SEPARATION OF IONS FROM ACID SOLUTIONS BY NANOFILTRATION

Examiners: Mika Mänttäri & Mari Kallioinen

Instructors: Mika Mänttäri & Mari Kallioinen

Date: 09.12.2016 Lappeenranta

Author: Oskari Salmenhaara

ACKNOWLEDGEMENT

TIIVISTELMÄ

Tekijä: Oskari Salmenhaara

Otsikko: Ionien erotus happamissa olosuhteissa nanosuodatuksella.

Osasto: LUT School of Engineering Science, Chemical Engineering

Vuosi: 2016

Hakusanat: Nanosuodatus, ionien erotus, ionien retentio, hapon suodatus, Donnan ilmiö

Nanosuodatus on suhteellisen uusi menetelmä membraanisuodatuksessa. Menetelmä yhdistää retentio-ominaisuuksia niin ultrasuodatuksesta kuin käänteisosmoosista, mahdollistaen selektiivisen membraanisuodatusprosessin UF ja RO suodatusten väliltä. Tyypillisesti nanosuodatusta on hyödynnetty veden pehmennyksessä, mutta kalvojen räätälöitävyyden ansiosta nanosuodatusta voitaisiin hyödyntää monilla teollisuuden aloilla.

Diplomityön tavoitteena oli tutkia ionien ja erityisesti raudan retentiota happamissa olosuhteissa sekä erottaa rautaioneja happoliuoksista. Kirjallinen osa käsittelee nanosuodatuksen perusteita ja suodatusta happamissa oloissa ja syventyy komponenttien erotukseen vaikuttaviin retentiomekanismeihin. Kokeellinen osassa tutkittiin ionien retentiota happamissa oloissa käyttäen kaupallisia GE-Osmonics ja AMS Technologies membraaneja. Ionien retentiota typpihappo liuoksessa tutkittiin pH skaalalla 5.4 – 1. Raudan retentiota puolestaan tutkittiin useilla rautakonsentraatioilla eri happoliuoksissa.

Tulokset osoittivat pH:n vaikuttavan ionien retentiojärjestykseen. Lisäksi tutkituilla membraanilla havaittiin erittäin korkea raudan retentio happamissa olosuhteissa. Tulosten valossa nanosuodatuksen hyödyntäminen metallien erotuksessa happoliuoksista vaikuttaa lupaavalta, tosin laajempaa tutkimusta aiheeseen liittyen tarvitaan.

ABSTRACT

Author: Oskari Salmenhaara

Title: Separation of ions from acid solutions by nanofiltration

Department: LUT, School of Engineering Science, Chemical Engineering

Year: 2016

Keywords: Nanofiltration, separation of ions, retention of ions, acid filtration, Donnan effect

Nanofiltration (NF) is relatively new concept in field of membrane filtration. NF combines retention characteristics from ultrafiltration (UF) and reverse osmosis (RO), thus providing intermediate filtration process between UF and RO. Conventionally, nanofiltration has been utilized widely in water softening application, but it could be tailored to numerous industrial applications.

The objective of this Master's Thesis was to investigate retention of ions in acidic conditions along with separation of iron from acidic solutions. Literature part presents the operational principle of nanofiltration along with deeper focus on retention mechanisms and reviews nanofiltration in acidic environment. Experimental part composed from studies regarding retention of ions and iron in acidic environment using NF membranes from GE-Osmonics and AMS Technologies. Retention of ions was investigated in pH scale 5.4-1 using nitric acid, while retention of iron was studies in various concentration of ions in different acidic solutions.

Results indicated than charge based retention mechanisms plays significant role in retention of ions. Studied membranes also showed promising retention of iron in highly acidic conditions. Obtained results indicates that nanofiltration could be utilized to separate metal ions in acidic environment, although more extensive research on the topic must be conducted.

ABBREVATIONS AND LIST OF SYMBOLS

$CaCl_2$	Calcium chloride
CP	Concentration polarization
DE	Dielectric exclusion
HF	Hollow fibre
IC	Ion chromatography
MPD	m-phenylene diamine
MWCO	Molecular weight cut-off
NF	Nanofiltration
HNO_3	Nitric acid
$(COOH)_2$	Oxalic acid
PA	Polyamide
RO	Reverse osmosis
NaCl	Sodium chloride
Na_2SO_4	Sodium sulphate
SW	Spiral wound
TFC	Thin-film composite membrane
TMC	Trimesoyl chloride
UF	Ultrafiltration
ZP	Zeta-potential

c_{feed}	Concentration of ion in the feed
c_{perm}	Concentration of ion in the permeate
$m_{c,p}$	Mass of collected permeate
J	Membrane flux
ΔJ	Membrane flux difference
P	Membrane permeability
Q	Permeate flow through membrane
Δp	Pressure difference
r_F	Retention Factor
R	Retention percentage
A_m	Surface area of membrane
δ	Thickness
$t_{c,p}$	Time of collected permeate

CONTENT

LITERATURE PART

1 INTRODUCTION

Due to increasing environmental awareness and tightening regulation in industrial water treatment the interest in nanofiltration has increased during past decades. Nanofiltration can be classified to be intermediate filtration process between ultrafiltration (UF) and reverse osmosis (RO) as it combines separation characteristics from both UF and RO filtrations. Due to selective retention of nanofiltration, it could be used in numerous industrial applications such as in water disinfection, heavy metal and contaminant removal. [1,2]

Nanofiltration in acidic environment have not been studied much in past decades due to small amount of commercially available acid resistant NF membranes. Also, industrial applications for nanofiltration in acidic conditions are scarce. However, Tanninen et al. have studied retention of salts and copper in acidic environment. [3,4]

Objective of this Thesis was to investigate retention of iron ions for nanofiltration membranes in acidic environment along with separation of metal ions from acid solutions using Ge-Osmonics and AMS Technologies membranes. Literature part presents the operational principle of nanofiltration along with deeper focus on retention mechanisms and reviews nanofiltration in acidic environment. To complement literature study, the experimental part composing from series of ion and iron retention studies in acidic environment were conducted. To understand results more thoroughly, theory behind NF retention phenomenon is essential to understand.

2   MEMBRANE FILTRATION

Membrane filtration is a pressure driven filtration process, which utilizes semipermeable membranes to separate chemical components from each other. Pressure aided membrane filtration processes can be divided to microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Nanofiltration can be considerate to be intermediate filtration process between reverse osmosis and ultrafiltration as it combines separation mechanisms from RO and UF. [5] Also, nanofiltration membranes have excellent retention capability to divalent ions and organic solutes, but monovalent ion retention is primarily between 20-70%. [6] In addition, NF provides considerable better retention than ultrafiltration membranes and higher permeate flux than conventional reverse osmosis. [7,8] In this chapter is presented the operation principle of membrane filtration and especially nanofiltration along with NF application areas.

2.1   Operation Principle of Nanofiltration

Pressure driven membrane filtration is a separation process, which utilizes a semipermeable membrane barrier to separate chemical compounds from feed solution to permeate and retentate streams. [9] Filtration process can be either dead-end or cross-flow process depending on how feed stream is directed towards membrane. In cross- flow filtration the feed stream is directed tangentially across the membrane surface where portion of the initial feed stream is permeated trough membrane and the rest goes to retentate stream. The retentate stream can be either collected or recycled back to filtration process. On the contrary in dead-end filtration, the feed stream is directed straight towards membrane and all feed solution is pushed through the membrane barrier. [10] The operation principle for cross-flow and dead-end filtrations are presented in Figure 1.
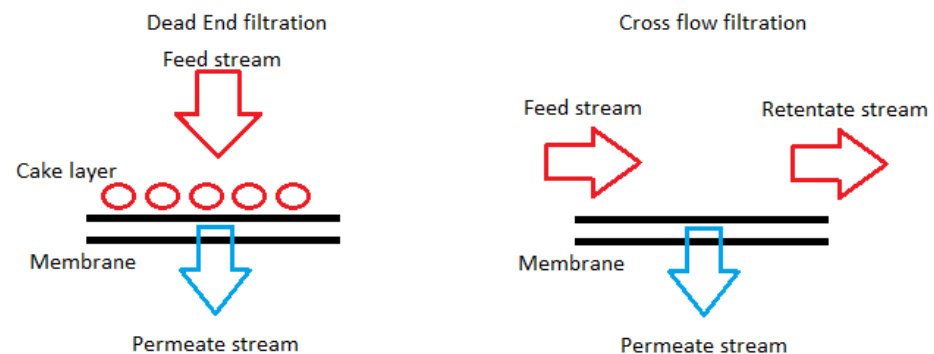
Figure 1. Principles of dead-end and cross-flow membrane filtration processes. [9]

In pressure driven membrane processes (excluding RO), component retention is occurring by sieving. Molecules and ionic compounds are retentates based on their size and shape. Compounds with smaller diameter than membrane pore diameter can pass membrane while larger compounds retentates to retentate stream. [9,10] Figure 2 Presents pressure driven membrane filtration processes, typical pore sizes and compounds that membranes retentates.
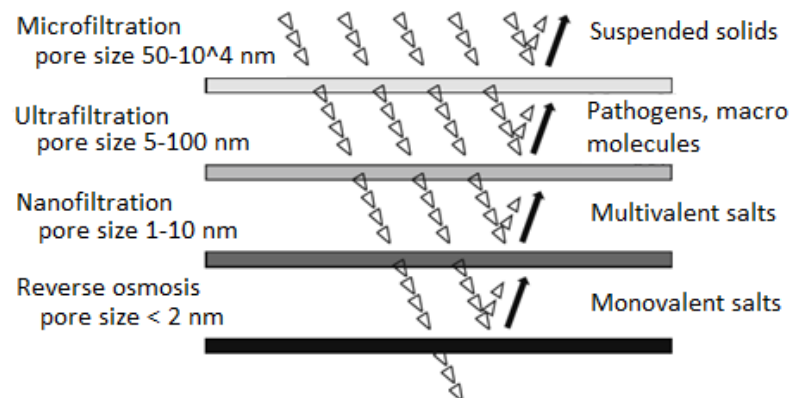
Figure 2. Pressure driven membrane processes, with estimated pore sizes and example compounds which can be retained. [9]

Nanofiltration is relatively new pressure driven membrane filtration process, which was introduced by Filmtech in 1980s. In nanofiltration the component retention is based on sieving, diffusion and electrostatic forces. Due to very small

pore size in nanofiltration, the nanofiltration pore are more accurately classified as "free space" inside the selective layers' polymer network rather than tubular capillary pores. Very small pores in nanofiltration membrane also enables permeation based on solution diffusion, which does not occur in UF. Since ultrafiltration membranes are clearly pore-flow type and reverse osmosis membranes are nonporous solution diffusion membranes, nanofiltration belongs to so called "transition zone" between these two. [11]

2.2   Membrane Types

Synthetic membranes can be manufactured from manufactured from large variety of materials such as polymers, ceramics, glass, metals and liquids. However only a portion of these materials have suitable permeability and selectivity properties along with required mechanical or chemical strength for specific applications. [1] Figure 3 illustrates the synthetic membrane classification base on membrane material.
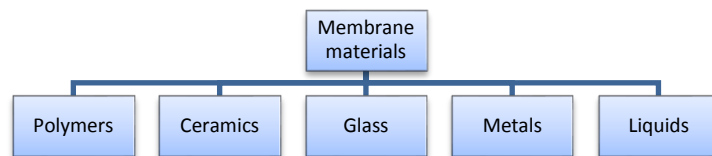
Figure 3. Synthetic membrane classification based on membrane material. [12]

Furthermore, membranes can also be divided to symmetrical or asymmetrical membranes based on their cross-sectional structure. Symmetrical membranes are membranes where mass transport properties are identical through the cross-section. Also, flux is determined by whole thickness of membrane. On the contrary, asymmetrical membranes such as thin film composite membranes (TFC) have porous or nonporous film layer and typically two additional supporting sub layers. [12] Figure 4 Presents the synthetic membrane classification based on membrane structure.
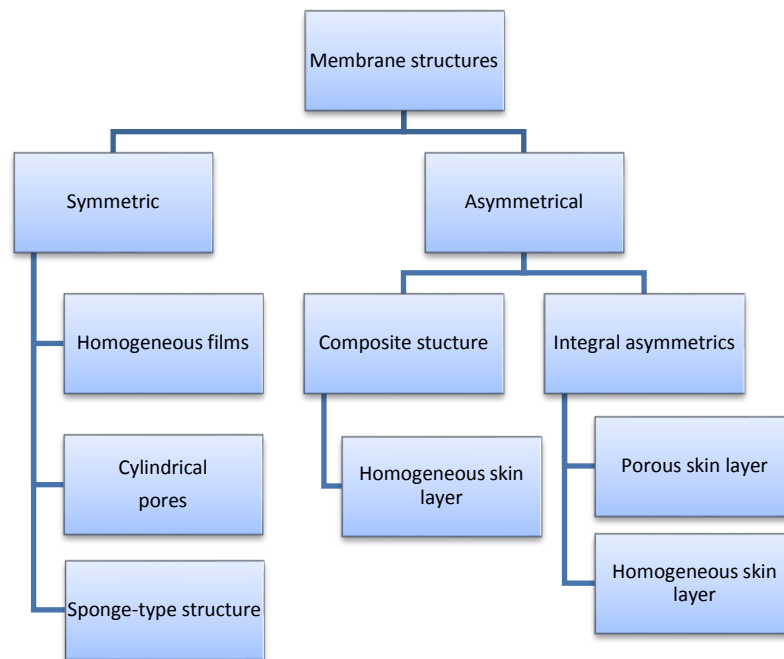
Figure 4. The synthetic membrane classification based on membrane structure. [12]

Nanofiltration commonly utilizes composite membranes with homogeneous skin layer also known as thin film composite membranes (TFC). The thin film composite membranes are asymmetrical membranes which consists from ultrathin top layer and two additional sub layer. [2] TFC membranes are highly flexible membrane class regarding their application areas since specific features for each layer can be independently tailored to achieve optimal TFC membrane for specific application. Asymmetrical membrane such as TFC, flux is determined by thickness of top layer. [1] The Figure 5 illustrates cross-section cut from TFC membrane, where can be seen: top layer, porous support layer and non-woven backing layer.
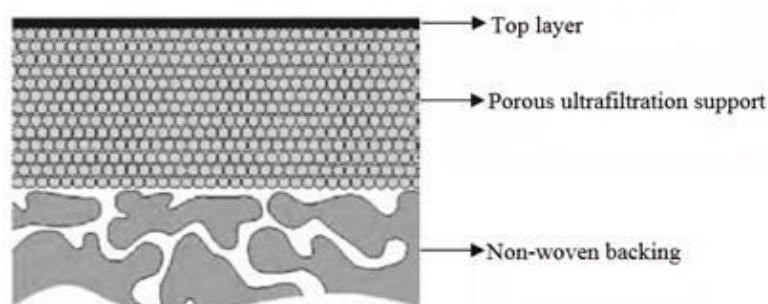
Figure 5. Thin film composite membranes structure. [2]

Top layer of a membrane is typically 0.1–3-µm-thick selective barrier where molecular rejection occurs. That is typically manufactured from crosslinked aromatic polyamides (PA). Mostly used monomers for manufacturing film layers are *m*-phenylene diamine (MPD) and trimesoyl chloride (TMC). [2,13] Sub layers are typically highly porous support layers. Usually first support layer is porous and smooth ultra- or microfiltration membrane, which makes it easier to graft selective barrier layer on top of it. The second sub layer is typically a non-woven reinforced fabric, which offers most of the membranes mechanical strength and compression resistance. [2,14]

In recent advance in field of membrane preparation, many nanofiltration membrane manufacturers have could produce acid resistant membranes. Acid resistant membranes are known to be able to withstand pH levels from 2 to 10 in continuous filtration processes, although in many cases in chemical and mining industry's treatable waste streams pH are more extreme [7,8]. In Table I is presented some of nanofiltration membranes along with used selective layers' surface material and operating ranges in acidic conditions.

