Ceramic Nano-filtration of NOM - rich brine

MASTER THESIS

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Ceramic nanofiltration of NOM rich brine

By

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This thesis is confidential and cannot be made public until October 28, 2021.

Preface

This research is a testament of my 2 years and 2 months in field of environmental engineering at TU Delft. It has been a bumpy ride, but in the end, it is all worth it. For my thesis, I wanted to work on topic related with micropollutants or organics in drinking water treatment. Eventually, I found the topic which was challenging and exciting at the time. During the thesis months I received support of many individuals whom I wish to acknowledge. My heartfelt gratitude to my supervisors, Prof. Dr. Ir. Luuk Rietveld and Dr. S.G.J.Heijamn, who, showed interest to my progress, explained the doubts and were available in the need of an hour. I would thank them for their encouragment, understanding attitude in all situations, support, and supervision. I am extremely grateful to my PhD mentor Ir. Irene Caltran for her constant encouragement, tips, patience, understanding, and supervision. Also, being there to provide guidance and advice when things didn't work as expected. I owe her my sincere thanks for being friendly, empathetic and supportive during all odds of research period and having productive discussions. Working with them, I have learned to love the work you perform, respect and always be critical about the research for what it is.

The lab process was easier and more comfortable to work in because of Lab technicians – Armand Middeldorp and Patricia van den Bos, who always helped happily, whom I could approach for the requirement of resources any time. I am thankful to have such friendly Lab technicians during my journey at Water Lab. Besides, I would like to thank DEMO lab staff, Sander and Frank who were instrumental in helping me with arranging and repairing for setup and equipment's, needed during the thesis. I would like to thank everyone else– colleagues and PhDs who either helped and or made Water Lab a better place to work in. A special thank you to Floriana for troubleshooting the problems with IC instrument.

I am blessed for the friends in Delft – especially Surabhi, Sagar, Maulik, Vimarsh, Kalrav, Kashyap, Kushal, Rishabh, Gaurav and Ashvij who were always ready to help, support and encourage me during these two years in Delft. I am thankful to Mrinal, Shreya, Sasidhar, Apoorva and Magnolia for their assistance. My flatmates – Sahana, Samyuktha, Shrutika to whom I could share my frustration about clueless moments during thesis and otherwise. It was a memorable experience to study in a multi-cultural and lingual crowd.

Last but not the least, I would like to express my biggest gratitude to my Parents – Manish and Sonal Halvawala, and best friend Umang who believed and encouraged me to study at TU Delft. I am forever grateful for their unflagging support, care, and love, which played an important role during my studies.
Finally, I hope that this research is useful for DOC2c's project.

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Abstract

The presence of organic and inorganic contaminants in aquatic ecosystem has been threat to public health and environment. To produce drinking water, removal of natural organic matter has been of importance due to formation of DBPs. Of the many available treatments, ion exchange (IEX) has the potential to remove natural organic matter (NOM). However, IEX resins need to be regenerated upon saturation with NOM, which generates brine. Usually, NaCl is used to regenerate the resins, hence the desorbed NOM ends in the brine with sodium chloride and other ions like sulphate and nitrate which are present in surface or ground water. The disposal of high saline brine is complex due to aftereffects on the environment and the associated costs. Therefore, an interesting physical alternative is to separate the NOM from brine that can be further reprocessed as fertilisers for agriculture.

Ceramic nanofiltration (NF) appears to be an alternative to treat the brine. This type of membrane is chemically and mechanically robust, can be operated at extreme pH conditions, withstands backwashing and chemical cleaning. Besides, ceramic nanofiltration membranes have the capability to separate multivalent ions which makes it suitable to treat the brine. However, NOM possess a complex matrix and relies on various factors for its high removal.

In this research, it was interesting to recognize the NOM fractions and the behaviour alleviating NOM retention. Various IEX brines from water treatment plants were studied. For this, NOM was characterised using two different methods i.e., LC-OCD and NSM. The LC-OCD characterization done by *Het Waterlaboratorium* characterized NOM fraction based on the size of fractions into Humic substances, building blocks, Low molecular weight neutrals and low molecular weight acids. Characterisation of NSM was done by Udine University, Italy wherein the characterization of humics was done on the principle of the selective resin adsorption and precipitation. The characterisation of NOM by LC-OCD predicted the NOM rejection on membrane quite accurately.

The effect of ionic strength was investigated to reflect NOM removal. NOM rejection for same NOM source and membrane pore size remained unaffected by the ionic strength of the brine. However, when different membrane pore sizes (600Da and 900Da) for different NOM source, NOM removal by ceramic nanofiltration was governed a combination of steric exclusion, electrostatic repulsion and hydrophobic nature of the humic content and. In longer duration, ceramic NF membranes may foul due to filtration process. To reflect the same, fouling test was conducted. Fouling test was conducted with the high ionic strength brine because during the filtration experiments, it showed highest permeability drop. The sudden drop in permeate flux was due to osmotic pressure difference. However, during NOM filtration period, the flux and permeability were quite steady which suggested no major fouling in that phase. Irreversible fouling did not affect the membrane pore size.

Keywords: Ceramic Nano-filtration; NOM rejection; IEX brine; LC-OCD; Humic substances; NaCl and Na_2SO_4; New standardised method; Osmotic pressure

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List of Acronyms

CP	Concentration Polarization
Da	Daltons
EfOM	Effluent Organic Matter
FA	Fulvic Acid
HA	Humic Acid
HOC	Hydrophobic organic carbon
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
IEX	Ion Exchange
IHSS	International Humic Substances Society
LC-OCD	Liquid Chromatography – Organic Carbon detector
MF	Microfiltration
MM	Molar mass
MW	Molecular Weight
MWCO	Molecular Weight Cut-off
NF	Nanofiltration
NOM	Natural Organic Matter
NSM	New Standardized method
OND	Organic nitrogen detector
PEGs	Polyethylene Glycols
PES	Polyethersulfone
POC	Particulate organic carbon
Ppb	Parts per billion
ppm	Parts per million
PSD	Particle Size Distribution
RO	Reverse Osmosis
TMP	Transmembrane Pressure
UF	Ultrafiltration

1 Introduction

1.1 Water Treatment

Safe drinking water is indispensable to humankind for health and to support productivity in agriculture and industry. Nevertheless, there is abundant scarcity of fresh water due to urbanisation, increase in population and industrialisation. To combat the scarcity of fresh water is to treat, recover, recycle, and reuse the dirty water in all feasible fields (Lee et al.,2015) and use fresh water efficiently.

Several techniques are currently applied with the aim to recover, recycle and reuse of the dirty water. Resources can also be recovered from water treatment, using, e.g., chemical precipitation, membrane filtration, biological treatments, activated carbon adsorption (Rajasulochana & Preethy, 2016). Of all, membrane process has been effective to separate broad spectrum of components from colloidal solids, small organic compounds to even ions (Bruggen et al., 2003). Membranes work on solid-liquid or liquid-gas separation principle. The range for nanofiltration membrane pore size is from 1 to 10 (Fane et al., 2011) and ≤ 1 whereas reverse osmosis does not have predefined pores and work based on solution-diffusion separation mechanism. This implies low permeability and high pressures are required for operation. Therefore, depending on the purpose, NF is preferred over reverse osmosis because they provide high productivity even at lower working pressures (Bruggen et al., 2003). NF membranes come in two types, Organic – polymeric membranes and inorganic membranes – ceramic membrane. At industrial scale polymeric membranes are preferred because of capital cost and brittleness of the ceramic membranes (Lee et al., 2015). However, high chemical, thermal and mechanical resistance is provided by ceramic membranes (Weber et al., 2003). They withstand organic solvents, chlorine, other oxidants and microbial attack which makes them suitable than polymeric membranes (Mallada and Menéndez, 2008). Due to its advantages, ceramic NF is used in this research to examine the rejection of salts and NOM for the treatment of NOM - rich brines.

1.2 Ion-Exchange Brine treatment

Natural Organic matter (NOM) is a bulk term used for all organic matter excluding living organisms and synthetic compounds (Buffle et al.,1982; Buffle, 1984). It imparts undesirable colour, taste and odour problems in drinking water and has been a major contributor to disinfection by-products (Sillanpää, 2014). There are numerous techniques which can remove NOM from drinking water. The techniques are Nano-filtration, coagulation and flocculation, chemical sorption (ion exchange), physical adsorption (activated carbon) and biofiltration (Ødegaard et al., 2010). Amongst these techniques ion exchange has proved to be competent in removal of NOM, because usually NOM carries charge (Finkbeiner et al., 2018; Galjaard & Koreman, 2015). Specifically, anion exchange has been capable to remove the fraction of NOM that is negatively charged. Anion exchange not only removes NOM, but also other anions like sulphate, nitrate and bicarbonate from water. (Sillanpää, 2014)

During anion exchange, negatively charged NOM is loaded in high concentration to the ion exchange resin column and NOM in return is exchanged with negatively charged ions, namely Cl_{-}, originally present on the resin surface. Also, SO_{42-}, and other anions existent in the raw water to be treated are loaded on the ion exchange resin. The anions with higher selectivity and affinity than Chloride ions are adsorbed by the resins (Bae et al., 2002; Calmon, 1986). Eventually the capacity of the resins decreases. When the resins are exhausted, unwanted ions (e.g., SO_{42-}) leak into treated water. This indicates that regeneration or restoring the exchange capacity of resins is needed. Generally, regeneration of the resins is done using a fresh regenerant. A widely used regenerant in drinking water applications is sodium chloride (NaCl). In regeneration phase, a high concentrate NaCl solution, e.g., 10 % (Dardel, 2018), is added to bring back the resins to its original condition. Therefore, the waste stream generated from IEX regeneration is called Brine which, contains anions removed by the resin(majorly sulphate if present in the drinking water source), NOM and the regeneration ions Na^+ and Cl^- (Drikas et al., 2011).

The brine disposal is problematic. Discharge of brine directly to surface water can make the fresh water brackish and in near future it may not be possible due to stricter governmental legislations (Lenntech, n.d.). It can also disrupt the aquatic ecosystem since the organic part of NOM acts as a nutrient for microbial growth (Teixeira & Sousa, 2013). Disposal into sewer system can corrode the sewers. Transportation of brine to sea incurs enormous transportation costs. Therefore, the best thoughtful alternative to get rid brine is its treatment.

Biological treatment of the brine might not be beneficial because humic substance present is not readily biodegradable (Grefte, 2013). An alternative is the physical treatment by membrane filtration. Membrane filtration will segregate the compounds thereby reducing the volume of brine. The added advantage of this choice is low energy demand unlike crystallization and vapour compression (Ghalavand et al., 2015).

NF membranes can retain organic substances and multivalent ions. Most studies conducted until recently used polymeric NF membranes however, very few researchers used ceramic membranes using low ionic strength solutions. An inclusive study on ceramic membranes dealing with high ionic strength (NaCl, Na_2SO_4) and NOM rich solution has not been conducted. The volume of the brine can be reduced by recovering NaCl and the NOM present in the Brine. NaCl can be further reused to regenerate resins for IEX process; NOM can be used for the agricultural purposes. For the same, the membrane should aim at retention of NOM and sulphate and passage of small cations and anions, usually monovalent ions like sodium and chloride to make a salt stream, which can be reused to regenerate IEX resins.

1.3 Research Gap

There has been a huge number of studies on the rejection of NOM in presence of divalent ions like Ca^{2+} and Mg^{2+} with low ionic strength solution using different Nano-filtration membranes. However, there is hardly any comprehensive research done on the rejection various types of NOM in high salinity solution (mainly presence of NaCl and SO_4^{2-}) using ceramic NF membranes. Rejection tests with different brines may foul the membrane and hence, the characterisation of fouled/uncleaned membrane is interesting to investigate.

1.4 Research objective

In this research, treatment of high ionic-strength water – brine solution, containing NOM and salts (NaCl and Na_2SO_4) by NF was investigated. The goal of the research was to understand NOM rejection and rejection mechanism, and fraction of NOM rejected. The first objective was to explore the inter-dependency of the salt and NOM on the NOM rejection. The second objective was to characterise the NOM fractions present in various IEX brines. That is, to characterise the NOM and thereby determine the rejection mechanism. The final objective was to explore the extent of fouling, and the effect of ionic strength and NOM on membrane fouling.

1.5 Research Questions

Based on the research objective, research questions were formulated to guide the research. The research questions are as follows:

Research Question 1

i. *What are the characteristics of the NOM present in different ion exchange brines?*
ii. *What are the characteristics of the membrane?*

⇒ The real IEX brines have various fractions of NOM. The characterisation of NOM was done by LC-OCD and New standardised method (NSM). The feed water of all the test experiments was analysed by LC-OCD and NSM. The results from these methods, that work on principles of size exclusion and fractionation by selective resin adsorption and precipitation respectively, were compared. It was aimed to select the method that is most useful to predict the behaviour of NOM membrane rejection. To characterise the membrane, the molecular weight cut-off of the membranes used was determined by conducting PEG tests on clean membranes.

Research Question 2

What is the effect of NaCl and Na_2SO_4 *and NOM on NOM rejection?*

i. *What NOM characterisation method is useful to predict NOM rejection?*

⇒ To answer this research question, NOM rejection was studied for different concentrations of salts, that is, different ionic strengths, using artificial brines and IEX brines which originated from different water treatment plants.

Research Question 3

What are the characteristics of NOM fouling?

i. *Is the fouling reversible or irreversible or a combination?*

ii. *Does the irreversible fouling affect the membrane pore size?*

⇒ Firstly, it was studied to identify the loss of permeability during nanofiltration compared to clean water. To learn, is the major loss of permeability due to salts? Or due to NOM? Secondly, to check whether the irreversible fouling reduced the pore size of the membrane, which was done by measuring the MWCO of the membrane after treating the brine, without cleaning it.

1.6 Thesis Outline

In this thesis, the ceramic NF performances for NOM and salt retention were studied, to understand rejection mechanism and fouling.

Chapter 2 describes the fundamentals of the ceramic membrane based on different types of structure and configuration of the membrane, and possible retention mechanisms of NOM and salts in ceramic membrane. Further, it describes NOM characterisation and measurement techniques of NOM. Lastly, it describes the characteristics of membrane fouling.

Chapter 3 mainly explains how the bench-scale experiments were conducted. It describes the materials, instruments and methodology to execute the research.

Chapter 4 explains the results and discussion of the NOM and salts filtration experiment, including flux and permeability variations, retention mechanisms, NOM characterisation and validation of experimental results using a model. It also includes the results from the fouling experiments on NOM and salt retention.

Chapter 5 mentions the conclusions for the filtration and fouling experiments derived from the results. In addition, recommendations for further research are suggested.

2 Literature Review

2.1 Pressure-driven Membranes

Pressure-driven membranes have gained rapid importance in drinking water production. They have also found their use in different industries like food, textile and medical. Pressure-driven membranes separate compounds based on selectivity and permeability of the solutes. These two parameters depend majorly on membrane's pore characteristics (pore size, pore-size distribution and porosity). Therefore, based on membrane pore structure they can be classified into MF, UF, NF and RO. Besides, properties like hydrophilicity, surface charge etc, are also important. These pressure-driven membranes can be categorised into porous and non-porous. MF and UF are porous because the pore structure can be seen under an electron microscope whereas, there does not appear any pores on rejection layer of RO membrane. Ultimately, NF membranes lie between tight UF membranes and loose RO membrane. (Fane et al., 2011)

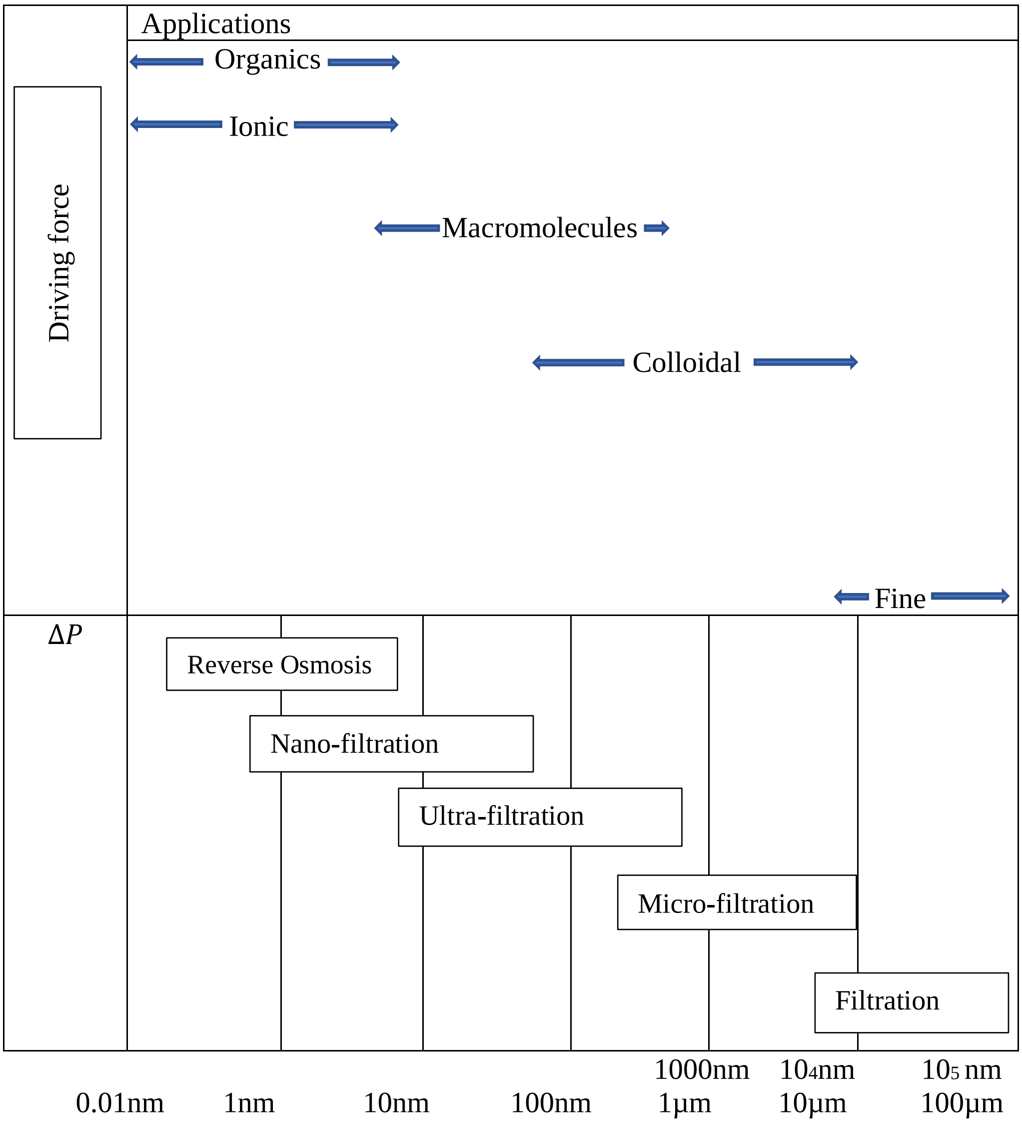


Figure 2.1: Summary of different pressure-driven filtration processes corresponding to sizes of compounds removed (Fane et al., 2011)

Table 2.1: Pressure-driven membrane properties. Adapted from (Fane et al., 2011)

Parameters	Microfiltration	Ultrafiltration	Nanofiltration	Reverse Osmosis
Pore size(nm)	50-10,000	1-100	≈ 2	<2
Water permeability (lm$_2$ h$_{-1}$ bar$_{-1}$)	>500	20-500	5-50	0.5-10
Operating pressure (bar)	0.1-2.0	1.0-5.0	2.0-10	10-100
MWCO (Da)	-	1000-300,000	>100	>10
Targeted contaminants in water	Bacterial, algae, suspended solids, turbidity	Bacterial, virus, colloids, macromolecules	Di-and multivalent ions, natural OM, small molecules	Dissolved ions, small molecules
Membrane materials	Polymeric and inorganic	Polymeric, few inorganic	Thin-film composite polyamide, cellulose acetate, ceramic, other materials	Thin-film composite polyamide, cellulose acetate

2.2 Nanofiltration membrane

As discussed, summarized in Table 2.1 the pore size for NF membranes is approximately 2nm. The natural organic matter namely humic acid, viruses and dissolved salts can be retained by nanofiltration membranes. (Halem, 2009; Fane et al., 2011) In general, the membranes can be classified based on the material used for its production. One is polymeric membrane (e.g. made of polyamide, polysulphone, cellulose acetate etc.) and second is inorganic membrane (e.g. made up of ceramic, zeolites materials). However, in drinking water applications the membranes used are polymeric (Gitis & Rothenberg, 2016). To widen the usage of membranes in extreme conditions, ceramic membranes are replacing polymeric membranes (Z. Wang et al., 2016).

