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Investigation of sub-micron particles and their impact on membrane fouling in drinking water treatment

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Extract: Low-pressure membrane (LPM) filtration is an alternative for producing high quality water. Understanding membrane fouling is the key aspect of the application of such a system. The purpose of the study is to gain a better understanding of the impact of NOM on membrane fouling in low pressure submerged membrane configurations.

Constructed raw water was used in a series of filtration experiments of three different types of low pressure membranes -hydrophilic cellulose esters (MF) and two hydrophobic PVDF membranes (UF). The raw water was made by mixing NOM concentrate into tap water to represent typical Norwegian surface water. The filtration unit was operated under various conditions in order to evaluate their effect on the fouling behaviour. This included the effect of flux variations and different membrane characteristics and, the effect of pre-treatment of the raw water.
Samples of raw water, membrane permeate, and desorbed NOM from fouled membranes were collected and subjected to analysis. NOM fractionation was conducted to distinguish four different NOM fractions, i.e. very hydrophobic acids (VHA), transphilic acids/ slightly hydrophobic acids (SHA), hydrophilic charged (CHA) and hydrophilic neutrals (NEU). Analyses of colour, UV_{254}-absorbance and zeta potential were also applied.

The study revealed some interesting results:

- Higher flux increased the fouling rate and the fouling by NEU. This was claimed to be a consequence of a more severe concentration polarization and gel layer formation.
- Hydrophobic-hydrophilic interactions seemed to be the dominating mechanism in NOM-membrane interaction.
- The main foulant were attributed the VHA in all filtration experiments except for the MF experiment operated at highest flux were the NEUs were dominating.
- Pre-treatment reduced the rate of fouling tremendously, indicating that the pre-treatment were efficient in removing some of the NOM fractions responsible for the fouling.

In summary, strategies to reduce fouling may include careful membrane selection and pre-treatment of the raw water. Sufficient knowledge about the composition of raw water is also important.

Stikkord:

1. Drinking water treatment
2. Low pressure membranes
3. Natural organic matter
4. Fouling

(sign.)

Abstract

The drinking water industry is gaining more interest in substituting conventional separation technologies for treatment of surface waters with membranes due to their separation capabilities. Low pressure membranes are particularly suitable for the removal of suspended solids, especially bacteria, algae, and protozoa namely Giardia and Cryptosporidium. However, they are less effective in removing dissolved contaminants, such as natural organic matter (NOM), which also is claimed to be the major cause of the TMP increase experienced during filtration of surface water.

The purpose of the study is to gain a better understanding of the impact of NOM on membrane fouling in low pressure submerged membrane configurations.

Constructed raw water was used in a series of filtration experiments of three different types of low pressure membranes -hydrophilic cellulose esters (MF) and two hydrophobic PVDF membranes (UF). The raw water was made by mixing NOM concentrate into tap water to represent typical Norwegian surface water. The filtration unit was operated under various conditions in order to evaluate their effect on the fouling behaviour. This included the effect of flux variations and different membrane characteristics and, the effect of pre-treatment of the raw water.

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Trondheim, June 14, 2010

Hanne Næss Høvik

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Abbreviations

Al	Aluminum
CE	Cellulose Esther
CHA	Charged hydrophilics
DOC	Dissolved Organic Carbon
HCl	Hydrogen Chloride
lmh	Membrane flux, expressed as $L\ m^{-2}h^{-1}$
MF	Micro filtration
MW	Molecular weight
MWCO	Molecular weight cut-off
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
NEU	Neutral hydrophilics
NF	Nano filtration
NOM	Natural organic matter
P'	Normalized transmembrane pressure
PAC	Powdered activated carbon
PVDF	Polyvinylidene Fluoride
RO	Reverse osmosis
RW	Raw water
SHA	Slightly hydrophobic acids
SUVA	Specific UV adsorption
TMP	Transmembrane pressure
UF	Ultrafiltration
UV254	Ultraviolet light
UVA	UV absorption
VHA	Very hydrophobic acids
V_s	Unit permeate throughput, expressed as $L\ m^{-2}$

Symbols

A	m^2
c	$mg\ L^{-1}$
G	s^{-1}
J	$L\ m^{-2}h^{-1}$
k	-
R	m^{-1}
t	s
V	m^3
V_s	$L\ m^{-2}$
ΔP	Pa
η	$N\ s\ m^{-2}$

1. Introduction

1.1 Background

Norwegian surface water is characterized by low turbidity, high content of natural organic matter (NOM), it is soft and it has low alkalinity and pH (Fabris et al. 2008). Typical treatment requirements of Norwegian surface waters therefore contain NOM removal, corrosion control and disinfection.

It is desirable to remove NOM due to the many negative environmental and health effects it may cause. The main concern is the potential to form harmful disinfection by-products during water treatment (Eikebrokk et al. 2004). Optimization and new regulations of the treatment process for drinking water with respect to NOM have therefore gained much attention the last years.