Table I. Presentation of nanofiltration membranes, selective layers' surface materials and operating ranges in acidic conditions. [15]

Manufacturer	Membrane	Surface material	pH operating range	
			continuous	Short-term
DOW-Filmtech	NF270	Polyamide	2-11	1-12
	NF90	Polyamide	2-11	1-12
AMS Technologies	Nanopro A series	-	0-12	0-13
	Nanopro S series	-	2-12	1-12
GE-Osmonics	DK series	Polyamide	3-9	2-10.5
	DL series	Polyamide	3-9	2-10.5
	Duracid	-	0-9	0-9
NITTO DENKO Hydranautics	ESNA series	Polyamide	3-10	1-11
	HydraCoRe	SPES	2-11	1-11
MICRODYN-Nadir	NP series	Polyether sulfone	0-12	0-12

2.2.1 Membrane Configurations

During last decades, membrane filtration has become more common in industrial scale which has increased the amount of commercially available membranes and module types. The most common membrane configurations also known as modules are tubular, spiral wound hollow fibre and plate and frame modules. Spiral wound and hollow fibre modules are often used due to their excellent operational efficiency and high membrane are to volume ratio. [16]

Typically, in industrial applications each membrane housing consists from multiple spiral wound modules. Spiral wound (SW) module is a cross-flow filtration module which is rotated around itself providing a leaf like geometry. The module consists from permeate spacer which is covered on both sided with membrane and feed spacers. The module structure is designed to enable two-sided mass transfer trough membranes into the permeate spacer. The feed spacer on the contrary is designed to enhance mass transfer near membrane. The downside of spiral wound modules is high pressure loss along the membrane leaf. As total

module housing length increases the systems driving force reduces (pressure drops) thus leading to concentration polarization fouling along membrane leaf. [16] Figure 6 presents the structure of spiral wound membrane module.
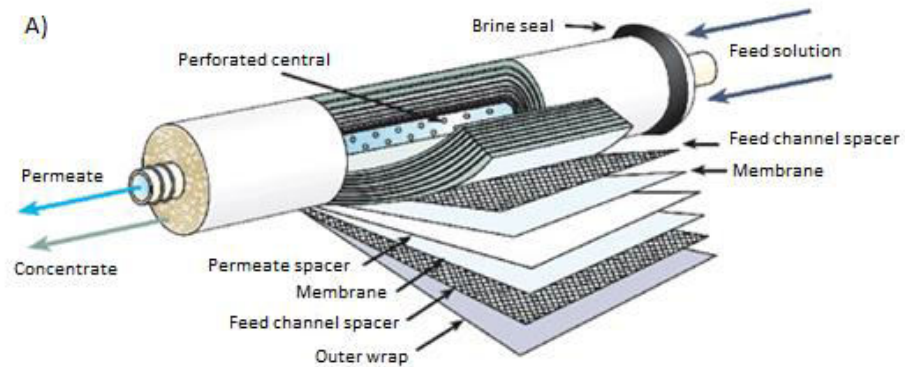
Figure 6. Structure of spiral wound membrane module. [17]

Like Spiral wound modules, the hollow fibre (HF) membrane modules have very high surface area to volume ratio and is used in cross-flow filtration. Hollow fibre module consists form numerous long and narrow membrane tubes, which are attached to each end of membrane module. Hollow fibre module can be used in two ways depending on the process. Feed solution can be directed straight into the membrane tubes where portion of the solution permeates the membrane and is transferred to outside of the membrane tube. On the contrary, the feed solution can also be directed outside of the membrane tubes. In this case permeate flow is collected from inside of the membrane tubes. The best advantage of the hollow fibre membrane module is its very high packing density and flexible membrane tubes. Utilizing membrane tubes also have some major drawbacks such as braking and fouling. [18] Figure 7 illustrates principle of hollow fibre membrane tube, where feed stream is directed into the membrane tube and permeate is collected from outside.
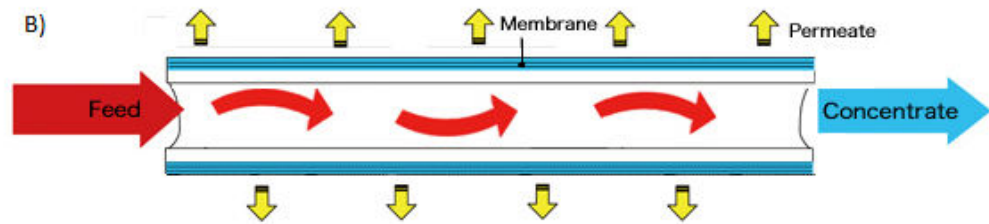
Figure 7. Hollow fibre membrane tube where fees stream is directed into the membrane tube and permeate is collected from outside of the tube. [19]

2.3   Industrial Applications of Nanofiltration

Nanofiltration has numerous applications in different industrial fields such as in water treatment industry and in mining industry. Although the NF processes are normally used in water softening applications there have been research regarding metal ion removal from wastewaters. [20] For example, nickel removal has been studied by Murthy and Chaudhari [21], chromium removal by Muthukrishnan and Guha [22] and copper removal by Ahmad and Ooi [23].

2.3.1   Water Treatment Industry

One of the largest application area for nanofiltration is water softening. Beside from removing multivalent ions from water to increase its softness, nanofiltration van also be used to: clean contaminated ground waters, remove colours from pulp and paper waste streams and remove heavy metals and small carcinogenic organic compounds from drinking water. Also, nanofiltration process meets the requirements for water disinfection. Up to 99% of bacteria and viruses can be removed with NF. [1]

Nanofiltration is a highly selective separation process and has several advantaged over ultrafiltration and reverse osmosis. Nanofiltration membranes have medium monovalent salt ion passage (50% or over) for ions such as sodium, chloride, nitrate and potassium while divalent ion retention remains over 95%. With very

high multivalent ion retention and nanoscale pore size, nanofiltration membranes have ability to retain low molecular weight (200-1000 DA) organic compounds from wastewater while allowing medium or high salt passage. [1]

2.3.2   Mineral Processing

Membrane separation has been studied in metallurgic and metal industry for wide range of applications. Typically, nanofiltration has low retention capability for acids while it allows separation of positively and negatively charged monovalent ions from multivalent ions. With low acid retention, concentration on both sides of membrane are quite similar leading to only small contribution to the differential osmotic pressure. Therefore, water and acid components of the solution can be considered as solvents. [5]

Several applications for utilization of NF in metal hydrometallurgy have been reported. In copper cathode manufacturing, nanofiltration is utilized to remove harmful trivalent ions such as manganese, chloride and iron while simultaneously increasing copper concentration in leaching liquor. [5] In gold processing industry, nanofiltration can be utilized to remove gold cyanide $Au(CN)_2^-$ complex ions from other metal complexes such as copper-cyanide $Cu(CN)_3^{-2}$ complex in leaching liquor. The leaching liquor containing gold and copper cyanide complexed is directed to nanofiltration module where gold-cyanide complex is effectively separated into from copper-cyanide complex. This method has been patented by Dennis H. Green & Jeffrey J Mueller. [24] The utilization of membrane filtration for removal of heavy metal complexed from cyanide barren liquors have also been patented by Debasish Mukhopadhyah. [25]

3 RESISTANCE MECHANISMS IN NANOFILTRATION

In membrane processes, resistance in mass transfer is a typical problem which can be caused by osmotic pressure, concentration polarization or fouling. In pressure driven filtration such as in nanofiltration, the process efficiency depends not only membrane properties but also process operational condition such as feed turbulence, and ionic concentration. Systems hydrodynamics directly influences the membrane transport resistance and these hydrodynamic conditions can be altered to reduce for example: concentration polarization and fouling. [26]

3.1 Osmotic Pressure

Osmosis and osmotic pressure are closely related to membrane processes. Osmosis is a physical phenomenon that is defined as water net movement from higher water chemical potential to lower water chemical potential through a semipermeable membrane. In membrane filtrations, the direction of osmotic flow is from permeate side towards feed side. [27]

Osmotic pressure is pressure generated from solvent moment trough membrane barrier, which is directly proportional to concentration difference of ions between feed and permeate sides. To counteract osmotic pressure, greater hydraulic pressure must be applied. Thus, in pressure driven membrane filtration, increase of osmotic pressure is a negative phenomenon due to the reduction of permeate flux. [1] Figure 8 illustrates the osmosis phenomenon, water movement towards osmotic equilibrium in membrane process along with hydrostatic pressure to counteract osmotic pressure.
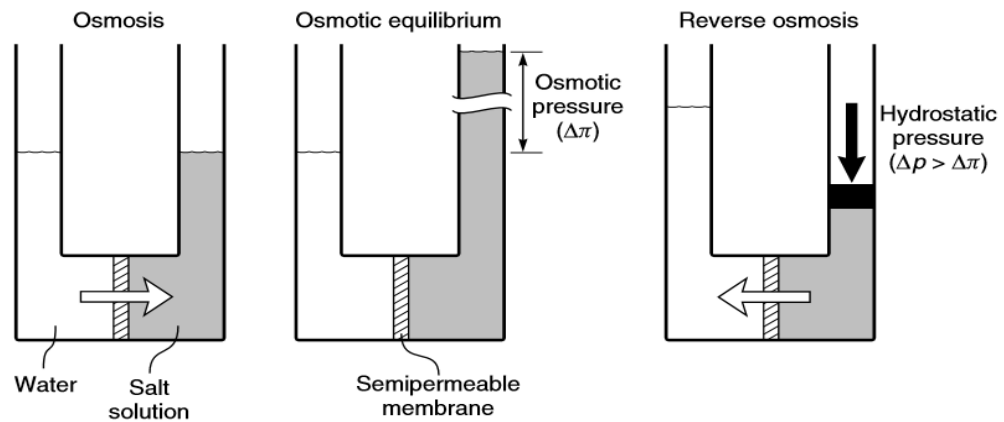
Figure 8. Osmotic phenomenon, water movement in membrane process along with hydrostatic pressure to counteract osmotic pressure. [1]

3.2 Concentration Polarization

Concentration polarization is a phenomenon in membrane filtration processes, which occurs when compounds permeate membrane at different rates. This creates a concentration gradient on both sides of the membrane. The concentration polarization creates concentration gradient on either side of membrane unless the solution is extremely well stirred. [6]

Pressure driven membrane processes utilizes one-sided concentration polarization model called boundary layer film model, where concentration gradient is formed only on the feed side. Boundary layer film model uses simplified description of concentration polarization by simplifying real hydrodynamics within membrane module. In the model is assumed that a layer of unmixed fluid with thickness (δ) exists in system between bulk solution and membrane surface. [6] Figure 9 represents the component enrich and deplete concentration polarization along with concentration gradients.
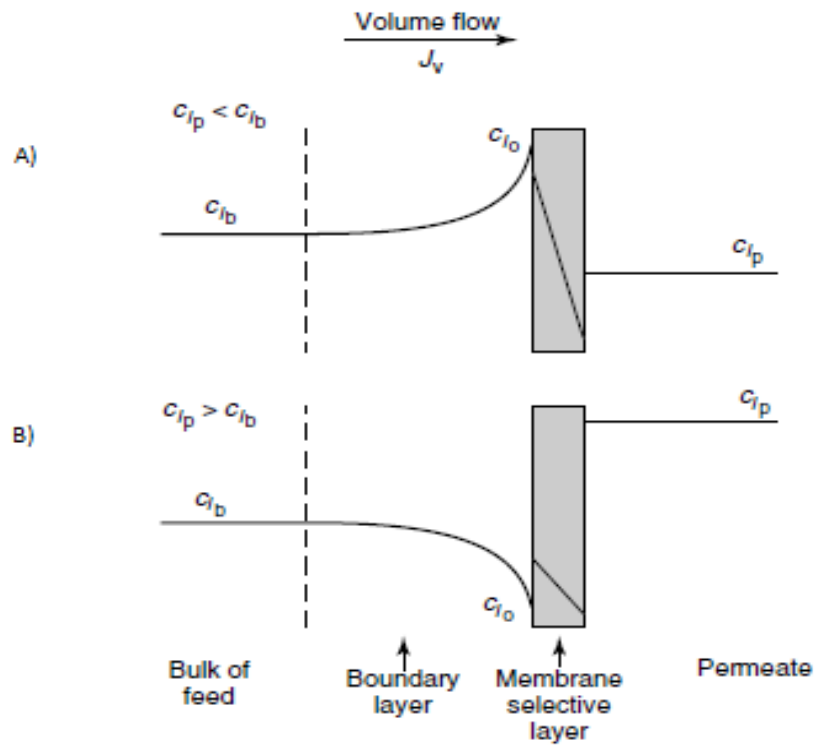
Figure 9. Concentration gradients for one component in membrane system A) Component enriched at membrane surface. B) Component depleted at membrane surface. [6]

Where J_v *Mass transfer trough membrane*

                  $c_{i,p}$ *Component concentration in permeate side*

                  $c_{i,b}$ *Component concentration in bulk solution*

                  $c_{i,o}$ *Component concentration in boundary layer*

Concentration polarization follows closely law of mass balance. If one component A is enriched at the membranes surface, the other component B must be depleted so that sum of component messes remains constant. When concentration polarization occurs, concentration of component A will increase until the systems steady state have been reached. Steady state means state where sufficient concentration gradient for component have been reached, allowing component diffusion back to bulk solution from boundary layer. [6]

In boundary layer model flux resistance is related to boundary layer thickness (δ). While decreasing the thickness of boundary layer, the flux resistance created by concentration polarization is also reduced. [6] By increasing turbulence at the membrane surface, the reduction of boundary layer thickness can be achieved. Most common ways to increase turbulence are: increase flow velocity (at membrane surface) in cross flow process, disrupting fluid flow with spacers and engage pulsing feed. Though pulsing feed leads increased energy consumption and great pressure drops which limit its uses. [11,28]

3.3   Membrane Fouling

Due to the ability of membranes to reject particles, colloids, solutes and ions, membrane processes are susceptible phenomenon called fouling. Fouling is a long-term flux decline which is caused by accumulation or adsorption of foulant material on membrane surface or inside the membrane matrix. [29] Typical fouling is precipitation of inorganic compounds, deposition of organic compounds or bacterial growth on membrane surface and within membrane pores. The difference between CP and fouling is that concentration polarization is reversible while fouling is irreversible. Fouling can also occur during very short or long period. [28,30] Figure 10 presents differences in flux decline between concentration polarization and fouling
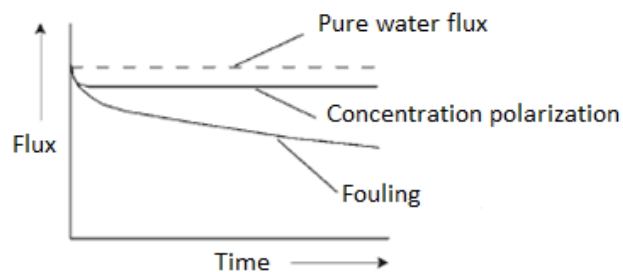
Figure 10. Schematic illustration of flux decline in concentration polarization and fouling. [28]

Fouling is a gradual decline of flux which is dependent on many process conditions and membrane properties such as: membrane material, porosity, roughness, surface chemistry, hydrodynamics (turbulences). [29] Due to fouling's irreversible nature membrane cleaning is required. Typical cleaning methods in industry are for example chemical cleaning or backflush. In backflush, clean solution is directed from membrane permeate side towards feed side to flush membrane pores and remove solids from membrane surface. [30]

4 RETENTION MECHANISMS IN NANOFILTRATION

Retention mechanism in nanofiltration is a combination retention of uncharged and charges molecules. Unlike in MF and UF, in nanofiltration charge based retention plays a major part in total retention capability. Retention of uncharged molecules in nanofiltration is mainly affected by molecule shape and size along with hydrophobicity and hydrophilicity. The major factors affecting retention of uncharged molecules are molecular size exclusion and diffusion, where size exclusion is based on sieving mechanism and diffusion is based on concentration gradient across the membrane. [5] In charge based exclusion, ions and other charged molecules are retained by membrane systems by electrostatic repulsion forces such as Donnan effect and dielectric exclusion. Even loose NF membrane can effectively retain charged ions due to electrostatic repulsion forces which are affected by membrane and solution properties such as charge density, solution pH, ion valence and concentration. [5,31]

4.1 Retention of Uncharged Species

Retention of uncharged molecules is based on sieving effect where physical size and shape of the component determines rejection efficiency. Nanofiltration membranes selective layer is three-dimensional cross-linked polymer network. The free space inside the polymer network determines membranes selectivity and permeability. [5]

Determining the molecular weight cut-off (MWCO) is a typical characterization method for nanofiltration membranes. Characterization method is used to determine separation capability (cut-off and pore size distribution) of membranes by defining what is the lowest molecular weight that membrane can retain with 90% retention. [5] Since membrane cut-off is determined to retention capacity of 90%, components smaller than membranes cut-off value can also be retained due to components geometrical shape and charge. Non-uniformly sized free spaces

inside the selective layer of membrane leads to fact that MWCO value for membrane is not and absolute and should be treated as directional value. [31,32]

Along with pore-flow mechanism, mass transfer trough membrane can occur by solvent diffusion. Diffusion is a process where very small molecules such as water can travel passively trough membrane by concentration gradient. [6] Solvent diffusion is also closely related to membrane swelling. Diffusion of solvent into selective layer of membrane expands the free space between polymer chains. This decreases membrane selectivity by allowing other components such as ions and very small molecules permeate more freely, while increasing membrane permeability. In aqueous solutions membrane hydrophobicity or hydrophilicity effects a water diffusion thus swelling of membrane material. [6,33]

4.2   Retention of Charged Species

Charge in nanofiltration membranes is generated when the membrane is brought in contact with aqueous solutions. Charge can be acquired with several different mechanisms such as dissociation of functional groups, adsorption of polyelectrolytes, ions, ionic surfactants and charged macromolecules. [5] The retention of ions mostly depends on ion concentration, valence and chemical nature of components along with membrane surface charge and charge density. [34] To understand charge dependent separation mechanism in NF it is essential to understand membrane surface charge and its relation to chemical nature of the treated solution. [35]

Due to electrostatic repulsion positively charged membranes will theoretically reject multivalent cation much better than monovalent cations and attract multivalent anions more strongly than monovalent anions. [5] It is also imperative to understand that rejection order is not absolute and it is effected by used membrane and its properties along with solutions properties. [34] Table II illustrates the theoretical retention order of monovalent and multivalent ions when

membrane surface charge is either positive or negative. (ion size is not considered).