2.2.1 Ceramic nanofiltration membrane

Ceramic membranes have become popular recently due to their properties. First MF ceramic membrane was developed in Germany for liquid separation in early 1980s. However, due to incompetence of the polymeric membranes with ceramic membranes at industrial levels, ceramic membranes have gained momentum. The robustness of the ceramic membrane has indulged several companies and research institutes for research on development of ceramic membranes. (Z. Wang et al., 2016) For instance, the ceramic membranes can withstand temperature as high as 500 degree Celsius and extreme operating conditions of pH range 1-14. Various benefits compared to polymeric membranes are high mechanical strength, high chemical and thermal resistance, narrow pore size distribution, long lifespan and recyclable material (Benfer et al., 2001)However, they also have limitations, e.g., high investment costs. Commercial ceramic membranes are ten times costlier than polymeric membranes (Ciora, 2003). During fabrication of membrane holders, a slight dash can affect the membrane's performance (Shang, R., 2014).

Ceramic nanofiltration membranes have not been used only in water purification but in various other industries. Industries like dairy, textile, biotechnology, pharmaceutical, food and beverage, petroleum, power generation and many others (Manohar, 2012).

2.2.2 Structure and configuration of ceramic membranes

Usually, ceramic membranes have asymmetrical structure and multi-channel element composed of minimum of three discrete porosity levels (Erdem, 2017; Fan et al., 2016; K. Li, 2007). These different layers are top, intermediate and separation layers. The intermediate layer reduces surface roughness while, the support layer provides mechanical resistance to the filter. The elements are grouped together in a case often called as housing.

Amongst the three layers the layer with finest pores is called the separation layer. The porosity decreases from support layer (bottom) to the top layer (top) in Figure 2.2.

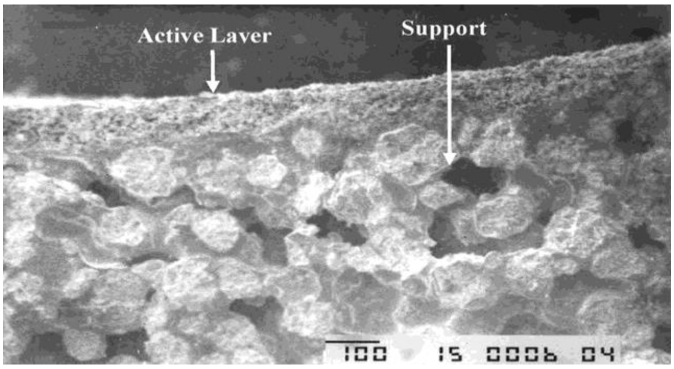


Figure 2.2: Cross-section micro-photograph of ceramic membrane (Almandoz et al., 2010).

In general, there are four types of membrane modules. Plate and frame module, hollow-fibre, spiral -wound and tubular. Commercially, ceramic membranes are in tubular, disc or plate configuration. The goal of these modules is to provide maximum surface area in less volume so that productivity of membrane is maximum. (K. Li, 2007)

Membrane modules

a. Plate and frame module

The feed is transported across the membrane surface. The feed travels from permeate channel to central permeate collection system. Between two end plates (top and bottom) membrane, feed spacers and product spacers are sandwiched. (Pal, 2017)

b. Tubular module

In this arrangement the membranes are built in a shell – and tube- arrangement. The tubes are installed as parallel bundles inside a shell. The characteristics of this module is 1) they are capable of retaining large particles and can be easily mechanically and chemically cleaned 2)require large pumping capacity, operated under turbulent conditions (Re > 10,000) and 3) have the lowest surface are to volume ratio amongst all configurations and has low packing density and large size. (Cui, Jiang, & Field, 2010; Nagy, 2019)

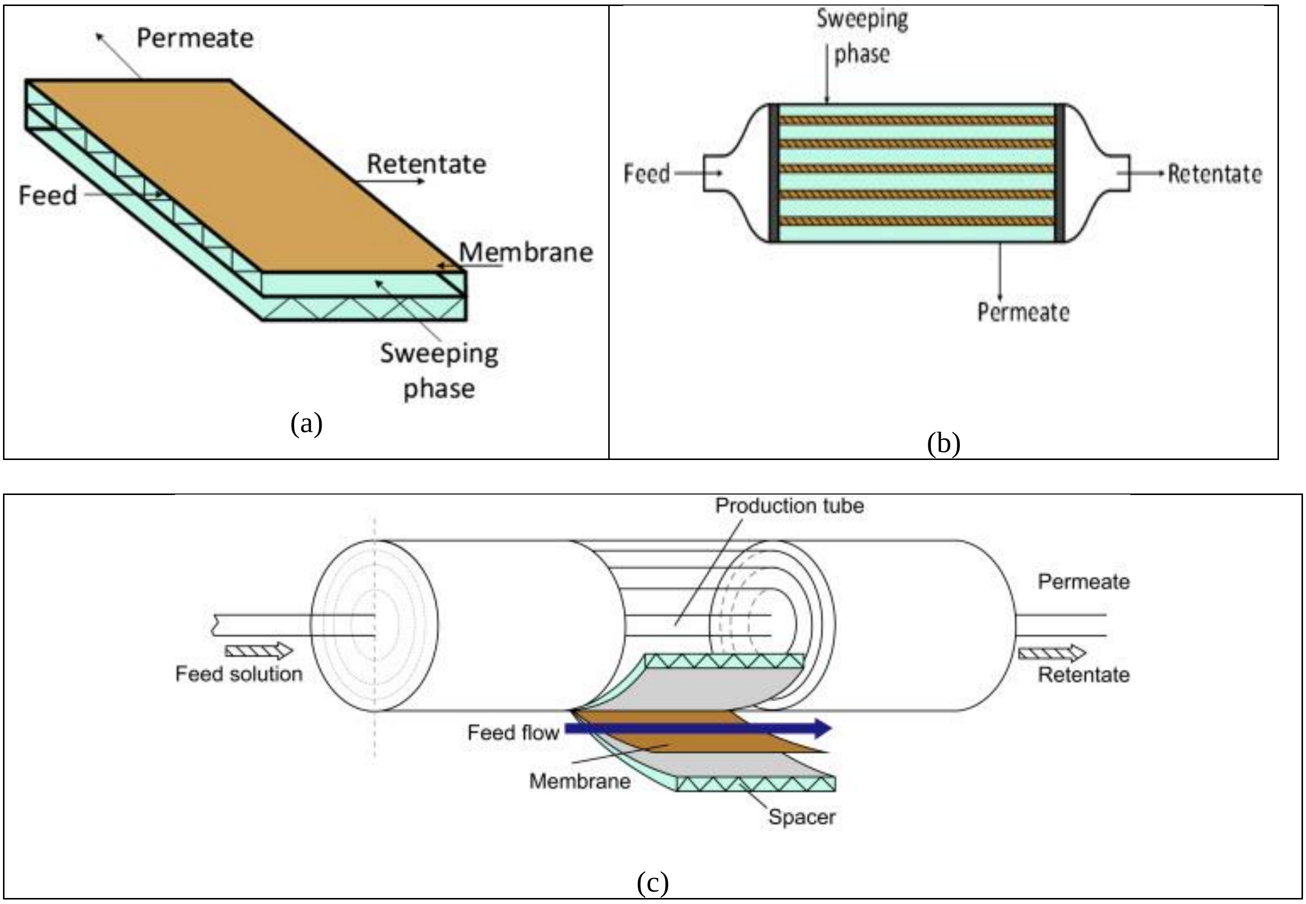
c. Hollow fibre module

In this arrangement, thin tubular membranes are assembled in a manner to self-support that can enable it to withstand high backpressure. Generally, the fibres are coupled in hundreds and thousands and sealed together in a membrane housing. They are recommended to be operated in Laminar region (Re 500 – 3000), at low pressure ≈ 2.5 bar, high packing density, economical energy consumption. However, due to thin diameters they are susceptible to be blocked by large particles hence, relatively clean water is required. (Cui et al., 2010)

d. Spiral-wound

The sheet membrane is rolled into a spiral around a permeate tube. Feed spacers, separate the membrane sheets, which is sealed at the edge and wound around the perforated centre tube. (Cui et al., 2010) The characteristics are: they can operated in turbulent region due to presence of feed spacer, the pressure drop is relatively high due to additional drag from the feed spacers, lowest capital cost, moderately high surface area-volume ratio, suspended particles block the spacers and eventually may clog the feed line therefore, require relatively clean feed is required. (Nagy, 2019)

Of the mentioned module configurations, except spiral-wound, all other configurations can be adapted by the ceramic membranes (M. Lee et al., 2015)



(a) (b) (c)

Figure 2.3: Different membrane modules (a) Plate and frame module (b) Tubular membrane module (c) spiral wound module (Nagy, 2019)

Table 2.2: Different module characteristics (Fane et al., 2011)

Characteristic	**Spiral-wound**	**Tubular**	**Hollow fibre**
Package density ($m^2\ m^{-3}$)	High (500-1000)	Low-moderate (70-400)	High (500-5000)
Energy use	Moderate	High (turbulent)	Low (laminar)
Fouling management	Good (no colloids); Poor (colloids)	Good	Moderate(in-to-out); Poor (out-to-in)
Replacement	Element	Tubes	Element
Cleaning	Difficult	Good- physical cleaning	Backflush (MF/UF)

2.3 Membrane rejection mechanisms

2.3.1 Steric exclusion

Steric exclusion is another name for rejection of solutes based on size, also called as sieving effect. The molecules or hydrated ions bigger than the membrane pore size are rejected by the membrane. However, the smaller solute molecules than the membrane pore size pass through the membrane.

The membrane pore size is determined by molecular weight cut-off (MWCO). The MWCO is defined as the “minimum molecular weight of a solute that is 90% retained by the membrane” (Drioli & Giorno, 2010). In the study of Winter et al., (2017) the MWCO of membranes used for NOM removal ranged from 300 to 8000 Da (polymeric NF- tight UF range membranes). The usual MWCO range for NF membrane is of 200-1000 Da (Winter et al., 2017). Ceramic NF are further divided into tight ceramic NF membrane, with MWCO < 400 Da, and loose ceramic membrane > 400Da. The latter NF membrane is the majority of the commercially available NF membranes (Shang et al., 2017)

2.3.2 Hydration

Hydration is one of the important thermodynamic and physical characteristics of ions. Hydration appears in aqueous solution between the water molecules and charged ions. The hydration potential determines the affinity an ion will have towards water molecule. (Birdi, 2010) Since water molecules are asymmetrical and polarised to some extent, they align themselves surrounding the ions to form a hydration shell as shown in Figure 2.4. Thus, they have small radius in crystalline form than in aqueous form.

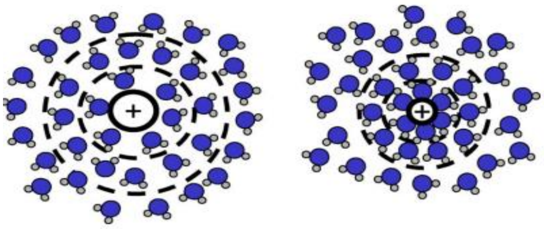


Figure 2.4: Hydration shell for large (left) and small (right) ions. (Tansel et al., 2006)

Larger ions form weak bonds with water molecules than the smaller ions (J. Havel, 1995) Crystallographic radii of central ions and charge density determine the size of hydrated radius (David et al., 2001). The hydration radii of the anions with similar atomic number as cations have smaller hydration radii. This is because the hydrogen atoms are closely positioned around the central ion resulting in lower ability of the anion to hold the water molecules in hydration shell.(Tansel, 2012) Studies shows that large water clusters are attracted to ions with high charge densities more than those with lower charge densities. (Tansel et al., 2006)

2.3.3 Electrostatic repulsion/ Donnan Exclusion

Rejection of ions by porous membranes in presence of fixed charge in pressure-driven systems at zero electric current is referred to as Donnan exclusion (Donnan, 1995). Generally bulk solutions contain both anions and cations to maintain electro equilibrium. When this bulk solution comes in contact with negatively charged membrane for instance, the cations like sodium, calcium etc are attracted to the negatively charged species of membrane surface whereas the anions are repelled and make their way backwards towards the bulk solution. This reduces the anions concentration near the membrane surface. The ion valence and membrane charge of the solutes determine the strength of ion exclusion or attraction. It is implicit that greater the membrane charges higher the retention of co-ions (ions same as of membrane charge). (Feng, 2018) Further, the electro balance is dependent on: a) ionic strength; b) fixed charge concentration on the membrane; c) valence of co-ion; and d) valence of the counter-ion (Peeters et al., 1998)

2.3.4 Dielectric exclusion

In NF membranes, rejection of solutes can occur due to Dielectric exclusion. It occurs due to differences in dielectric constants of the solvent in the bulk within the membrane pore (Pal, 2017). Additional repulsion of the charged ion is caused due to same sign of ions present in the media (Vezzani & Bandini, 2002). The dielectric property of the solvent ions and the rejection of ion is influenced by changes inside the membrane pores in comparison to the bulk solution. Vezzani & Bandini, (2002) saw that solutions containing various co-ions, di-electric exclusion was not distinct with rejection of monovalent counter ions.

2.3.5 Convection and diffusion

For pressure driven systems like NF the solute transport can occur either convective or diffusive. NF lies between UF and RO in which the solute transport is by convection and diffusion respectively. (Pontalier et al., 1997) Solute transport by convection occurs due to applied pressure gradient across the membrane, whereas a concentration difference across the membrane causes mass transport by diffusion (Schaep et al., 1998) At low membrane charge and high permeate volume flux dominant mechanism for electrolyte transport is convection while, strongly charged, low permeate volume flux dominant mechanism is diffusion (Szymczyk et al., 2003). Szymczyk et al., (2003) reported that convection is directly proportional to ionic concentration within the membrane whereas diffusion is directly proportional to concentration gradient across the membrane.

2.3.6 Concentration polarisation

Transport of solute in partly porous and party dense NF membrane occur either by convection, diffusion or electro-migration (Pal, 2017). Concentration polarization occurs because of accumulating solutes near the membrane surface. During filtration in NF, the solute and solvent travel towards the membrane from the bulk solution by water flux. Nevertheless, the solutes which are rejected by different mechanisms namely, size exclusion and electrostatic repulsion amass near the membrane surface. It means the solute concentration near the membrane surface increases over filtration time. Upon accumulation near membrane surface, the concentration of solute near membrane surface is more than in the bulk solution. Due to this concentration gradient near the membrane surface, the solute diffuses back to the bulk solution. Now, when back diffusion is at par with forward solute transport a constant CP profile is formed as seen in Figure 2.5. This layer is reversible by altering the driving factors for this phenomenon. The driving factors are high water flux and low mass transport coefficient. (Fane et al., 2011) As per Van't Hoff equation, osmotic pressure is directly proportional to ion concentration. This implies that raise in osmotic pressure is dependent on rejection of ions in feed water. With increase in osmotic pressure, effect of driving force decreases, causing flux decline. Scaling is a likely limitation due to CP in NF. (Judd & Jefferson, 2003) To reduce the undesirable effect of CP, it is advised to operate NF membranes in crossflow filtration. Lastly, concentration polarisation can never be eliminated but only mitigated (Halem, 2009).

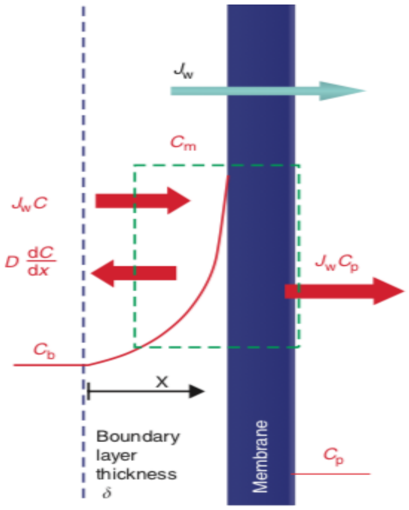


Figure 2.5: Concentration polarisation in membrane (Fane et al., 2011)

2.4 Natural Organic Matter

2.4.1 Characteristics of Natural Organic matter

Natural Organic matter (NOM) is diverse bulk term for all organic compounds found in natural waters like ground and surface waters which derives from dead plants and tissues, microorganisms, animals and biological and chemical degradation of these sources. NOM negatively affects various water treatment processes like coagulation, adsorption, oxidation and membrane filtration (Lee, Amy, & Croué, 2006) and decreased removal of other compounds (Baghoth, 2012). Besides, aesthetic problems like colour, odour and taste it is one of the major foulant in membrane filtration process, a precursor for the formation of carcinogenic disinfection by-products (DBP's) during disinfection/oxidation process (Owen et al., 1995), promote biological growth in distribution system and show increased levels of complexed heavy metals and adsorbed organic pollutants (Matilainen et al., 2011).

The concentration of NOM in water is increasing over two decades now due to multiple reasons. Moreover, with increasing concentrations of NOM, the NOM character differs with time, origin and season (Matilainen et al., 2011). In general, NOM can be categorized into three main types based on origin: (Baghoth, 2012; Sharma et al., 2011)

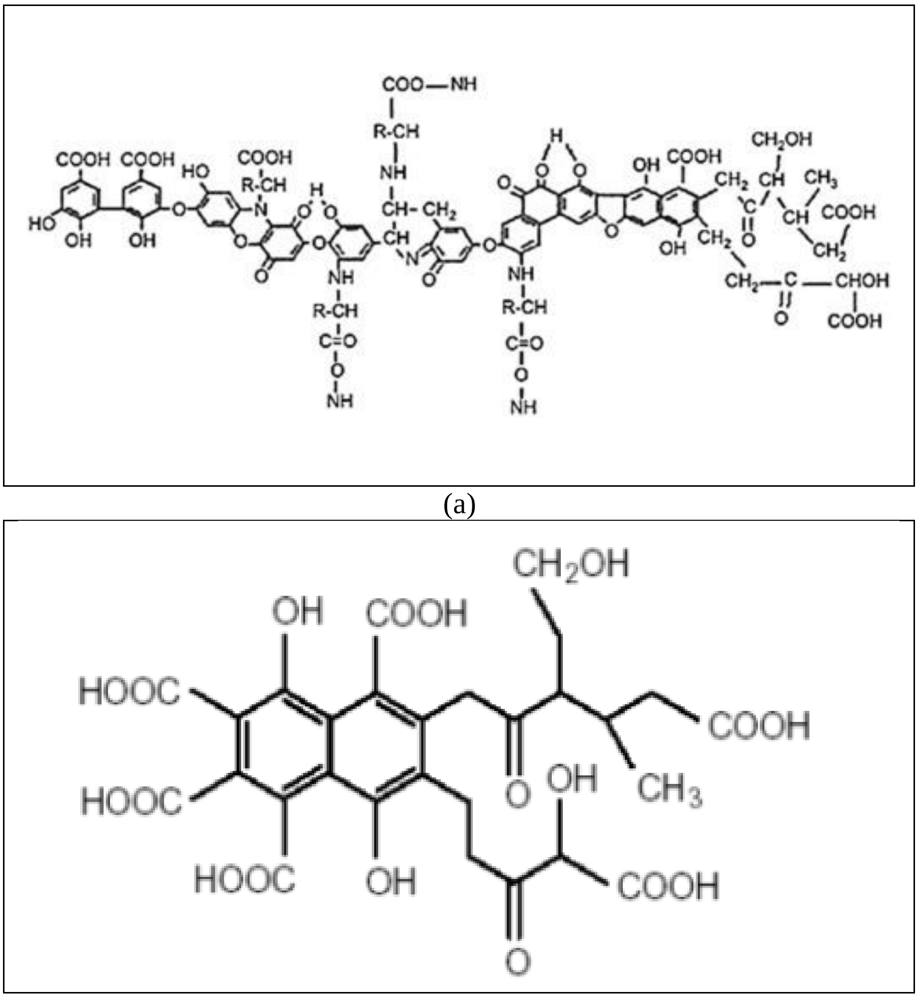
a) Allochthonous NOM: This type of NOM emerges from the biodegradation of terrestrial biomass or soil leaching, but mainly from the vegetative debris, exhibits humic nature (Uyguner et al., 2006). The production is dependent on the vegetative cycles and the hydrologic and geological characteristics of the terrestrial biomass.
b) Autochthonous NOM: This type of NOM emerges from the photosynthetic activity and biodegraded products from algal matter. This NOM is produced from sources like algal organic matter (AOM), phytoplankton, macrophytes; components consisting of exocellular or intracellular organic matter consisting of macromolecules and cell fragments.
c) Effluent organic matter (EfOM): This type of NOM is dependent on the drinking water source and treatment and wastewater treatment applied. This type of NOM consists of NOM not removed during water treatment in addition to soluble microbial products (SMPs) produced during the biological treatment of wastewater.

Characterisation of NOM in water sources is important since it is largely dependent on the time and origin; it will help in proper removal of NOM fractions from the drinking water. (Baghoth, 2012) Besides, NOM can also be categorised and characterized based on different properties which are hydrophobicity, humidity, size and charge.