According to the Norwegian Drinking Water Regulations (Norwegian Ministry of Health and Care Services 2001), drinking water should be clear and without any prominent smell, taste or colour when delivered to the customer. In addition it should not contain any physical, chemical or biological components that could be harmful to people's health. In order to fulfil the drinking water regulations with respect to NOM, the maximum colour and organic carbon level in the water after treatment is set to 20 mg Pt/l and 5 mg TOC/l, respectively.

Observations indicate increasing natural organic concentration levels in several water sources in Norway the past 10-12 years (Eikebrokk et al. 2004). This, in addition to the new regulations, has led to a greater effort in the water industry directed towards the removal of NOM by the development of alternative and more sustainable treatment schemes.

The industry is gaining more interest in substituting conventional separation technologies with membranes due to their separation capabilities. They represent an absolute cut-off of particles of a certain size relative to the pore size of the membrane, and are therefore effective at removing chemical resistant pathogens such as Cryptosporidium and Giardia (Ødegaard 2009).

The development of nanofiltration made it possible to also remove NOM by membranes in surface waters. The first Norwegian full scale nanofiltration plant was put into operation in 1990 and by the year of 2010 more than 100 plants were in operation (Ødegaard et al. 2010). However, membrane fouling, low fluxes and recovery, frequent cleaning and relatively high energy consumption due to operation at a high pressure, are major disadvantages of nanofiltration.

It is of great interest to overcome these challenges by designing new alternative membrane filtration modules and operation modes to be able to take advantage of the many benefits of membrane filtration. Zularisam et al. (2006) mention small footprint, compact module, production of water of superior quality, little or no sludge production and the capability of handling wide fluctuations in feed quality among the benefits.

The use of low pressure submerged membranes is a relatively new approach with respect to module design and energy requirements. It is beneficial in that the overall energy consumption is low and that the capital costs are competitive (Li 2008). Microfiltration and ultrafiltration membranes are low-pressure membranes able to remove turbidity (particulates and bacteria) and to some extent NOM. However the technology has showed good treatment results with respect to NOM in combination with other conventional technologies such as coagulation, although rapid flux decline due to fouling by submicron particles and NOM is a big challenge.

1.2 Report scope, objectives and structure

This research comprises a study on low-pressure submerged membranes applied for drinking water treatment of surface water of high NOM content. The focus in this study has been on membrane fouling.

A small laboratory scale pilot plant test unit has been utilized to conduct the membrane filtration and fouling studies. The unit has been equipped with different types of flatsheet membranes operated in an outside-in mode. Experiments have been run with and without pre-treatment (flotation), and the feed water has been of typical Norwegian raw water quality.

The purpose of the report was to gain a better understanding of the impact of NOM membrane fouling in low pressure submerged membrane configurations. Two main goals were established:

1. Identification of which NOM fractions are the main foulants at different operating conditions:
    - Effect of flux
    - Effect of having membranes of different characteristics
    - Effect of pre-treatment

2. Identification of fouling rate and fouling mechanisms under the various conditions

In order to achieve the different goals, an extensive literature review was necessary. Membrane filtration processes in general have been discussed, the many properties of natural organic matter and membranes have been identified, and typical NOM/membrane interactions have been covered. The topics are presented in a literature review in *Chapter 2*.

Chapter 3 gives an overview of the methods and analytical tools utilized for data evaluation. The experimental setup and filtration protocol are described in detail.

The results are presented and discussed in *Chapter 4* based on observations made from the experiments and the addressed topics in the literature review.

Chapter 5 concludes the study and suggests topics for further research.

2. Literature review

2.1 Membrane separation technology

A membrane is defined by Mulder (1996, p.7) as “a permselective barrier or interface between two phases”. It has the ability to discriminate between types of molecules when a driving force is acting on the components in the feed, hence being more permeable to some of the constituents of the water. The driving force can either be a difference in pressure, concentration, temperature or electrical potential which leads to a transportation of compounds through the membrane from one phase (feed) to the other (permeate) as illustrated in Figure 1 (Mulder 1996).

