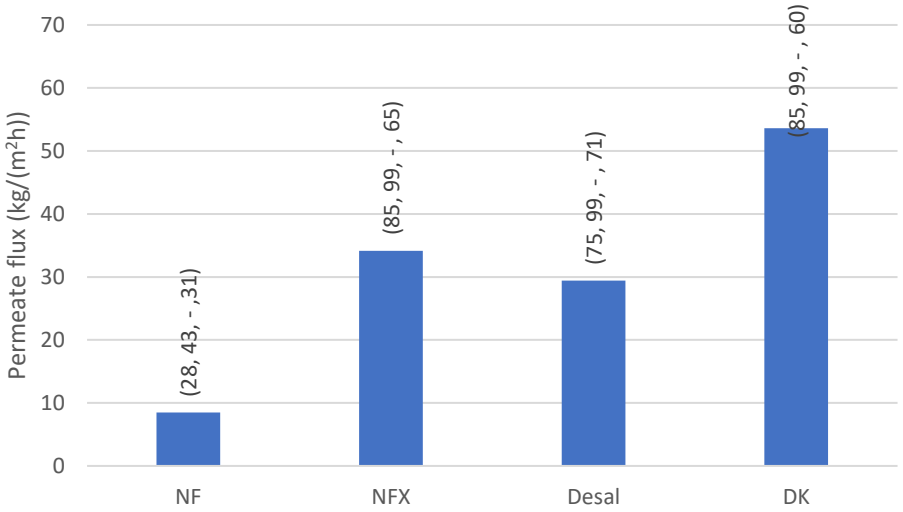

Figure 32. Sample 2 measured permeate fluxes and Na_2SO_4, $ZnSO_4$ and TOC rejection at 40 bars for each membrane.

Sample 3 had higher concentrations of Na_2SO_4, $ZnSO_4$ and had considerable amount of sulphuric acid. Results for experiments done sample 3 are presented in figure 33.

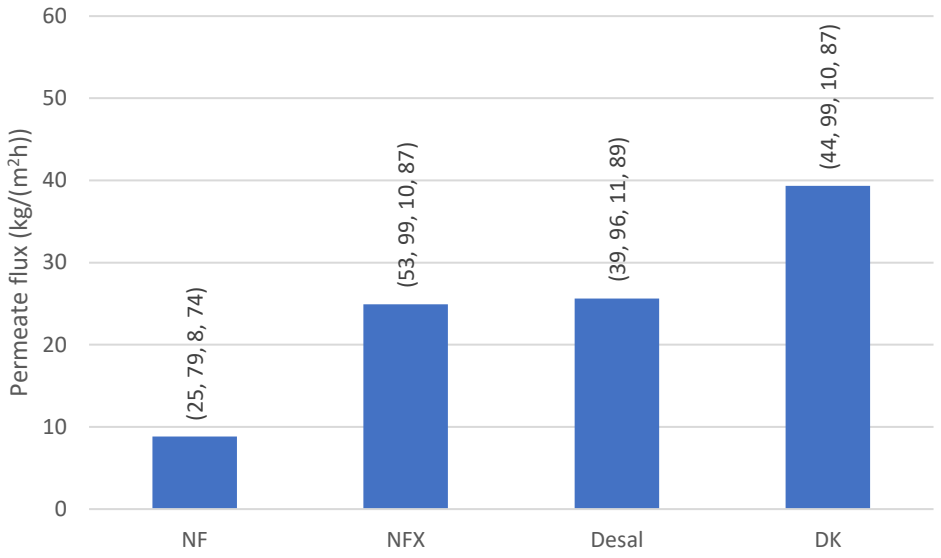

Figure 33. Sample 3 measured permeate fluxes and Na_2SO_4, $ZnSO_4$, sulphuric acid and TOC rejection at 40 bars for each membrane.

Rejection for real solutions was similar to previous results. Addition of organic matter did not considerably affect rejection or permeate flux. DK membrane had the highest permeate flux as well as highest Na_2SO_4 and $ZnSO_4$ rejection with all feed solutions. $ZnSO_4$ rejection staid at 99 % with every feed solution and Na_2SO_4 rejection was around 80 % with samples 1 and 2. Like noticed before Na_2SO_4 rejection decreased a lot when feed solution with higher sulphuric acid concentration was used. NFX and Desal membranes had similar results with each other. Both had over 90 % $ZnSO_4$ rejection with all feed solutions and around 75 % Na_2SO_4 rejection with samples 1 and 2. Biggest difference they had to DK membrane was up to 20 kg/m^{2}h lower permeate flux. NF membrane had again low rejection to Na_2SO_4 and $ZnSO_4$ as well as low permeate flux. TOC removal was similar with all membranes being around 65 % -75 % on samples 1 and 2 and around 75 % - 89 % on sample 3.

12.8. Changes in permeate flux

After all measurements were done control measurements for pure water permeability and one Na_2SO_4 solution were carried out. This is done in order to find out if membrane permeability has changed at some point of the experiment period. Changes can be caused by

fouling, flattening and damage caused by acid which are possible due to high salinity solutions, high pressure, extreme pH and solutions containing organic matter. Measuring was done at exactly same conditions as the measurement earlier with 3.7% Na_2SO_4 solution, but only at 40 bar pressure. New solution with approximately 3.7% Na_2SO_4 was used, and results were compared. This comparison between these measurements is presented in figure 34.