NOM comprises of humic and non-humic fraction. Humic fraction is found in both soil and sediments and in aquatic surrounding. Soil humic consists of humic acid (HA), Fulvic acid (FA) and Humin, whereas aquatic HS consists of only HA and FA (IHSS, 2007). Humic acid (HA) does not dissolve at pH<1 whereas fulvic acid (FA) is soluble at all pH (Baghoth, 2012). Humic acid is separated from Fulvic acid by adding strong acid, resulting in precipitation of the Humic acid. Furthermore, the supernatant consists of Fulvic acid and is extracted by adding strong base (NaOH or KOH). Therefore, humic acid can be defined as "the portion of soil organic matter which is soluble in base and insoluble in mineral acid and alcohol." It is a dark-brown polyelectrolyte with a molecular weight ranging from 800-500,000 but commonly cited is range is 2.0-5.0 x 10^4. (Steelink, 1963) The functional groups include alcohol, amine, amide, carbonyl, and quinone. The adapted structures for HA and FA can be found below in Figure 2.6.The empirical formula of HA is $C_{36}H_{30}N_2O_{15}.xH_2O$ (x= 0-15), also the humic acids can aggregate to an apparent weight ≥ 5kDa (Davies, Ghabbour, & Steelink, 2001). The size ranges of humic substances by various researchers can be found in the Table 2.3.

Table 2.3: Size ranges of Humic substances by various researchers

	Fulvic Acid	Humic Acid	Reference
Size (Da)	650-950	2000-3000	By (MALCOLM, 1985) in (Schafer, 2001)
Size (Da)	600- 2000 (maximum)		By (Leenheer, 1985) in (Schafer, 2001)
Size (Da)	500-10000	1000-10000 and above	By (Thurman et al., 1982)



(a)

(b)

Figure 2.6: (a) Adapted Humic acid model (Source: (de Melo, Motta, & Santana, 2016) (b) Adapted Fulvic acid model (Uyguner et al., 2006)

There are two types of components of NOM present in water, i.e. Hydrophobic and Hydrophilic. Hydrophobic fraction comprises aromatic carbon, having phenolic structures and conjugated double bonds whereas hydrophilic covers higher proportion of aliphatic carbon and nitrogenous compounds, such as carbohydrates, proteins, sugars and amino acids. (Matilainen et al., 2011) Transphilic NOM is defined as NOM intermediate between hydrophobic and hydrophilic NOM. Amphiphilic NOM has characteristics of both hydrophilic and lipophilic as shown in Table 2.4. Reactivity based on structure can be branched into aromatic and aliphatic. An aromatic molecule is less reactive because its planar cyclic structure is stable whereas an aliphatic molecule is less stable and can be both cyclic and chain structure.

About 50% of organic matter comprises of humic substances in aquatic NOM. Natural anionic polyelectrolytes of aromatic and aliphatic hydrocarbon structures with several functional groups including carboxylic and phenolic groups are categorised as humic substances. Conversely, carbohydrates, fats, lipids, sugar, amino acids and transphilic acids are grouped as non-humic substances. (Metsämuuronen et al., 2014) In addition, humic substances are polar while non-humic substances are non-polar (Baghoth, 2012).

Further, NOM can be fractionated into three fragments based on polarity: hydrophobic (humic substances), transphilic and hydrophilic substances. (Metsämuuronen et al., 2014)

a) Hydrophobic: NOM with high molecular weight are usually hydrophobic in nature. They are aromatic and have capacity to adsorb on the membrane surface (Zularisam, Ismail, & Salim, 2006) and are mostly hydrophobic acids. The examples are carboxylic acid, methoxyl and phenolic groups. In addition, selected groups of neutral compounds with relatively lower MM having condensed aromatic moieties; examples are aromatic and aliphatic amines and amino acids.
b) Transphilic: NOM with MW in between the hydrophobic and hydrophilic NOM falls under this category. The relatively hydrophilic and aliphatic acids come under this group.
c) Hydrophilic: NOM with low molecular weight are hydrophilic in nature. The characteristics of this class is NOM with aliphatic, linear molecular structure and are non-humic, this includes several acids and bases with low molecular mass (MM), especially derived from lignin constituents and a degree of condensed aromatic moieties. Also, hydrophilic neutral and few bases represent this fraction. Examples are hydroxyl and sugar acids, aromatic and aliphatic amines and amino acids, polysaccharides proteins, carbohydrates and high nitrogen containing compounds (Matilainen et al., 2011). Due to less aromatic character, this fraction is major contributor to biodegradable organic carbon (Baghoth, 2012).

Gel permeation chromatography, ultrafiltration and freezing point depression are common methods to determine molecular weight of aquatic humic substances. However, molecular weight by colligative method is best amongst state-of-art. Molecular weight of aquatic humic acid fraction ranges from 1000 – 10000 and above (Thurman et al., 1982). Aquatic fulvic acid fractions are coloured, polyelectrolytic acids, highly soluble (Schafer, 2001), weighs lower than 2000 and is in dissolved state. Thurman et al., (1982) concluded that size of humic substances increases significantly with ionic carboxylic functional group compared to hydroxyl functional group.

2.5 Measurement Techniques for NOM

2.5.1 Conventional Measurement techniques

a) TOC

The widely and most elementary used method to measure NOM is carbon measurements. Basic characterisation of NOM is division of TOC into two subfractions. The fraction of organic carbon which retains on the 0.45µm filter is called the particulate organic matter (POC) while the fraction which is smaller than the 0.45 µm pore size remains dissolved and is called the Dissolved Organic carbon (DOC) (Baghoth, 2012). However, this technique gives information only on the quantity of NOM and not on the quality of water (Matilainen et al., 2011). POC is the matter from plants and animals and coatings on the clay and silt. It contributes to 10 % or below of the TOC. While DOC is chemically more reactive and accounts for the dissolved fraction of the TOC. DOC concentration ranges from 0.1 mg C/L in groundwater to 50 mg C/L in swamps. (Thurman et al., 1982)

b) UV- vis
Ultra-violet and visible absorption spectroscopy are measurement of reduction in the amplitude of the signal of a beam light after it passes through the sample or after reflection from sample surface. Using the Beer- Lambert law the absorbance of an analyte in a solution at a wavelength can be determined. The most appropriate wavelength for NOM measurements has been between 220 – 280nm, in spite of the fact that absorbance spectra will be dependent on the range of chromophores in NOM. Chromophores is term referred to functional groups responsible for NOM absorbance light (Baghoth, 2012). Carboxylic, aromatic chromophores absorb UV at 220nm, aromatic groups typically absorb at 254nm. However, there are significant errors in measurement between 200nm to 230 nm in cases when nitrates and sulphates are present. Also, it is sensitive to pH and ionic strength (Matilainen et al., 2011)

c) SUVA
SUVA is defined as the UV absorbance of a given sample at 254nm divided by the DOC concentration of the sample. It describes the hydrophilicity and the hydrophobicity of the NOM fraction. A SUVA > 4 indicates high aromatic, hydrophobic and MW aquatic humic NOM, while SUVA ≤ 2 indicates hydrophilic, mostly non-humic, low hydrophobicity and MW NOM and SUVA 2– 4 L/m -mgC indicates mixture of aquatic humics, other NOM, mixture of hydrophobic and hydrophilic NOM and of molecular weights (Baghoth, 2012; Matilainen et al., 2011). A close relationship between HS molecularity and HS aromaticity can be depicted by HS-diagrams. Aromaticity is measured in terms of ratio of SAC and OC where SAC is the Spectral Absorption Coefficient obtained with UVD and organic carbon. The HS-diagrams give information about the origin of water.

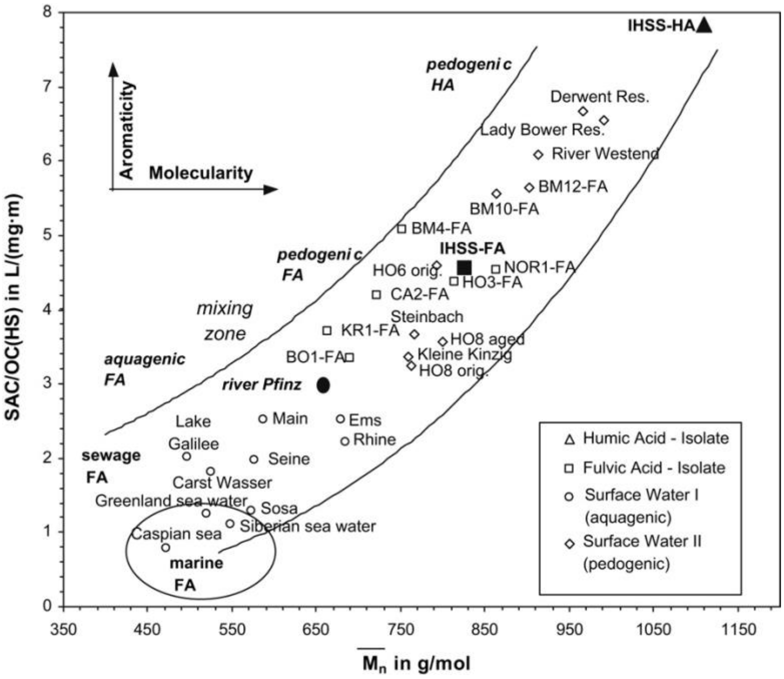


Figure 2.7:Humic Substances diagram: The profile for natural organics plotted between aromaticity and molecularity (Huber et al., 2011)

From the above Figure 2.7 it can be concluded that HS with high MW and aromaticity resembles to pedogenic HA and allochthonous HS. And, HS with low MW and aromaticity resembles to aquagenic FA and autochthonous HS.

2.5.2 LC-OCD-OND method

Despite the conventional methods, the characterisation of NOM can be done using combination of size exclusion chromatography with organic carbon detector. This method helps to separate the NOM into fractions based on molecular size and chemical characteristics which aids in NOM quantification based on Organic carbon. The most popular approach is Liquid Chromatography with organic carbon and nitrogen detector. (Schafer, 2001) Size exclusion chromatography can also be coupled to UV-absorbance (Huber et al., 2011). Detection with UV depends on the structure of OC and cannot be quantified. However, detection with both UV and OCD is advantageous since it gives information mass-based as well as based on measure of aromaticity and extent of conjugation within OC (Allpike et al., 2007). SEC-OCD has detection limit of 1-50 µg C/L (Baghoth, 2012). Preceding any measurements for NOM characterisation, the samples are made particle free by passing through 0.45µm PES-filter. In LC-OCD-OND system there are series of detectors to assess the characterisation of NOM. After SEC, (with liquid chromatography-LC), the samples are analysed with UV absorbance by 254nm. Afterwards, organic carbon (OC) is detected with organic carbon detector. To detect nitrogen organically bound on humics, a side stream after UV detector is analysed. The organically and inorganically bound (ammonium, nitrate, urea) nitrogen is converted to nitrate since nitrate absorbs strongly at 220nm in UVD. (Huber et al., 2011) Based on size, polarity and charge (Huber et al., 2011)defined several fractions: hydrophobic organic carbon (HOC), biopolymers (BP), humic substances (HS) building blocks (BB) low molecular weight acids (LMW a), low molecular weight neutrals (LMW n). It can be seen that HOC fraction does not include humic substances, defined as in resin fractionation. A general LC-OCD-OND chromatogram can be found in Figure 2.8.

Table 2.4: NOM fractionation with SEC techniques (Huber et al., 2011)

Method	**Name NOM type**	**SEC + UVD**	**SEC + OCD**	**SEC + OND**
SEC+UV+DOC = LC-OCD	Hydrophobic organic carbon (HOC)	-	Difference between bypass and sum of chromatographic fractions	-
	Biopolymers: Like polysaccharides, polypeptides, proteins and amino sugars	No response	Elutes close to the exclusion volume of the SEC column	-
	Humic substances: FA, HA*	Responses	Responses to OCD; peak of UVD and OCD unidentical	-
	Building blocks: Smaller fractions of humic substances*	-	-	-
	LMW acids and amphiphilic compounds: Low MW humic and acids*	Responses	Elution influenced by anionic repulsion with SEC. All LMW-acids elute near the salt boundary zone	-

	LMW neutrals and hydrophilic to amphiphilic compounds: Such as alcohols, aldehydes, ketones, amino acids*	No response	Anionic: Elutes before or with the salt boundary zone. Cationic: Elution slightly after permeation volume of the column	-
SEC+UV+DOC+N = LC-OCD-OND	Similar to LC-OCD	Same as LC- OCD	Same as LC-OCD	Biopolymers: few responses to OND
	Nitrate and ammonium bound to NOM: Organic and inorganic species	Same as LC-OCD	Same as LC-OCD	Response to OND

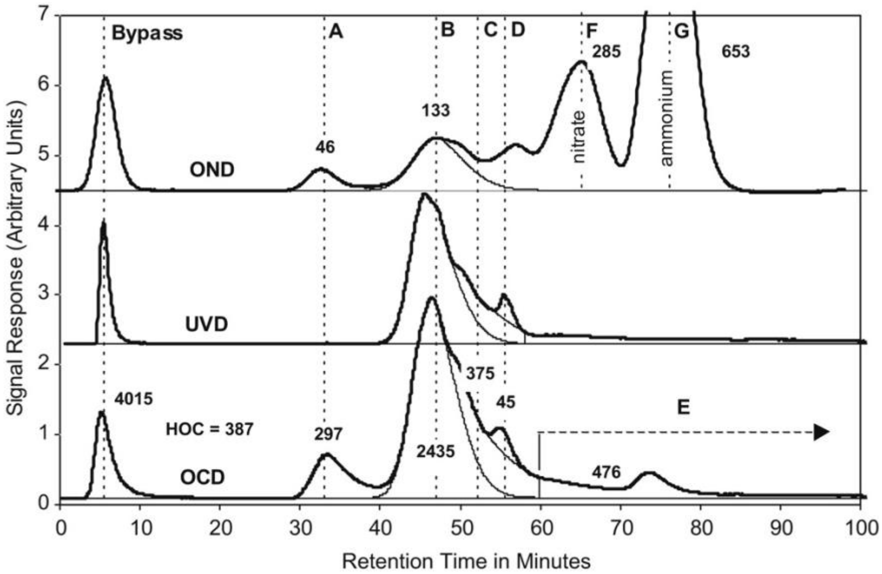


Figure 2.8: SEC- OCD-OND chromatogram for surface water. A = Biopolymers; B = Humic Substances; C = Building blocks; D = Low-molecular weight acids; E = Low molecular weight neutrals; F and G = nitrate and ammonium (detected only by OND). Concentration values in OCD and OND chromatogram are in µg/L C and µg/L N respectively, (Huber et al., 2011)

2.5.3 New Standardised method for quantification of Humic and Fulvic acids

The new standardised method (NSM) is used to quantify HA and FA in solid and liquids commercial products and humate-containing geological deposits. The conventional method of separation of HA and FA makes use of a strong base to separate alkali-soluble components; remove the non-soluble components; acidify the alkali solution to precipitate HA. The NSM defines FA "as the material that binds to a non-ionic macro-porous acrylic ester resin of moderate polarity at low pH, i.e., DAX-8". This is different than the classical definition of FA as organic matter soluble in both base and at all pH. NSM develops distinction of the hydrophobic FA and hydrophilic organic components polysaccharides, amino sugars, amino acids, proteins, fatty acids, carbohydrates, lipids, etc., which are extracted along with the Humic acid. It measures the ash-free HA and FA via gravimetric method.

This method is more useful to testify the commercial products (HA and FA) used in agriculture to know the degree of adulterants. Another difference between the conventional and NSM is alkaline extraction is done under N_2 atmosphere, quantification is done on dry-ash basis, and non-ionic resin separation. Basic difference between the LC-OCD -OND method can be found in the table . Also, further literature and HA and FA extraction procedure can be found in (Lamar et al., 2014).

Table 2.5: Basic differences between LC-OCD-OND and NSM method

Parameters	LC-OCD - OND	NSM**
Principle	Gräntzel thin film reactor, high performance liquid chromatography, NOM components – based on size, charge and polarity of compounds*,***	Selective adsorption on resin, modified method of IHSS
Pre – preparation	Sample filtration by 0.45µm PES filter	Sample filtration by 0.2µm
Quantification	Carbon and Nitrogen containing compounds present in NOM	Quantifies only HS i.e. HA and FA – on gravimetric concentrations on ash-free basis. FA further quantified on polarity;
Detection limit	1-50 ppb/L C * and can detect N compounds	Detection limit: HA = 4.62 ppm; FA = 4.8 ppm Quantification limit: HA =14.7 ppm; FA = 15.3 ppm
Uses	To fractionate the surface and ground waters containing NOM***, majorly beneficial to water production companies.	To distinguish HA and FA from adulterants, beneficial to agricultural industries.

*= (Baghoth, 2012) , **=(Lamar et al., 2014), ***= (Huber et al., 2011)

2.6 Fouling of membrane

Membrane fouling is a challenge in all membrane technology (Le & Nunes, 2016). It is the deposition of substances on membrane surface or inside the membrane. This accelerates membrane resistance and decline in flux.

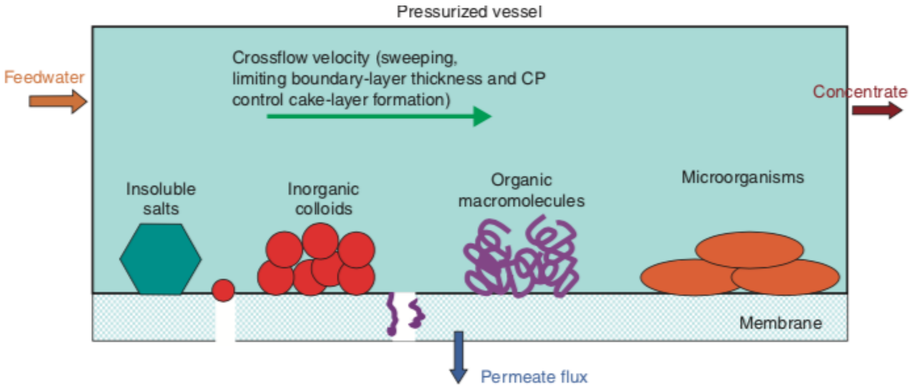


Figure 2.9: Membrane fouling illustration in pressurised cross-flow module (Fane, 2011).

Due to fouling additional hydraulic resistance is generated which lowers membrane productivity. The foulant substances can be organic matter, inorganic substances and microbes as shown in Table 2.6. Adsorption of dissolved matter in the membrane pores or onto the membrane surface can only be removed by chemical cleaning, referred it to as irreversible fouling (Mustafa et al.,2014). On the contrary, the foulant removed by hydraulic backwash is reversible fouling. Flux decline can occur either due to CP or fouling. When constant pressure is applied, CP occurs near the membrane surface (Fane et al., 2011) and doesn't increase with time, referred to as reversible fouling. On the contrary, fouling causes long term flux decline. Factors affecting the extent of fouling include, membrane properties, module design, feed water characteristics and hydrodynamic conditions (Fane et al., 2011). Mechanisms of fouling can be complete blocking, stand pore/ Intermediate blocking, cake filtration and intermediate blocking (cake filtration + pore blocking) (Al-Amoudi, 2010)

Table 2.6: Overview of type of Fouling and its foulant (Al-Amoudi, 2010).

Type of fouling	Foulant
Inorganic fouling	Caused by salts deposition, colloidal matter on membrane surface.
Organic fouling	Caused by Natural Organic Matter such as humic acid substances or its fractions and derivatives.
Biofouling	Caused by microbial attachment on membrane surface followed by its growth in presence of organic nutrients.

Generally, hydrophilic membranes have lower tendency for fouling (Tian et al., 2013). Tran et al., (2015) reported that the most significant foulants are hydrophilic and neutral fractions of organic matter. Besides, the universal indicator of fouling in MF and UF is Biopolymers (Tian et al., 2013; Tran et al., 2015). Many authors have reported that fouling is enhanced by low pH, high ionic strength, high concentration of humic acids and high concentration of divalent and trivalent ions (Braghetta et al., 1997; Metsämuuronen et al., 2014). E. K. Lee, Chen, & Fane, (2008) reported that major fouling can be originated by medium size NOM (300-1000 Da) and extend up to high size NOM (>50,000 Da). Based on DOC concentration, fouling potential of fractionated NOM can be hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic charged (Guo, Ngo, & Li, 2012).

The degree of fouling also depends on the size and hydrophobicity of the NOM. Different NOM fractions foul under various conditions. Wiesner et al., (1992) reported four categories of NOM which highly foul the membrane – proteins, polysaccharides, amino sugars, polyhydroxyaromatics. Polysaccharides were even identified by Amy & Cho, (1999) to foul the UF and NF membranes. The type of fouling caused by these macromolecules is partial hydraulic reversible which is not affected by calcium. It is generally seen in low pressure membranes like UF and MF (Amy, 2008). Many researchers mentioned in Winter et al., (2017) reported that biopolymers have been major foulants in UF. This was supported by Tran et al., (2015) and Tian et al., (2013) as well. They added mentioning biopolymers as the universal indicator for membrane fouling potential of surface waters in low pressure membranes – UF and MF. The next bigger fraction, HS of terrestrial origin is found to contribute to membrane fouling reported by various researchers (Winter et al., 2017). Tian et al., (2013) observed that humic content has no notable correlation with membrane fouling potential during UF. He also noted that HS did not exhibit correlation with irreversible fouling during UF. This is probably corresponding to larger pore size of the UF membrane. But, Q. Li & Elimelech, (2006) noticed HS as one of the major foulant in tight UF and loose NF. The observation by Q. Li & Elimelech, (2006) was contradicted by Amy & Cho, (1999) where they observed that despite effective HS rejection, they haven't contributed to NF membrane fouling. On the whole, it can be concluded though humic substances play minor role in UF membranes (Tian et al., 2013) but in tight UF and loose NF they are the major foulants.