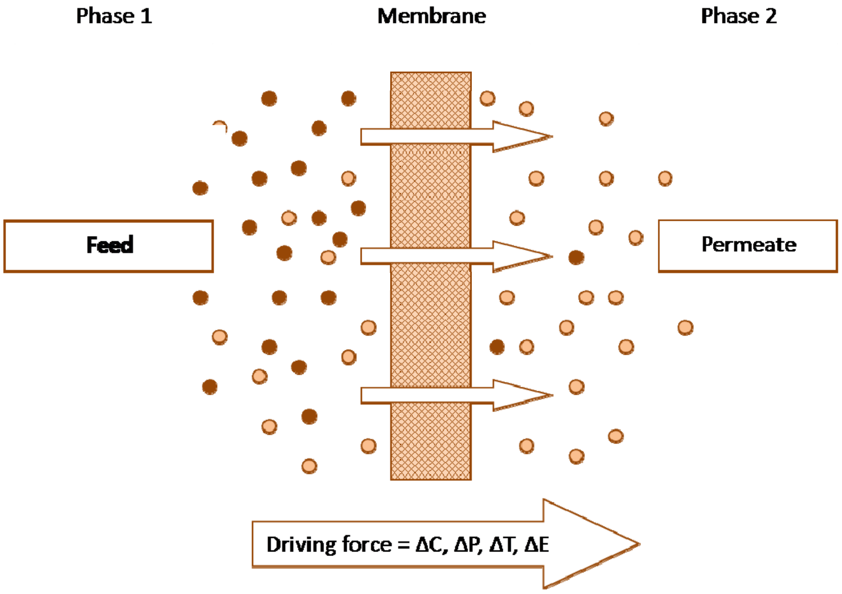


Figure 1: Illustration of a membrane separating a two-phase system based on schematic representation by Mulder (1996, p.7).

Membrane separation processes have become technically important the past 40 years. Rapid development and improvements have made the separation technique applicable to a wide range of industries. It is found in industries like food and beverages, metallurgy, pharmaceutical, dairy, chemical and in the water industry for treatment of both drinking water and waste water (Mulder 1996).

The properties, and therefore the applications, of a membrane are mainly determined by the structure (symmetric/asymmetric, porous/nonporous) and material (polymeric, ceramic, glass, metal) of the membrane. Depending on its properties, a physical and/or chemical interaction between the membrane and the components in the feed takes place. This in turn leads to a more effective transportation of some components through the membrane than other (Mulder 1996).

The most common membrane separation processes applied to the industry involve microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Cheryan 1998). They are all pressure driven but they are distinguished by the means of pore size of the membrane as shown in Figure 2. The pore size represents, in common practice, the size of the rejected particle or molecule (Zeman and Zydney 1996).

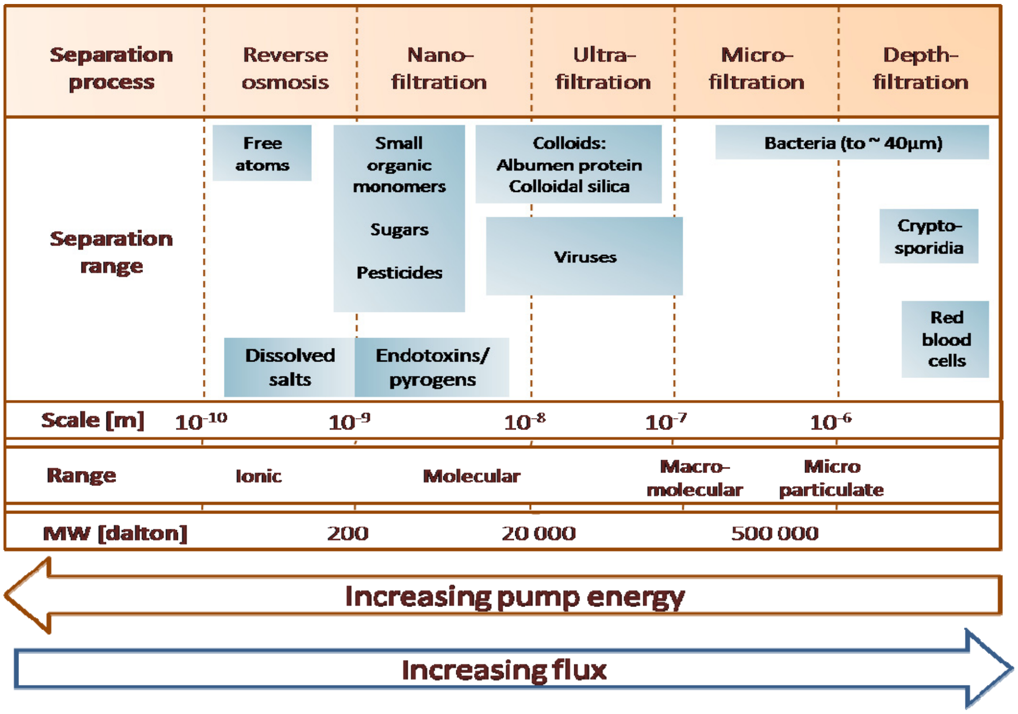


Figure 2: Classification of membrane separation processes based on illustration by Judd and Judd (2006).