Table II. Theoretical monovalent and multivalent ion retention order in system where membrane surface is positively and negatively charged.

Membrane surface charge	Retention order					
	--> --> Ion retention increases --> -->					
Positive (+)	- - -	- -	-	+	+ +	+ + +
Negative (-)	+ + +	+ +	+	-	- -	- - -

Where   -   *Monovalent anion*
           - -   *Divalent anion*
           - - -   *Trivalent anion*
           +   *Monovalent cation*
           + +   *Divalent cation*
           + + +   *Trivalent cation*

In nanofiltration processes, the retention of charged species are mainly effected by phenomena called Donnan effect and dielectric exclusion. Donnan effect is also present in ultrafiltration while dielectric exclusion is present in reverse osmosis. [36]

4.2.1   Isoelectric Point in Membrane Filtration

Characterization of membrane material is important when studying and predicting filtration behaviour such as selectivity and fouling. Typical ways to characterize membranes interactions with solute is to evaluate zeta potential (ZP) of the membrane from electro-osmosis and streaming potential analyses. Streaming potential analysis is often used analysis method, since the analysis is very sensitive to concentration changes in low solute concentration. [35]

Electromigration is a result from streaming potential difference across the membrane. On the contrary, the streaming potential difference in generated by

electric current which occurs as electrolyte moves through membrane matrix. [37] The main parameters effecting on electromigration are membrane charge density and polarity which can be characterized analysing zeta potential (ZP) of the membrane surface. Streaming potential and thus zeta potential are dependent on properties of the used electrolyte solution and membrane material. [35] pH for example is one of the most important factors effecting on ZP evaluation and streaming potential since it dictates charge on molecules in solute and membranes functional groups. Also, pH may affect to membrane pore size thus effecting membrane size exclusion. [37]

Isoelectric point (IEP) in membrane technology refers to membrane specific pH value of solution where membrane surface net charge is zero. In isoelectric point, the charged groups of membrane equally consist from both negatively and positively charged groups. The charged groups in membrane matrix are not necessarily distributed evenly. This leads to possibility of local charge variations throughout membrane surface, although membrane net charge would be zero. Thus, surface charge of membranes is closely related to pH of the feed solution and can be changed by changing feed solutions pH. In neutral solution charged groups inside selective layer of the membrane are charged negatively. As pH is lowered with acid the functional groups of the membrane start to dissociate thus changing the polarity of functional groups. When pH of the solution is higher than IEP, membrane surface polarity is negative thus leading to negative ZP value. Otherwise membrane surface charge polarity is positive. [37]

Due to physical and electrochemical separation characteristics of NF, minimal for ionic compounds should be expected at isoelectric point since size exclusion is dominant separation mechanism in this pH value due to membranes zero net charge. Previous studied have shown indeed that salt retention is often at its minimum near IEP of the membrane. However, there are exceptions when minimal ion retention is acquired from other than near IEP, but explanation or

theoretical base have not yet been produced regarding this matter. To completely understand and optimise NF separation process it is essential to understand and study membrane charge relationship with solution pH, since pH effects various performance characteristics. [37]

4.2.2 Donnan Effect

Donnan effect is based on Donnan equilibrium theory which describes an ion movement trough semipermeable membrane in a two-phased ionic system. Since nanofiltration membranes often have fixed charges on polymeric structure, Donnan effect frequently contributes to separation performance. [5]

When ionic solution containing cations and anions is introduced to a negatively charged membrane, positively charged cations tends to travel towards membrane surface increasing cation concentration on membrane surface. At the same time anions are rejected toward bulk solution reducing their concentration at membrane surface due to electrostatic repulsion forces as illustrated in Figure 11. This ionic shift is called Donnan potential. This whole phenomenon is called Donnan effect or exclusion. [5,34]
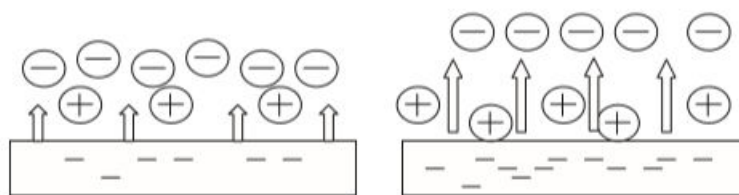
Figure 11. The principle of Donnan exclusion for negatively charged membrane. [11]

Based on the theory of Donnan effect, the retention of ions with negatively charged membrane is dependent on membrane charge and ion valence of the solutes. Membrane with greater charge will have better ion retention capacity compared to membrane with weak charge. [5]

Along with the membrane charge density Donnan potential is affected by salinity of the solution. In low to mid salinities (< 3000 mg/L) Donnan potential is greatest, thus leading to increased salt retention on the contrary, solutions with very high salinity (salinity > 3000 mg/L) reduces Donnan potential, thus leads to decrease in retention. [34] This can be based on theory that increased solution ionic concentration also increases ion concentration on membrane surface therefore "shielding" solutions anions from membranes repulsion. Further increase in solute concentration gradually reduces Donnan potential to a point where it is no longer effective rejection mechanism, which leads to increased ion permeation. [11, 34] In Figure 12 is illustrated the principle of shielding effect in solution of high ionic concentration
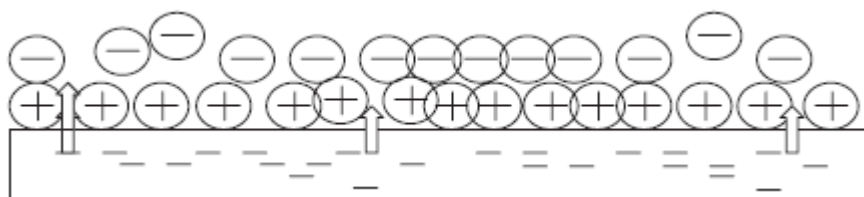
Figure 12. The principle of shielding effect in solution of high ionic concentration. [11]

By increasing ionic concentration, ion valence also effects to retention. Multivalent ions effectively shield solutions anions from membranes negative charge leading to weaker Donnan potential and reduced ion repulsion. Although portion of ionic compounds can pass the membrane material regardless of the shielding due required electroneutrality across the membrane. [11, 34] Figure 13 presents the Donnan effect in solution which contains monovalent and multivalent ions.
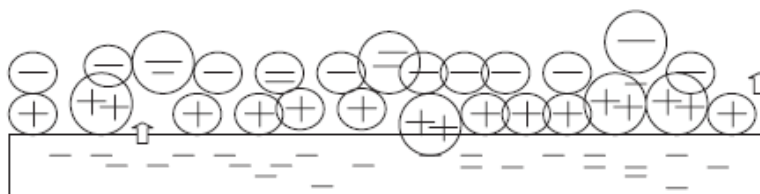
Figure 13. Donnan potential in solution with multivalent ions. [11]

4.2.3   Dielectric Exclusion

The concept of dielectric exclusion (DE) mechanism have been introduced in 1965 by Gluekauf. [38] (38) Dielectric exclusion is a phenomenon which is caused by different dielectric constants between bulk solution and membrane matrix creating a repelling force which hinders ion movement through membrane material. [36, 39] When ion is in medium with higher dielectric constant (in this case in polar solvent such as water), ion induces electric charge at the interface with membrane pore. The ions induced electric charge are same sign as its own charge, which leads to repulsion and exclusion. [40]

Along with Donnan effect, dielectric exclusion can be stated to be one of nanofiltration' charge based separation mechanisms. Originally it was believed that Donnan effect was the main rejection mechanism in NF due to rejection rate of double-charged anions compared to single-charged. This same characteristic can be found at dielectric exclusion also. Due to NF membranes nanoscale pore size, dielectric exclusion force can be considerable and should be considered when investigating nanofiltration separation mechanisms. [40]

4.2.4   Hydration

As mentioned in chapter: "Retention of Uncharged Species" size exclusion is most important rejection mechanism for uncharged molecules. Size exclusion is also relevant and plays significant role in ion rejection in form of hydration. Hydration is charge based phenomenon which occurs in aqueous ionic solutions between ions and water molecules. Ions in the solution attracts water molecules to their immediate vicinity by electric attraction forces This increases ionic radius. [41] The principle of hydration is presented in Figure 14.
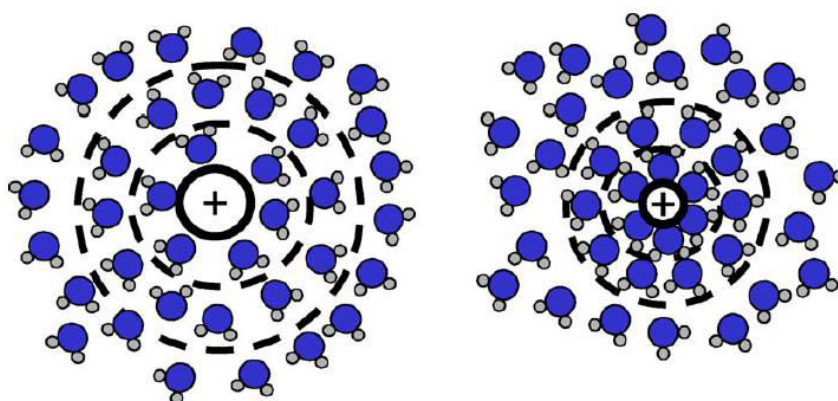
Figure 14. Illustrated hydration shell for larger and smaller monovalent cations. [41]

Due to slightly polarized configuration of water molecules, they align themselves around ion so that positive ion attracts negative oxygen ends and negative ions attracts positive hydrogen ends. This formation around the ion is called hydration shell. The hydration radius has been concluded to be dependent on crystallographic radius and charge of the central ions. [41]

The hydration strength of the ions is dependent on multiple factors such as ion structure and concentration and pH, temperature and ionic strength of the solution. Studies show that ions with high charge density tend to bind larger hydration shells more strongly than ions with lesser charge density. [41] The hydration shell is also held more firmly by anionic central ion compared to cationic central ion. Ions with weak hydration bonds with water molecules can lose all or a portion of hydration shell to permeate trough membrane. On the contrary, ions with strong hydration bonds might not fit through gaps in membranes selective layer. [41]

5 ION SEPARATION IN ACIDIC ENVIRONMENT

As described in chapter 2.3 "Industrial Applications of Nanofiltration", the typical application for nanofiltration lies in water treatment technology. Due to unique separation capabilities, nanofiltration could be utilized efficiently also in metal processing industry to separate metal ions from acidic waste streams. Nanofiltration can be even used in processes which contain high concentration of strong acids. [5] Nanofiltration and reverse osmosis are generally known to have similar retention capacity towards metal ion contaminants. [37] Figure 15 presents the principle of ion permeation in cases where membrane surface charge is above and below its isoelectric point.
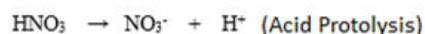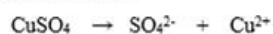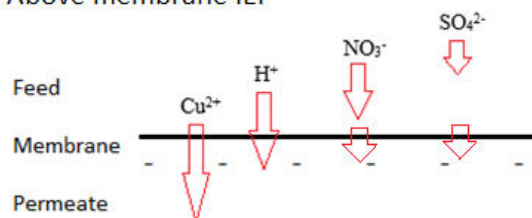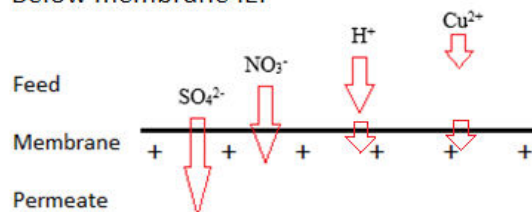
Figure 15. Example of ion permeation in positively and negatively charged membranes.

5.1   Principle of Ion Retention in Acidic Environment

In nanofiltration, retention is mostly based on Donnan effect and size exclusion. [5] Studies shows that isoelectric points for many commercial nanofiltration membranes are between pH 3 and 6. At the isoelectric point membrane net charge is zero. By further reducing solution pH with acid, the amount of positively charged functional groups increases thus changing the membrane net surface charge to positive. Positive surface charge reduces retention of anionic compounds (dissociated acids), while increasing retention of cationic compounds (metal ions). Positive surface charge of the membrane leads to separation process where acid fractions are typically permeated while metal ions are retained to some extent. In acidic condition Donnan equilibrium can also be seen when dissociated acids concentrates on the permeate side while metal ions are retained. [4]

5.2   Filtration Characteristics in Acidic Conditions

In this chapter highlights from earlier studies regarding nanofiltration performance in very acidic conditions are presented. Aspects regarding nanofiltration performance can be roughly divided to flux through the membrane (solvent permeability) and retention of solutes. [30] Nanofiltration membranes have an ability to recover metals and acid without concentrating the full total dissolved solids of the solution. [37] The ion rejection capacity of membrane is effected on feed pH, concentration and ionic strength of the solution. [42]

Nanofiltration membranes appears to have negative retention for ions. Due to Donnan equilibrium, the negative retention can be achieved when solution contains highly retainable multivalent ions. For example, negatively charged membrane has higher retention towers multivalent anion compared to monovalent anions. As multivalent anions are retained, monovalent ions are concentrated on the permeate side of the membrane due to electroneutrality. [43, 44]

Previous studies have shown that sodium chloride (NaCl) can be forced to concentrate on permeate side when sodium sulphate (Na_2SO_4) is introduced to feed solution in certain concentration. Molecular size and salt diffusivity difference between ions in high concentrations becomes significant factor which affects to membrane salt rejection capacity. Thus, leads to selective separation of NaCl in salt solution which contains mono- and multivalent salts. [45] This principle can be utilized also in acidic conditions to obtain excellent permeation for acid fraction when membrane surface charge is positive and it rejects cations. [4]. This phenomenon is mainly dependant on salt or acid concentration ratio and concentration of feed solution according to earlier studies. [45]

The use of sulfuric acid in metal industry is very common. Flux studies have shown that addition of metal salt (e.g. Copper sulphate) increases solutions osmotic pressure build-up because of multivalent salt rejection. This leads to reduced flux. Donnan effect and negative retention for sulfuric acid were observed. Tanninen et al. [3] reported decrease in the effect of salt on acid retention, when ion concentration along with ratio of acid/salt was increased. Also, the effect created by Donnan equilibrium was affected by partial dissociations of acid and metal salts. [3]

5.3   Related Studies in Acidic Conditions

Recent advance in membrane preparation field have provided the means to manufacture more stable and acid resistant membranes. These new acid resistant membranes have renewed interest utilizing nanofiltration in metal industry due to their ability to permeate sulphate ions easily because of electroneutrality rule. [44]

Tanninen et al. [44] studied membrane stability with long term filtration process in acidic conditions. They used the commercial membranes Desal-5 DK and Desal KH from GE-Osmonics and NF270 from DOW FilmTec and two experimental membranes from BioPure Technologies. NF270 and Desal-5 DK were known to

have insufficient acid resistance. According to Tanninen et al. [44] commercial membranes had copper retention of at least 60% in 8 wt.-% sulphuric acid for first 500 hours. After the 500 hors drastic decrease in copper retention were observed for membranes, which were not specifically manufactured for acidic conditions. Also, membranes which were manufactured for acidic conditions had higher isoelectric points than the rest. Thus, increased positive charge on membrane surface should enhance membranes separation capability. [44]

EXPERIMENTAL PART

The objective of the experimental part was to investigate retention of ions in acidic environment along with separation of metal ions from acid solutions using commercially available Ge-Osmonics and AMS Technologies nanofiltration membranes.

6   MATERIALS AND METHODS

6.1   Membranes and Chemicals

AMS Technologies Nanopro A-series (A3012 and A3011) and GE-Osmonics Duracid were chosen to the experiments. These membranes have been manufactured specifically to acidic conditions. Along with A3012, A3011 and Duracid membranes Ge-Osmonics Desal-5 DK membrane was also chosen to the experiment as non-acid resistant reference membrane due to extensive research about its properties and performance along with quite similar permeate flux compared to other membranes. Table III Presents the used membranes in the experiments.

Table III. Used membranes in the experiments.

Manufacturer	Membrane
GE-Osmonics	Duracid
	Desal-5 DK
AMS Technologies	Nanopro A 3012
	Nanopro A 3011

Solution preparation and experiments were carried out using purified water from Elga's CENTRA-R 60/120 equipment, which produces ultrapure water with

resistance of 15MΩ. Used chemicals can be categorized in salts, metal salts and acids, which all are presented in Table IV with their CAS numbers.

Table IV. Used chemical and chemical abstract numbers.