3 Materials and Methods

In this research, artificial brines and IEX brine containing salts and NOM were used as feed water in nanofiltration experiments. The artificial brines had ionic strength of 0.1 and 1M, and different DOC concentration of NOM previously recovered from spent IEX brine by a drinking water company (Vitens). A bench-scale crossflow filtration system setup, as shown in scheme of Figure 3.1, was used to execute the filtration experiments. Filtration was carried out for two ceramic nanofiltration membranes with initial MWCO of 600Da and 900Da. A fouling experiment was also conducted, with an artificial brine and with an IEX brine, with nearly the same DOC, NaCl and Na_2SO_4 concentration.

3.1 Chemicals

The feed solution was prepared using two salts and natural organic matter in demineralised water. The chemicals used were Sodium Sulphate (Na_2SO_4) anhydrous from Carl Roth ≥ 99%, granular sodium Chloride (NaCl) salt from (PoolSel), and the Natural Organic Matter used for the artificial brines originated from the spent brine from a drinking water company (Vitens). To carry out membrane characterisation, Polyethylene Glycols (PEGs) of 200, 300, 400, 600 and 1000Da was used. 0.01M and 1M of Sodium hydroxide and Hydrochloric acid was used to adjust the pH during the experiments. In Fouling experiments to maintain the pH 1mM sodium bicarbonate (because of its buffer properties) was used and small amounts of sodium hydroxide and or hydrochloric acid to attain the target pH during the experiments.

3.2 Setup

The experiments were performed using an experimental setup: membrane NF filtration. This setup was later modified to perform membrane NF fouling. The diagram of the setup for the membrane NF filtration experiments can be found in Figure 3.1.

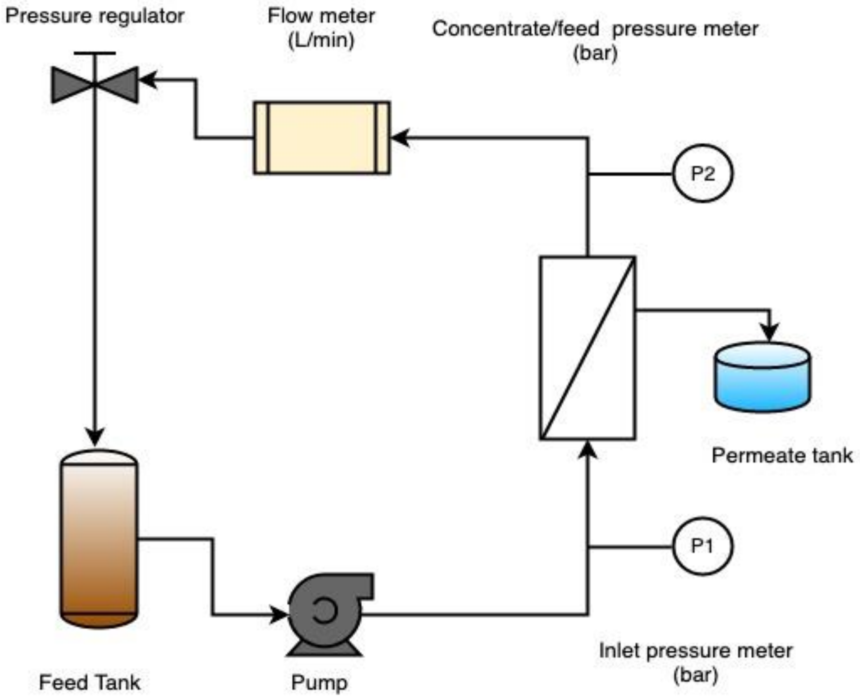


Figure 3.1: Diagram of the Nanofiltration system operated in crossflow mode

The components of the membrane NF experiments consisted of feed tanks, a gear pump (Getriebebbau NORD GmbH & Co. KG, type SK 180E-550-340B), pressure meters (ESI USB Transducer), membrane housing, valve, weighing balance (Radwag WTC 200) and flow meter (Sea Zhongjiang, type ZJ – LCD-M). The feed water from the feed tank was pumped to membrane module via a gear pump. The feed pressure and concentrate pressure were measured by pressure meters P1 and P2 respectively. The transmembrane pressure is the average pressure of the feed and the concentrate pressure shown on the pressure meter. The opening and closing of the valve and regulating the rotations per minute of the pump controlled the TMP. The permeate flow was measured on the weighing balance based on the weight of water, that was eventually converted to volume unit based on density of water. Permeate collected was transferred to another container after filtration with 0.45 µm for ions and dissolved organic carbon (DOC) analysis. The flow meter measured the recirculation flow of the feed/concentrate as the pH and temperature were monitored using a pH meter and temperature sensor.

3.3 Ceramic NF membranes

The ceramic nanofiltration membranes used in this research were manufactured by Inopor GmbH, Germany. As per the information provided by the producer, the membrane separation layer is made of TiO_2 whereas, the support layers are made of Al_2O_3 and the front-side of the membrane is made of silica glass. The nanofiltration membranes, as shown in Figure 3.2 had a MWCO of 600Da and 900Da, measured previously by other researchers. The membrane was placed inside the membrane housing made of PVC module which had maximum operating pressure of 10 bar. The membrane had a tubular singular channel configuration, with a channel diameter of 7mm and outer diameter of 10mm with a filtration length of 75mm with the effective filtration area of 0.00163 m_2. Both ends of the membrane (after installed in the membrane housing) were sealed with rubber bearings, see Figure 3.2.

Figure 3.2: PVC membrane housing with rubber bearings (left) and Membrane T03 and T09 (right)

3.3.1 Chemical cleaning

After nanofiltration of brines and fouling experiments the membrane permeability declined. Thus, membrane was chemically cleaned. Membrane cleaning was done with sodium hypochlorite (NaClO) solution (0.2 wt.%) for 2 hours for the filtration and the fouling experiments. Then the membrane was immersed in ultra-pure water twice for half an hour each to remove the residual chemicals from the membrane surface. Post cleaning, the cleaned membrane was tested for its permeability. If the membrane recovery was too less, the cleaning process was repeated until the membrane regained the permeability close to original permeability. System cleaning was carried out using NaClO solution (0.2 wt.%) to flush the system for 1 hour (recycled) and demi-water 10L flushing (flushed out).

3.4 Membrane Characterisation

3.4.1 Membrane Permeability

Permeability is defined as the flux of the membrane divided by the transmembrane pressure (TMP). The membrane permeability was determined by ultra-pure water at room temperature (24-27˚C) and pH for 30 minutes. The crossflow velocity of the system was 1.3 ± 0.5 $m \cdot s^{-1}$ and the transmembrane pressure was set to 3.0 ± 0.5 $m \cdot s^{-1}$ (Feng, 2018). The permeate flux, pressure, temperature and crossflow were recorded manually every 5 minutes. The permeability test was conducted before and after each filtration test. Due to additional energy transferred from the pump increased the temperature of the water during the permeability, filtration and fouling tests. Therefore, a temperature correction formula was used to standardise the permeability at 20˚C. The equation (3.1) is as follows:

$$L_{p,20°C} = \frac{J}{TMP} \cdot \frac{\eta_T}{\eta_{20}} = \frac{J \cdot e^{-0.0239(T-20)}}{TMP} \tag{3.1}$$

Where, $L_{p,20°C}$ is permeability at 20˚C, $Lm^{-2}h^{-1}bar^{-1}$, T is temperature, ˚C, J is the permeate flux ($L \cdot m^{-2} \cdot h^{-1}$) and ΔP is the transmembrane pressure (bar). After about 15 mins the permeability was constant, and the average was calculated. Sometimes, when the permeability was lower than the original value then an additional cleaning was performed. Membrane was always soaked in ultrapure water overnight so that the membrane pores do not dry out.

3.4.2 MWCO

The size of the membrane pores is termed as MWCO and measured in unit Daltons (Da). The MWCO of a membrane is the molecular weight of a compound that shows 90% retention. Therefore, to measure the pore size of the membrane, the solute should follow a mechanism based only on steric rejection. Hence, non-ionic PEGs were selected to be the solute for the MWCO measurement. (S. Lee et al., 2002; Sarrade, Rios, & Carlès, 1994) Thus, the rejection mechanism is not influenced by electrostatic repulsion. To measure the MWCO of the tubular ceramic membrane, as used in our filtration tests, a feed solution of demineralized water and polyethylene glycol (PEG) with a mixture of five sizes, 200, 300, 400, 600 and 1000 Da , as similarly done by Shang et al., (2017) and Kramer et al., (2019) was used. The PEG of each size had a concentration of 0.6g/L. The filtration was in cross-flow mode and the concentrate was recirculated as feed. The TMP of the experiment was operated at 2.9 – 3.1 bar and the cross-flow velocity was operated at 1.3 ± 0.5 $m \cdot s^{-1}$ with a flux of 41 - 43 LMH to produce a turbulent flow in order to decrease the CP influence and have proper dilution of the feed. The MWCO measuring period was 2.5h for each experiment on the fouled membrane with 3 sampling points. After 60, 70 and 80 min of filtration three permeate samples were collected. The feed was collected twice, during the collection of the first and third permeate.

After samples collection, the samples were filtered with 0.45µm filters MACHEREY-NAGEL GmbH & Co. KG and stored in the fridge. Later, the concentration of PEGs was analysed using High-performance liquid chromatography system (Prominence, Shimadzu, Japan) with a refractive index detector (RID-20A, Shimadzu, Japan) and two gel permeation chromatography columns for size exclusion (5 µm 30 Å, PSS GmbH, Germany). Knowing the elution time of the single sizes of PEG, the signal of the refractive index detector for permeate and feed samples were compared to calculate the membrane retention of each PEG size.

During the PEG analysis in HPLC, different molecular weight PEG has different elution time. Each molecular weight represents a different specific elution time and can be plotted, as shown in Figure 3.3. The signal intensity is proportional to the PEG concentration in the samples.

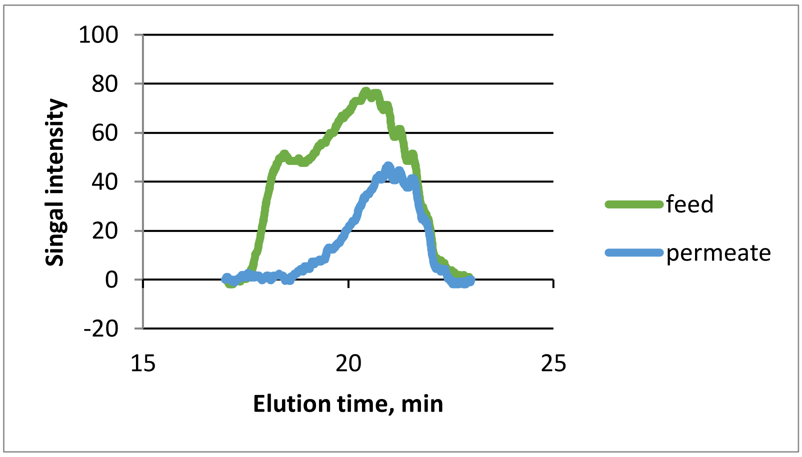


Figure 3.3: PEG signal from HPLC

The molecular weight distribution curve or the sieving curve was produced from the measured concentrations of PEGs in the feed and permeate. The retention rates for PEGs with different molecular weight were calculated based on the equation (3.2).

$$R_i(\%) = \frac{C_f - C_p}{C_f} \cdot 100 \tag{3.2}$$

where, C_f is the PEG concentration in the feed stream, C_p is the PEG concentration in the permeate. The retention curve as shown Figure 3.4 (1) from the experiment can be described by the model (3.3) below (Van der Bruggen & Vandecasteele, 2002).

$$\sigma(\mathrm{MW_s}) = \int_0^{\mathrm{MW_s}} \frac{1}{S_{\mathrm{MW}}\sqrt{2}} \frac{1}{\mathrm{MW}} \exp\left(-\frac{(\ln(\mathrm{MW})-\ln(\mathrm{MWCO})+0.56 S_{\mathrm{MW}})^2}{2\, S_{\mathrm{MW}}{}^2}\right) d\mathrm{MW} \tag{3.3}$$

where σ(MW_S) is the reflection coefficient for different molecular weight (MW_S) of PEGs, S_{MW} is the standard deviation of molecular weight. The molecular size of PEG (dp in nm) can be calculated with its molecular weight (MW in Da) by following equation (3.4).

$$d_p = 0.065\ (MW)^{0.438} \tag{3.4}$$

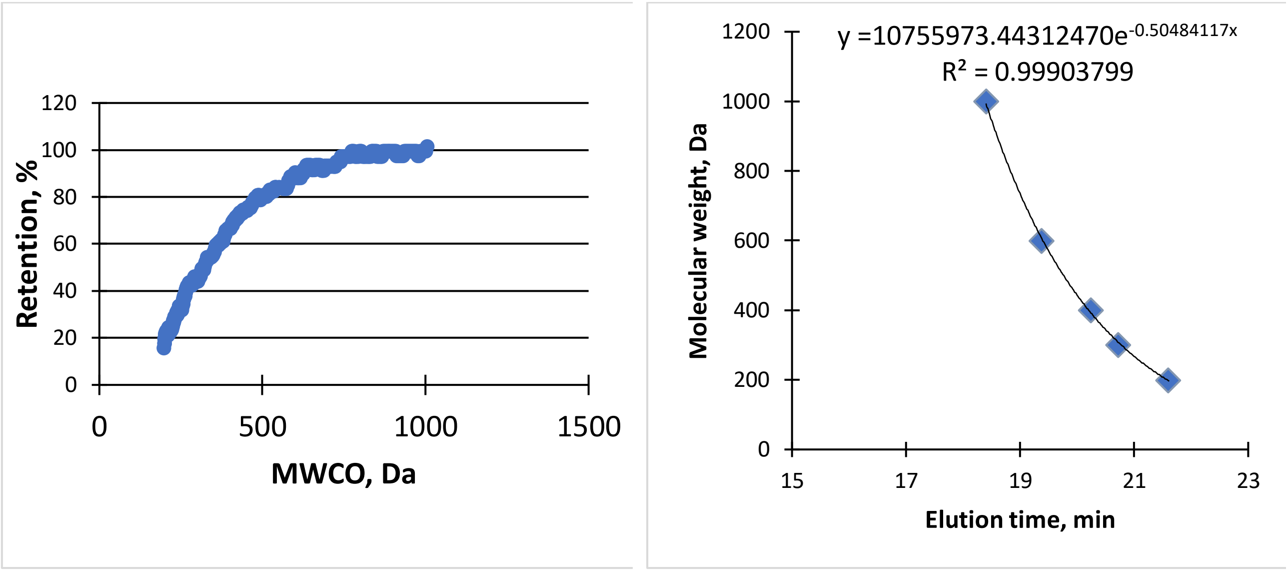


Figure 3.4: An illustration (1) Retention curve and (2) Calibration curve

The calibration curve is determined by the relationship between elution time (mins) and molecular weight (Daltons) using the power model. An example of calibration curve is shown in Figure 3.4.

3.5 Filtration experiments for NOM and Salt rejection in IEX brines and synthetic brines

3.5.1 Feed Water characteristics and Experiment Table

The feed water for the filtration experiments was synthetic brine and the real IEX brine. The synthetic media was prepared by dissolving solid salts in demineralised water. or 0.1M and 1M ionic strength. The two salts used were sodium chloride (NaCl) and sodium sulphate (Na_2SO_4). In addition to the salts, natural organic matter – Humic Substances from Vitens was used at a concentration of 0.5 g DOC/L and 0.05 g DOC/L in the synthetic brines. The pH of the artificial brines was maintained at 8, because the IEX brines had a pH of 8-8.1. If required additional 0.1M of NaOH or HCl was used to keep the same pH. The chemical composition of the real IEX brine was unaltered throughout the experiment(s). The pH of the real IEX brine was 8 ± 0.2 during the experiments.

Table 3.1: Table showing filtration test and chemical cleaning of membrane

Brines	**T03 (600Da)**	**T09 (900Da)**
Sweden		
England		
PWNT		
	Chemical cleaning (CIP)	
0.1M HS_Vitens		
1M HS_Vitens		
	Chemical cleaning (CIP)	
Belgium		
	Chemical cleaning (CIP)	

3.5.2 Filtration experiments

The membrane filtration was carried in inside-out mode with a crossflow configuration. The concentrate and permeate from the membrane were recycled back to the feed of 5L volume. The sampling volume was very little for analysis and the rest was recycled back.

The NOM investigated was NOM extracted from anion exchanger brine in drinking water treatment (Vitens, The Netherlands). The feed solution was prepared by dissolving the two salts and NOM from Vitens into 5L demineralised water. From previous studies, it was concluded that the ionic strength of the IEX brines ranged between 0.1M to 1M except the Belgium brine which had ionic strength greater than 1M. The composition and the predetermined ionic strength can be found in the Table 3.2. The real IEX brines were tested with their original chemical composition. All the rejection tests were conducted at constant flux and pH 8.

For all the test runs, the permeate flux was regulated at 30 ± 2 $L\cdot m^{-2}\cdot h^{-1}$ and cross flow velocity at 1.3 ± 0.04 $m\cdot s^{-1}$. After 60 min of stabilisation, the samples were taken thrice at an interval of 30min. The feed samples were collected when the first and the last permeate sample was taken. The collected samples were filtered through 0.45µm filters and stored in the fridge. The system was cleaned with flushing 10L of demineralised water. Afterwards, the ultrapure water permeability was measured; the ultrapure water permeability was measured even before the filtration test.

Table 3.2: Matrix for salt and NOM experiment

NOM type	**Concentration**	**0.1M**		**1M**	
	(g DOC/L)	0 NaCl + 4.73 Na_2SO_4 (g/L)	2.92 NaCl+ 2.37 Na_2SO_4 (g/L)	0 NaCl + 47.34 Na_2SO_4 (g/L)	29.22 NaCl + 23.74 Na_2SO_4 (g/L)
HA (Vitens)	0.5				
Brine PWNT	Conc. In brine	-	-	Conc. In brine	Conc. In brine
Brine England	Conc. In brine	Conc. In brine	-	-	-
Brine Sweden	Conc. In brine	Conc. In brine	-	-	-

Brine Belgium	-	-	-	Conc. In brine	Conc. In brine

3.6 Filtration experiments to analyse fouling of membrane

3.6.1 Setup

The membrane NF filtration setup was modified to conduct the fouling experiments. The setup and components remained the same except that now there were two tanks for two feeds and an overhead mixer, as shown in Figure 3.5. One tank consisted of the electrolyte and the second tank consisted of brine. To make certain of the homogeneity of the solutions, a continuous overhead mixer (RW 20DZM.n, IKA Labortechnik) was employed. The mixing was done at 225rpm during the whole experiment for both the solutions.

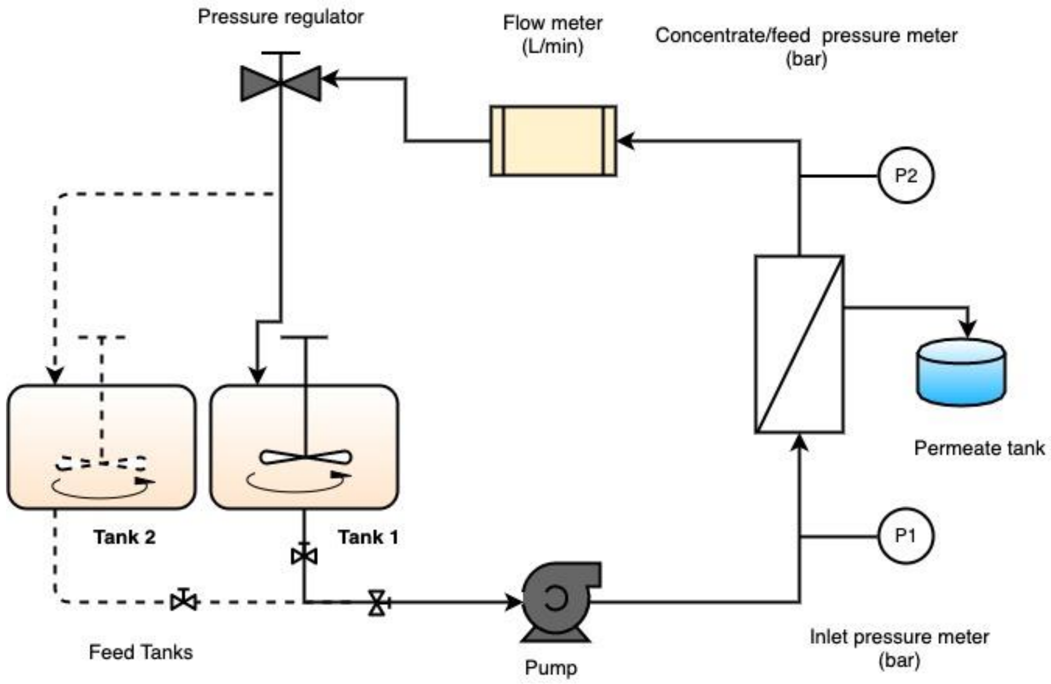


Figure 3.5: Schematic diagram of the nanofiltration system for the fouling experiment.