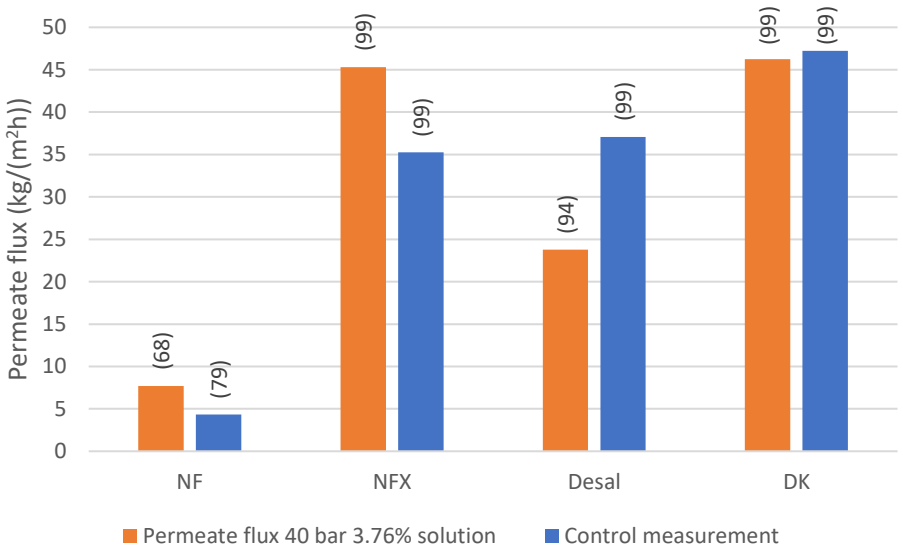

Figure 34. Comparison between first measurement and control measurement for each membranes permeate flux and Na_2SO_4 rejection when using feed solution containing approximately 3.7 % Na_2SO_4.

Next, pure water permeability was measured in the same way as it was done before. Measurements were done at 10, 15 and 25 bar pressures and the cumulating permeate water was weighed. Permeate flow was then calculated with equation 1. From these results pure water permeate flux was calculated with equation 2. Comparisons between the results of first permeate flux analysis and this one is presented in figures 35 and 36.

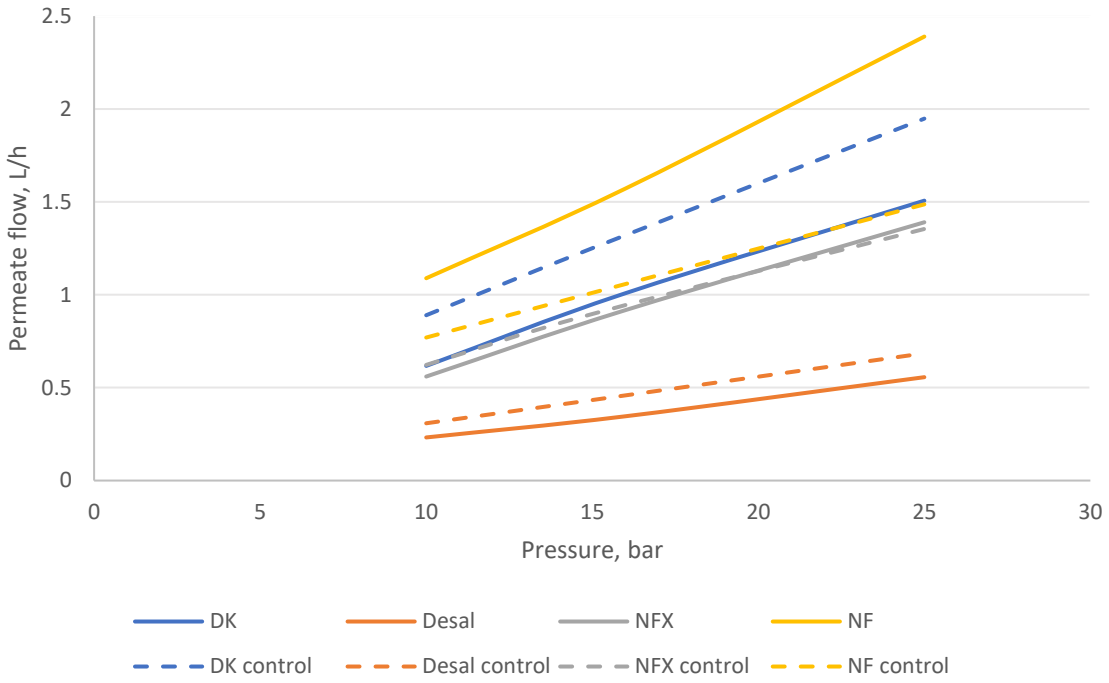

Figure 35. Comparison of permeate flow between first and control measurements for all membranes.

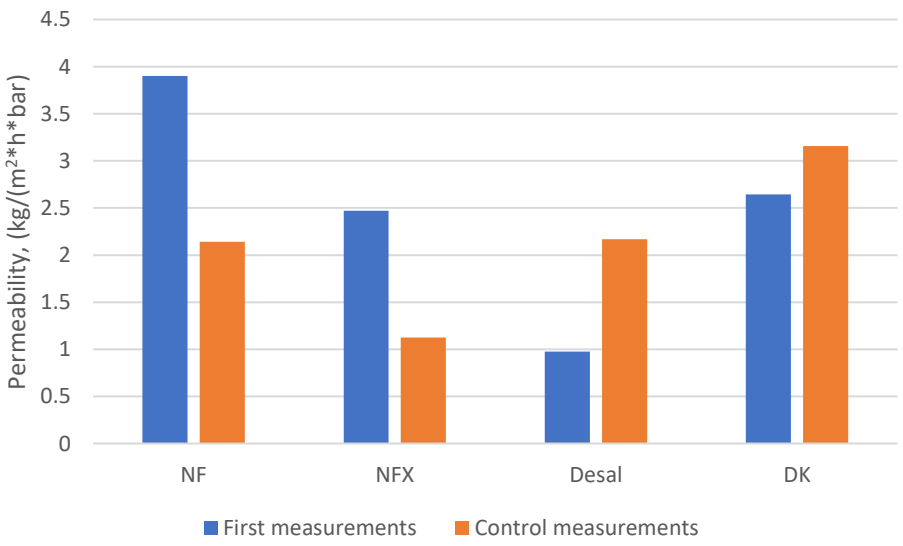

Figure 36. Comparison between first and control measurements of permeability on each membrane.

As seen from these results permeability was decreased for NF and NFX membranes. However NF did not seem to work properly at any point for this study. Decrease in NFX permeability can be caused by fouling, flattening or cake formation. Desal and DK membranes had increased permeability which can also be resulted from fouling, flattening or cake formation, or the membranes were not pressured well enough at the beginning of experiments and opened up more during measurements. Possible damage in membranes is caused by highly acidic solutions, high salinity solutions and/or organic matter. It is also possible that the membranes suffered from flattening because used pressures and temperatures were relatively high. Flattening causes changes in permeate flow.