Category	IUPAC Name	Formula	CAS Number
Salt	Sodium chloride	NaCl	7647-14-5
	Calcium chloride	$CaCl_2$	10043-52-7
	Sodium sulphate	Na_2SO_4	7757-82-6
Acids	Nitric acid	HNO_3	7697-37-2
	Oxalic acid	$C_2O_4H_2$	144-62-7
Metal salts	Iron(II) sulphate	$FeSO_4$	7720-78-7

Chemicals from salt category were only used in retention studies, where goal was to study membrane salt retention in constant flux with varying pH. Nitric acid was the main acid in conducted experiments due to dissociation to hydrogen (H^+) and nitrate ions (NO_3^-). It was used in pH adjustments and preparation of model solution in every experiment. Utilization of nitric acid provides a good opportunity to measure total sulphate concentration which is provided by other components of the solution.

6.2 Filtration Equipment

The Used cross-flow filtration equipment had four modules in parallel. Figure 16 illustrates detailed PI-chart from filtration equipment. Detailed specifications and figure descriptions can be found below.
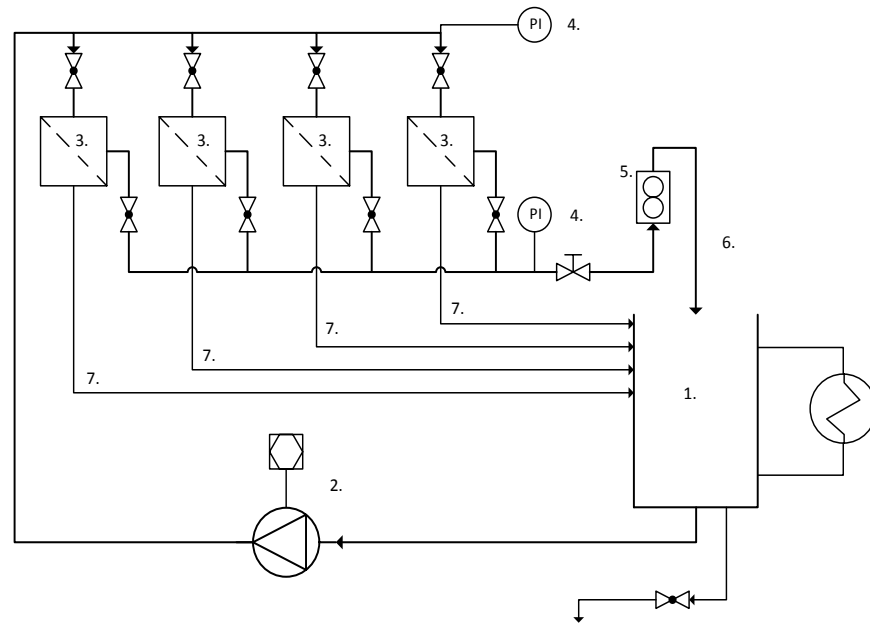
Figure 16. PI chart used four modules cross-flow filtration equipment.

The used cross-flow filtration equipment consisted from feed tank, pump, membrane modules and pressure indicator on either side of the modules, pressure valve, flow meter and channels permeate collection and retentate recycle. The solution temperature in the feed tank were measured with external thermometer and controlled with attached water circulation heater/cooler unit (1). From the feed tank, solution was pumped with Hydra Cell G25X pump (2.) to membrane modules (3.). Each membrane module held 0.02 m^2 sized membrane sheet with dimensions of 500mm x 40mm. On each side of membrane modules were pressure indicators (4.). Pressure inside the filtration equipment was controlled with valve (4.). After the pressure valve, retentate stream were directed through the flowmeter (5.) and retentate channel (6.) back to feed tank. The permeate from each membrane module was directed straight back to feed tank via permeate channels (7.).

The used pump and in experiment was Hydra Cell G25X pump with capability of producing 70 bar pressure. Pump motor was ABB 7.5 kW, 750 rpm electric motor

with maximum flowrate of 4800 dm^3/hour. Constant feed flowrate of 46% from maximum was used in all experiments. The whole filtration equipment was made from AISI 316 stainless steel. Before membranes were taken into use pre-treatment was done by pressurizing them at 30 bar for 30 minutes. No other pre-treatment was used. when all four membrane modules are in use empty volume inside filtration unit have been measured to be 4.4 kg

6.3   Measurements and Experiments

6.3.1   Sample Collection and Analysis

Permeate flux was measured manually by weighing method. Mass of permeate was collected and weighted from each membrane tree times during 30-minute measurement period. After the permeate mass measurement, pressure was changed and flux was let to stabilize for 10-20 minutes before conducting the next flux measurement. Figure 17 presents the collection method of permeate sample.

Figure 17. Collection method of permeate samples.

From permeate flow measurements, 20 ml samples were collected which were used to analyse permeate and feed ion concentrations Ion concentration analyses were conducted using Thermo Scientific Dionex ICS-1100 ion chromatography. For anion analysis Dionex AS22 column and cation analysis Dionex CS12A were used. Sample dilutions were made per column linearity zone which were between 1- 10/50 ppm depending on the ion.

Metal concentration analyses were conducted with Thermo Scientific ICE 3000 series AA spectrometer using iron hollow cathode with 78 mA current. Linearity zone for accurate iron concentration analysis was between 0.2 and 7 ppm. Due to high iron concentration in the samples, high dilution was used, which might have affected to the accuracy of analysis

6.3.2 Pure Water Permeability

Pure water permeability of the membranes was monitored with measurements before each experiment. This was done to study flux changes of the membranes during experimental part. Pure water permeability measurements between filtration experiments would provide valuable knowledge regarding membrane fouling and deterioration of the selective layer of the membranes.

Pure water permeability measurements were conducted at three different pressures for each membrane as presented in Table V. Permeate flows for each membrane were measured as described in the chapter 6.3.1 "Sample Collection and Analysis".

Table V. Pure water permeability measurement pressures for each membrane.

Membrane	Measurement pressures			
	3 bar	5 bar	12 bar	20 bar
Duracid	x	x	x	-
Desal-5 DK	-	x	x	x
AMS A3012	-	x	x	x
AMS A3011	-	x	x	x

The measured permeate masses were used to calculate permeate fluxes which were plotted as a function of pressure to obtain membrane pure water permeability. Calculation of permeate flow is presented in the Equation 1.

Equation 1.

$$\frac{m_{c,p}}{t_{c,p}} = Q,$$

Where $m_{c,p}$ *Mass of collected permeate*   [kg]

                    $t_{c,p}$ *Time of collected permeate*   [h]

                    Q *Permeate flow through membrane*   [kg/h]

Obtained permeate flows for each membrane in different pressures and pH (Q) were then used to calculate flux as presented in Equation 2.

Equation 2.

$$\frac{Q}{A_m} = J$$

Where A_m *Surface area of membrane*   [m^2]

                    J *Membrane flux*   [kg/m^2*h]

The calculated fluxes for each membranes were then used to calculate membrane specific pure water permeability as presented in Equation 3

Equation 3.

$$\frac{\Delta J}{\Delta p} = P$$

Where ΔJ *Membrane flux difference*   [kg/m^2*h]

                    Δp *Pressure difference*   [bar]

                    P *Membrane permeability*   [kg/m^2*h*bar]

6.3.3   **Measurement of Ion Retention at Different pH**

Retention of ions for membranes was studied with ionic solution composing of NaCl, CaCl$_2$ and Na$_2$SO$_4$. Prepared solution pH was 5.4 and concentration of each salt was 0.5 mmol/dm^3. Due to pH 5.4, slightly acidic solution provided starting point above IEP for each membrane, thus pH adjustments toward neutral solution were not needed. PH adjustments towards acidic end (to pH 1) were conducted using nitric acid (HNO$_3$).

Membrane fluxes were measured at 4 different pressures 3 bar, 5 bar 12 bar and 20 bar at different pH values. The pressure scale was chosen in the wat that each membrane had flux value of 20 kg/(m^{2}h) at their measured flux area. Permeate flux measurement were conducted as described in chapter 6.3.1 "Sample Collection and Analysis". After completing flux measures from whole pressure sequence pH was gradually dropped from pH 5 to pH 1 repeating pressure and flux measurement sequence at every step. pH steps were 5.4 (native), 5, 4.5, 4 3.5, 3, 2 and 1. At each pH step, feed samples were taken 10 minutes after the pH adjustments, thus the system had time to stabilize. Permeate samples for each of the membranes were taken during flux measurements at every pressure.

After the filtration experiment, concentration from feed and permeate samples were analysed using ion chromatography. Measured concentration were then used to calculate membrane retentions. In equation 4 is presented the calculation of ion retention.

Equation 4.

$$\left(\frac{c_{feed} - c_{perm}}{c_{feed}} \right) = r_F, \qquad r_F * 100\% = R$$

Where c_{feed} *concentration of ion in the feed*   [ppm]

                    c_{perm} *concentration of ion in the permeate* [ppm]

                    r_F *Retention Factor*   [-]

                    R *Retention percentage*   [%]

6.3.4   Measurements of Iron Retention in Acid Solutions

Retention of iron ions in acid solutions was studies two experimental series. Filtration were started with pure water permeability measurement, followed by filtration of first experimental series. Due to the structure of the filtration equipment it was very difficult to completely remove all water from the equipment. Thus, previously determined estimation of water inside of filtration equipment (when four modules we in use) were used in preparation of acid solution as described.

In the first experiment, the filtrated solution composed from 2 wt.-% nitric acid (HNO3) solution with added iron sulphate heptahydrate ($FeSO_4 * 7H_2O$). Calculated amount of 0.1 g/l of iron was added into the feed tank. After the iron sulphate was completely dissolved, the pressure was increased to 3 bar which was followed by stabilization period. Flux measurements were performed for Duracid, AMS A3012 and A3011 membranes at 5 bar, 12 bar and 25 bar. For Desal-5 DK Flux measurements were conducted in 3 bar, 5 bar and 12bar. After the flux measurement at 25 bar, the pressure was dropped back to 3 bar and iron concentration was increased to 0.5 g/l. The process was repeated and iron concentration were further increased to 1g/l and 2 g/l. Based on the AAS analysis of the feed samples, the iron concentrations in the first experiment were 0.15, 0.67, 1.4 and 2.6 g/l. The second filtration was conducted identically, although the prepared acid solution contained 2 wt.-% nitric acid (HNO_3) and 1 wt.-% oxalic acid ($(COOH)_2$). During the filtration process precipitation occurred. The

information regarding the precipitation can be found at chapter 7 "Results and discussion".

Amount of precipitated solid from filtration series containing oxalic acid was also measured. After the filtration, feed solution was circulated in filtration equipment and 3x 1 litre sample was taken from retentate stream. Because the used pressure was minimal, the flux was close to zero, thus the composition of retentate solution was equal to the composition of the feed solution. The parallel feed samples were then filtrated and washed using vacuum bottle with glass fibre filter. Solid samples were dried and weighted. The average weight was calculated and is presented in Results chapter

6.3.5   Experiment to Separate Acid and Iron

Separation of iron from acid was studied using GE-Osmonics Duracid membrane. The acid solution used in this experiment composed from 2 wt.-% nitric acid (HNO_3) solution and 1 wt.-% oxalic acid (($COOH)_2$). Due to the precipitation in previous experiment, the 50µm dead-end mesh filter were added into the filtration equipment. The mesh filter was installed into the retentate channel after the flow meter. From the mesh filter retentate solution was directed back to the feed tank. Figure 18 presents the installed mesh filter used to remove precipitated solids from the solution.

Figure 18. 50 µm dead-end mesh filter was used to collect precipitated solids from the retentate stream.

The acid solution was prepared into the feed tank and $FeSO_4 * 7H_2O$ added to in the way that iron concentration in the feed solution reached 2g/l. Solution was let to mix at 25 bar for 30 minutes. After the mixing period, the initial feed and permeate samples were taken and feed turbidity, permeate flux, conductivity, pH, temperature, time and permeate volume parameters were measured. During the filtration process sample collection and parameter measurement were conducted approximately in every 20 minutes.

7   RESULTS AND DISCUSSION

7.1   Retention of Ions at different pH

Retention order of the salts was studied in broad pH scale. Goal of the experiment was to determine do the chosen membranes, Duracid, Desal-5 DK, A3012 and A3011 follow theoretical salt retention order between pH 5.4 and 1. Figure 19 presents the retention of ions as function of flux in pH 5.4
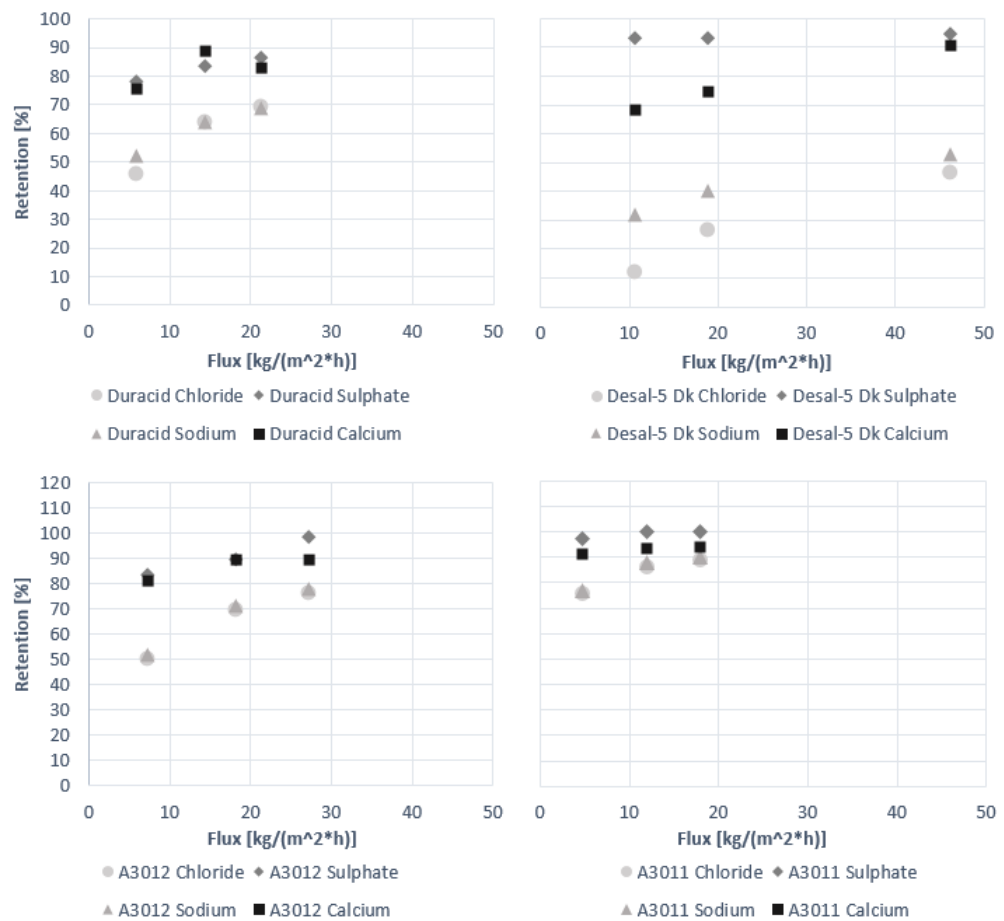
Figure 19. Retention of ions as function of pH when solution containing NaCL, $CaCl_2$, and Na_2SO_4 were nanofiltrated with Duracid, Desal-5 DK, A3012 and A3011 membranes at pH 5.4

As Figure 19 shows the ion retention increases non-linearly as a function of flux at the natural pH of the solution (pH 5.4). Increase in transmembrane pressure affects directly permeate flux, thus water transport trough the membrane is considerably faster than charged ion transport due to different diffusion coefficients as presented in theoretical part. This theory could be implemented to explain curving ion retention graphs when flux is increased.

Figure 20 Presents the retention of ions as function of pH for Duracid and Desal-5 DK. Measurement points are at flux 20 kg/m^{2}h or as close as possible.
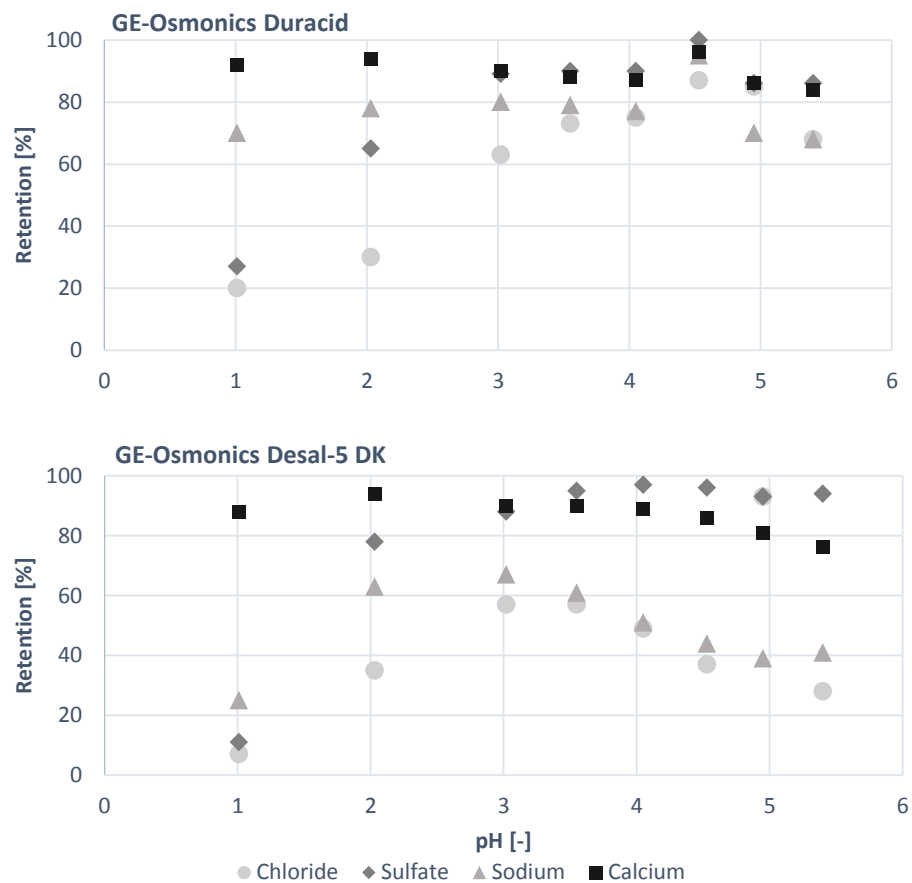
Figure 20. Duracid and Desal-5 DK retention of ions for Cl, SO$_4$, Na and Ca in function of pH at the flux of 20 kg/(m^{2}h).