3.6.2 Feed water characteristics and experiment table

The fouling filtration experiment was conducted to examine the possibility of fouling on the membrane. In this experiment, there were two feed solutions to be prepared. First, electrolyte composed only of the two salts dissolved in demineralised water to 1.3M ionic strength – similar to the ionic strength of the Brine from Belgium. Second, the synthetic brine prepared by dissolving the two salts to 1.3M and NOM – HS Vitens to 1.7 g DOC/L. The timeline of the experiment can be found in Table 3.3. The original pH of the electrolyte solution was approximately 5.7; 1mM Sodium bicarbonate (buffer properties) (SIGMA-ALDRICH) along with small amounts of 1M NaOH was added to attain pH 8.1 during the experiment. The brine had a pH more than 8.1 and therefore, 1M HCl was added in small quantities to reach pH 8.1.

Table 3.3: Phases of fouling experiment with the timeline duration

Steps	**Time(hours)**
UP water permeability	0-1

Electrolyte baseline	1-3
Brine fouling	3-7
PEG permeability	0-2.5
Flush	2.5-2.66
UP water permeability	2.6-3.6

3.6.3 Fouling filtration experiment

The fouling experiment was conducted in several steps in crossflow system. Initially, the membrane was tested for Ultra-pure water permeability for an hour or until the flux was stabilised at a TMP of 6 bar and crossflow velocity of 1.3 $m \cdot s^{-1}$. In following stage, an identical electrolyte solution containing same salt concentrations to be used in the fouling run was passed through the membrane module. This ensured fouling-free baseline for 2h. The permeate flux was kept constant in all experiments (electrolyte feed) at 84 ± 3 $L \cdot m^{-2} \cdot h^{-1}$, with applied pressure from 6.5 bar. After the membrane was equilibrated with the electrolyte solution and a constant flux was achieved, the brine was filtered through the membrane at the same pressure to initiate fouling. Fouling continued for 4 hours. During the fouling stage, the solution was continuously stirred at 225 rpm. Samples were taken from the permeate and feed line of electrolyte and the brine at an interval of 30 mins each. The samples were filtered through 0.45µm before being measured for TOC and salt retention in the TOC and IC analysis. The next step of the protocol was to measure the MWCO of the fouled membrane. A solution containing mixed solute with the MW of PEG fractions of 200, 300, 400, 600 and 1000 Da with 0.6g/L was filtered through the fouled membrane. The PEG solution was filtered at a crossflow velocity of 1.3 $m \cdot s^{-1}$ for 2.5h. The permeate samples were taken at pre-determined time and tested for TOC in TOC analyser. The final stage, membrane was chemically cleaned and tested for ultra-pure water permeability. The applied pressure was similar to that of the first step; prior to the ultrapure water permeability the system was flushed using demineralised water for 10 minutes. The permeability before and after the fouling test was compared to understand the possibility of fouling.

3.7 Characterisation of NOM

3.7.1 Procedure LC-OCD

The samples were sent to Het Waterlaboratorium, that performed the LC-OCD analysis according to the procedure of Huber et al., (2011). It classifies DOC compounds based on their hydrophobicity, charge and molecular weight. This method determines the percentage of biopolymers, Humic substances, Building blocks, Low molecular weight neutrals and low molecular weight acids on TOC. Also, this method can detect concentrations in low ppb range, about 1.5 µg/L. (Krzeminski et al., 2019) In case of approximated values lying outside the detection limits, the samples are diluted. A sample of about 3 mL is fed to the LC-OCD instrument and then filtered through 0.45µm filter. The particles retained on the filter is back washed and analysed to determine POC with TOC analyser. The inorganic carbon is stripped in the top of the reactor. The organic carbon detector oxidises the organic carbon to CO_2 via radiological method of splitting water molecules at 185nm. The CO_2 is analysed using non-dispersive infra-red. (Schäfer, Pihlajamäki, Fane, Waite, & Nyström, 2004)Concurrently, UV absorbance is also measured. UV absorbance at 254nm, divided by DOC content gives SUVA value which is beneficial to know the hydrophobic/aromaticity of the NOM.

Hydrophilic and hydrophobic fraction of DOC is chromatographable fraction of TOC. Molecular weight distribution is obtained from the chromatograph peak of Humic substances. A symmetrical Poisson distribution fitting is used to determine the average weight (Mw) and average number (Mn). The ratio Mw/Mn gives the range of size distribution as shown in Figure 2.7. The detailed method description can be found in (Schafer, 2001)

3.7.2 Procedure FA-HA characterisation using NSM

The samples for NSM were sent to Udine University, to be analysed according to the procedure mentioned by Lamar et al., (2014). The analytical steps followed to measure HA and FA are as follows:
Step1: Alkaline Extraction
Step2: Separation of HA
Step3: Determination of HA content
Ste4: Determination of Ash content
Step 5: Separation of Fulvic Acid
Step 6: Column Regeneration
Step7: Calculations
The detailed procedure can be found in (Lamar et al., 2014)

3.8 Analytical methods

3.8.1 TOC analysis

The carbon content present in feed and permeate is Total Organic Carbon. However, when the samples are filtered using 0.45 µm filter, NOM was measured as dissolved organic carbon in feed and permeate. The filtered samples were measured by a total organic carbon (TOC) analyser (TOC-VCPH, Shimadzu, Japan). The rejection of DOC was calculated using equation (3.2). Further characterisation of the NOM, was done by Het water Laboratorium (The Netherlands), using Liquid chromatography-organic carbon detector (LC-OCD) analysis as explained by Huber et al., (2011).

3.8.2 IC analysis

The concentration of ions such as sulphate, chloride, sodium and nitrate in feed and permeate were measured by Ion Chromatography (Metrohm. Instruments, Swiss). The analysis of anion and cation is done completely separately. For anion analysis, 818 Compact IC pro was used, and for cation analysis 883 basic IC plus was used. The ions are analysed based on the retention time in the respective columns. The column used for anion analysis was Supp 5 150/4.0 and for cation analysis C4 cation 150/4.0. The samples were filtered through 0.45µm filters before diluting them within the detecting range of 0 -100 ppm or mg/L. Generally, the samples were diluted between 40-50 mg/L.

To determine the concentration of the ions, a calibration curve is obtained in the start of the analysis. The calibration curve is produced for desired ions at different concentrations using IC standards. In this research, the concentrations for standards were 1, 10, 25, 50, and 100 mg/L. The time taken to analyse one sample inclusive of cation and anion is dependent on the ions to be analysed; in this research it was 20 minutes. Further, the ion retention was determined using the equation (3.2), which is the difference between feed and permeate ion concentrations.

4 Results and Discussion

4.1 Characterization of NOM

4.1.1 Characterization of NOM in the artificial Brine

The artificial brine is made using the NOM from Vitens. The Table 4.1 shows the fractionation of NOM of Vitens based on LC-OCD measurement. It is observed that the NOM is highly humic in nature with about 90% HS fraction. The other detectable fractions were Building Blocks, which are also humic, and Low molecular neutrals which are negligible in comparison to the HS.

Table 4.1: Organic composition of NOM from Vitens based on molecular weight[1]

MW (Da)			**~ 1000**	**~ 300 - 500**	**<350**
Proportion		TOC	Humic Substances (HS)	Building Blocks (BB)	Low molecular neutrals (LMN)
Vitens	g/L - C	99.66	90.02	6.76	5.76
	% TOC	100	90.3	6.8	5.8

The NOM solution from Vitens was also investigated by NSM as shown in Table 4.2.

Table 4.2: Characterisation of NOM from Vitens by NSM

NSM	**g/L**	**% C**
DOC	86.09	
Humic Substances (HA +FA)	68.95	
Vitens FA	59.7	69.3
Vitens HA	9.25	10.76
Non-humic substances	17.14	

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[1] The total sum of the percent fractions is not always 100% because the fractions analyzed are in % TOC. The DOC is bit higher than TOC because of inaccuracy of LC-OCD method. LC-OCD is more of qualitative method than quantitative.

Loss	13.57 [2]	

From Table 4.2 it was observed that the DOC concentration detected by LC-OCD and NSM differed considerably. Different methods yield slightly different DOC values. The DOC measured by LC-OCD and NSM was 99.13 g · L^{-1} and 86.09 g · L^{-1} respectively. The fractions are pictorially represented in
Figure 4.1. Prior to testing the samples, the samples were filtered with 0.2 µm PES – filters unlike the 0.45 µm PES- filters used for LC-OCD. The less measured DOC could be due to elimination of cells and or coagulated colloids. The other major difference is the measurement of HS content by the two methods. It was reported by Lamar et al., (2014) that the NSM method measured ash (i.e., the inorganic fraction complexed by the HA and FA) free quantities of Humic substances (HA and FA). In other words, the measured HA and FA calculated was without ash content which may have minor influence on the final HS quantified by NSM. Besides, extraction of FA was not only defined to the conventional method of organic matter extracted with strong base that is soluble in both acid and base but a step further i.e. classifying the FA into hydrophobic and hydrophilic fraction of the soluble matter. (Lamar et al., 2014) This breakdown reduced the concentration of FA measured – due to partial loss of specific fraction. The inconsistency between the LC-OCD and resin fractionation includes chemical or physical alterations of NOM due to extreme pH changes, gravimetric measurement on ash-free basis, contamination from resin bleeding, irreversible adsorption of compounds on resin, size-exclusion effects and different operational conditions which account for the loss of organic content. On the contrary, significant loss was not observed in LC-OCD method because the characterization was primarily based as a function of size (Baghoth, 2012; Huber et al., 2011) and did not alter the environmental conditions to extremities.

The two methods of comparison are based on different principles and therefore yield different results for NOM characterization. Based on NSM, it was observed that major fraction (~69 % C) of HS consisted of FA. Likewise, it was observed by Thurman et al., (1982) that fractionation of NOM based on sorption method yields high Fulvic acid than Humic acid also because these fractions are characterized based on water solubility (Fulvic fraction being more hydrophilic than Humic fraction). But, when the characterization of NOM is based on molecular weight this quantification by NSM contradicts, this was confirmed by Aoustin et al., (2001) and Hayes et al., (1989). Hayes et al., (1989) even confirmed that FA has lower molecular weight and carbon content than HA which complements with our results of NOM rejection (shown in next section). In a nutshell, LC-OCD is based on pore size and charge (little charge from the column) and NSM is based on hydrophobicity and precipitation. To this, we can deduce that characterization by NSM could be good method for agricultural reuse purposes, whereas LC-OCD is beneficial for comparison, prediction and validation of membrane filtration. Since the membrane technology shows rejection based on molecular size and weight, charge and polarity of NOM. These parameters are (except polarity to some extent) not accounted by the selective sorption methods (NSM and classical IHSS method) and hence, LC-OCD is used further for comparison with the experimental results.

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[2] Loss is calculated by subtracting the DOC obtained from NSM from DOC by LC-OCD method. It is attributed to losses in rinsing the column and unrecoverable material in the resin.

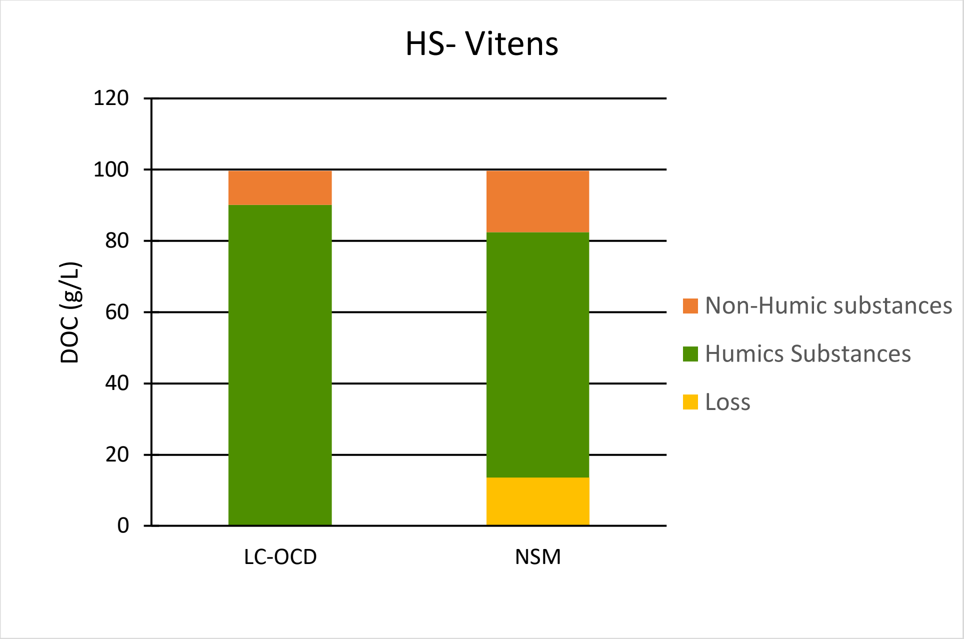

Figure 4.1:Vitens NOM characterisation into HS, non-HS and Loss by LC-OCD and NSM method.

4.1.2 Characterization of NOM in the Real brine

The characterization of NOM for varied brines by LC-OCD can be found in Table 4.3. Each brine depicted humic nature of NOM which was confirmed by the LC-OCD method. The humic substances with ~ 1000Da molecular weight were the main NOM fraction in each brine ranging from ~63% in England to ~ 81% in Belgium brine. This was because the negatively charged humic substances adsorb on the anion-exchanger during ion exchange. In return, they are concentrated in the spent regenerate during the regeneration process of IEX- resins. Next, the second major contributor to NOM was the building blocks fraction. Huber et al., (2011) referred BB as the low molecular weight HS. In the NOM tested for the brines, BB range from ~ 7 % to ~ 18 % of carbon. Another fraction detected was the Low molecular neutrals which are low molecular weight with low to zero ionic density (Huber et al., 2011) and are unlikely to be adsorbed on the IEX-resins (Matilainen et al., 2011) and therefore not expected in the real IEX brines. A possibility of minor concentration of neutrals was perhaps due to the residual water of IEX-process containing neutrals (hydrophilic in nature) which could be mixed with regenerant during regeneration process and therefore traces of neutrals were detected in brines. However, in this research they are excluded and considered as a measurement or instrument error.

Table 4.3: Organic composition of various real IEX brines based on molecular weight

MW (Da)		**~ 1000**	**~ 300 - 500**	**<350**
Proportion (%)	TOC	Humic Substances (HS)	Building Blocks (BB)	Low molecular neutrals (LMN)
Sweden	100	76.3	16.4	9.2
England	100	63.3	18.3	15.7
PWNT	100	69.8	15	10.9
Belgium	100	80.5	6.8	5.8

LC-OCD also detected the specific UV absorbance of NOM at 254 nm. The brine Belgium and NOM from Vitens exhibited SUVA > 4 L (mg·m)$_{-1}$ which indicates relatively high hydrophobic and aromatic content in NOM whereas the rest three brines showed a SUVA between 2-4 L (mg·m)$_{-1}$ which indicates mixture of hydrophilic and hydrophobic NOM and mixture of molecular weights (Baghoth, 2012) and a SUVA less than

3 low removals of DOC can be expected (Edzwald & Van Benschoten, 1990; Matilainen et al., 2011), PWNT in our case.

Table 4.4: SUVA values for NOM of various real IEX brines and HS-Vitens

Brines	**SUVA = SAC/OC (L/(mg·m))**
Sweden	3.19
England	3.77
PWNT	2.23
Belgium	4.10
HS-Vitens	4.32

From the partitioning of organic carbon (Table 4.5), it was observed that Brine Belgium consisted of highest DOC of about 1.589 g·L$_{-1}$, while the most diluted brine – England had a DOC of about 0.036 g·L$_{-1}$. The order followed by brines based on DOC content was Belgium > Sweden > PWNT > England.

Table 4.5: NOM characterisation for real IEX brines by NSM and LC-OCD.

	NSM		**LC-OCD**	
BRINES	DOC (g/L)	% C	DOC (g/L)	% C
SWEDEN BRINE	0.451		0.4663	98.1
SWEDEN BRINE FA	0.277	61.3		
SWEDEN BRINE HA	n.d.			
SWEDEN BRINE HS			0.3625	76.3
ENGLAND BRINE	0.036		0.04044	100
ENGLAND FA	n.d.			
ENGLAND HA	n.d.			
ENGLAND BRINE HS			0.0256	63.3
PWNT BRINE	0.161		0.1707	99.5
PWNT BRINE FA	n.d.			
PWNT BRINE HA	n.d.			
PWNT BRINE HS			0.1197	69.8
BELGIUM BRINE	1.2		1.589	100
BELGIUM BRINE FA	0.548	45.7		
BELGIUM BRINE HA	0.107	8.9		
BELGIUM BRINE HS			1.285	80.5

n.d. being not detected (concentration below quantitation limit)

The characterization obtained from NSM was quite scarce and incomplete. Despite the quantification limit for HA and FA being 14.7 and 15.3 mg·L$_{-1}$ (Lamar et al., 2014) NSM could not detect the humic substances for diluted brines, thus more water – more NOM content is needed to have HA and FA detected. From experiments, it was seen that feed NOM for the brines ranged between 200-1700 mg·L$_{-1}$, so the method should be able to detect HS even for the diluted brine. Nevertheless, the data obtained for Belgium brine by NSM was compared with LC-OCD method shown in Figure 4.2. Clearly, the DOC content measured was undermined than the LC-OCD and experimental results shown in

Table 4.7. The possible reasons were mentioned in section 4.1.1.

Table 4.6: Characterisation of NOM in Belgium Brine using two different methods (i) LC-OCD and (ii) NSM

	LC-OCD	**NSM**
DOC (g/L)	1.6	1.2
Humic Substances (HA +FA) (g/L)	1.28	0.66
Non-humic substances (g/L)	0.3	0.55
Loss (g/L)		0.4 [3]

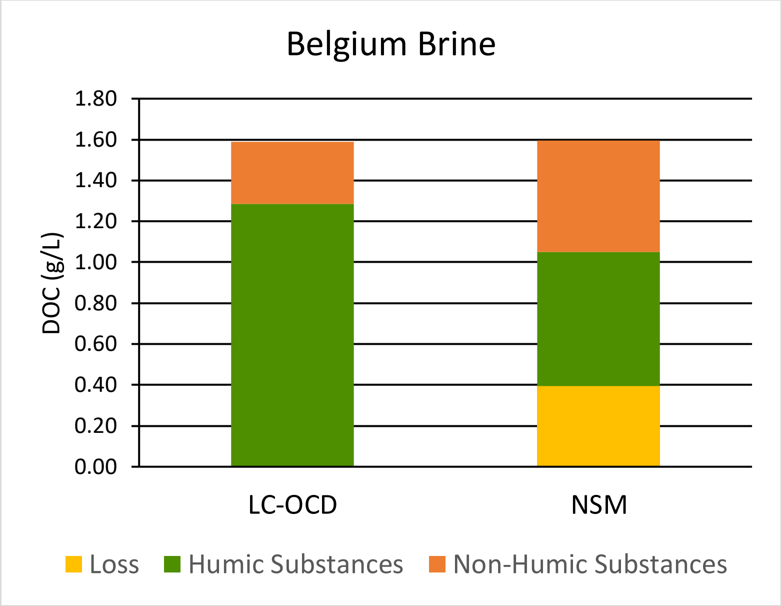

Figure 4.2: Belgium brine NOM characterisation into HS, non-HS and Loss by LC-OCD and NSM method

It was interesting to observe the ratio of non-humics to humic substances by NSM was 3.5 times higher than the LC-OCD method. It indicated NSM was unsuccessful to measure true humic nature of NOM in the brine. This observation agrees to previously mentioned statement. NSM could be good for agricultural reuse purposes while LC-OCD is better for the membrane rejection prediction.

Table 4.7:Comparison of average DOC from 600Da and 900Da with LC-OCD method.

Feeds of Brines	**600Da**	**900Da**		**LC-OCD**	**Error**
	DOC (g/L)		Average DOC (g/L)	DOC (g/L)	(%)
Sweden	0.4494	0.4577	0.45355	0.4663	2.73
England	0.0425	0.0439	0.0432	0.0404	6.93
PWNT	0.1474	0.1643	0.15585	0.1707	8.7
Belgium	1.6874	1.6878	1.6876	1.5896	6.17

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[3] Loss is calculated by subtracting the DOC obtained from NSM from DOC by LC-OCD method. It is attributed to losses in rinsing the column and unrecoverable material in the resin

Table 4.7 suggested that concentration of DOC in the feeds/concentrates (recovery of the membrane 0.2%) of the filtration experiment was in good agreement with the LC-OCD analysis. The deviation between the values are within the error limit of 10%.