Some error on these results can be caused by short 5-minute measuring period which had to be used because the pure water permeate flux was so high. This multiplies possible errors and can cause unreliability.

12.9. Zeta potential results

Zeta potential calculated by the used software and isoelectric point for each membrane are presented in figures 37 - 40.

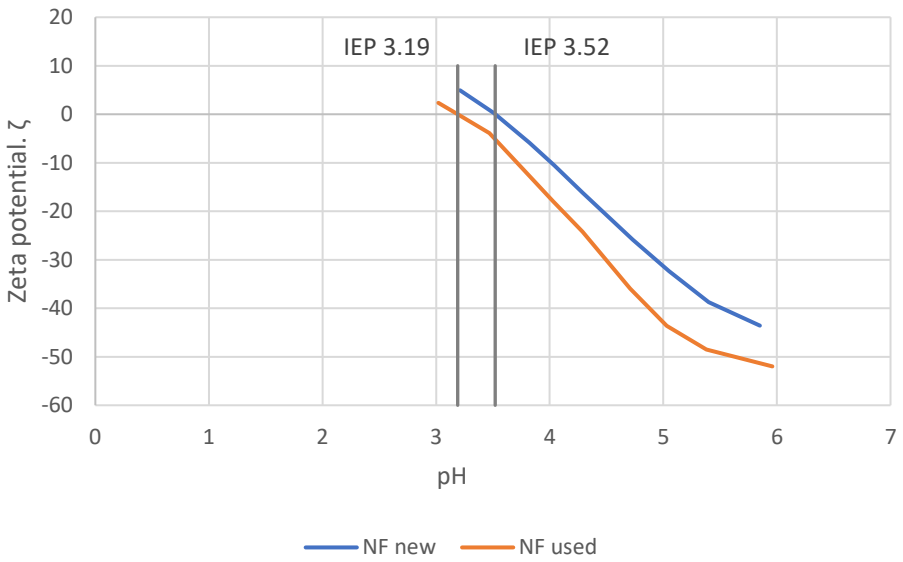

Figure 37. Zeta potential as pH´s function and IEP for new and used NF membrane

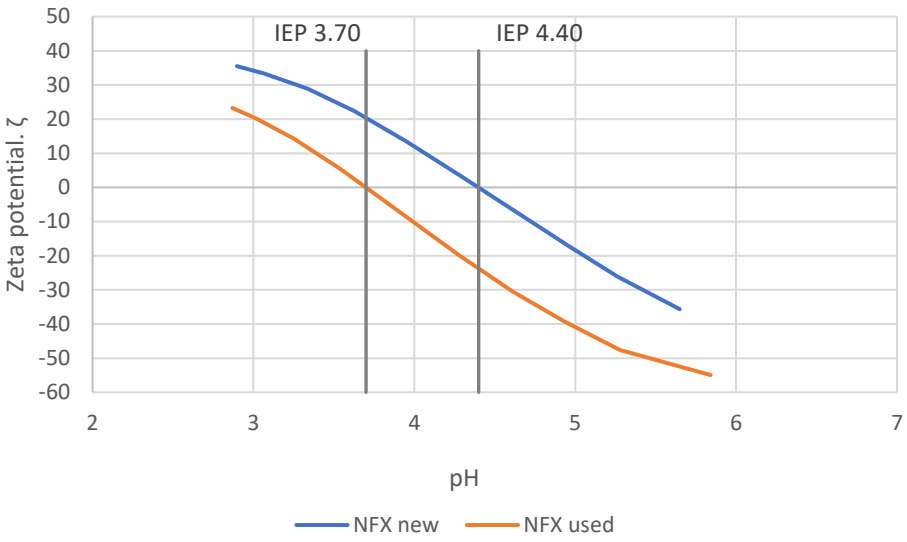

Figure 38. Zeta potential as pH´s function and IEP for new and used NFX membrane

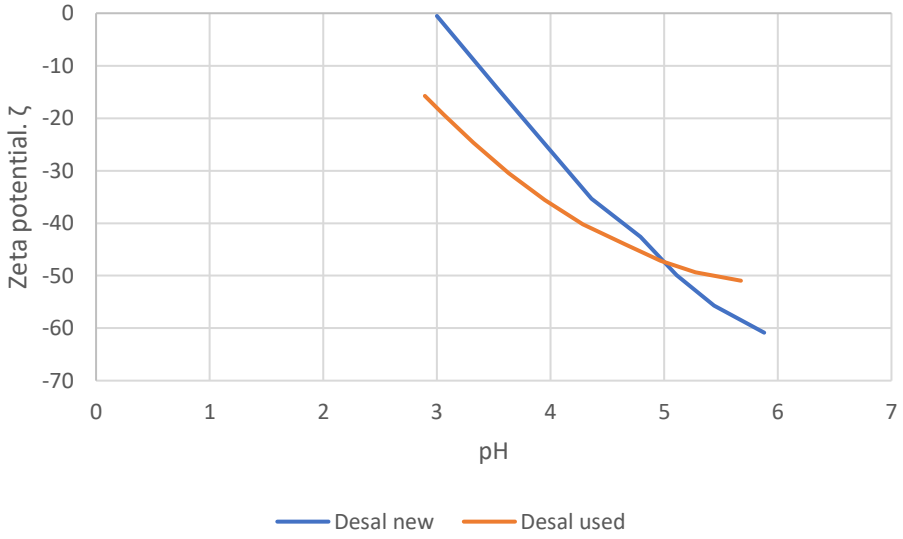

Figure 39. Zeta potential as pH´s function for new and used Desal membrane

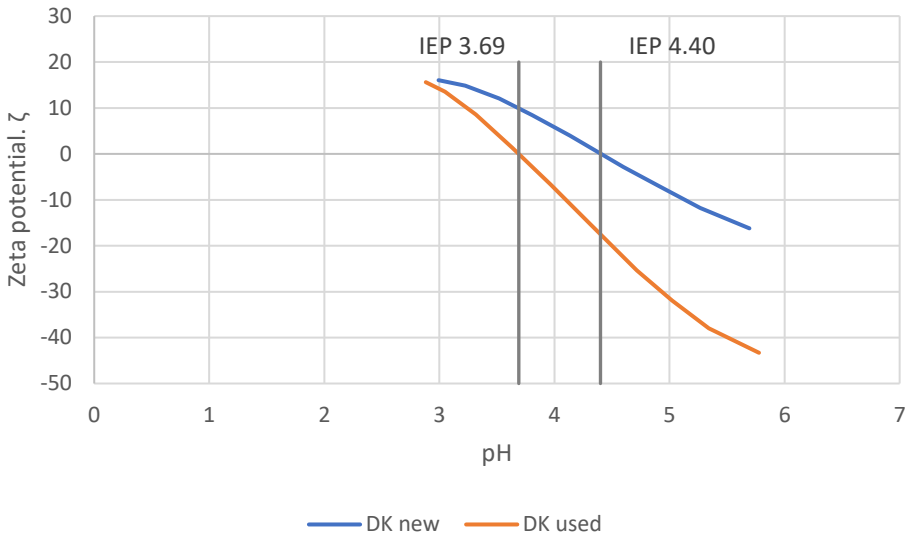

Figure 40. Zeta potential as pH´s function and IEP for new and used DK membrane

Zeta potential for all membranes lowered after use. This is resulted from surface charge changes caused by low pH solutions. IEP was also lower in every case because profile of the zeta potential curve stayed similar even though it was lower. Surprisingly Desal membrane has IEP so low that it was not even reached in the pH range of 7 to 3. From these results it can be seen that when acidic solutions were used in this study zeta potential for all membranes was above zero. Although IEP for Desal membrane was not determined it can be assumed that it was positive at such high acidity solutions. As membranes acquired positive zeta potentials, they also acquired positive surface charges, which can explain increased permeate flux and rejection values.

12.10. Contact angle results

Contact angle was measured 10 times for each membrane and the median and standard deviation SD was calculated. Results are presented in table 11.

Table 11. Median and standard deviation (SD) for measured contact angles on used and unused membranes.

	Left angle		**Right angle**	
	Median	**SD**	**Median**	**SD**
NF used	59.1	1.2	59.7	1.5
NF new	23.1	3.4	24.8	3.3