Both MF and UF membranes have a porous structure. As shown in Figure 2, microfiltration is designed to retain micro particulates in the range of approximately 0,1-10 µm whereas ultrafiltration is applied to retain macromolecules in the range of approximately 2-100 nm (Mulder 1996, 52). Hence, MF and UF are processes capable of removing microorganisms (e.g. Giardia and Cryptosporidium), suspended and colloidal particles and to some extent NOM (Li 2008). NF and RO membranes are non-porous and are able to separate low molecular weight components, e.g. singly charged ions like sodium and chloride (Judd and Judd 2006). Rejection or retention is one of two parameters used to quantify the effectiveness of membranes and is defined by Cheryan (1998, p.293) as:

$$R = 100 \times \left(1 - \frac{c_P}{c_F}\right) \quad [\%] \qquad [1]$$

c_p is the solute concentration in the permeate and c_F is the solute concentration in the feed water.

The hydrodynamic resistance of MF and UF membranes is quite low due to their relatively large pore size. Thus a small driving force is sufficient to obtain a high flux (J). However, NF and RO processes have a much smaller pore size and they require a higher driving force in order to obtain the same flux because of an increased hydraulic resistance in the membrane (Mulder1996). Flux is the second parameter used to quantify the effectiveness of membranes and is defined by Darcy's law as the volume flowing through a unit area of the membrane per unit time (Li 2008), Equation 2:

$$\frac{1}{A}\frac{dV}{dt} = J = \frac{\Delta P}{\eta R_m} \quad \left[\frac{L}{m^2 h}\right] \qquad [2]$$

In equation 2, , ΔP [N/m^2] refers to a constant applied TMP, while η[Ns/m^2] is the viscosity of the liquid. R_m refers to the permeability or membrane resistance of the clean virgin membrane.

The rejection of contaminants ultimately places a fundamental constraint on all membrane processes (Judd and Judd 2006). Rejected compounds tend to block the membrane pores during filtration by a variety of phenomena collectively referred to as fouling. Fouling of the membrane leads to a flux decline when operated at constant transmembrane pressure (ΔP or TMP) or an increase in TMP when operated at constant flux.

Fouling is one of the major factors limiting the use of all membrane filtration processes. It worsens the membrane performance by altering its retention and shortening its lifetime (Li 2008). This is also the case for membrane application in surface water treatment where NOM and its components are characterized as being the major foulants (Zularisam et al. 2006).

Membrane filtration was applied by the water industry for drinking water treatment about 40 years ago. At that time it was mainly for desalination of seawater, brackish water and groundwater. However, during the late 1980s the technology developed, which resulted in an increase in membrane filtration plants also for treatment of surface water (Thorsen 1999).

2.2 Drinking water treatment with low pressure membranes

In 1960 a low pressure industrially suitable filtration membrane was introduced by Loeb and Sourirajan (Li 2008). Since then UF and MF have been applied to a variety of industries, some mentioned above, and the technology has expanded greatly. A major contribution to this expansion is its application to the water industry, where the membranes have been used for clarification of drinking water and sewage as an alternative to conventional sand filtration (LI 2008). However it was not until after it was found that the membranes were capable of retaining pathogens like Giardia and Cryptosporidium that their use exploded (Furukawa 2002).

2.2.1 MF and UF in general

Furukawa (2002) has in a recent global study showed that the trend of using low pressure membranes accelerated noticeably from the mid 1990s. This was mainly due to the new drinking water regulations, The US 1989 Surface Water Treatment Rule (LeChevallier et al. 1991), which required 3-log cycle removal (99,9%) of Giardia and a 4-log cycle removal (99,99%) of Cryptosporidium. The new regulations were adopted after cryptosporidium outbreaks in the United States.

The expansion in use of MF and UF is mainly due to their capability to remove pathogens while avoiding the formation of disinfection by-products. MF and UF is also applied as pre-treatment to RO, e.g. for desalination of water (Li 2008), an application in growth as a result of the increased water scarcity many countries around the world experience.

As mentioned in the introduction, Norwegian surface water is characterized by high NOM content and low calcium and magnesium concentration (soft water). In addition, 90% of the raw water sources are surface waters (Thorsen 1999). These are the main reasons for the early investigation and development of membrane technology for NOM removal in Norway, and also some of the reasons why NOM removal has been emphasized in treatment of drinking water.

Coloured surface water contains organics of a broad range of molecular sizes and molecular weights. In order to be able to retain the organics, the membranes should have a pore size related to the molecular size of the NOM (Thorsen 1999). Direct filtration by NF has successfully been applied for the removal of NOM, although energy consumption increased. MF and UF are, although very suitable for the removal of suspended solids and colloids, less successful for the removal of dissolved NOM in surface water due to a larger relative pore size compared to the size of NOM. However, the combination of UF and MF with pre-treatment based on coagulation has proven to be effective for NOM removal at the same time as a decreased hydraulic resistance and increased critical flux ("the flux below which a decline of flux does not occur; above it fouling is observed" (Field et al. 1995)) is achieved (Zularisam et al. 2006).