The GE-Osmonics Duracid and Desal-5 DK membranes showed quite similar retention of multivalent ions during the whole experiment. Between pH 5.4 and 3 the percentage of retention for sulfate and calcium ions were measured to be above 78%. As closing on the acidic end of the pH scale sulfate retention is decreased drastically while calcium retention remains above 80%. Retention of monovalent ions on the contrary were very different for the GE-Osmonics membranes. With Duracid, sodium retention remained over 60% during the whole experiment while chloride retention decreased as the pH dropped. On the contrary Desal-5 DK membranes showed increase in monovalent ion retention as pH decreased from 5.4 to 2.5. Also between pH 3-1 Desal-5 DK membranes monovalent ion retention decreased to quarter. The decrease in retention of monovalent ions could be affected by membrane swelling. As membrane material swells, the size of the gaps inside the polymer network of the selective layer increases thus allowing more free passage for small sized ions.

For both membranes at higher end of pH scale (pH 3.55 − 5.4) retention of ions was based on their size. By decreasing pH from 3.55, the change towards charge based retention order could be seen. Between pH 3 and 1, retention of anions reduces significantly while retention of cations remains high. With Desal-5 DK membrane, the retention of sodium also reduces unlike with Duracid membrane. Since membranes are positively charged below membranes IEP, theoretically retention of multivalent anions should be lowest, if retention of ions is only affected by charge.

In very acidic conditions sulphate ions should have smaller retention than chloride ions due to greater attraction towards positively charged membrane. Since nanofiltration retention mechanism is based on both electrostatic repulsion and size exclusion, it is possible that membranes dense surface layer is hindering transportation of sulphate ions based on their size thus allowing chloride to permeate more freely. This also leads back to the Donnan theory of electro

neutrality, where in equilibrium state both sides of membranes should have equal amount of positive and negative charge. [5, 34] Figure 21 presents the retention order of ions when AMS Technologies Nanopro A series A3012 and A3011 membranes were used in similar experiment as GE-Osmonics membranes. Percentages of ion retention are shown as function of pH. Data points are at flux 20 kg/m^{2}h or as close as possible.
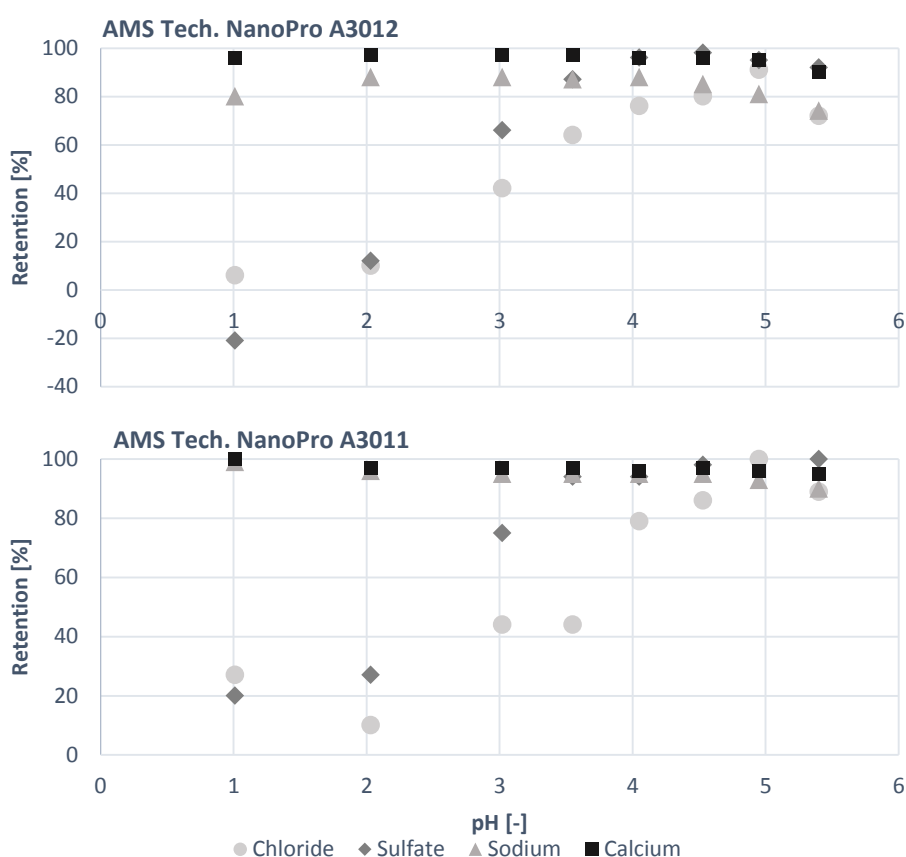
Figure 21. AMS A3012 and 3011 retention of ions for Cl, SO4, Na and Ca in function of pH at the flux of 20 kg/(m^{2}h).

Retention of ions for AMS membranes presented in Figure 21 are quite similar compared to the Duracid and the Desal-5 DK membranes, although some variations exists. Both AMS Technologies membranes showed very high retention of cations during the whole experimental series. Calcium retention was measured

to be over 90% for both AMS membranes in native solution and further increasing when pH was lowered. Sodium retention with A3011 membrane was almost similar to calcium retention as its retention remained very high. With 3012 membrane Sodium retention was over 70%, which was slightly lowered than with A3011 membrane.

Anion retention on the contrary, decreased gradually towards acidic end of pH scale. For A3012 membrane, the decrease in anion retention started at pH 4 – 4.5 and for A3011 membraned at pH ~4.5. The point where anion retention starts to decrease is theoretically the point where membranes surface charge polarity changes from negative to positive. As comparing ion retention graphs of AMS membranes to ion retention graphs of GE-Osmonics membranes, the pH value in which ion retention starts to decrease is approximately 1 pH unit higher with AMS membranes than GE-Osmonics membranes. The earlier decrease in anion retention capability indicates that AMS membranes have higher IEP values than GE-Osmonics membranes. Also, decrease in retention of anions is much steeper compared to GE-Osmonics membranes, which could indicate that AMS membranes have stronger surface charge density. Greater surface charge could result to separation where charge plays more significant role than size exclusion. In pH 1 retention order with both membranes follow theoretical retention order based on charge. Also with A3012 membrane negative retention for sulphate can be seen. Negative retention of ions occurs when ions are concentrated in permeate side of membrane to retain electro neutrality across the membrane as explained earlier. Generally, ion retention of the AMS A3011 is higher than of the A3012 membrane, which could be a result from different MWCO values and membrane charge densities.

During the experimental series, noticeable changes in permeate flux occurred when pH was lowered. Table VI presents the membrane flux change during the experiments, where pressure normalized flux is I presented as a function of pH.

Table VI. Permeate fluxes for membranes at measured pH

Permeate fluxes for membranes, [kg/(m^2*h*bar)]

pH	Duracid	Desal-5 DK	AMS A3012	AMS A3011
5.40	1.15	3.71	1.44	0.95
4.95	1.20	3.86	1.46	0.97
4.53	1.19	3.87	1.40	0.93
4.05	1.15	3.89	1.35	0.89
3.55	1.13	3.90	1.29	0.84
Å3.02	1.12	3.96	1.23	0.79
2.03	1.17	4.21	1.15	0.70
1.01	1.09	4.39	1.02	0.59

Table VI shows that Duracid and AMS A3012 and AMS A3011 permeate fluxes of the membranes reduce, while permeate flux of the Desal-5 DK increases as pH is decreased. The largest reduction of flux can be seen to occur with AMS A3011 membrane, where permeate flux reduced almost 40% when pH was adjusted from 5.4 to 1. The increase of flux as pH was reduced for Desal-5 DK membrane could have been occurred due to degradation of membranes selective surface, since pure water permeability for Desal-5 DK increases from 3.83 to 4.63 kg/(m^{2}h) after the filtration. In further experiments the increase of pure water flux for Desal-5 DK was minimal.

7.2   Retention of Iron in Acid Solutions

7.2.1   Retention of Iron in HNO₃ Solution

Retention of iron ions experiment were conducted in fixed acid solution of 2 w-% HNO₃. Figure 22 and Figure 23 presents the percentage of iron ion retention at function of flux for GE-Osmonics and AMS Technologies membranes.

Figure 22. Retention of iron ions for Duracid and Desal-5 DK membranes in 2 w-% HNO₃ solution at function of flux.

Figure 23. Retention of iron ions for AMS A3012 and AMS A3011 membranes in 2 w-% HNO$_3$ solution at function of flux.

Figure 22 presents Iron (Fe) retention capabilities for GE-Osmonics membranes in four different concentrations of iron ions. Both Duracid and Desal-5 DK membranes showed similar increasing iron retention capabilities, when flux and iron concentration were increased. Generally, retention of iron ions for studied membranes was directly proportional to increase of flux, thus increase of pressure.

AMS 3011 iron retention graph for highest concentration of iron was slightly different compared to other the membranes. As Duracid, Desal and A3012 membranes showed increase in retention of iron as flux increased from first measurement point of to the second, the retention of iron for A3011 membrane slightly decrease. Experimental series with 2.59 g/l iron concentration required 1/200 dilution to be accurately measured with AAS due to linearity zone were between 1-5 ppm. In major dilutions, even small errors in pipetting procedure could be multiplied and thus effect several percentages on rejection capability. This could explain reduction of retention of iron for A3011 membrane Figure 23.

Notable increase in retention of iron were observed when concentration of iron was increased from 0.15 g/l to 0.67 g/l. The overall retention of iron for each membrane was very good. After the first iron concentration increase, addition of iron did not affect to iron retention capability. The lowest iron retention was observed for Desal-5 DK in iron concentration of 0,15 g/l, which started from 82% increasing to 91.5% as pressure was increased. Also, with the Desal-5 DK membrane the reduction of flux was highest as concentration iron was increased from 0,15 g/l to 2,59 g/l. As can be seen in Figure 22 the 3 bar pressure used in experimental series with lowest concentration of iron (0,15 g/l) produced flux of 15 kg/m^2h, while highest concentration of iron series (2,59 g/l) produced flux of 5 kg/m^2h. This can be explained by osmotic pressure build-up in the feed solution. Increase in ionic concentration also increases the osmotic pressure inside the system thus hindering the mass transfer trough the membrane.

Due to highly acidic condition of the filtration, the pH measurements were conducted to study acid permeation in filtration system. Table VII presents the retention of iron and pH of the permeate at different fluxes and concentrations of iron when solution contained HNO_3 and $FeSO_4$ were filtrated. For iron concentration series of 0.15, 0.67 and 1.39 g/l pH was 0.45 while for iron concentration series of 2,59 g/l the feed pH was 0.46

Table VII. Retention of iron and pH of the permeate at different fluxes and concentrations of iron when solution contained HNO_3 and $FeSO_4$ were filtrated

	GE-Osmonics Duracid			GE-Osmonics Desal-5 DK		
Fe c. [g/l]	Flux kg/(m2h)	Retention [%]	Perm. pH	Flux kg/(m2h)	Retention [%]	Perm. pH
	5.0	86.3	0.47	15.0	82.1	0.45
0.15	11.7	91.5	0.50	25.1	86.6	0.46
	25.4	92.8	0.50	42.2	91.3	0.47
	4.4	91.4	0.46	13.4	93.7	0.46
0.67	10.8	93.9	0.46	23.3	95.3	0.46
	24.8	95.1	0.49	59.2	96.3	0.46
	3.8	89.8	0.46	10.5	92.2	0.45
1.39	10.6	94.0	0.47	20.8	95.5	0.45
	23.9	95.5	0.49	56.0	97.0	0.46
	2.8	91.2	0.47	5.4	89.5	0.45
2.59	9.6	93.6	0.48	17.0	94.7	0.46
	23.0	95.7	0.50	49.5	97.2	0.46

	AMS Technologies A3012			AMS Technologies A3011		
Fe c. [g/l]	Flux kg/(m2h)	Retention [%]	Perm. pH	Flux kg/(m2h)	Retention [%]	Perm. pH
	4.2	85.3	0,47	2.2	85.1	0.60
0.15	10.9	94.1	0,47	5.9	94.1	0.47
	23.2	96.6	0,47	12.6	96.7	0.48
	4.1	91.5	0,45	2.2	96.8	0.45
0.67	10.5	96.2	0,45	5.8	97.2	0.45
	23.1	98.2	0,46	12.9	98.5	0.46
	3.9	88.9	0,45	1.9	94.2	0.45
1.39	10.0	95.9	0,45	5.5	97.4	0.45
	22.5	98.2	0.46	12.7	98.8	0.46
	2.8	90.8	0.46	1.5	99.1	0.46
2.59	9.1	95.2	0.46	5.1	96.9	0.46
	22.0	98.1	0.47	12.5	98.7	0.47

During the experiments, pH of the permeate was relatively stable all the time. Also, pH of the permeate was slightly higher compared to pH of the feed solution. Since pH of the permeate is not significantly lower compared to pH of the feed, acid does not seem to concentrate on the permeate side of the membrane during the experiment.

7.2.2 Retention of Iron in HNO$_3$ + (COOH)$_2$ Solution

Retention of iron ions was also studied in acidic solution composing from mixture of 2 w-% HNO$_3$ + 1 w-% (COOH)$_2$. Figure 24 and Figure 25 presents the percentage of iron retention as a function of flux for GE-Osmonics and AMS Technologies membranes.
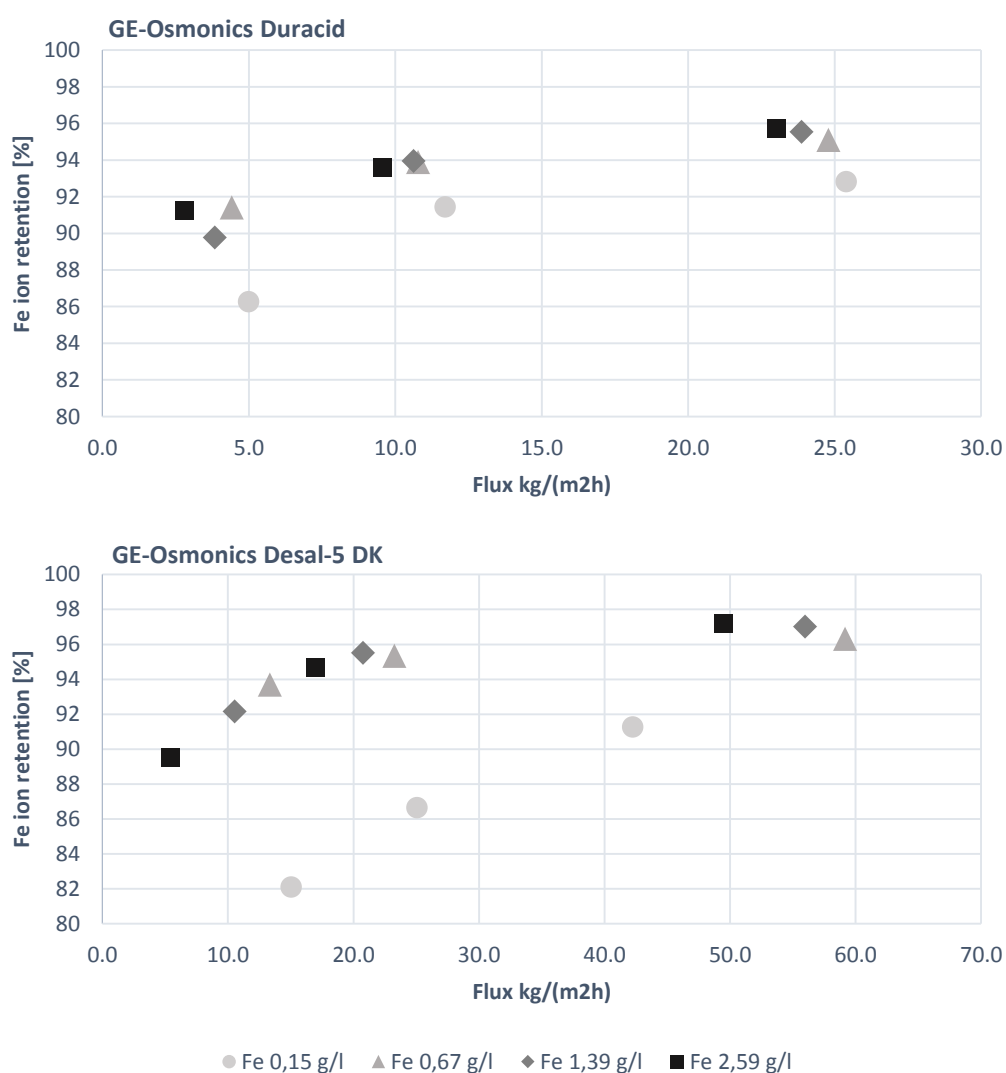