4.2 Characterization of membrane

4.2.1 Membrane permeability and MWCO

In this research, membranes of two different pore sizes were used for filtration experiments. The membranes were characterized by previous researchers. Figure 4.3 shows the ultrapure water permeability of the tested membranes.

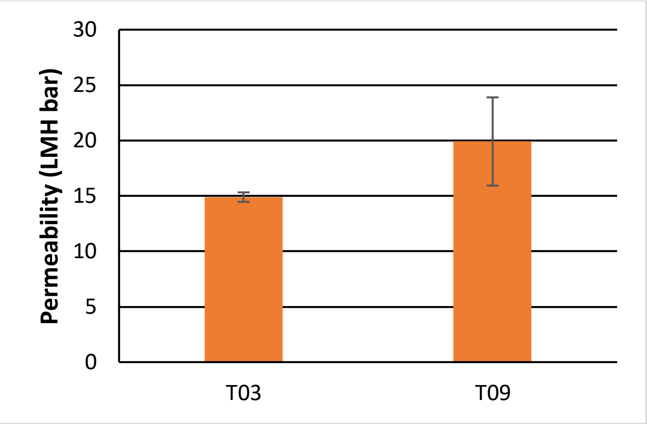


Figure 4.3: Ultrapure water permeability of the tested membranes

The two investigated membranes have a permeability of ~ 15 $L\cdot(m^{-2}\cdot h^{-1})$ · bar and 20 $L\cdot(m^{-2}\cdot h^{-1})$ · bar respectively which is between the range of 10 $L\cdot(m^{-2}\cdot h^{-1})\cdot$bar to 24 $L\cdot(m^{-2}\cdot h^{-1})\cdot$ bar, as reported in several research for ceramic nanofiltration membranes. (Shang et al., 2017; Weber, Chmiel, & Mavrov, 2003c) These two membranes were chosen because the research focused on removal of NOM. The size range of target NOM removal is ~500 Da to ~1000Da and above (Thurman et al., 1982). Membrane T09 and T03 were selected because they have different MWCO, to compare the rejection mechanism based on membrane pore size. Besides, bigger pore size possibly means higher permeability and higher flux and, consequently, less energy consumption, which is beneficial for use at large scale.

Pore size distribution of the membrane can be obtained when the mechanism for rejection involves only steric exclusion. For this reason, PEG is considered to be representative uncharged macromolecule for pore size distribution of the membrane (S. Lee et al., 2002). For T03 membrane: PEG molecules of 1000Da are all removed, 600Da PEG molecules are removed by 90% and 200Da PEG molecules by less than 25%. Similarly, for T09 membrane: 1000Da PEG molecules will be removed by 95%, 900Da removed by 90% and less than 200Da is removed by less than 15%. This can be explained pictorially in the Figure 4.4.

Table 4.8: Result of Membrane characterisation

Membrane	**Ultrapure water permeability $L\cdot m^{-2}\cdot h^{-1}$ · bar**	**MWCO (Da)**
T03	14.89	560
T09	19.91	879

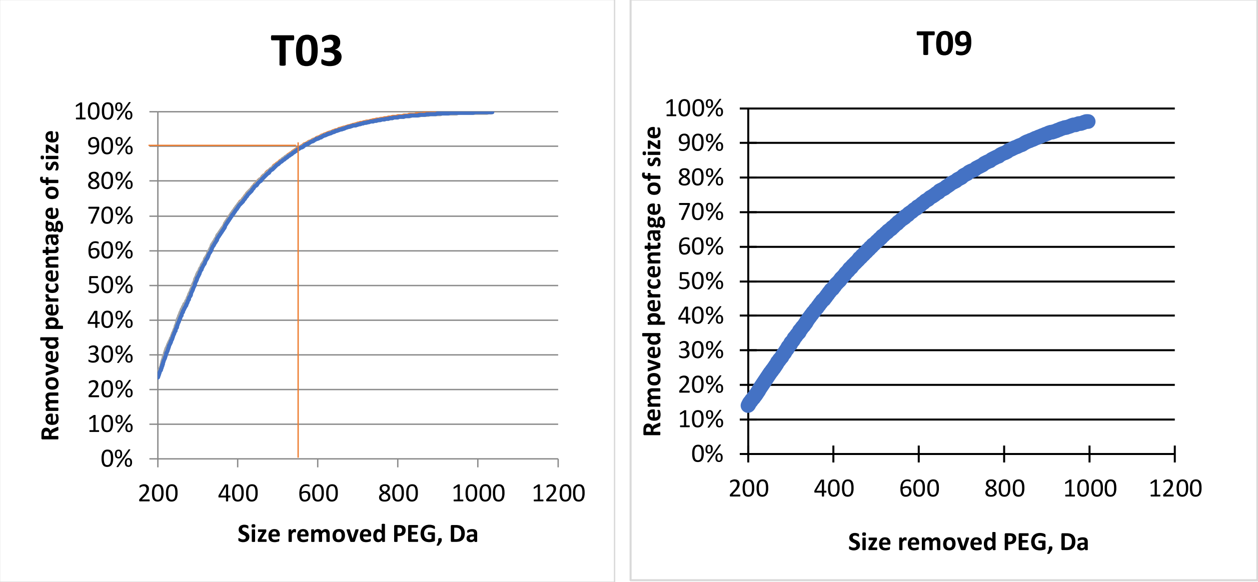


Figure 4.4: Rejection curve of (1) 600Da – T03 (left) and (2) 900Da – T09 (right) membrane from MWCO measurement

4.3 Effect of Salt on NOM and ions rejection

4.3.1 Effect of ionic strength on NOM rejection

Table 4.9: Rejection of Vitens NOM with different ionic strength and 600Da and 900Da pore size. The measured NOM concentration in feed solution was 0.5 ± 0.4 g/L

Membrane Pore size	Measured Ionic strength	Vitens NOM rejection
Da	**(mol/L)**	**(%)**
600	0.09	98.44 ± 0.13
	0.756	97.52 ± 0.2
900	0.088	98.03 ± 0.06
	0.762	95.64 ± 0.67

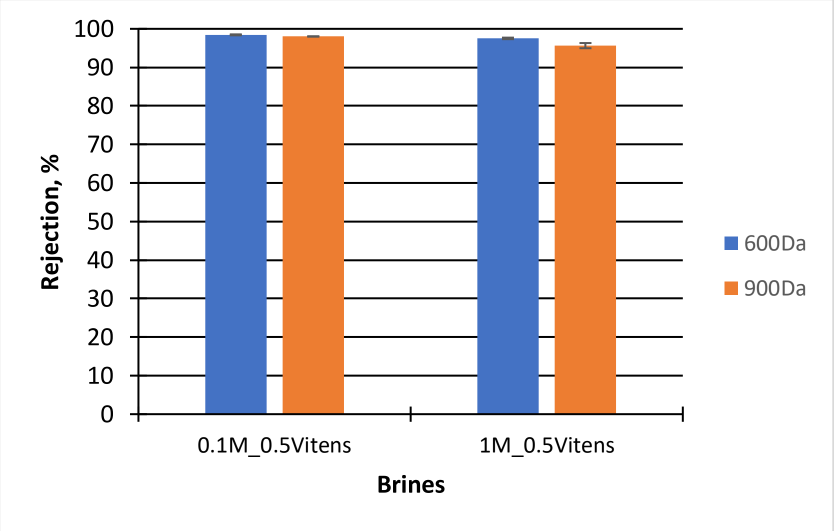


Figure 4.5: Rejection of Vitens NOM at different ionic strength but same NOM concentration. Error bars show SD of triplicate measurements.

Various researchers and literature works based on experiments considered NOM rejection based on DOC as a function of size exclusion, electrostatic repulsion and hydrophobicity/aromaticity between the NOM and the membrane surface and pore (Amy & Cho, 1999; Braghetta et al., 1997; Cho, Amy, & Pellegrino, 1999). As shown in Table 4.9, both membranes 600 Da and 900Da membrane showed rejection of NOM from Vitens greater than 95%. This is expected because, in general, high humic-water dominated by hydrophobic acids (FA and HA) exhibit high NOM removal (Amy & Cho, 1999). This in good agreement with the fact that the Vitens NOM used in the artificial brines contained about 90 % of Humics, mentioned in section 4.1.1. Also, this NOM was characterized to have a SUVA > 4 which translates to high hydrophobic NOM content (Matilainen et al., 2011). This suggested effective removal of hydrophobic acids (Amy & Cho, 1999). Further, it was observed that for different ionic strength but same pore size membrane, the NOM rejection was almost same (~ 97 – 98%). This suggested that NOM removal was independent of membrane charge, considering that that membrane surface charge changes with ionic strength. The results show that the rejection of NOM was mostly unaffected by the ionic strength of the solution for the same pore size and suggest that rejection was mainly due to steric exclusion.

However, when NOM rejection from the filtration experiments was compared between the two pore sizes (600Da and 900Da) at same ionic strength (for instance, ~ 0.1M), it could thus be expected that T03 will project higher NOM rejection than T09. However, consistent rejection at ~ 0.1M ionic strength was observed; also, similar NOM rejection was observed for 1M ionic strength. This suggests that minor electrostatic repulsion between the membrane surface and NOM fraction in addition to steric exclusion could play a role in NOM rejection, especially at ~ 0.1 M ionic strength or lower ionic strength. This can be supported by the relationship between the zeta potential of membrane and ionic strength of the solution which will be explained further.

Table 4.10: Rejection of NOM in various IEX brines (different ionic strength) by 600Da and 900Da membrane pore size.. The measured NOM concentration in feed solution was 0.5 ± 0.4 g/L

Membrane Pore size	**Brines**	**Measured IS**	**NOM rejection**
Da		**(mol/L)**	**(%)**
600	Sweden	0.192	95.27 ± 0.37
	England	0.079	86.97 ± 0.69
	PWNT	0.265	89.998 ± 0.284
	Belgium	1.287	97.4 ± 0.18
900	Sweden	0.197	90.89 ± 0.19
	England	0.083	86.45 ± 0.8
	PWNT	0.255	86.66 ± 0.51
	Belgium	1.417	92.55 ± 0.2

The trend for NOM removal followed by the IEX brines is same as the HS content present in each brine. Higher the HS content better the NOM removal. As mentioned previously in section 4.1.2, these brines are primarily humic in nature and thus more the humic substances (hydrophobic content) higher the NOM removal. The series of NOM removal is Belgium > Sweden > PWNT > England which is the same order as the humic fraction content. The measured DOC for all the brines can be found in

Table 4.7. From above, it was concluded that ionic strength of solution has low or no effect on NOM removal for the same membrane pore size with same NOM being used, and NOM rejection was possibly due to steric exclusion. However, with real IEX brine tested, they are different in ionic strength, NOM type, source of NOM and the NOM content. Therefore, there is no single trend which is followed by all brines. It was observed that the NOM rejection for T09(900Da) membrane was slightly less than the T03(600Da). For obvious reasons that 600Da has tighter pores and smaller pore size than 900Da.

As mentioned in Table 4.3, the Belgium brine has highest humic content amongst the real IEX brines. The molecular size of the NOM fraction of HS present in the brine could possibly be larger than the MWCO of the membranes. From previous study by Feng, 2018 it was found that ceramic membrane was neutral charged at high ionic conditions, while, exhibit negative charge in normal conditions. Therefore, the rejection of NOM for the Belgium brine can be attributed to the Steric exclusion. Furthermore, it was expected that the brine with least ionic strength – England brine will show high rejection due to steric exclusion and electrostatic repulsion between the NOM and membrane surface due to membrane potential. However, it shows the least NOM rejection. This is possible because the brine is diluted in NOM content. Various studies have shown, NOM rejection largely depends on the NOM content (Amy & Cho, 1999). That is rejection increases with increasing NOM content.

An interesting interplay of steric exclusion, hydrophobicity and electrostatic repulsion is shown by Sweden Brine. The ionic strength of the brine is ~ 0.2M. The rejection for both the membranes is above 90%. The zeta-potential of the membrane is still negative at neutral pH and ionic strength of ~ 0.2M, which means the membrane is negatively charged in the proximity of its surface. The negatively charged (presence of carboxylic and phenolic groups) NOM are possibly repulsed by the negative membrane charge thereby, increasing the NOM rejection. However, this effect can be more evident when there is sufficient hydrophobic matter to be rejected, because accumulation of hydrophobic NOM near the membrane surface may increase the negative charge. This might explain the high NOM rejection of Sweden Brine. Figure 4.6 shows pictorial representation of the NOM removal from different brines.

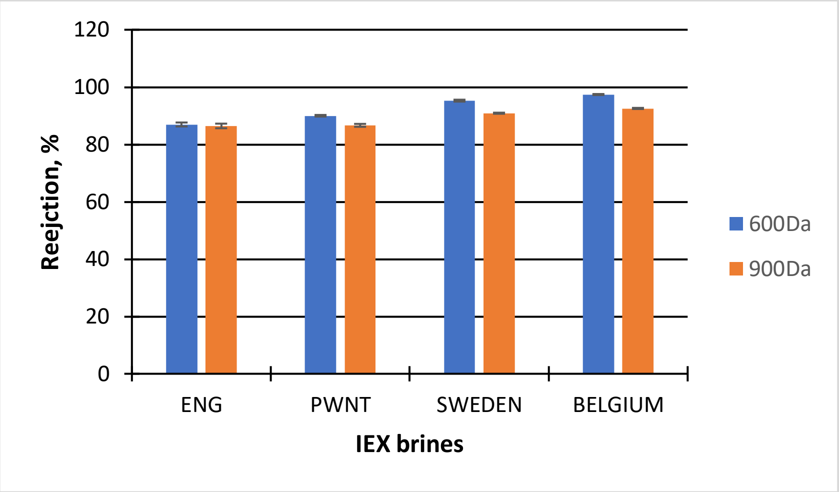


Figure 4.6: Rejection of NOM from different IEX brines. The SD shows the deviation from triplicate measurements.

4.3.1.1 Modelling

To investigate the contribution of steric exclusion in the rejection of NOM observed in the filtration experiment, modelling was done. The fractionation data from LC-OCD analysis was applied on the PEG rejection curve. Since PEG follows a size - exclusion rejection modelling was done to identify which mechanism governs the NOM removal in brines. The fractions smaller than ~1000Da are the Building blocks of ~400Da (average of ~300Da to 500Da), the expected rejection for T03 and T09 is 70% and ~50% respectively. For fractions smaller than 350Da – low molecular weight neutrals, rejection lower than 40% and 30% is expected from 600Da and 900Da respectively. This means that rejection of LMN by these membrane pore sizes is difficult and negligible The membranes T03 and T09 displayed 90% rejection of fractions larger than their respective pore size, meaning the humic substances (~ 1000Da) were almost rejected by both the membranes. For modelling, upper and lower limits were calculated. The lower limit being (rejection from HS and BB) and upper limit being (rejection from HS, BB and LMN). The experimental rejection (%) corresponding to the analytical rejection (%) is shown in Table 4.11.

Table 4.11: Comparison of modelled NOM rejection with experimental NOM rejection for artificial and IEX brines

	T03 (600Da)		T09 (900Da)	
	Analytical rejection (%)	Experimental rejection (%)	Analytical rejection (%)	Experimental rejection (%)
Vitens	95-99	98	90-92	97
Sweden	88-93	95	80-84	91
England	76-86	87	69-75	86
PWNT	81-88	90	74-78	87
Belgium	85-89	97	84-86	92

From Table 4.11 it is seen that there are discrepancies between the analytical values and the experimental rejection. It shows that the experimental rejection is either same or slightly higher than analytical values. This is because the modelling considers rejection based on the unionized PEG macromolecules but in real the NOM is negatively charged, this means in real the rejection is dependent on steric rejection, chemistry of the solution (pH and ionic strength), behavior and nature of NOM. However, on the whole the rejection mechanism can be attributed to steric exclusion (also since it contributes to rejection in all conditions despite possibilities of other mechanism). It can be said that LC-OCD is thus a useful tool to predict NOM rejection by NF membrane when treating IEX brines (especially high ionic strength).

Furthermore, the model can be improved by involving the NOM characterization in order to have precise idea about the size of the fractions. For instance, in the present model, we have assumed that the size of HS is 1000Da, but the size of organics can be bigger and smaller, varying as per the NOM source and properties. Also, Da is the unit for molecular weight and not "size", so it might make difference by considering the geometrics of the molecules. Dimensional parameters of the molecule play a crucial role in rejection of organics because, retention of organics with similar molecular weight but different structural configuration may differ (Nghiem & Schäfer, 2004).

4.3.2 Effect of ionic strength on Salt rejection

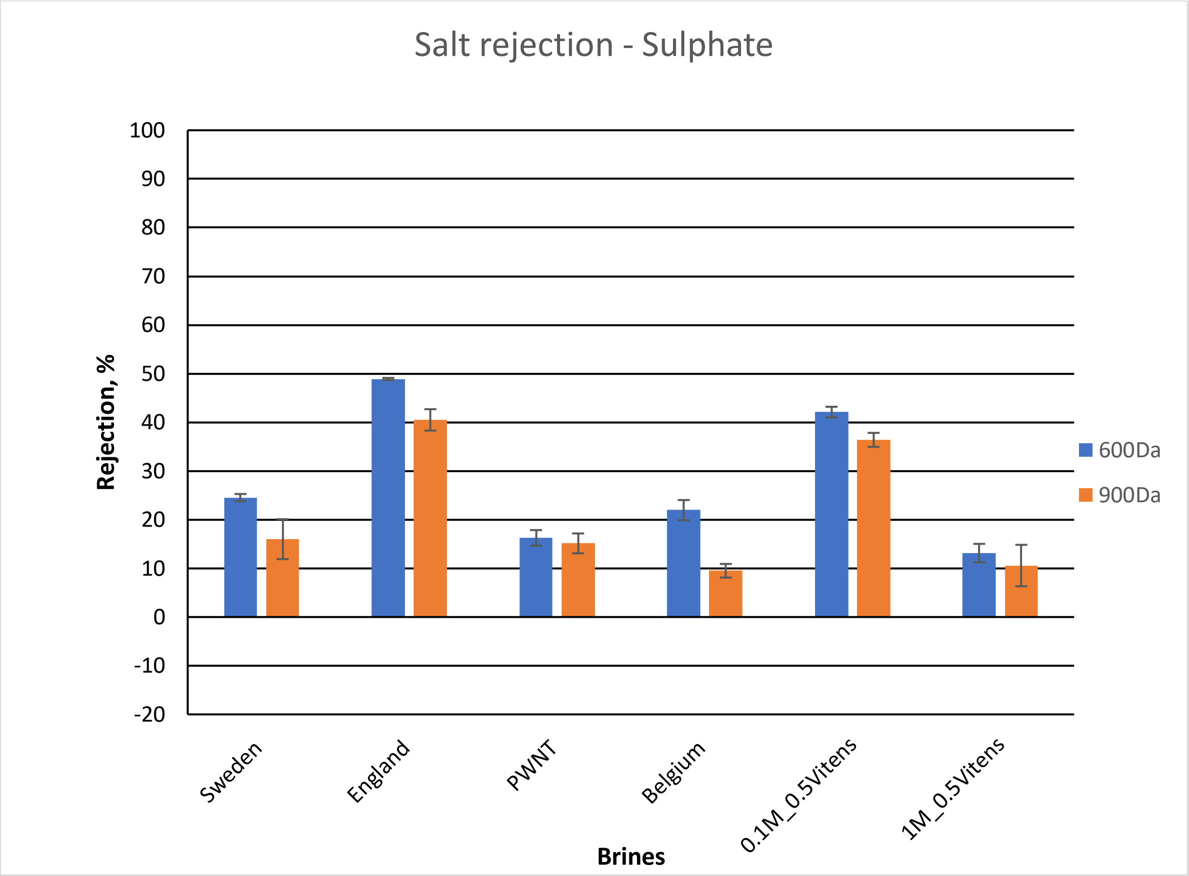
As shown in Figure 4.7, the ions rejection is much lower compared to the rejection of NOM. This is due to ionic strength of the brines. In ceramic NF membranes, salt retention depends on the charge near the membrane surface, which is measured by zeta potential of the membrane surface (Weber et al., 2003). Due to charge of the membrane electrostatic repulsion plays a vital role in rejection mechanism (Wang, et al., 2005), lower salt rejections can be explained by changes in electrical double layer on the membrane surface.

At higher ionic strength solutions, the thickness of double layer on the membrane surface becomes smaller. Due to this, the overlapping of double layer between the ions and the membrane surface lessens, causing weakening of the electrostatic repulsion between the co-ion (SO_4^{2-}) and a negatively charged membrane surface. When the electrical double layer shrinks the area of permeation of water increases through the membrane. (Wang et al., 2005; Yan et al., 2016) As shown in Figure 4.7, sulphate rejection decreased with increasing ionic strength. The less rejection of sulphate, at high ionic strength is due to presence of less membrane surface charge, whereas at low ionic strength, the membrane charge is not shielded, and the rejection is based on electrostatic repulsion and attributes to high rejection of sulphate. Consequently, the charge and sieving effect diminishes with increase in ionic strength of the brines.