NFX used	63.4	0.8	63.3	0.8
NFX new	30.6	3.3	32.2	3.8
Desal used	70.2	3.5	72.4	3.5
Desal new	44.0	3.8	45.6	2.5
DK used	84.4	2.8	84.4	2.6
DK new	38.0	7.4	37.1	5.6

All membranes used in this study were hydrophilic. Clear increase in contact angles can be seen after the experimental part. Some wearing off could have happened during the filtration which would explain the increase because roughness off the contact surface has an impact on the contact angle especially when using sessile drop method (Rosa, de Pinho 1997). Increase in contact angle is not wanted since the increase in contact angles implicate decreased hydrophilicity which usually increases fouling speed.

12.11. FTIR results

Differences between different membranes are small but some can be seen in absorbances at 3450-3200 cm^{-1}, 1620 cm^{-1} and 1150 cm^{-1} as seen in figures 42 - 44. NF and NFX membranes have lower absorbance at 3450-3200 cm^{-1} which indicates less N-H stretching in primary and secondary amines. Higher absorbance in Desal and DK membranes tells of a higher amount of these functional groups. At 1620 cm^{-1}, absorbance curve takes different shape in NF and NFX compared to DK and Desal and also reaches higher absorbance. This can be caused by bending of N-H bond or stretching of C = C bond in an alkene functional group. Especially NF has high absorbance compared to other membranes. Desal membrane has higher absorbance peak at 1150 cm^{-1} compared to other membranes which can be caused by stretching of C-O or C-N bonds in either aliphatic ether (C-O), tertiary alcohol (C-O) or amine (C-N) functional groups. Amine is the most likely one because the membranes are

made from polyamine materials. (Sigma Aldrich , Skrovanek, Howe et al. 1985, Tang, Kwon et al. 2007)

Comparison between membranes at these wavenumbers is presented in figures 41-43.

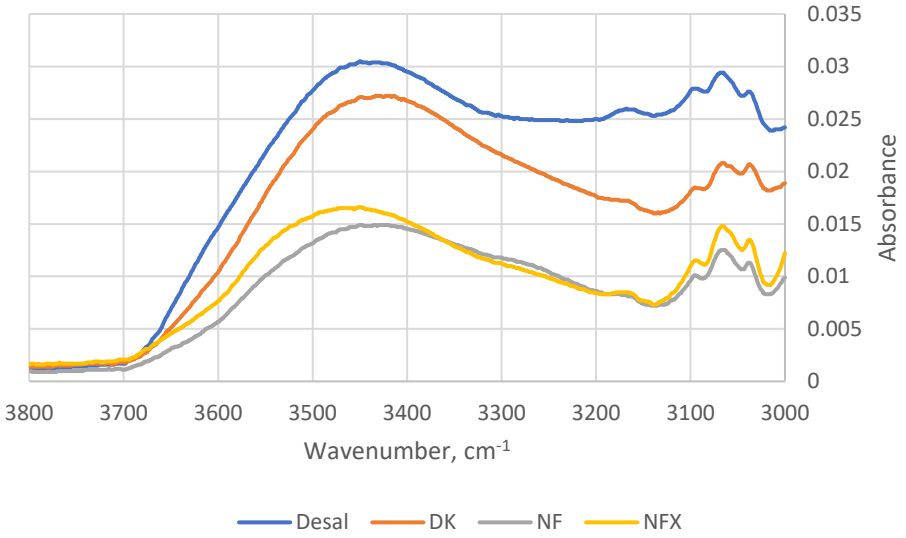

Figure 41. Difference in absorbance curve between new membranes at 3800 - 3000 cm^{-1}.