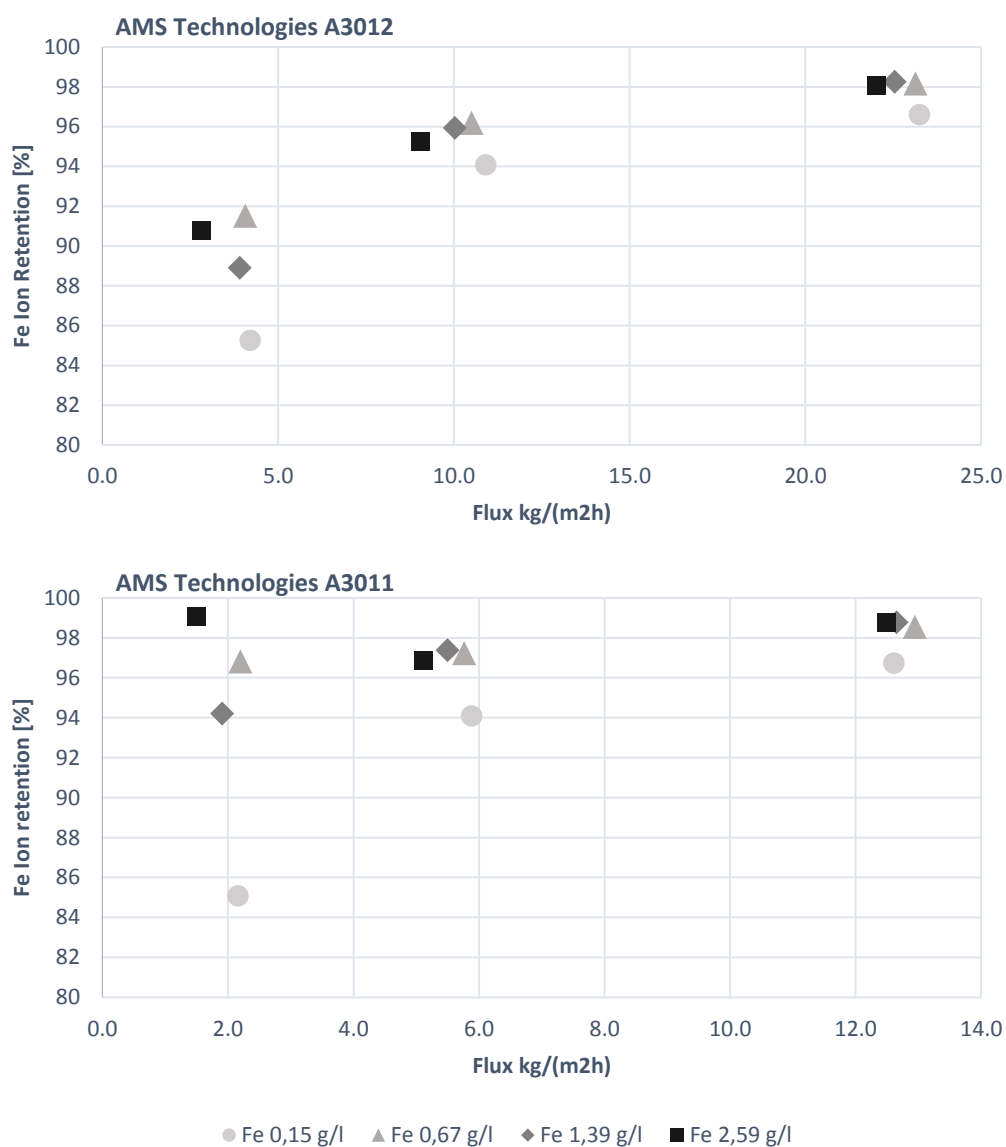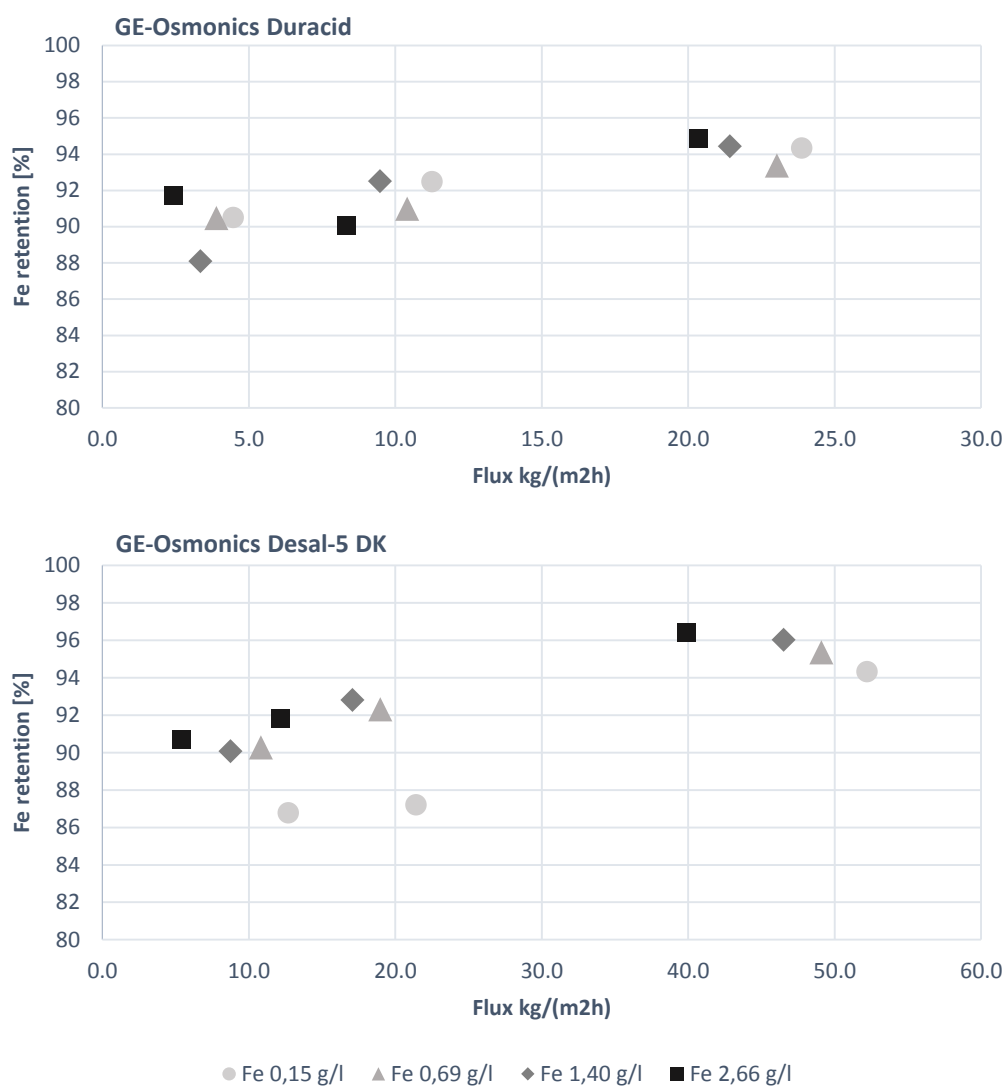Figure 24. Retention of iron ions for Duracid and Desal-5 DK membranes in 2 w-% HNO$_3$ and 1 w-% (COOH)$_2$ solution as a function of flux.
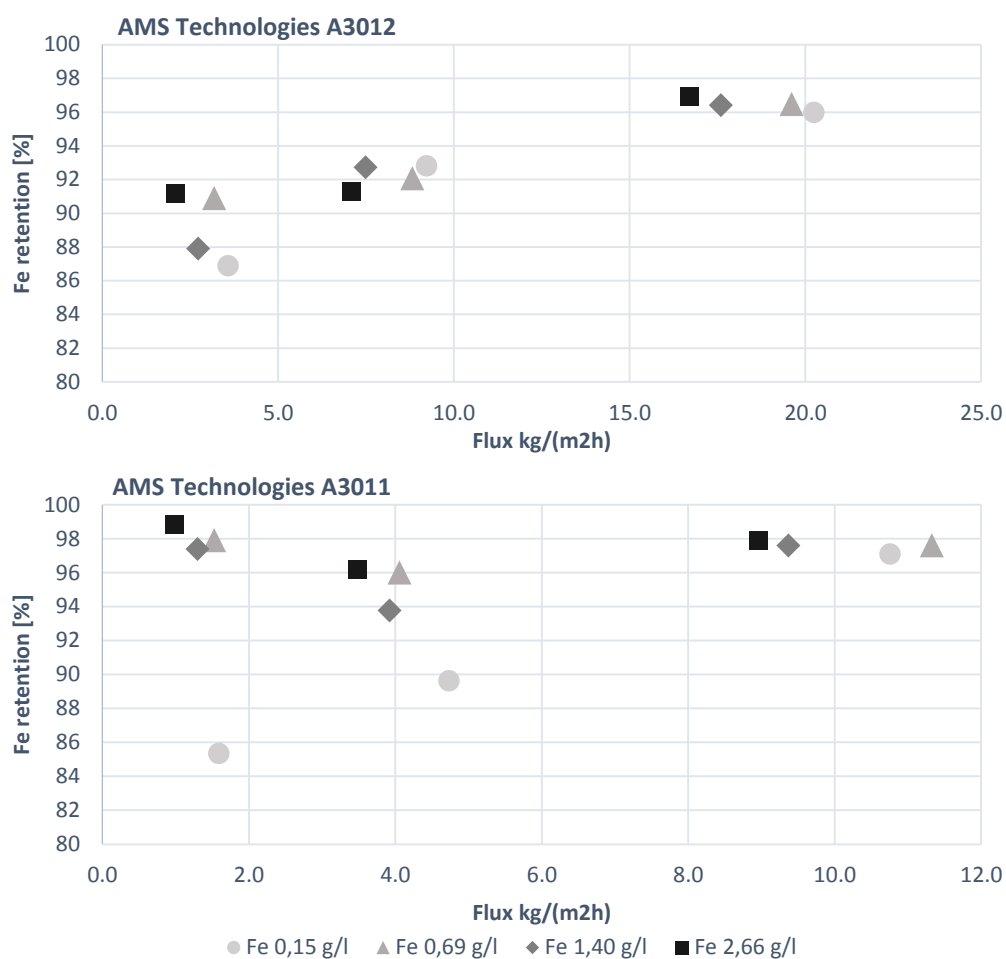
Figure 25. Retention of iron ions for AMS A3012 and AMS A3011 membranes in 2 w-% HNO_3 and 1 w-% $(COOH)_2$ solution as a function of flux.

The addition of 1 w-% of oxalic acid into feed solution showed slight changes in retention of iron for membranes compared to the experiment with pure 2 w-% HNO_3 solution. Profiles of the retention graphs are more stable and linear compared to retention graphs in HNO_3 solution. Also, retention of iron with A3011 membrane reduced first when pressure was increased to second measurement point (from 5 bar to 12 bar). Further increase in pressure increased the iron retention slightly.

During the filtration process, precipitation was observed in the feed solution. Precipitation occurred during the experimental series where concentration of iron was 1.4 g/l. Figure 26 presents the sample of feed solution after the filtration experiment.

Figure 26. Sample of the feed solution at the end of filtration process.

Precipitation did not occur in experimental series in nitric acid solution, thus it is formed due to complex formation between iron and dissociated oxalic acid, producing ferrous(II)oxalate. Complex ions are formed when positively charged metal ion forms coordination bond with negatively or neutrally charged ligand, in this case with oxalate ion thus producing complex ion with neutral net charge. (46) Precipitation produced by complex formation could affect to flux of nanofiltration experiment. Mass of the precipitated complex ion was measured to be approximately 3.7 g/l from the feed solution after the filtration process. Overall iron retention for GE-Osmonics and AMS A3012 membranes remained above 85%, which was similar when compared to experimental series in nitric acid solution. In Table VIII presents the fluxes and concentrations of iron for acid solution containing 2 wt.-% HNO_3 solution and acid solution containing 2 wt.-% HNO_3 and 1 wt.-% $(COOH)_2$.

Table VIII. Fluxes and concentrations of iron for acid solution containing 2 wt.-% HNO_3 solution and acid solution containing 2 wt.-% HNO_3 and 1 wt.-% $(COOH)_2$

Fluxes in 2 wt.-% HNO3 solution					Fluxes in 2 wt.-% HNO3 and 1 wt.-%(COOH)2 solution				
Fe [g/l]	Flux [kg/(m2h)]				Fe [g/l]	Flux [kg/(m2h)]			
	Duracid	Desal-5 DK	A3012	A3011		Duracid	Desal-5 DK	A3012	A3011
0.15	4.99	15.03	4.20	2.16	**0.15**	4.46	12.68	3.58	1.59
	11.69	25.06	10.90	5.88		11.25	21.42	9.22	4.73
	25.39	42.23	23.24	12.61		23.88	52.20	20.24	10.76
0.67	4.42	13.36	4.06	2.20	**0.69**	3.90	10.83	3.18	1.53
	10.78	23.26	10.51	5.76		10.40	18.97	8.82	4.06
	24.79	59.17	23.14	12.94		23.04	49.10	19.61	11.33
1.39	3.84	10.54	3.91	1.91	**1.40**	3.34	8.75	2.72	1.30
	10.62	20.77	10.03	5.50		9.48	17.08	7.49	3.92
	23.87	55.97	22.55	12.65		21.43	46.53	17.60	9.37
2.59	2.79	5.40	2.83	1.49	**2.66**	2.41	5.40	2.09	0.98
	9.56	16.96	9.07	5.12		8.34	12.18	7.08	3.49
	23.03	49.48	22.04	12.49		20.36	39.89	16.72	8.97

As comparing fluxes at both acidic solutions, flux of permeate is higher in experimental series containing only HNO_3 solution. This could indicate that addition of oxalic acid does affect to flux of permeate. Reduced flux can be indication of membrane fouling, although significant fouling was not observed when membranes were removed from filtration equipment.

pH of the feed solution was measured during the experiment. For iron concentration series of 0.15 g/l and 0.68 g/l the pH was 0. 44 while for iron concentration series of 1.4g/l and 2.66 g/l the pH was 0.43. When compared pH values of the feed solutions to ones in nitric acid solution, the pH was slightly higher when acid solution contained nitric acid. Table IX presents the retention of iron and pH of the permeate at different fluxes and concentrations of iron when solution contained HNO_3, $(COOH)_2$ and $FeSO_4$ were filtrated.

Table IX. Retention of iron and pH of the permeate at different fluxes and concentrations of iron when solution contained 2w-% HNO_3 and 1w-% $(COOH)_2$.

	GE-Osmonics Duracid			GE-Osmonics Desal-5 DK		
Fe c. [g/l]	Flux kg/(m2h)	Retention [%]	Perm. pH	Flux kg/(m2h)	Retention [%]	Perm. pH
0.15	4.99	90.49	0.49	15.03	86.79	0.47
	11.69	92.48	0.48	25.06	87.22	0.47
	25.39	94.33	0.49	42.23	94.32	0.48
0.69	4.42	90.47	0.45	13.36	90.28	0.45
	10.78	90.97	0.45	23.26	92.30	0.44
	24.79	93.37	0.46	59.17	95.36	0.44
1.40	3.84	88.09	0.43	10.54	90.07	0.42
	10.62	92.50	0.43	20.77	92.80	0.42
	23.87	94.42	0.44	55.97	96.03	0.42
2.66	2.79	91.72	0.42	5.40	90.72	0.40
	9.56	90.05	0.42	16.96	91.83	0.41
	23.03	94.83	0.44	49.48	96.40	0.43

	AMS Technologies A3012			AMS Technologies A3011		
Fe c. [g/l]	Flux kg/(m2h)	Retention [%]	Perm. pH	Flux kg/(m2h)	Retention [%]	Perm. pH
0.15	4.20	86.88	0.47	2.16	85.36	-
	10.90	92.81	0.47	5.88	89.63	0.48
	23.24	95.98	0.47	12.61	97.10	0.47
0.69	4.06	90.90	0.43	2.20	97.90	0.44
	10.51	92.07	0.44	5.76	96.01	0.43
	23.14	96.48	0.44	12.94	97.62	0.44
1.40	3.91	87.90	0.41	1.91	97.39	0.43
	10.03	92.72	0.41	5.50	93.77	0.41
	22.55	96.40	0.42	12.65	97.59	0.42
2.66	2.83	91.17	0.42	1.49	98.86	0.42
	9.07	91.25	0.42	5.12	96.17	0.41
	22.04	96.92	0.42	12.49	97.89	0.42

pH of the permeate and retention of iron presented in Table IX shows slight decrease in pH of permeate as iron concentration of feed was increased. Same phenomenon occurred for all membranes but is seen more clearly in cases of: Desal-5 DK, AMS A3012 and A3011, where permeate pH decreases under feed

solutions pH at every flux measurement. As a conclusion from iron retention studies in combined nitric acid and oxalic acid solution, it could be stated that iron retention throughout experimental series was very high for studied membranes.