Complementary to ionic strength effect on sulphate removal, the rejection of Chloride was found to be either zero or negative in many brines (maximum ~6%) and independent of the ionic strength (Pérez-González et al., 2015). Negative chloride rejection in mix salt solution was also observed by (Yan et al., 2016) It is found in open literature that Cl^- has higher the ion exchange selectivity of ionic compounds retention by NF/ RO membranes than SO_4^{2-} (Nghiem & Schäfer, 2004). This lower rejection of chloride can be described by the electrostatic effect at the membrane surface which is explained by Donnan equilibrium theory. The Cl^- diffuses through the membrane due to its selectivity over sulphate, lower valence, and smaller radius (Peeters et al., 1998). Since, the sulphate ions are mostly retained because they cannot cross the membrane, while sodium ions can pass through the membrane, leading to an excess positive charge on the permeate side. Chloride ions are dragged towards the permeate side, to achieve electrostatic neutralization or equilibrium, on both (feed and permeate) sides of the membrane.(Nghiem & Schäfer, 2004; Pontalier et al., 1997; Yan et al., 2016) Thus, this even explains the decrease of sulphate rejection with increasing ionic strength (Pérez-González et al., 2015).

Table 4.12: Sulphate and Chloride rejection with increasing order of ionic strength.

Brines	**Average measured IS (mol/L)**	**Average SO_4^{2-} rejection, (%)**	**Average Cl^- rejection, (%)**
England	0.08	45	3
0.1M_HS Vitens	0.1	40	4
Sweden	0.2	20	-2
PWNT	0.3	16	-3
1M_HS Vitens	1	12	-3
Belgium	1.3	16	-0.2



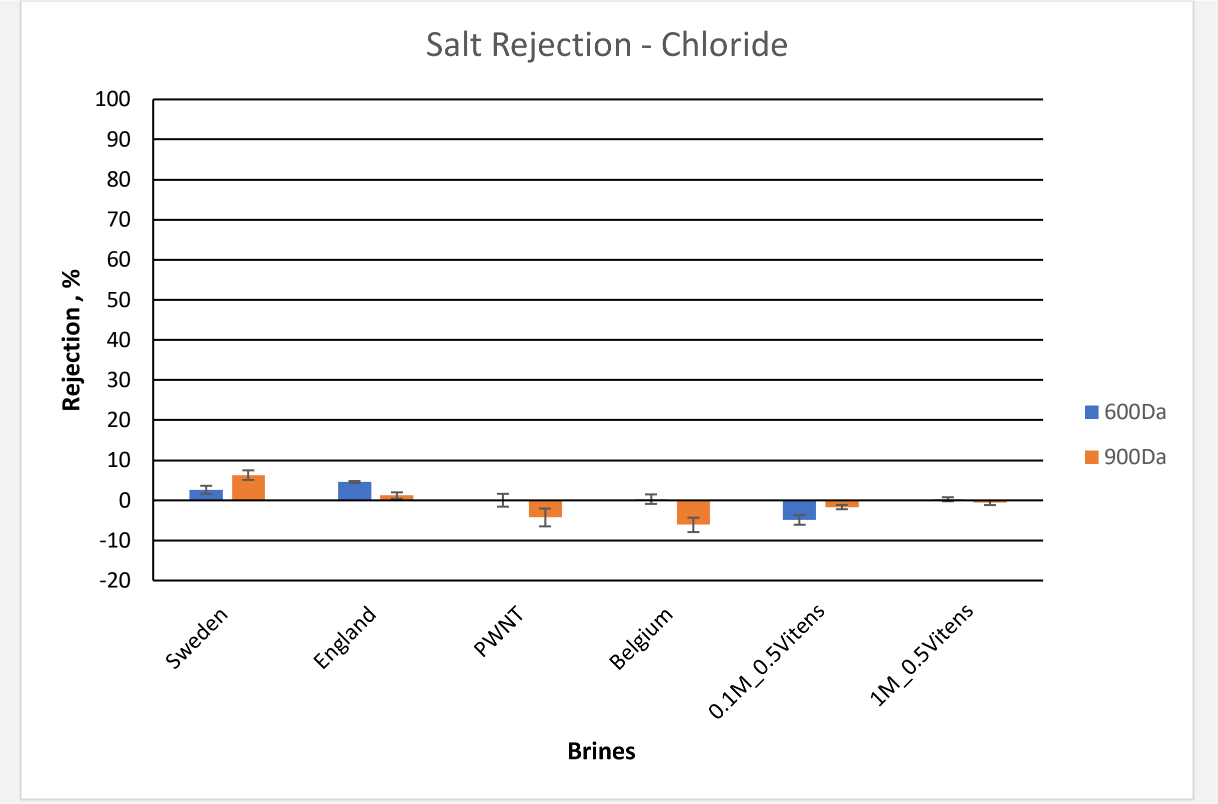
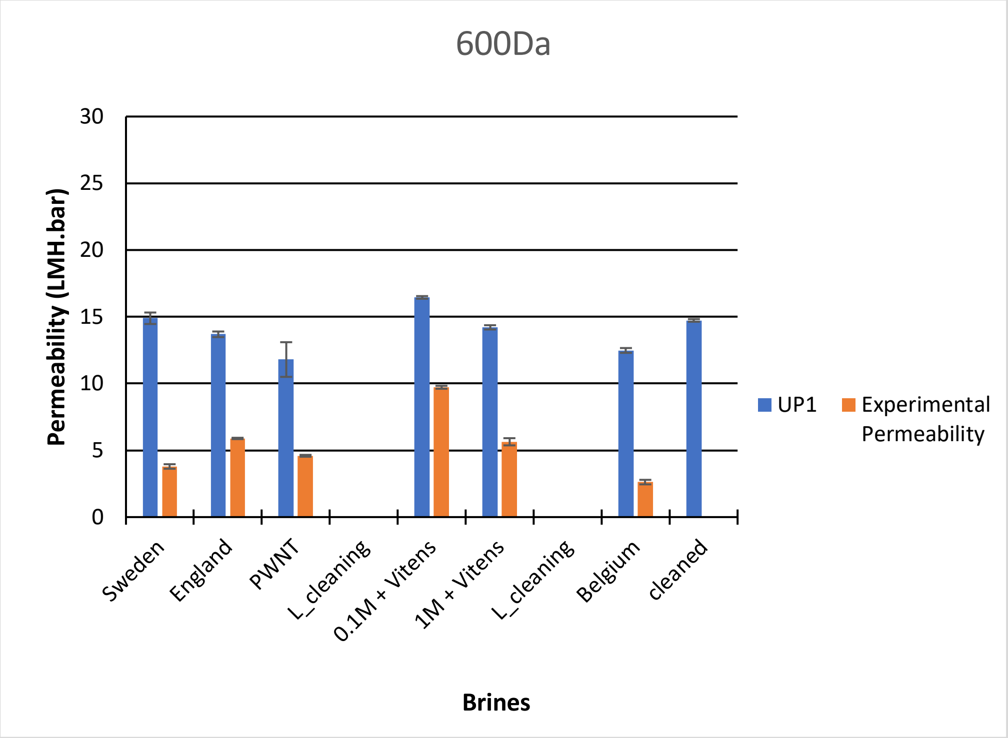


Figure 4.7: Rejection of salts by ceramic membrane in presence of NOM at different ionic strength

4.4 NOM fouling characteristics

4.4.1 Loss of permeability during filtration

As shown in Figure 4.8, the permeability of the membranes drops during the nanofiltration experiments of solutions containing NOM. The drop in the permeability of the membrane is considered with respect to the water permeability of the membrane before the filtration experiments. In this study, permeability drop is defined as the difference between the clean water permeability and the permeability during filtration experiments, calculated in percentage. The membrane was intermittently cleaned chemically several times during the series of experiments (Appendix A: Series of experiments and membrane cleanings done to regain its permeability before next filtration. The range of permeability drop observed was in the range of 40 – 80 %, as shown in Table 4.13, for both the membranes. It was observed that Belgium brine showed the highest permeability drop of about 79 % and 78 % in 600Da and 900Da respectively. This implies that solution with high HS content and high salt concentrations have a higher permeability drop**.** This result was observed by Hong & Elimelech, (1997), Jarusutthirak et al., (2007) and many other researchers that with increase in salt and NOM concentrations there is increased permeate flux decline, NOM and salt rejections. For this reason, Belgium brine was tested for fouling potential.



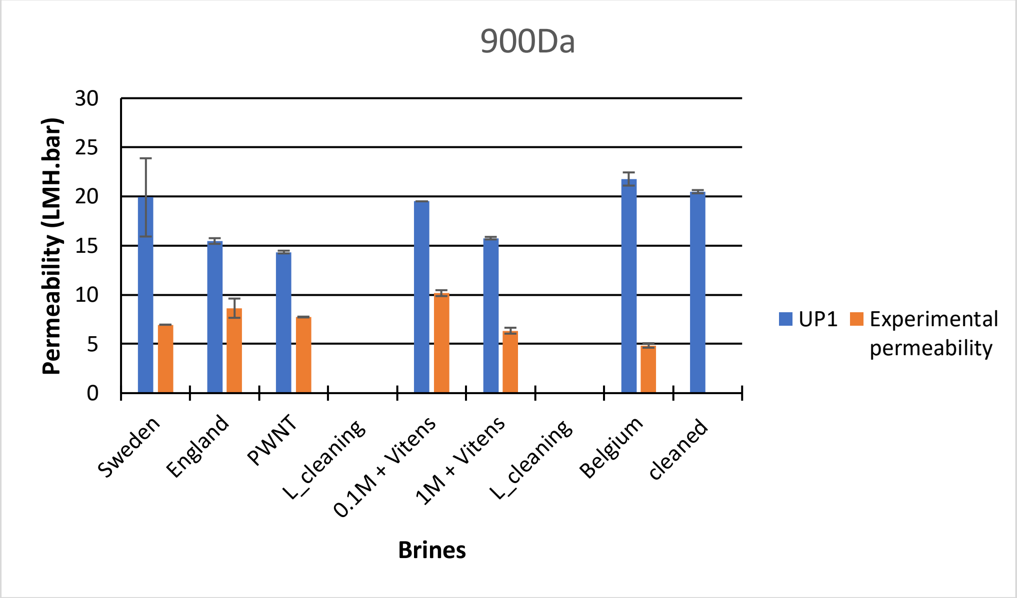


Figure 4.8: Water permeability and permeability during experiments for T03 and T09 membranes. The SD is from the triplicate measurement. For artificial brines the DOC is 0.5 ±0.3 g · L-1.

Table 4.13: Permeability drop for two membranes 600Da and 900Da

Brines	**Permeability drop (%)**[4]	
	600Da	**900Da**
Sweden	74	65

[4] Permeability Drop is the percentage reduction which results from the difference between water permeability and experimental permeability

England	57	44
PWNT	61	46
0.1M + Vitens	41	48
1M + Vitens	60	60
Belgium	79	78

4.4.2 Concentration polarisation and osmotic pressure in the salt and NOM experiments

Concentration polarization factor (β) was calculated to suggest the extent of concentration polarization near the membrane surface during filtration experiments. It can be calculated in two ways; one is using the Sherwood theory and the other is simply from the ratio of the osmotic pressure at the membrane to the osmotic pressure at the feed. In our case, CP was calculated using osmotic pressure near the membrane surface (π_m) and of the feed (π_f). The CP factor (β) can be expressed as in equation (4.1).(Halem, 2009)

$$\beta = \frac{\pi_m}{\pi_f} \tag{4.1}$$

The water permeability factor for the membrane can be calculated using the equation (4.2), where the J_w is the flux of ultra- pure water in LMH, μ is the absolute viscosity of water in Pa·s , TMP is the transmembrane pressure of water in Pa.

$$k_w = \frac{J_w \, \mu_w}{TMP_w} \tag{4.2}$$

$$\mu = \frac{497 \cdot 10^{-6}}{(42.5 + T)^{1.5}} \cdot \rho_{solution} \tag{4.3}$$

From the water permeability coefficient, osmotic pressure difference can be calculated from the equation (4.4). All the values change due to different feed water (salt solution), temperature and TMP of the system.

$$k = \frac{J \, \mu}{TMP - \Delta\pi_m} \tag{4.4}$$

The osmotic pressure for feed and permeate was calculated using the equation (4.5) where, c_i and M_i are the concertation and molecular mass of the ion I in g·m$_{-3}$ and g·mol$_{-1}$ respectively. Finally, the osmotic pressure near the membrane can be calculated using equation (4.6).

$$\pi = \sum_i \frac{c_i \cdot R \cdot T}{M_i} \tag{4.5}$$

$$\Delta\pi_m = \pi_m - \pi_p \tag{4.6}$$

The calculated CP is representative of the degree of CP occurred by ions near the membrane surface. However, both NOM and salt contribute to concentration polarization in NF (Winter et al., 2017).

Table 4.14: CP factors in fouling phase experiments for electrolytes.

Electrolyte	Ionic strength	Temperature	Density	Absolute viscosity	CP factor

	M	˚ C	$g\cdot L^{-1}$	$x10^{-4}$ Pa · s	
$NaCl + Na_2SO_4$ – (test Vitens Brine)	1.3	32.95	1070	8.12	1.02
$NaCl + Na_2SO_4$ – (test Belgium Brine)	1.4	29.3	1070	8.74	1.1

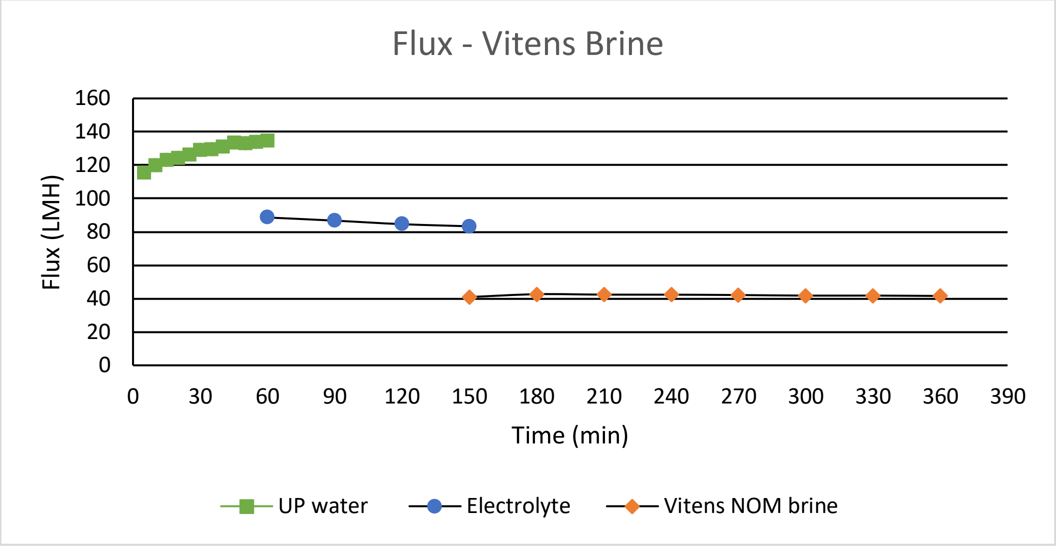
As shown in Table 4.14, the CP factor for both the electrolyte approached to 1, which suggests that accumulation of ions caused no CP near the membrane surface.

4.4.3 Effect due to solution composition

For charged membranes, ion composition and ionic strength contribute to flux decline, due to development of osmotic pressure, by influencing ion rejection by Donnan exclusion. A study by Jarusutthirak et al., (2007) showed that with increase in ionic strength, flux decline increased perhaps due to osmotic pressure from higher feed salts concentration. Besides, it eventually leads to reduction of membrane permeability (Kilduff et al., 2004).

In this research, the salts present in the feed solution were NaCl, Na_2SO_4 and 1mM $NaHCO_3$ with ionic strength of 1.34M and concentration of 1.7 g C /L Vitens NOM. Unlike many studies on membrane fouling due to salt and NOM interaction mainly due to presence of divalent cations, there are no divalent cations and only mono-valent cations present in the solution composition. When mono-valent cations are present in the solution, the fouling activity is determined by hydrophobic and electrostatic interaction between the foulant and the membrane surface at the initial stage. As it progresses, the interaction between the foulant molecules in the feed solution and foulants on the fouling layer surface determine the fouling rate and mechanism. (Li & Elimelech, 2004)

As shown in figure below, initially only electrolyte consisting of NaCl, Na_2SO_4 and 1mM $NaHCO_3$ at ionic strength of 1.34M was passed through the membrane. This was done to generate an electrolyte baseline before passing the solution with salt and NOM, with the purpose to increase the chances of fouling. From Figure 4.9. shown below, it was observed that there was relatively stable permeate flux during this phase. This can be explained by difference in the osmotic pressure between feed and permeate. The low salt rejection is also attributed to low net electrostatic repulsive between the membrane and the salts at high ionic strength. Therefore, high salt concentrations of ions reduce the rejection rate of ions in charged membranes. This was even observed by Pontalier et al., (1997).



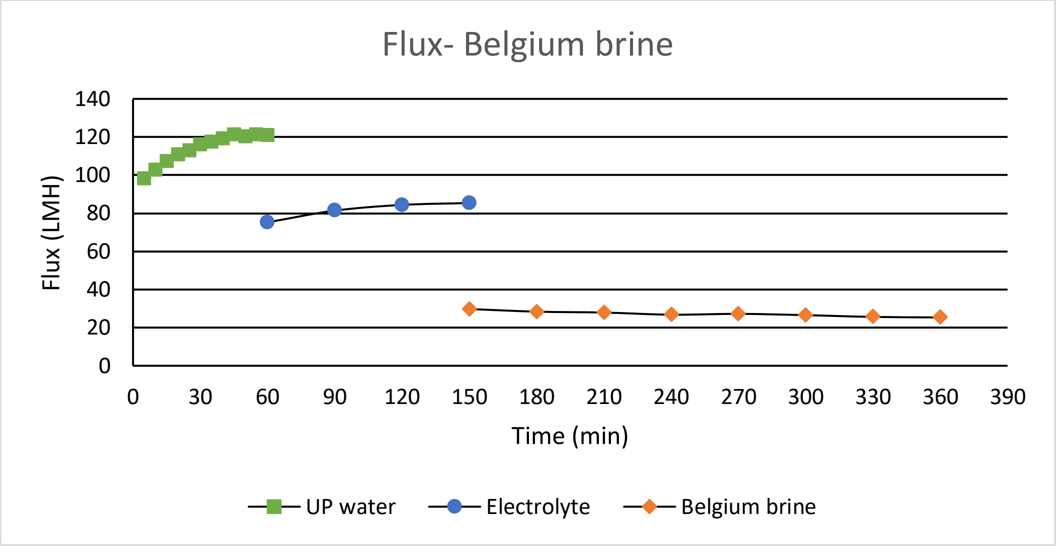
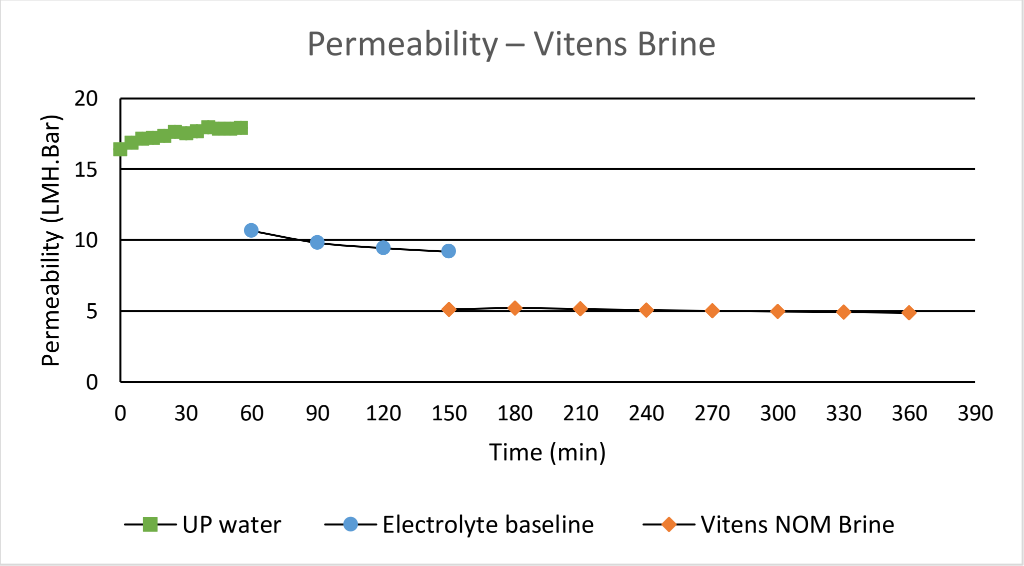


Figure 4.9: Flux of T03 membrane during fouling for Vitens brine (top) and belgium brine (bottom)