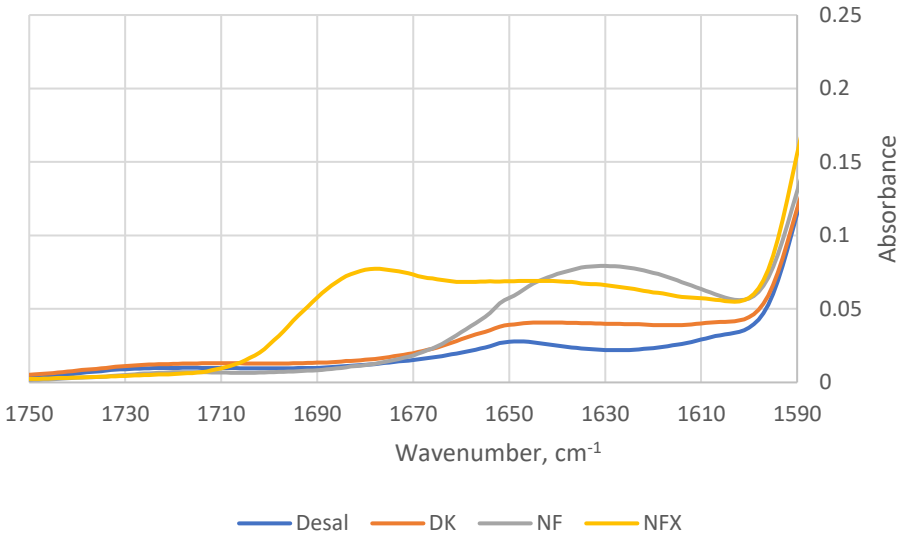

Figure 42. Difference in absorbance curve between new membranes between at 1750-1590 cm^{-1}.

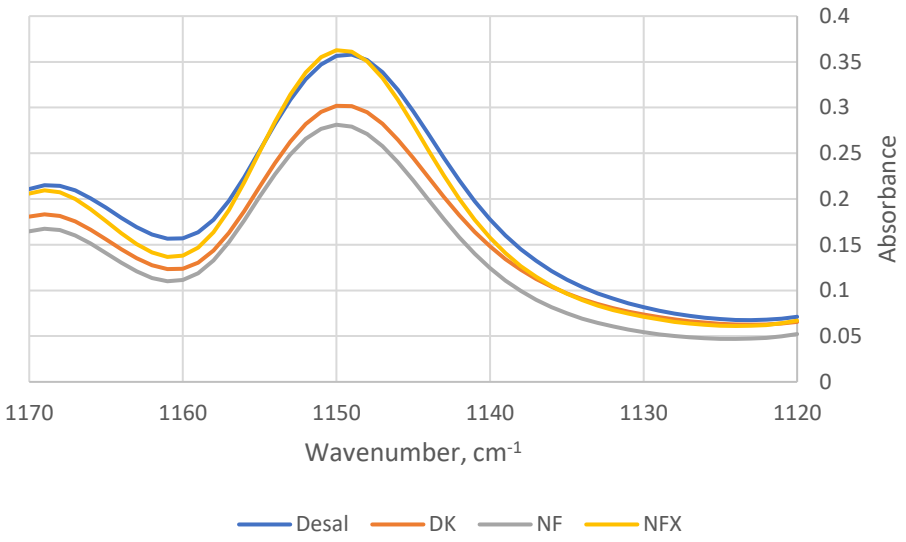

Figure 43. Difference in absorbance curve between new membranes between at 1170-1120 cm^{-1}.

As it can be seen the differences between membranes are not large and for the most part differences are even smaller than these presented. FTIR analysis was also done to used membranes in order to specify possible fouling agents from the membranes. Differences were again small and no real fouling agents were found. Largest difference was seen with Desal and DK membranes at 34500-3200 cm^{-1}, where absorbance increased. Comparison between used and new Desal and DK membranes is presented in figures 44 and 45.

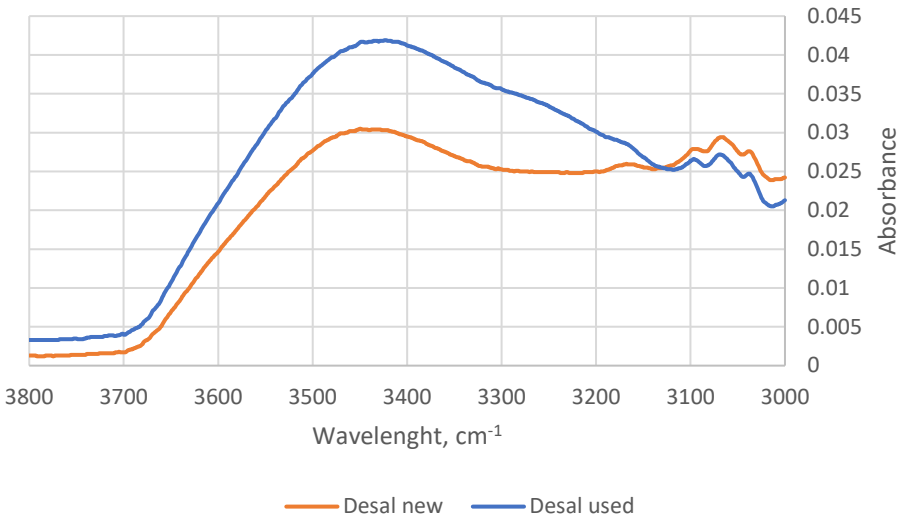

Figure 44. Difference in absorbance curve between used and new Desal membranes at 3800-3000 cm^{-1}.