2.2.2 Low pressure submerged membranes

Submerged membranes are relatively new developments first introduced in Japan in the late 1980s (Li 2008). It started as more of a curiosity, but ten years after its introduction it has by far become the most common approach for low-pressure membrane systems in the water and wastewater industry. In 2003, submerged membranes constituted more than 50% of the installed capacity of MF/UF in the water industry (Li 2008).

In submerged membrane filtration, also referred to as vacuum filtration, membranes are placed in an open tank at atmospheric pressure filled with feed water to be treated, see Figure 3 (Li 2008). It is operated in an outside-in mode. Vacuum is generated by a pump in order to obtain a transmembrane pressure to filter the feed water through the membrane and to remove the permeate. The TMP is kept below one atmosphere and the flux is normally constant. Air scouring may be applied for fouling control.

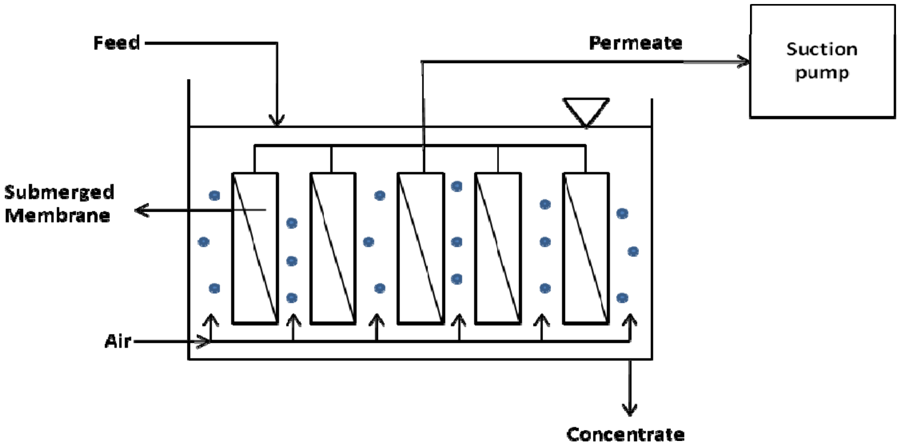


Figure 3: Common features of submerged membrane system (Li 2008).

Norman (Li 2008) states that the majority of submerged membranes are either hollow fibers or flatsheets, the latter being used in the experiments conducted in this study. Figure 4 shows an example of a flatsheet module. Although MF and UF are considered a promising processes in the further development of high quality drinking water, membrane fouling, especially by NOM, constraints the technological development.

Figure 4: Flatsheet membrane (Judd and Judd 2006).

2.3 Fouling of low pressure submerged membranes

Fouling is one of the main limitations in membrane separation processes. It is defined by Li (2008, p.150) as: “The blockage of membrane pores during filtration caused by the combination of sieving and adsorption of particles and compounds onto the membrane surface or within the membrane pores”. The phenomenon is further classified as reversible or irreversible. Reversible fouling is caused by solid accumulation on the membrane surface and can be removed by backwashing or chemical cleaning, whereas irreversible fouling refers to adsorption or pore plugging of solutes in or within the pore matrix and is not removable by any means (Li 2008; Zularisam et al. 2006).

Fouling of membranes by NOM is a complex mechanism. The membrane and NOM have separate sets of properties which interact in different ways and cause fouling depending on the quality of feed water, inorganic solution chemistry (pH, ionic strength), the type and level of any pre-treatment, and the hydraulic configuration applied (Carroll et al. 2000).

The situation described previously by Darcy’s law (Equation 2), is a situation where no fouling occurs. In real life operation, however, the clean water permeability is typically very small compared to other resistances which appear as results of different fouling mechanisms (Cheryan 1998). Fouling of membranes therfore leads to a deviation from the linear flux pressure relationship represented by Darcy’s law.

2.3.1 Fouling mechanisms

The fouling mechanisms that might take place in low-pressure membrane filtration are concentration polarization, gel layer formation, direct and long term adsorption, plugging of the pores and cake filtration. The adsorption mechanisms are also recognized as standard and intermediate blocking, respectively, while plugging of the pores is known as complete blocking (Ruohomaki and Nystrom. 2000).

The “resistance-in-series” model is commonly applied to describe the flux of a fouled membrane:

$$J = \frac{\Delta P}{\eta\left(R_m + R_{cp} + R_g + R_a + R_{cf}\right)} \quad \left\lfloor \frac{L}{m^2 h} \right\rfloor \qquad [3]$$

where R_m is the membrane resistance and R_{cp}, R_g, R_a and R_{cf} are the additional resistances due to concentration polarization, gel layer formation, adsorption mechanisms and cake formation respectively (Schäfer 2000).