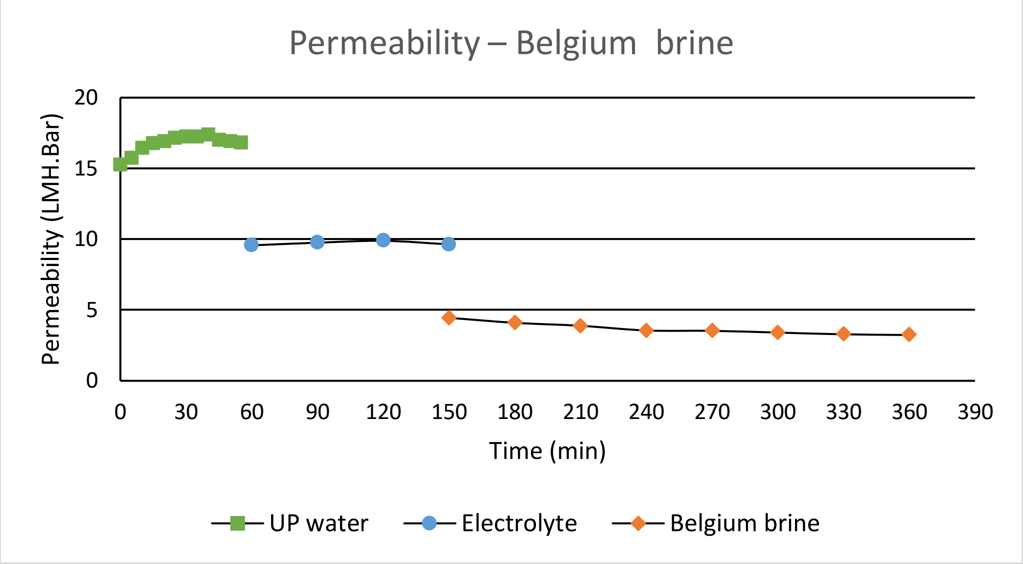


Figure 4.10: Permeability of T03 membrane during fouling phase for Vitens brine (top) and Belgium brine (bottom)

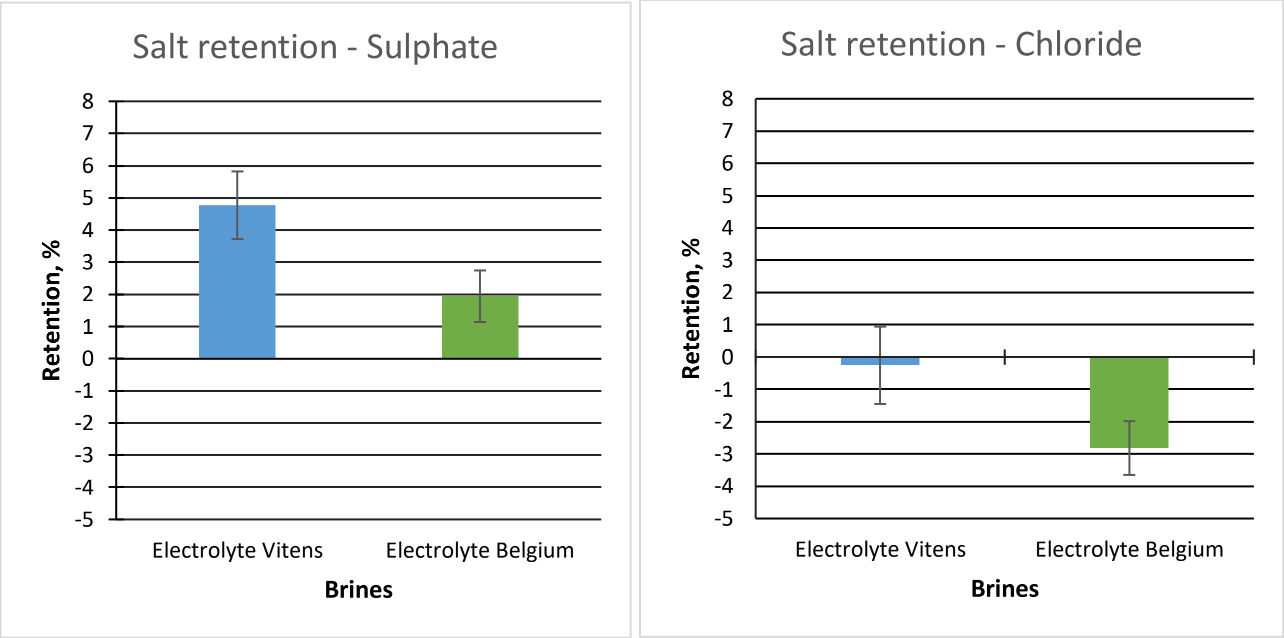


Figure 4.11: Ions retention during conditioning for both brines, sulphate (left) and chloride (right)

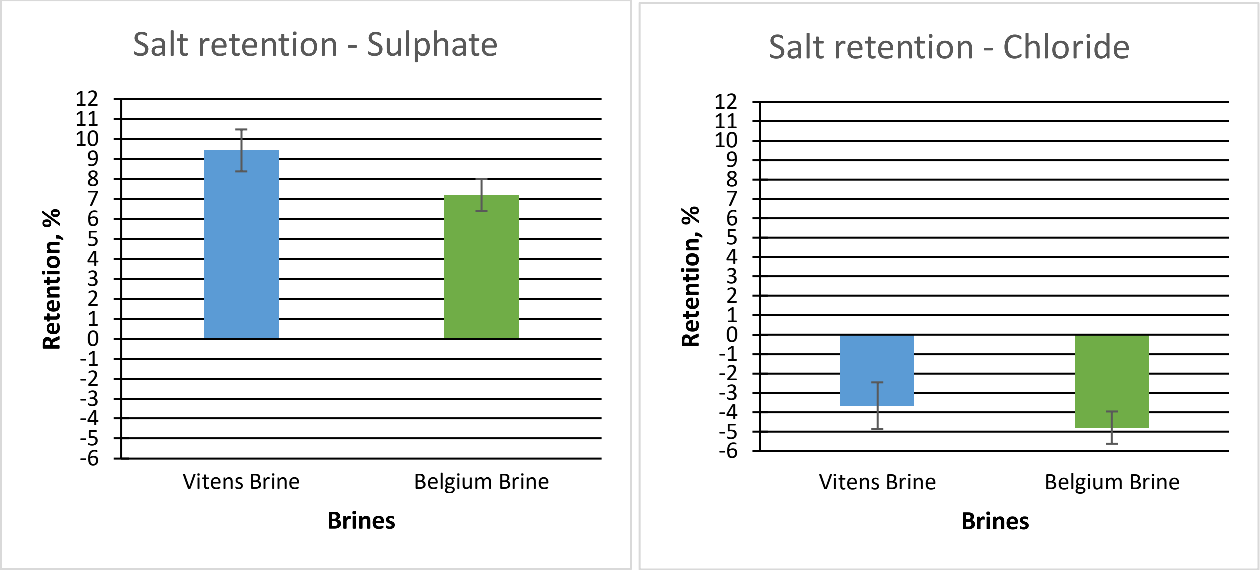


Figure 4.12: Ions retention during fouling phase, sulphate (left) and chloride (right)

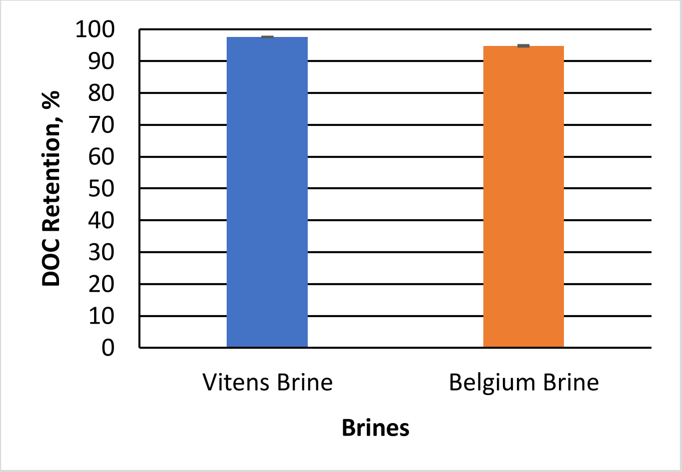


Figure 4.13: DOC retention for Vitens and Belgium brine. The SD is from multiple (8) measurements.

For the same ionic strength, solution with Vitens NOM concentration (1.7 g/L) was passed through the membrane after 2 hours. From Figure 4.13 above, it is apparent that there was sudden drop of 51% in flux and 65% in permeability for Vitens brine. Similarly, the flux drop for Belgium brine was 45% and 54 % in the permeability, of the membrane when the feed solution changed from electrolyte to brine. One reason to the sudden drop of flux and eventually the permeability in transition of feed solution from electrolyte to the brine. Upon changing the feed (switching the valves) water from only salt to brine, the pressure of the system might be disturbed due to gush of air bubbles, affecting flux and the permeability to decline sharply. Over the period of next hours, the system is self-stabilised and almost consistent flux and permeability was observed. Previously, we assumed that NOM from Vitens and Belgium may contain major hydrophobic fractions which are likely to deposit on the membrane surface. This was seen by Schäfer et al., (1998) in their study; from an electron micrograph image, they could observe that UV values were always higher than DOC values obtained. That meant more deposition of hydrophobic and aromatic compounds, at almost all pH. However, deposition is quite dependent to the amount of hydrophobic character already present in the feed and the chemical characteristics of the different hydrophobic fractions. But again, the fouling rate due to brine is relatively low, considering the concentration of NOM (1.7 g/L). Owing to high ionic strength, charge screening was negligible and might have not played a significant role in NOM fouling. Therefore, the negligible decline in flux and permeability during 4 hours of filtration in the fouling stage in presence of NOM can be attributed due to NOM and membrane surface interaction. A study by Q. Li & Elimelech, (2004) confirmed the very slow fouling. It also suggested that the fouling layer is weak, thin, loose and perhaps reversible in presence of monovalent cations. It must be assumed that the flux decline is not always related to amount of deposit but, the structure of the deposit, as mentioned by Schäfer, Fane, & Waite, (1998). Despite minimal fouling, a clear difference in rejection of ions was observed with and without NOM. The rejection of ions increased (doubled) in presence of NOM, previously supported by many researchers (Shang et al., 2014).

4.4.4 Effect on membrane pore size

Furthermore, to understand the effect of irreversible fouling on the membrane pores, a MWCO of uncleaned membrane was conducted. The weak, feeble layer formed on the membrane was flushed away and therefore, MWCO of irreversible fouling, if any, was measured by PEG tests. From the PEG test, it was surprising and contrasting result than expected. The MWCO obtained of the uncleaned membrane can be found in Table 4.15.

Table 4.15: MWCO of 600Da membrane in different conditions

Membrane condition	MWCO
Virgin/clean membrane	560
After fouling test - Vitens	626
After fouling test - Belgium	700

As shown in Table 4.15 above, the MWCO of the membrane has increased. The possible reasons for increase in the pore size could be attributed to either extensive cleaning of the membrane regularly or the membrane may have a defect. The defect for the membrane is checked at 1000Da molecular weight. Defect is defined as the inability of the membrane to reject the 1000Da PEG up-to 90% due to cracks that cause short circuiting of feed water to permeate water (Kramer et al., 2019) Defect (%) is calculated as the difference of the rejection of the membrane at the highest molecular weight of PEG from 90% rejection. The calculated defect for the membrane is shown in
Table 4.16, which suggested that the damage to the membrane due to defect is negligible and cannot be accounted for. However, it was to be noted that before MWCO was measured for the membrane the membrane has been repeatedly used and cleaned chemically. The series of chemical cleaning can be found in
Figure 4.14. It was observed that the UP-water permeability of the membrane before the HS Vitens brine and Belgium brine fouling test was increased in comparison to the initial UP water permeabilities in the series. The increase in pore size over time can be understood from the Ultra-pure water permeability of the membrane.

Table 4.16: Percentage defect in T03 membrane

Membrane Condition	Defect (%)
after Vitens brine test	0.71
after Belgium brine test	2.34

From the results, it can be suggested that the pore size of the membrane was not constricted by irreversible fouling. Further, tests are needed because, for the membrane, the permeability after chemical cleanings suggests that the pore size increased.

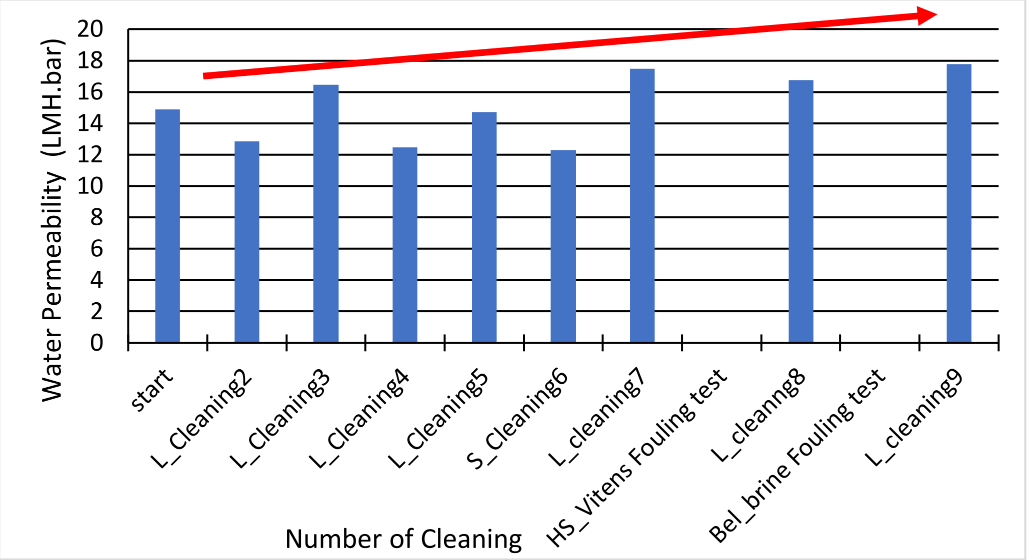


Figure 4.14: Water Permeability of T03 after each chemical cleaning. L_cleaning9 is done after all filtration tests including the NOM fouling.

5 Conclusions and Recommendations

5.1 Conclusion

As a conclusion of this research, the research questions are answered as follows:

1. What are the characteristics of the NOM present in the different ion exchange brines?

   The IEX brines from different water treatment plants had varying NOM content, in terms of concentration and NOM characteristics, although for all brines the main NOM had humic character. The NOM was characterized using two fractionated methods, i.e., LC-OCD and NSM. The two methods are based on different principles and definitions of NOM fractions. The LC-OCD method was predicting the behaviour of NOM on membrane rejection quite accurately. NSM had a different definition of NOM fraction and it is potentially useful to analyse waters with preferably high concentrations of humic matter (humic and fulvic acids). NSM fractionation can be useful for agricultural use of NOM. Compared to LC-OCD, part of NOM was lost during the NSM analysis. The deviation of DOC measured by a conventional organic carbon analyser and the DOC measured by LC-OCD was within 10%. From the fractionation of NOM in IEX brines, the series for SUVA and humic fraction as based on percent TOC was Belgium > Sweden > PWNT > England. The NOM extracted from drinking water company Vitens had highest TOC humic fraction, i.e., 90%; for the other brines, the humic fraction was between 63 and 80 %.

2. What is the effect of salts (NaCl and Na_2SO_4) and NOM on NOM rejection?

   The ionic strength of the solution of artificial brines in the range of 0.1 to 1M did not influence the NOM rejection, when membranes of the same pore size and NOM with the same source were used. The results showed that rejection is mainly governed by steric exclusion. The comparison of NOM rejection using two different pore sizes at same ionic strength, is possibly influenced slightly by electrostatic repulsion in addition to steric exclusion. For IEX brines from drinking water companies with different characteristics, NOM rejection increased with increasing ionic strength, SUVA and NOM content. The rejection observed was possibly a combination of steric exclusion, electrostatic repulsion and hydrophobicity of humic mater. For effect of NOM on NOM rejection, ionic strength had little to zero influence on NOM rejection. However, humic matter content played a crucial role in NOM rejection. Moreover, NOM improved sulphate rejection, which was confirmed by previous researchers as well. Maximum sulphate retention could be obtained at lower ionic strength.

3. What are the characteristics of NOM fouling? Is it reversible or irreversible or a combination? Does fouling affect the membrane pore size?

   Permeate flux decreased when solutions of increasing salt and/or NOM concentration were used, and when membranes with decreasing pore size were used. The decreased permeability was mainly explained by osmotic pressure difference. The CP factor obtained for two different feeds showed very less CP and can be concluded that the fouling occurred could have been majorly reversible.
   After a short initialization time, during the filtration of the brines, the observed flux was mostly quite stable, suggesting no major fouling in this phase.
   Investigations on uncleaned membranes after brine filtration experiments suggested that irreversible fouling did not decrease the pore size of the membrane. However, the increasing permeability of one of the membranes during the months of experiment might indicate an increase of the pore size of the membrane due to frequent chemical cleaning.

5.2 Recommendations

This research used two NOM characterisation tools namely, LC-OCD and NSM. To improve the existing and further research on NOM removal, few recommendations are made on this research's result.

1. Low molecular weight fractions
   This research has shown that LC-OCD is a successful tool for characterizing NOM and it's removal. LC-OCD of the permeates from the nanofiltration would give better understanding on the fraction of removal which could bolster the reasoning based on hydrophobicity, charge and molecular size of NOM present. However, there is requirement of research on fractionation, quantification and detection of low molecular weight neutrals and acids. Further research could consider using chromatographic columns which specifically target the fractionation of the LMW organics.

2. Size range of NOM
   Further research can be based on shift in molecular size range of NOM in high ionic strength conditions, which can affect the NOM removal.

3. Detailed NOM characterisation
   Elemental analysis of NOM present in the feed water can provide in depth insight on the hydrophobicity and hydrophilicity of the fractions present in NOM.

4. Fouling experiment
   To induce purposive fouling to know the degree of fouling by the NOM present in different IEX brines, longer duration of filtration and relative virgin membrane should be tested since it was observed, fouling rate is slow. Besides, better setup configuration can be built for the fouling experiment.

5. Temperature
   During the fouling experiment, the permeability was corrected for temperature at 20 ˚C. However, it will be recommended to maintain the temperature at 20˚ C of the feed water especially for longer durations to avoid influence of temperature on the fouling layer.

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Appendix

Appendix A: Series of experiments and membrane cleanings done

Membrane name and MWCO	**Name of test, permeability or cleaning**
T09_900	BrineSWEDEN_Filtration (UP1 , FIL, UP2)
T09_900	BrineENGLAND_Filtration (UP1 , FIL, UP2)
T09_900	BrinePWNT_Filtration (UP1 , FIL, UP2)
	CLEANING_LONG
T09_900	0.1M_CS_0.5Vitens_900Da_ok (UP1 , FIL, UP2)
T09_900	1M_CS_0.5Vitens_900Da_ok (UP1 , FIL, UP2)
	CLEANING_LONG
T09_900	0.1M_CS_0.5FA_900Da. (UP1 , FIL, UP2)
T09_900	1M_CS_0.5FA_900Da. (UP1 , FIL, UP2)
	CLEANING_LONG
T09_900	Brinebelgium_Filtration_900Da_ok (UP1 , FIL, UP2)
	CLEANING_LONG
T03_600	PERMEABILITY TRIAL
T03_600	BrineSWEDEN_Filtration_OK_NF (UP1 , FIL, UP2)
T03_600	BrineENGLAND_Filtration_OK_NF (UP1 , FIL, UP2)
T03_600	BrinePWNT_Filtration_OK_NF (UP1 , FIL, UP2)
T03_600	0.1M_CS_0.5FA_600Da_NF_Filtration (UP1, FIL, UP2)
T03_600	1M_CS_0.5FA_600Da_NF_Filtration (UP1, FIL, UP2)
	CLEANING_LONG
T03_600	0.1M_CS_0.5Vitens_600Da_NF
T03_600	1M_CS_0.5Vitens_600Da_NF
	CLEANING_LONG
T03_600	BrineBELGIUM_600Da_OK_NF
	CLEANING_LONG
T03_600	0.1M_CS_0.5Vitens_600Da_OK
T03_600	1M_CS_0.5Vitens_600Da_OK
	SHORT_CLEANING
T03_600	0.1M_CS_0.5FA_600Da (UP1, FIL, UP2)
T03_600	1M_CS_0.5FA_600Da_Filtration (UP1, FIL, UP2)
	CLEANING_LONG
T09_900	0.1M_CS_0.5FA_900Da (UP1, FIL, UP2)
T09_900	1M_CS_0.5FA_900Da_Filtration (UP1, FIL, UP2)
	CLEANING_LONG
T03_900	Permeability trials_900Da
T03_600	Permeability trials_600Da
T03_600	BrineVitens_fouling_600Da_ok (UP1,electrolyte, brine)
T03_600	PEGbrineSYNTHETIC_Vitens_fouling_600Da_ok + UP2_brineSYNTHETIC_Vitens_fouling_600Da_ok
	CLEANING_LONG
T03_600	Brinebelgium_fouling_600Da_not
T03_600	Brinebelgium_fouling_600Da_ok (UP1, electrolyte, brine)
T03_600	PEGBrinebelgium_fouling_600Da_ok
	CLEANING_LONG