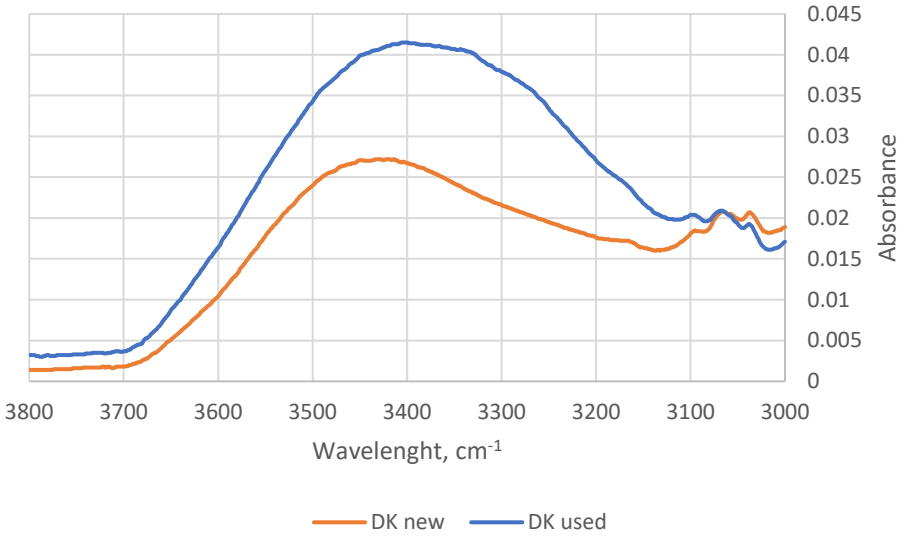

Figure 45. Difference in absorbance curve between used and new DK membranes at 3800-3000 cm-1.

These differences were most likely caused by increased amount of N-H bonds in primary and secondary amines. All and all results from FTIR analysis did not give any surprising differences between membranes or identify any fouling agents, which most likely is because no fouling occurred in sense of clogging or cake formation. Full FTIR spectrums are presented in appendix 1.

13. Conclusions

The aim of this study was to find the most fitting separation method for high volume acidic wastewater containing metal salts. Comparison between conventional separation methods quickly indicated that membrane separation would be the most fitting to the conditions this study focuses on. Out of different possible membrane separation processes the relatively new nanofiltration process showed the most promising theoretical separation performance and was chosen to be the main focus on this study. Four different nanofiltration membranes were chosen to be used in the experimental part, each with slightly different properties.

Membrane performance was on a decent level when first solutions containing only Na_2SO_4 were used. Best results were obtained with NFX and DK membranes at 40 bar pressure. Na_2SO_4 rejection for these two membranes reached 98 % with 2.2 %, 3.7 % and 5.2 % feed solutions and permeate flux was up to 70 kg/m^{2}h with 2.2 % feed solution and decreased when feed solution concentration increased. Desal membrane also performed decently with Na_2SO_4 rejections of 86 % to 94 % in 40 bar pressure and permeate flux up to 40 kg/m^{2}h. NF membrane performed poorly, and none the membranes performed well when 10.5 % feed solution was used. With 10.5 % feed solution, NFX and DK had rejections of over 80 % but permeate fluxes were only around 0.5 kg/m^{2}h. Desal and NF had rejections of around 45 % and permeate fluxes between 0.8 and 2 kg/m^{2}h. This indicates that the 40-bar pressure was not high enough to overcome osmotic pressure of the solution. Addition of $ZnSO_4$ did not affect Na_2SO_4 rejection significantly and the NFX and DK membranes had $ZnSO_4$ rejection of 95 to 99 % at 40 bars. Desal had $ZnSO_4$ rejection of 57 to 90 % at 40 bars. These rejection efficiencies are on a good enough level for both Na_2SO_4 and $ZnSO_4$ to be recycled back to the process feed. Permeate flux is also on a good level when lower concentration feed solutions are used but especially with 5.2 % feed solution a pressure above 40 bars could be used to reach better permeate flux what is needed in a large-scale process.

When acid was added to these solutions containing both salts multiple things happened. Firstly the permeate flux increased significantly. When a feed solution containing approximately 5 % total salt and 5 % acid was filtered at 40 bar pressure, the permeate flux increased on NF from 2 to 15 kg/m^{2}h, on NFX from 6 to 18 kg/m^{2}h, on Desal from 8 to 32 kg/m^{2}h and on DK from 8 to 30 kg/m^{2}h. When acid concentration was increased further the

permeate flux started to decrease but remained higher than when non-acidic feed solution was used. Na_2SO_4 rejection efficiency also decreased when acid was introduced to the feed solution, but $ZnSO_4$ rejection slightly increased although it was already on a really high level. Na_2SO_4 rejection decreased from 93 to 60 % on NFX membrane, from 50 to 38 % on Desal membrane and from 91 to 51 % on DK membrane. Rejection also decreased more when acid concentration increased. Acid rejection was also studied measured for all membranes, but it stayed at only around 10 % percent. Effect of acid was studied further with solutions containing only Na_2SO_4 and smaller amounts of acid. Results from these filtrations were similar as results obtained from filtrations done before with feed solution containing Na_2SO_4, $ZnSO_4$ and acid. Acid rejection was higher with these solutions reaching 89 % with Desal membrane when feed solution containing 0.3 % acid was used. Even though permeate flux increased addition of acid presented a new problem as too much Na_2SO_4 goes through the membrane into the permeate. $ZnSO_4$ was really well rejected as expected.

Results staid consistent with the previous ones when real industrial wastewater samples were used. It seemed like the addition of organic material did not affect filtration performance. Same issues of low Na_2SO_4 rejection remained. NFX and DK membranes performed best

Membrane characterization showed that the use of membrane had lowered the zeta potential of all the membranes, but no clear signs of fouling or cake formation was seen in the FTIR spectra. Contact angle values increased for all membranes during the use. No clear signs of damage were seen in the membranes The exposure time was really short and possible damage caused by acid and organic matter needs to be considered in long term use. Tanninen et al. have studied filtration performance in a long-term acid exposure for NF, Desal and DK membranes and according to their results only Desal maintained its rejection during the whole experiment (Tanninen 2004).

As a conclusion, DK and NFX membranes had high enough $ZnSO_4$ and Na_2SO_4 rejection when nonacidic feed solution was used but their permeate flux was relatively low especially when higher initial concentrations were used. With acidic feed solution $ZnSO_4$ rejection as well as permeate flux is on a level where they could be used on a wastewater treatment system but too much Na_2SO_4 passed the membrane into the permeate and therefore the permeate cannot be recycled back to the process without additional treatment. Based on the experiments done another filtration or other treatment method would be needed in order to

remove remaining Na_2SO_4 and acid from the permeate. On the other hand, at acidic conditions membranes could be used to separate zinc from acid and sodium sulphate.