7.3   Separation of Iron from Acid Solution

Enrichment filtration using Duracid membrane was conducted in solution containing 2 w-% HNO3 and 1 w-% oxalic acid ($(COOH)_2$) with $FeSO_4 * 7H_2O$. Figure 27 presents the permeate flux and feed solutions turbidity as a function of permeate yield, which is permeate volume fraction from total feed solution.
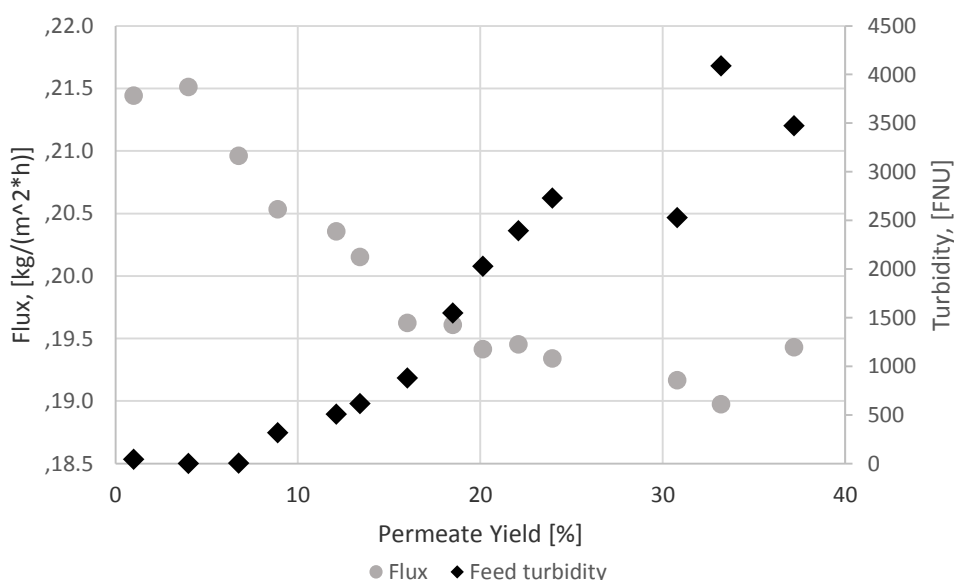
Figure 27. Flux and Feed turbidity as a function of permeate yield.

As presented in Figure 27 the flux starts to decrease after 5% of total feed solution is filtrated trough membrane followed by increase in feed turbidity at 7% permeate yield. In previous studies using combination of nitric acid and oxalic acid precipitation started to occur after 1-2 hours from addition of Fe (in form of FeSO4) to concentration of 2 g/l. Initial concentration of iron in the feed was 2.2 g/l (Figure 27), which was increased to 2.9 g/l at the end of filtration. Between

permeate yield of 4% – 16% (20 – 120 minutes), permeate flux decreases very rapidly along with steady increase in feed turbidity. As filtration continued from the permeate yield of 16%, velocity of flux reduction decreased and feed turbidity start to increase more rapidly. At this point feed solution seemed to be very turbid. The change in velocity of flux reduction could indicate that the precipitation of iron and oxalate ions reduces the osmotic pressure inside the system thus providing better permeate passage. Since ferrous (II) oxalate is non-soluble in water, complex formation should remove ionic compounds from filtration system thus hindering osmotic pressure build-up.

Along with turbidity of the feed solution, conductivity and pH from feed and permeate samples were measured. Figure 28 presents the conductivity and pH measurements from the collected feed and permeate samples.
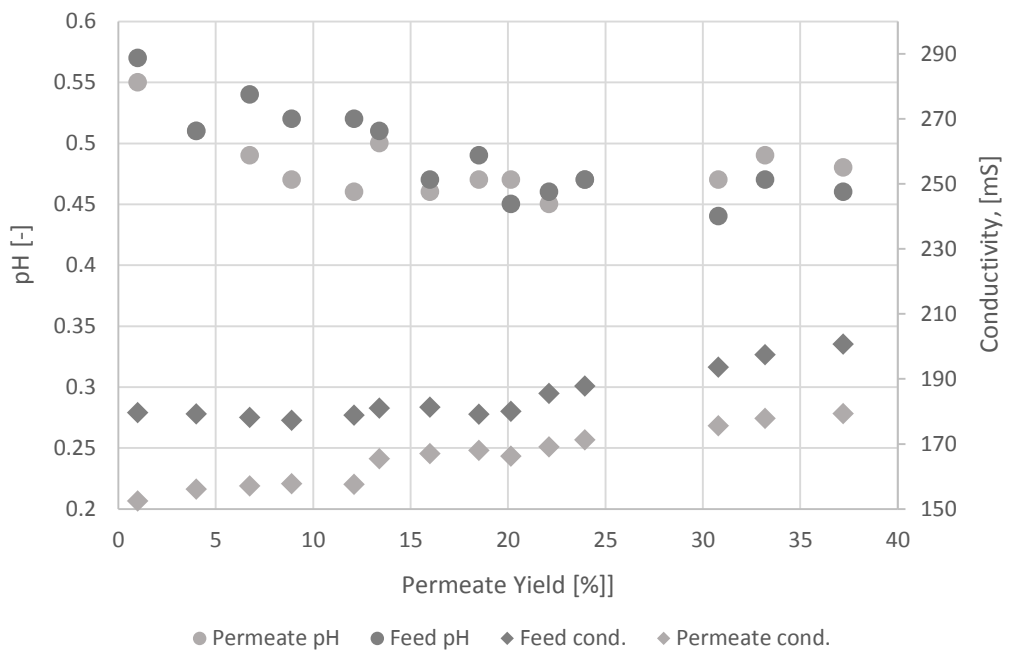
Figure 28. pH and conductivity of feed and permeate at function of permeate yield during filtration.

As the filtration progressed pH from both feed and permeate reduced while conductivity increased. The pH is slightly reducing between permeate yields of 0% and 13%. Small increase in conductivity can be observed also at permeate yield of 13%. After permeate yield of 20% feed and permeate conductivity starts to increase while pH remained stable.

Figure 29 presents the retention of iron and concentration of iron in the feed solution at function of permeate yield, Figure 30 presents the flux and retention of iron at the function of permeate yield.
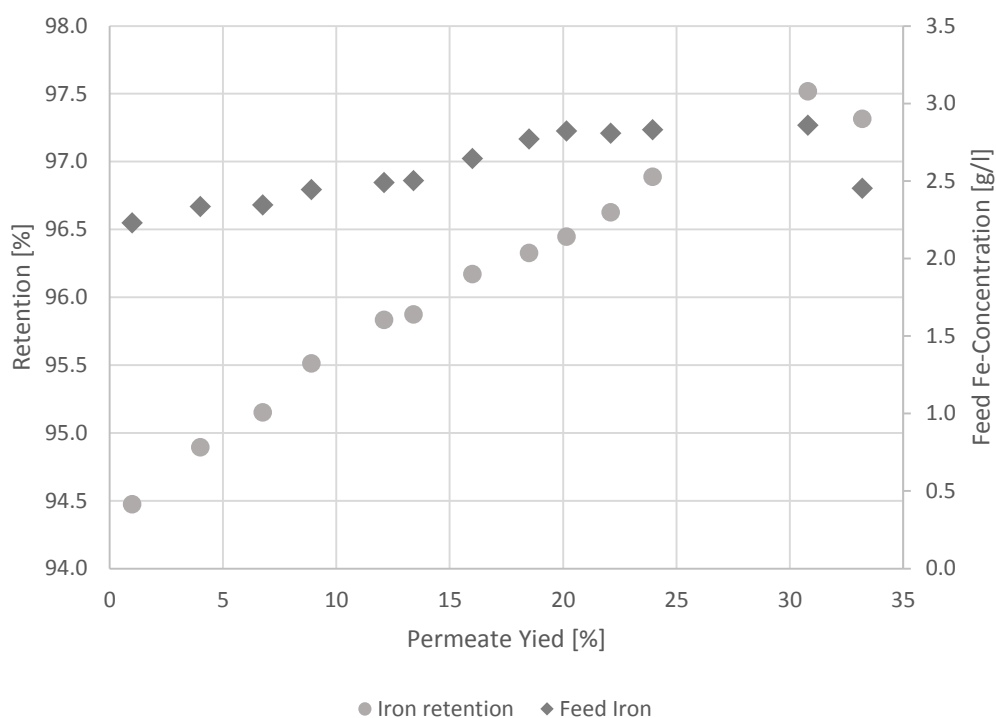
Figure 29. Retention of iron and concentration of iron in the feed solution at function of permeate yield
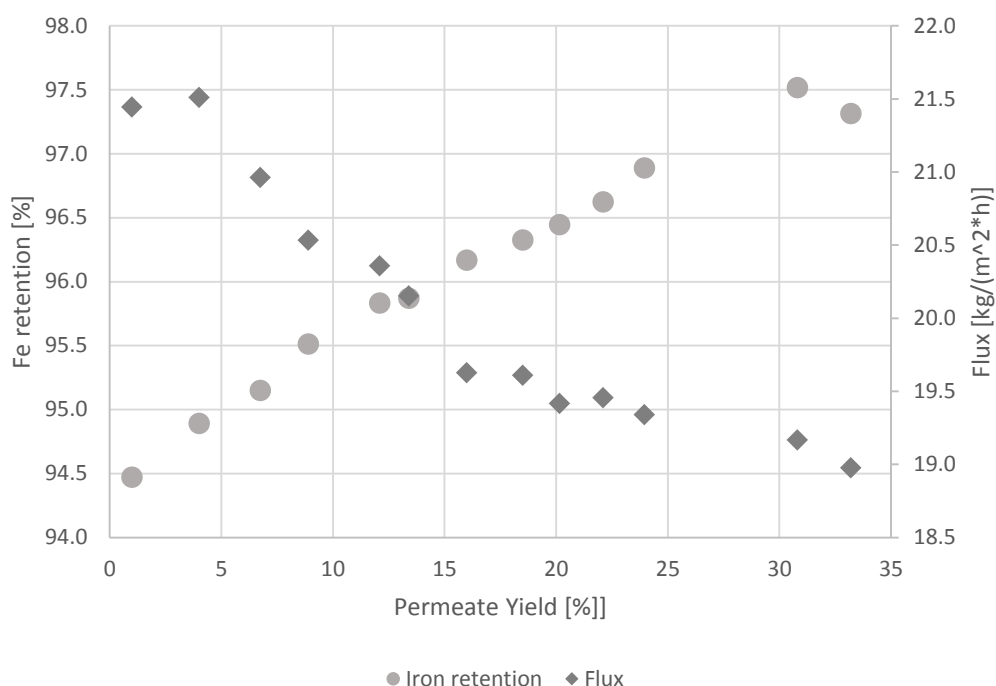
Figure 30. Flux and retention of iron as a function of permeate yield.

In Figure 29 the concentration of iron in the feed solution increases, the steady increase in retention of iron can be observed. The overall iron retention during the filtration is very high, which means that iron ions are mostly retained in the feed side. Due to law of electroneutrality the equal positive and negative charge must be on both side of membrane. When multivalent cations (e.g. iron) are retained in the feed side, the positive charge in the permeate side must come from protons due to dissociation of acids. The reduction of pH in Figure 28 is very small (~0.1 pH) so no reliable conclusion can be drawn from whether protons are concentrated on the permeate side of the membrane.

Steady increase in retention of iron can be observed during the filtration, as can be seen in Figure 30. The reduction of flux seems to faster at the beginning, which is followed by slower reduction of flux. No correlation in change of flux reduction velocity and increase in iron retention can be seen.

As a conclusion, the retention of iron was very good in acid conditions and acid permeated the membrane. To further study separation of iron from acid solutions the corresponding concentration mode filtration using HNO_3 must be made. Also, complete ion analysis from feed and permeate sample must be made.

After the enrichment filtration, feed solution was removed from filtration equipment and solid content were analysed by further filtrating it. Mesh filter was used as dead-end filter to remove precipitated solids from filtration equipment. The used mesh filter (50µm) did not work as planned, since it only removed portion of precipitated compound. After the filtration, the mass of precipitated compound was measured to be approximately 4.5 g/l. Measured mass of precipitated compound is not completely accurate due to do portion of solids were trapped into the 50 µm mesh filter. Figure 31 presents the dead-end mesh filter used to remove solids from filtration equipment.
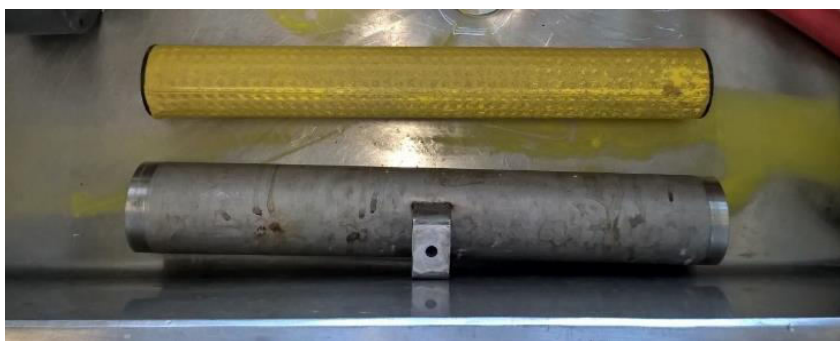
Figure 31. Dead-end 50 µm mesh filter used to remove precipitated complex compound form filtration.

8 CONCLUSIONS

The aim of this work was to study retention of ions in acidic environment along with separate iron ions from acid solutions using commercially manufactured GE-Osmonics membranes and AMS Technologies Nanopro A-series membranes. In the experimental part, the series of filtrations were conducted using nitric acid and combination of nitric and oxalic acid solutions. Retention of different ions was studied in pH scale of 5.4-1, while retention of iron was studied in fixed acidic solutions. Also, separation of iron from acid solution was studied in concentration mode of nanofiltration.

Nanofiltration combines molecular sieving of uncharged molecules, diffusion and retention based on charge. The most dominant separation characteristic for ionic compounds in nanofiltration is Donnan effect, which is based on theory of Donnan equilibrium. Along with Donnan effect, di-electric double layer and ion hydration affects to ion retention of membranes.

In acidic environment, the retention order of ions followed fully or partially charge based retention order, which indicated that Donnan effect affect the ion retention more significantly as pH of the solution is reduced. Also, the retention of iron increased as concentration of iron in the feed solution increased. Experimental series containing oxalic acid produced precipitated iron(II)oxalate complex. Due to precipitation, unmeasurable portion of iron was removed from liquid phase. Also, the addition of oxalic acid, had influence on permeate flux. The flux was slightly lower when oxalic acid was introduced in the solution. On the contrary, the addition of oxalic acid effect to retention of iron was negligible.

To obtain comprehensive data from filtration experiments, the concentration of all ions in the feed and permeate sides must be measured. To study nanofiltration further in acidic condition, a complete ion analysis from feed and permeate samples need to be made. Also, corresponding concentration mode filtration using only HNO_3 solution must be made, in order to study effects of precipitation in the feed solution.