2.3.1.1 Concentration polarization and gel layer formation

Concentration polarization (CP) in membrane processes is a result of a membranes ability to reject some of the feed water componentes (Li 2008). This gives rise to an accumulation of retained species at the membrane surface which will exert an additional hydrodynamic resistance to the flow of water through the membranes, i.e. R_{cp}.

A basic Equation for CP showing how the phenomenon of concentration polarisation is depending on two parameters, namely the flux, J, and the mass transport coefficient, k, has been presented by Mulder (1996):

$$\frac{c_m}{c_b} = \exp\left(\frac{J}{k}\right) \qquad [4]$$

In this relationship, c_m is the concentration of solutes at the membrane surface and c_b is the concentration in the bulk.

Convective transport brings the solutes to the membrane surface, while diffusive effects bring the solutes back to the bulk, the latter being a result of the higher solute concentration close to the membrane surface. The diffusive effects are represented by k in Equation 4 (Li 2008). The phenomenon of concentration polarization is illustrated in Figure 5.

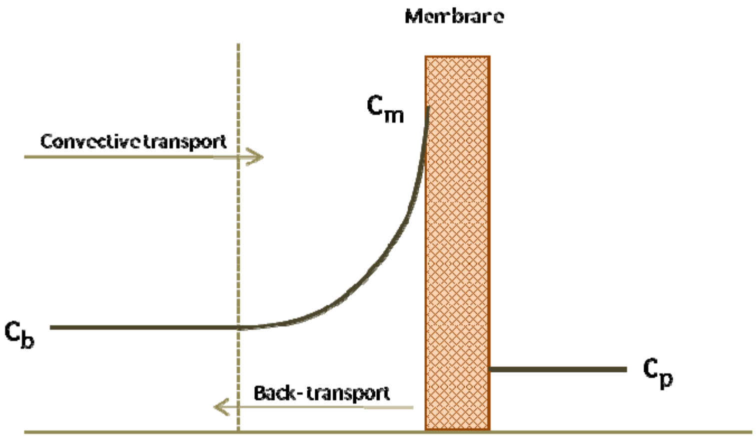


Figure 5: Concentration polarization, based on illustration by Mulder (1996). Convective transport brings the solutes to the membrane surface, while diffusive effects transport the solutes back to the bulk.

In MF and UF processes k is expected to be small. This is because diffusional effects caused by the retained particles, colloids and macromolecules are negligible (Li 2008). The effect of CP therefore becomes quite significant in low pressure membrane filtration, and amplified by high operational fluxes as seen in Equation 4 (Mulder 1996).

If the concentrations of the accumulated solutes in the CP layer exceed the solubility of the NOM, a new phase (gel) on the membrane surface may be formed and exerts an additional resistance to the flow of water through the membrane. This additional resistance is recognized as the gel layer resistance, R_g (Mulder 1996). Figure 6 illustrates the two phenomena of CP and gel layer formation.

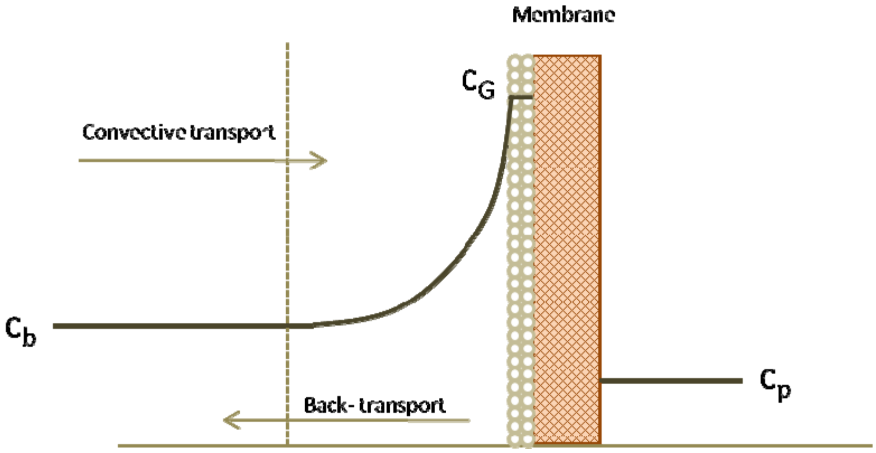


Figure 6: Concentration polarization and gel layer, based on illustration by Mulder (1996). A gel layer forms if the solute concentration at the membrane surface exceeds the solubility of the NOM.

2.3.1.2 Blocking mechanisms

Hermia (1982) developed a blocking model based on the four different fouling modes applicable for constant pressure filtration systems, in order to analyze how and when the membrane pores are blocked by fine particles. The blocking model is expressed by an Equation which relates filtration time, t, and cumulative permeate volume, V:

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \left[\frac{s}{m^3}\right] \qquad [5]$$

In Equation 5, k is the resistance coefficient while n is the blocking index related to the fouling mechanism: n = 2 for complete blocking, n = 1.5 for standard blocking, n = 1 for an intermediate blocking, and n = 0 for the cake filtration.