14. References

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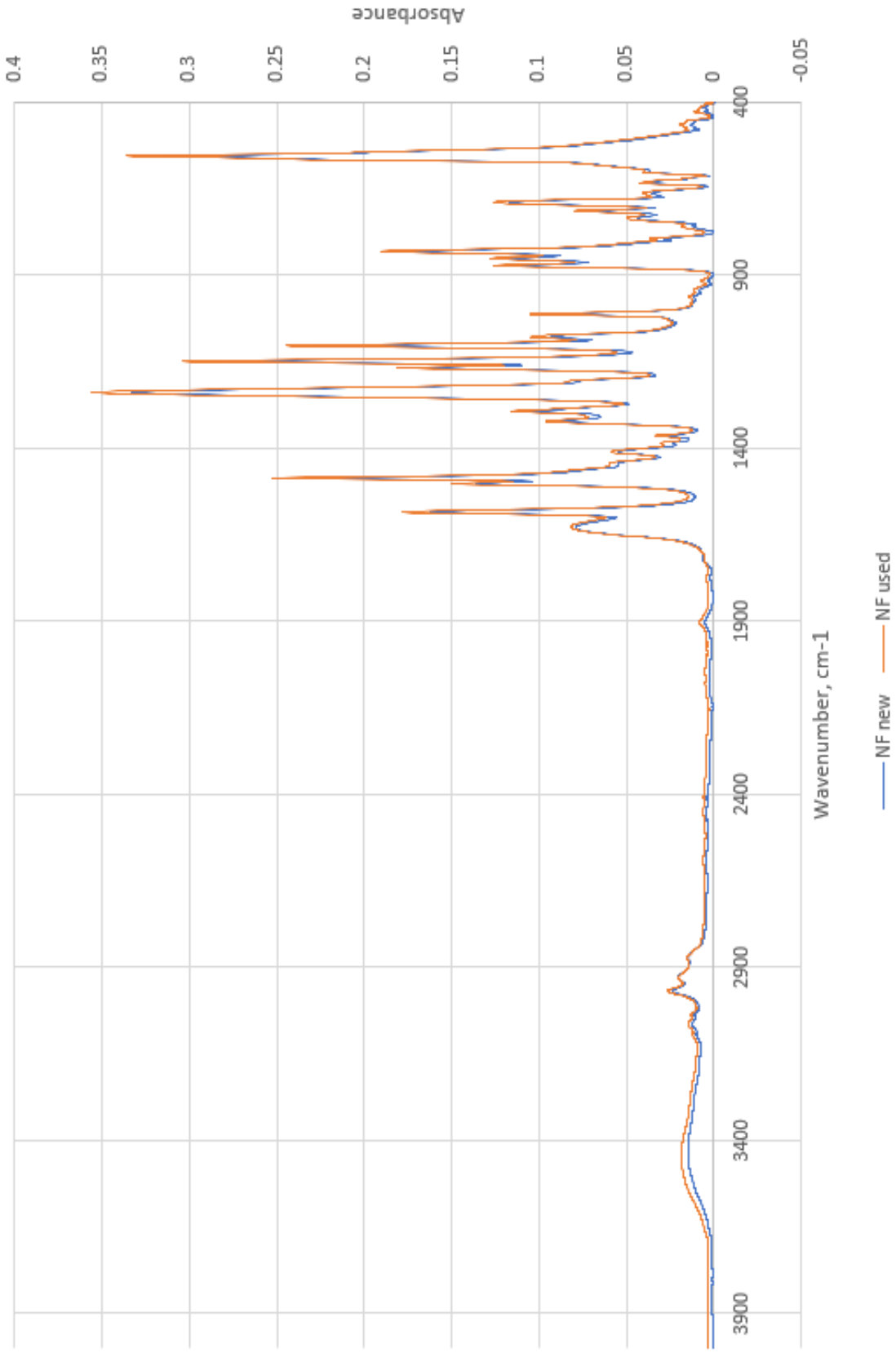
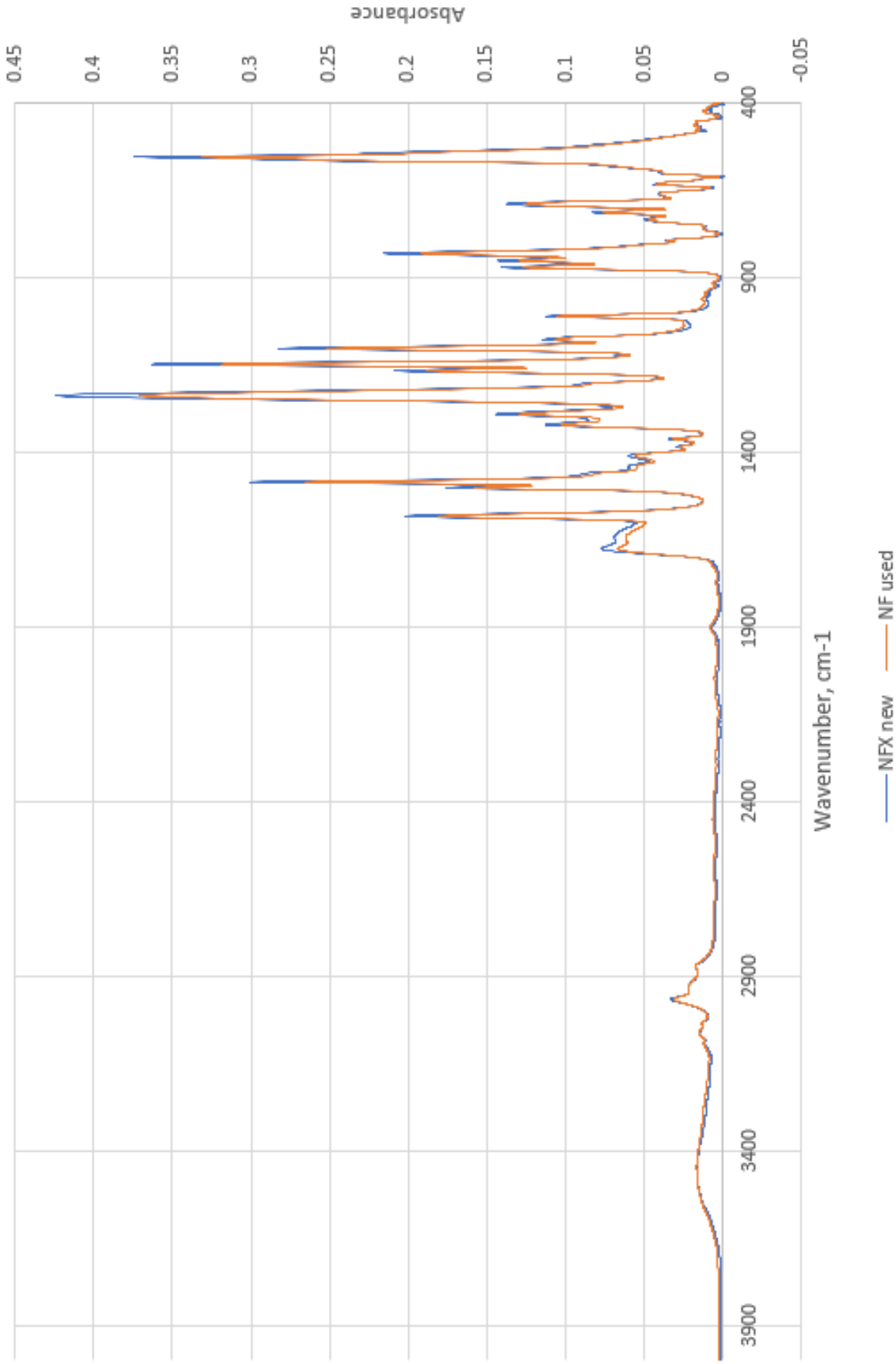
15. Appendices