APPENDIX I

pH 5.4	Pressure	Flux	Ion Retention [%]				Retention order			
Membrane	[Bar]	[kg/(m^2*h)]	Cl $^-$	SO2 $^{2-}$	Na $^+$	Ca $^{2+}$	1st	2nd	3rd	4th
Duracid	5	5,89	45,9	78,2	52,1	75,8	-	+	++	--
	12	14,37	63,8	83,2	64,2	89,0	-	+	++	--
	20	21,21	69,3	86,4	68,6	82,9	+	-	++	--
Desal-5 DK	3	10,57	12,2	93,2	31,9	68,6	-	+	++	--
	5	18,81	26,7	93,2	40,0	74,6	-	+	++	--
	12	46,16	46,5	94,5	52,6	90,9	-	+	++	--
AMS Tech. A3012	5	7,24	50,4	83,5	51,9	81,5	-	+	++	--
	12	18,11	69,6	89,5	71,4	89,4	-	+	++	--
	20	27,13	76,2	98,5	77,7	89,4	-	+	++	--
AMS Tech. A3011	5	4,72	75,8	97,2	76,9	91,2	-	+	++	--
	12	11,93	86,4	100,0	88,3	93,6	-	+	++	--
	20	18,02	88,7	100,0	90,1	94,1	-	+	++	--

pH 5.0	Pressure	Flux	Ion Retention [%]				Retention order			
Membrane	[Bar]	[kg/(m^2*h)]	Cl $^-$	SO2 $^{2-}$	Na $^+$	Ca $^{2+}$	1st	2nd	3rd	4th
Duracid	5	6,01	78,2	80,4	51,9	71,1	+	++	-	--
	12	14,45	83,2	85,7	66,8	88,4	+	-	--	++
	20	24,01	86,4	86,2	71,9	81,4	+	++	--	-
Desal-5 DK	3	11,30	93,2	94,4	29,4	73,3	+	++	-	--
	5	19,50	93,2	93,1	38,6	80,5	+	++	--	-
	12	46,94	94,5	99,7	52,0	92,6	+	++	-	--
AMS Tech. A3012	5	7,10	83,5	80,4	54,4	87,0	+	--	-	++
	12	17,49	89,5	93,4	78,9	95,4	+	-	--	++
	20	29,99	98,5	99,7	84,3	94,3	+	++	-	--
AMS Tech. A3011	5	4,66	97,2	?	77,2	92,7	+	++	-	?
	12	11,60	99,0	?	90,8	96,2	+	++	-	?
	20	20,01	100,0	?	93,0	95,8	+	++	-	?

pH 4.5	Pressure	Flux	Ion Retention [%]				Retention order			
Membrane	[Bar]	[kg/(m^2*h)]	Cl $^-$	SO2 $^{2-}$	Na $^+$	Ca $^{2+}$	1st	2nd	3rd	4th
Duracid	5	5,87	47,3	81,0	57,7	71,3	-	+	++	--
	12	14,09	65,9	85,2	70,9	88,5	-	+	++	--
	20	23,67	73,6	87,1	75,8	82,1	-	+	++	--
Desal-5 DK	3	11,42	24,2	91,6	35,0	82,9	-	+	++	--
	5	19,38	36,4	96,6	43,6	86,6	-	+	++	--
	12	47,21	53,2	96,2	56,5	94,2	-	+	++	--
AMS Tech. A3012	5	6,75	60,0	91,5	64,5	92,1	-	+	--	++
	12	16,92	77,7	97,5	83,1	96,9	-	+	++	--
	20	29,00	81,1	99,9	88,7	96,0	-	+	++	--
AMS Tech. A3011	5	4,48	76,2	99,6	83,2	94,6	-	+	++	--
	12	11,16	85,4	99,8	91,8	96,9	-	+	++	--
	20	19,32	87,3	100,0	94,4	96,3	-	+	++	--

pH 4.0	Pressure	Flux	Ion Retention [%]				Retention order			
Membrane	[Bar]	[kg/(m^2*h)]	Cl^-	$SO2^{2-}$	Na^+	Ca^{2+}	1st	2nd	3rd	4th
Duracid	5	5,66	51,1	68,0	60,2	72,9	-	+	++	--
	12	13,98	69,4	88,5	74,4	90,1	-	+	--	++
	20	23,28	76,6	88,8	78,5	83,8	-	+	--	++
Desal-5 DK	3	11,54	35,3	88,2	39,8	84,9	-	+	++	--
	5	19,30	48,4	97,7	50,9	88,9	-	+	++	--
	12	47,75	63,6	96,8	65,7	95,3	-	+	++	--
AMS Tech. A3012	5	6,43	60,2	87,4	67,5	93,0	-	+	--	++
	12	16,52	74,6	96,0	85,8	97,1	-	+	--	++
	20	27,94	78,5	100,0	90,1	96,5	-	+	++	--
AMS Tech. A3011	5	4,25	72,7	97,5	85,1	95,2	-	+	++	--
	12	10,88	77,6	98,4	93,0	96,9	-	+	++	--
	20	18,53	78,8	93,9	95,2	96,7	-	+	--	++

pH 3.5	Pressure	Flux	Ion Retention [%]				Retention order			
Membrane	[Bar]	[kg/(m^2*h)]	Cl^-	$SO2^{2-}$	Na^+	Ca^{2+}	1st	2nd	3rd	4th
Duracid	5	5,55	53,6	77,4	64,7	76,7	-	+	++	--
	12	13,58	66,6	87,5	75,0	90,5	-	+	--	++
	20	22,77	75,7	89,2	80,6	86,0	-	+	++	--
Desal-5 DK	3	11,51	44,4	89,4	48,9	86,2	-	+	++	--
	5	19,56	57,2	95,2	60,0	90,0	-	+	++	--
	12	47,39	72,6	96,3	74,4	95,9	-	+	++	--
AMS Tech. A3012	5	6,10	50,3	72,8	68,6	93,0	-	+	--	++
	12	15,62	61,4	85,0	84,4	97,1	-	+	--	++
	20	26,68	65,3	89,8	90,6	96,6	-	--	+	++
AMS Tech. A3011	5	4,03	38,3	95,0	87,8	95,0	-	+	--/++	--/++
	12	10,17	43,4	90,0	92,1	96,7	-	--	+	++
	20	17,46	43,3	93,5	95,0	96,5	-	--	+	++

pH 3.0	Pressure	Flux	Ion Retention [%]				Retention order			
Membrane	[Bar]	[kg/(m^2*h)]	Cl^-	$SO2^{2-}$	Na^+	Ca^{2+}	1st	2nd	3rd	4th
Duracid	5	5,52	41,6	73,3	63,1	79,4	-	+	--	++
	12	13,55	55,7	81,8	75,8	91,3	-	+	--	++
	20	22,71	65,3	91,2	81,2	87,8	-	+	++	--
Desal-5 DK	3	11,51	41,4	82,0	55,4	87,2	-	+	--	++
	5	19,89	56,9	89,4	67,1	90,0	-	+	--	++
	12	48,80	73,6	96,4	79,5	96,0	-	+	++	--
AMS Tech. A3012	5	5,86	34,4	54,2	66,6	93,0	-	--	+	++
	12	14,94	39,8	63,2	84,6	97,1	-	--	+	++
	20	25,52	43,5	68,8	90,7	96,7	-	--	+	++
AMS Tech. A3011	5	3,74	38,3	68,4	82,2	92,8	-	--	+	++
	12	9,57	43,4	67,6	92,0	96,6	-	--	+	++
	20	16,45	43,3	72,0	94,9	96,7	-	--	+	++

pH 2.0	Pressure	Flux	Ion Retention [%]				Retention order			
Membrane	[Bar]	[kg/(m^2*h)]	Cl $^-$	SO2 $^{2-}$	Na $^+$	Ca $^{2+}$	1st	2nd	3rd	4th
Duracid	5	5,73	13,9	27,1	58,5	86,3	-	--	+	++
	12	14,23	25,1	57,0	73,8	94,5	-	--	+	++
	20	23,73	33,0	69,8	81,0	92,5	-	--	+	++
Desal-5 DK	3	12,34	23,7	71,0	51,6	92,0	-	+	--	++
	5	20,86	36,1	78,9	63,2	93,2	-	+	--	++
	12	52,15	56,9	89,5	78,0	94,5	-	+	--	++
AMS Tech. A3012	5	5,49	3,9	11,7	66,5	93,9	-	--	+	++
	12	13,99	9,8	14,1	83,1	97,3	-	--	+	++
	20	23,75	8,6	9,4	90,5	96,8	-	--	+	++
AMS Tech. A3011	5	3,32	5,2	12,0	83,1	95,2	-	--	+	++
	12	8,52	7,6	16,9	91,0	96,8	-	--	+	++
	20	14,67	9,8	22,0	94,9	96,7	-	--	+	++

pH 1.0	Pressure	Flux	Ion Retention [%]				Retention order			
Membrane	[Bar]	[kg/(m^2*h)]	Cl $^-$	SO2 $^{2-}$	Na $^+$	Ca $^{2+}$	1st	2nd	3rd	4th
Duracid	5	5,31	8,7	-10,6	37,6	90,6	--	-	+	++
	12	13,09	12,3	12,8	60,4	94,9	-	--	+	++
	20	22,08	20,9	30,3	71,8	92,4	-	--	+	++
Desal-5 DK	3	13,28	3,7	2,7	18,2	86,6	--	-	+	++
	5	21,42	8,3	11,6	25,5	88,7	-	--	+	++
	12	53,59	19,4	42,3	45,8	94,0	-	--	+	++
AMS Tech. A3012	5	4,87	2,8	-44,6	46,0	88,0	--	-	+	++
	12	12,42	4,3	-26,5	70,1	94,9	--	-	+	++
	20	21,30	6,2	-20,3	81,6	95,5	--	-	+	++
AMS Tech. A3011	5	2,79	-2,1	-100,0	72,5	93,2	--	-	+	++
	12	7,06	5,9	-29,8	81,1	95,2	--	-	+	++
	20	12,20	13,2	-5,9	91,1	96,1	--	-	+	++

9 REFERENCES

1. R, Singh. Membrane Technology and Engineering for Water Purification: Application, System Design and Operation. Chapter 1-2. 2nd edition. Butterworth-Heinemann Publications (2015)

2. M, Dalwani. Thin film composite membranes for extreme conditions. Enschede: Institute for Sustainable Process Technology (2011) ISBN: 978-90-365-3276-1

3. J, Tanninen. M, Mänttäri. M, Nyström. Nanofiltration of concentrated acidic copper sulphate solutions. Desalination 189 (2006) 92-96.

4. J, Tanninen. M, Nyström. Separation of ions in acidic conditions using NF. Desalination 147 (2002) 295-299.

5. A, I, Schaefer. T,D, Waite. A,G, Fane. Nanofiltration - Principle and Applications. 2nd edition. Elsevier 2005

6. R, W, Baker. Membrane Technology and Applications, 2nd Edition. Chapter 1-5. John Wiley & Sons Ltd (2004) ISBN 0-470-85445-6

7. M, Dalwani. N, E, Benes. G, Bargeman. D, Stamatialis. M, Wessling. A method for characterizing membranes during nanofiltration at extreme pH. Journal of Membrane Science 363 (2010) 188-194.

8. J, Luo. Y, Wan. Effects of pH and salt on nanofiltration - a critical review. Journal of Membrane Science 438 (2013) 18-28.

9. L, K Wang. J, P, Chen. Y-T, Hung. N, K, Shammas. Handbook of Environmental Engineering volume 13: Membrane and Desalination Technologies. Springer Science (2011).

10. M, Mulder. Basic Principle of Membrane Technology. 2nd edition. Kluwer Academic Publishers (1996)

11. D, G, Rao. R, Senthilkumar. B, J, Anthony. S, Feroz. Wastewater Treatment: Advanced Processes and Technologies. IWA Publishing (2013).

12. E, Drioli. L, Giorno. Comprehensive Membrane Science and Engineering Volume 1. Elsevier (2010)

13. A, F, Ismail. M, Padaki. N, Hilal. T, Matsuura. W, J, Lau. Thin film composite membrane - Recent development and future potential. Desalination 356 (2015) 140-148.

14. J, W, Lau. A, F, Ismail. N, Misdan. M, A, Kassim. A recent progress in thin film composite membrane: A review. Desalination 287 (2012) 190-199.

15. Lenntech. Lentech Water Treatment Solutions (2016) [Viitattu: 8. 8 2016.] http://www.lenntech.com/.

16. J, Schwinge. P, R, Neal. D, E, Wiley. D, E, Fletcher. Spiral wound modules and spacers: Review and analysis. University of Sidney, Department of Chemical Engineering (2006) 129-153.

17. Sapphire Water. Membrane Filtration. 2016. Referred 29. 2 2016. http://www.sapphire-water.ca/water-treatment-technology/membrane-filtration/.

18. Synder Filtration. Hollow Fibre Membranes (2016). Referred: 26. 02 2016. http://synderfiltration.com/learning-center/articles/module-configurations-process/hollow-fiber-membranes/.

19. TSKE Ltd. Membrane separation processes (2016). Referred 29. 2 2016. http://www.tske.co.jp/english/technology/seizou_bunri.html.

20. F, Fu. Q, Wang. Removal of heavy metal ions from wastewaters: A Review. Journal of Environmental Managemant 92 (2011) 407-418.

21. Z, V, P, Murthy. L, B, Claudhari. Separation of binary heavy metals from aqueous solutions by nanofiltration and characterization of the membrane using Spiegler-Kedem model. Chemical Engineering Journal 150 (2009) 181-187.

22. M, Muthukrishnan. B, K, Guha. Effect of pH on rejection of hexavalent chromium by nanofiltration. Desalination 219 (2008) 171-178.

23. A, L, Ahmad. B,S, Ooi. A study on acid reclamation and copper recovery using low pressure nanofiltration membrane. Chemical Engineering Journal 56 (2010) 257-263.

24. D, H, Green. J, J, Mueller. Method for separating and isolating gold from copper in a gold processing system. US 5961833 (1999).

25. D, Mukhopadhyay. D, Bergamini. Method for treating process streams containing cyanide and heavy metals. US 5266203 (1993).

26. J, Mallevialle, P, E, Odendaal. M, R, Wiesner. Water Treatment Membrane processes. McGraw-Hil (1996).

27. T, Y, Cath. A, E, Childress. M, Elimelech. Forward Osmosis: Principle, applications, and recent development. Journal of Membrane Science 281 (2006) 70-87.

28. B, Elvers. Ullmann's Encyclopedia of Industrial Chemictry. H, Strathmann. Membranes and Membrane Separation Processes, 4. Concentration Polarization and Membrane Fouling. Wiley Online Library (2011) 513-525.

29. G, Mustafa. K, Wyns. A, Buekenhoudt. V, Meynen. New insights into the fouling mechanism of dissolved organic matter applying nanofiltration membranes with a variety of surface chemistries. Water Research 93 (2016) 195-204.

30. N, N, Li. A, G, Fane. H, W, S, Winston. T, Matsuura. Advanced Membrane Technology and Applications. John Wiley & Sons, 2008.

31. M, Mänttäri. A, Pihlajamäki. M, Nyström. Effect of pH on hydrofobicity and charge and their effect on the filtration efficicnecy of NF membranes at different pH. Journal of Membrane Science 280 (2006) 311-320.

32. Synder Filtration. Molecular Weight Cut Off (2016). Referred: 23.2.2016. http://synderfiltration.com/learning-center/articles/membranes/molecular-weight-cut-off/

33. A, Verhoef. A, Figoli. B, Leen. B, Bettens. E, Drioli. B, Van der Bruggen. Performance of a nanofiltration membrane for removal of ethanol from aqueous solutions by pervaporation. Separation and Purification Technology 60 (2007) 54-63.

34. C, Batels. R, Franks. S, Rybar. M, Schierach. M, Wilf. The effect of feed ionic strength on salt passage through reverse osmosis membranes. Desalination 184 (2005) 185-195.

35. A, Martín. F, Martínez. J, Malfeito. L, Palacio. P, Prádanos. A, Hernández. Zeta potential of membranes as a function of pH - Optimization of isoelectric point evaluation. Journal of Membrane Scince 213 (2003) 225-230.

36. K, Zhao. Y, Li. Dielectric Characterization of a Nanofiltration Membrane in Electrolyte Solutions: Its Double-Layer Structure and Ion Permeation. Journal of Physical Chemistry 110 (2006) 2755-2763.

37. M, Mullett. R, Fornarelli. D, Ralph. Nanofiltration of Mine Water: Impact of Feed pH and Membrane Charge on Resource Recovery and Water Discharge. Membranes 4 (2014) 163-180.

38. S, Bandini. D, Vezzani. Nanofltration modeling: the role of dielectric exclusion in membrane characterization. Chemical Engineering Science 58 (2003) 3303 – 3326.

39. A, E, Yaroshchuk. Dielectric exclusion of ions from membranes. Advances in Colloid and Interface Science 85 (2000) 193-230.

40. A, E, Yaroshchuk. Non-steric mechanisms of nanofiltration: superposition of Donnan and dielectric exclusion. Separation and Purification Technology 22-23 (2001) 143-158.

41. B, Tansel. J, Sager. T, Rector. J, Garland. R, F, Strayer. L, Levine. M, Roberts. M, Hummerick. J, Bauer. Significance of hydrated radius and hydration shells on ionic permeability during nanofiltration in dead end and cross flow modes. Separation Purification Technology 51 (2006) 40-47.

42. O, Agboola. J, J, Schoeman. J, Maree. R, Mbaya. A, Kolesnikov. Performance of an acid stable nanofiltration membrane for nickel removal from aqueous solutions: effect of concentration, solution pH and ionic strength. Waste Management and the Environment IV (2012) 415-424.

43. M, Mänttäri. M, Nyström. Negative retention of organic compounds in nanofiltration. Desalination 199 (2006) 41-42.

44. J, Tanninen. S, Platt. A, Weis. M, Nyström. Long-term acid resistance and selectivity of NF membranes in very acidic conditions. Journal of Membrane Science 240 (2004) 11-18.

45. J, Tanninen. M, Mänttäri. M, Nyström. Effect of salt mixture concentration on fractionation with NF membranes 283 (2006) 57-64.

46. F, A, Cotton. G, Wilkinson. Basic Inorganic chemistry. John Wiley & Sons Inc (1976).