The blocking mechanisms that might take place in MF and UF are illustrated in Figure 7.
The different blocking modes often coincide (Huang et al. 2007) and the fouling mechanism may change from one to another.

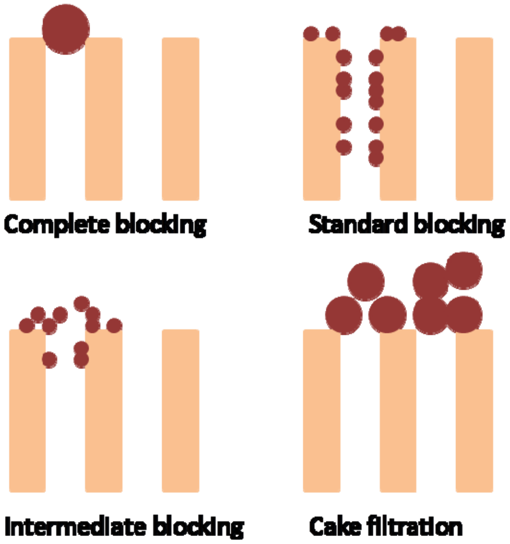


Figure 7: Illustration of membrane fouling mechanisms in MF and UF filtration adapted from (Ruohomaki and Nystrom 2000).

Complete blocking takes place when the particle arriving at the membrane surface is of approximately the same size as the membrane pores and plugs it without accumulation of particles on top of each other or on the solid area between the pores (Aoustin et al. 2001). If particle accumulation in addition to pore plugging takes place, it is recognised as intermediate blocking or long term adsorption. Standard blocking, or direct adsorption, is the deposition of particles at the internal pore walls which gives a reduction in the effective pore diameter of the membrane. This mechanism may take place if the particles have a smaller diameter than the pores. Finally, cake filtration is a fouling mechanism that doesn't involve any changes in the pore structure of the membrane. Particles bigger than the pore diameter are retained by sieving and will form a cake on the surface of the membrane which is already covered and blocked by other particles.

In the case of drinking water filtration by low pressure membranes, fouling by particulate and dissolved material may be due to different fouling blocking mechanisms (Howe and Clark 2002). Dissolved material, which is the part of the material that passes a filter with a pore size in the range of 0,2-0,45 µm (Eikebrokk et al. 2006), is claimed to foul the membrane depending on its shape and size relative to the membrane pores. Some are very small and will adsorb within the pores, while others are larger and will therefore result in plugging of the pores or surface cake formation. Particulate matter, however, is too big to penetrate the pores of MF and UF membranes, hence fouling is associated with surface cake formation only (Schäfer 1999; Howe and Clark 2002). Surface cake formation gives rise to an increased resistance related to the permeability of the surface cake, while material that adsorbs within the membrane pores gives an increased resistance as a result of reduction of the effective pore diameter.

How the fouling mechanisms change from one to another will be discussed in greater detail later in the report.

2.3.2 Membrane surface characteristic

The membrane surface characteristics determine the properties associated with the membrane, e.g hydrophilicity, surface charge, binding affinity for solutes or particles, etc. (Zeman and Zydney 2006). Knowledge about certain membrane characteristics is therefore necessary in order to be able to analyse fouling mechanisms taking place during membrane filtration.

2.3.2.1 Hydrophobicity

Hydrophobicity is expressed by the water contact angle, which varies depending on the interfacial tension of the membrane-water interface (Li 2008). A membrane surface is characterized as being hydrophilic if it exhibits a water contact angle close to zero. The smaller the contact angle, the more hydrophilic is the membrane, while a water contact angle close to or above 90° is characteristic for a hydrophobic membrane (Zeman and Zydney 2006). This is indicated in Figure 8.

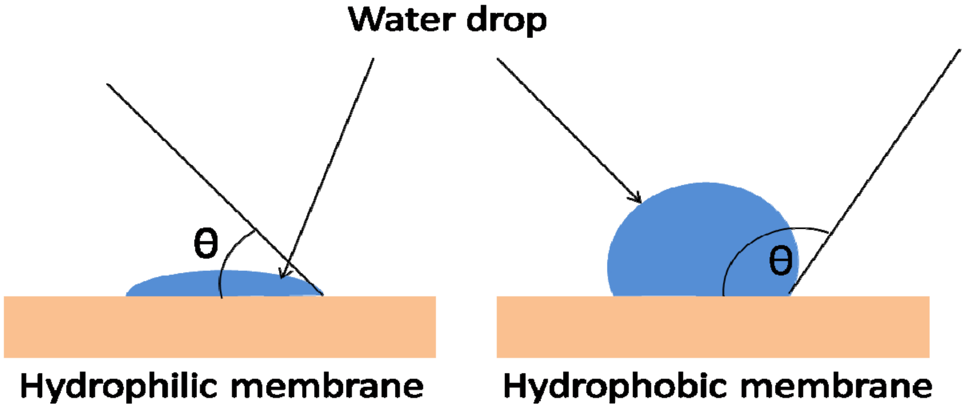


Figure 8:Contact angle is an expression of the hydrophobicity of a membrane.