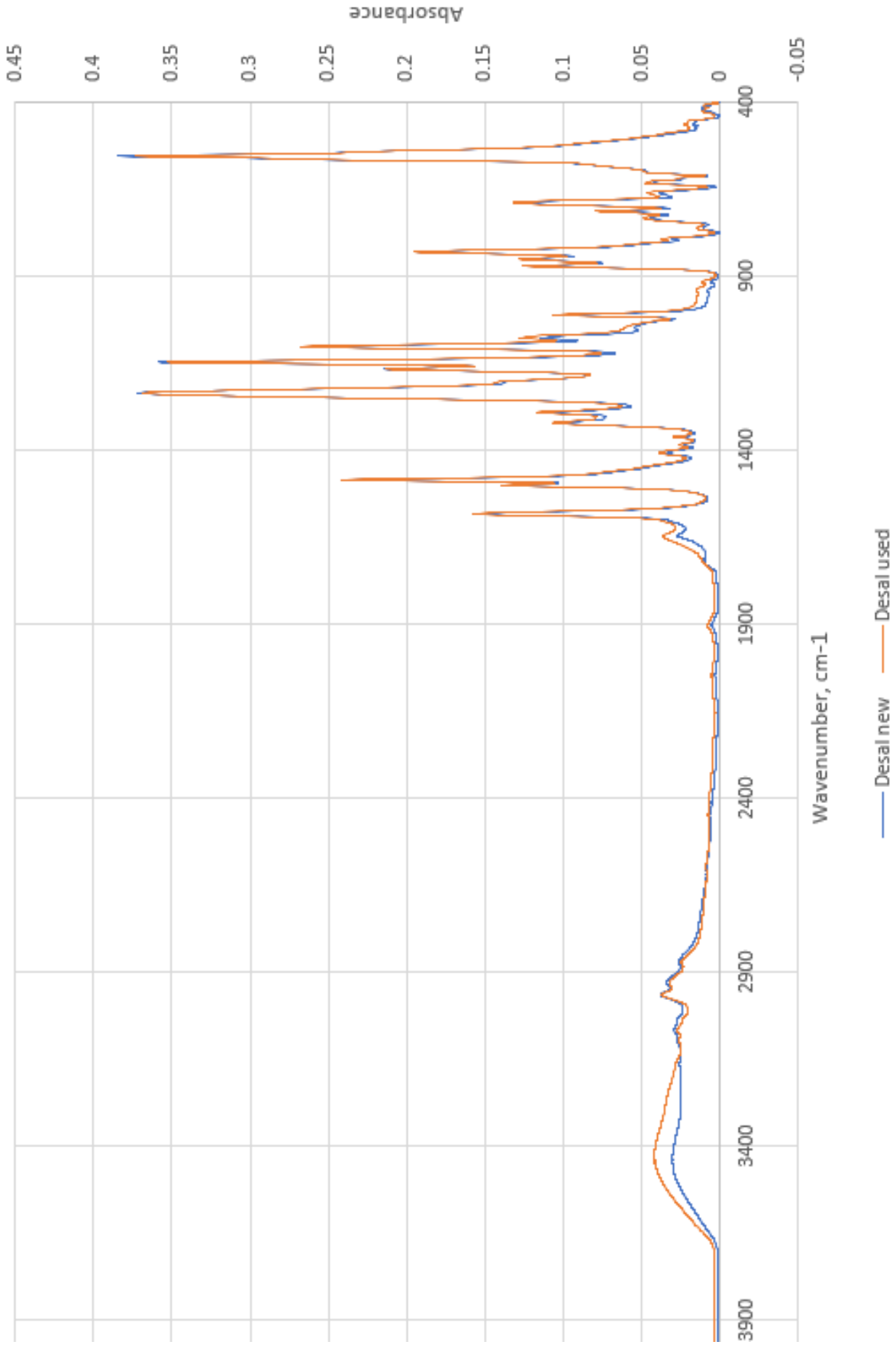
Appendix 1.1. NF membrane FTIR spectrum



Appendix 1.2 NFX membranes FTIR spectrum



Appendix 1.3. Desal membranes FTIR spectrum



Appendix 1.4. DK membranes FTIR spectrum.