Membranes may have attractive or repulsive response to water depending on the composition of the material. Hydrophilic membranes are water attracting due to a high surface tension which enables hydrogen-bonding with water, while hydrophobic membranes are water repelling (Filtration Solutions, Inc. 2000). The fouling potential of hydrophobic membranes is high because of the binding affinity to particles of hydrophobic character (e.g. proteins and humic substances), which is a result of the tendency of particles to attach to any material less hydrophilic than water. Membrane fouling may therefore be prevented by having membranes with a surface chemistry that prefers binding to water over particles, i.e. hydrophilic membranes.

The degree of hydrophobicity is commonly estimated by the sessile drop method using a goniometer (Li 2008).

2.3.2.2 Surface charge

The surface charge of a membrane is expressed by its zeta potential. The zeta potential is the electrical potential at the surface of shear between the solid and the liquid, and is typically in the range of approximately -50 to 40 mV (Zeman and Zydney 1996).

Depending on the surface charge, the character of the membrane-liquid interface changes and will affect the filtration properties and the fouling of the membrane (Li 2008). It is possible to take advantage of electrostatic repulsion between particles in the feed and the membrane of the same charge. Due to phenolic and carboxylic functional groups, NOM is negatively charged at neutral pH and rapid fouling by NOM is therefore prevented by modifying the membranes to carry a negative charge.

The most utilized method for determination of the zeta potential of a membrane is by streaming potential measurements (Li 2008).

2.3.2.3 Pore size and nominal molecular weight cut off

Membranes with a certain pore size were previously presented to give an absolute cut-off of particles of a certain size relative to the membrane pore size. However, this is a simplification as the pores in reality are not perfect parallel cylindrical capillaries like the model description. See Figure 9.

Figur 9: (a) Modelled pore structure, (b) actual pore structure (Mulder 1996).

UF membranes are frequently characterized by nominal molecular weight cut off (MWCO) rather than pore size. The MWCO is a performance-related parameter and it refers to the molecular mass of the particles retained by the membrane (Mulder 1996). However, MWCO may be a misleading indication of UF membranes' ability to remove a given compound. The molecular shape of compounds having the same molecular weight does not necessarily correlate, and hence affects the retention. The particle size used for the rating of MF membranes is also misleading since a particle is hardly described by a single parameter unless its geometry is very simple. Hence, the use of pore size and MWCO to describe the retention in MF and UF respectively is inadequate (Zeman and Zydney 1996).

Additional effects of membrane-solute interactions should be considered at the same time as pore size and MWCO in order to be able to determine the expected removal of compounds in the feed by the membrane (Zeman and Zydney 1996). These additional effects are electrostatic interactions, dispersion forces near the pore wall and hydrophobic bonding (Taylor and Wiesner 1999).

2.3.2.4 Clean water permeability

An important indicator of the functionality of a MF and UF membrane is its clean water permeability or membrane resistance, R_m (Zeman and Zydney 1996). It is often included in models for determination of the rate of fouling of membranes and is therefore essential to identify.

The R_m parameter is valid for ideal membranes and feed solutions, and is expressed by Darcy's law presented earlier by Equation 2.

The value of R_m for new membranes may vary as much as ±20-25%, simply because of manufacturing differences, variations in measurement techniques etc. (Cheryan 1998). The clean water permeability is therefore normally not provided for a particular membrane and must be determined manually. It is important to keep good control on the temperature during determination of R_m in order to be able to correlate the viscosity which is included in Darcy's law.

2.3.3 Hydraulic configuration

Submerged membranes are mostly operated in dead-end mode when applied to low solids feed, e.g. NOM removal in drinking water (Li 2008). Dead-end mode allows particle deposition on the membrane surface to grow, and a significant increase in TMP develops when operated at constant flux. Membrane fouling is controlled by a short periodically backwash, thus the energy consumption is reduced to a minimum of what is associated with cross-flow filtration.

Cross-flow filtration applies a continuous shear stress to the membrane surface in order to reduce the rate of fouling. It is therefore associated with high energy costs and is typically applied when having high solids feed (Membrane bio reactor)(Li 2008). Figure 10 shows the two ways to operate a filtration experiment. The graphs in the Figure illustrate the reduced flow in water through the membrane (i.e. flux, J) observed when operating at constant TMP, a result of fouling.

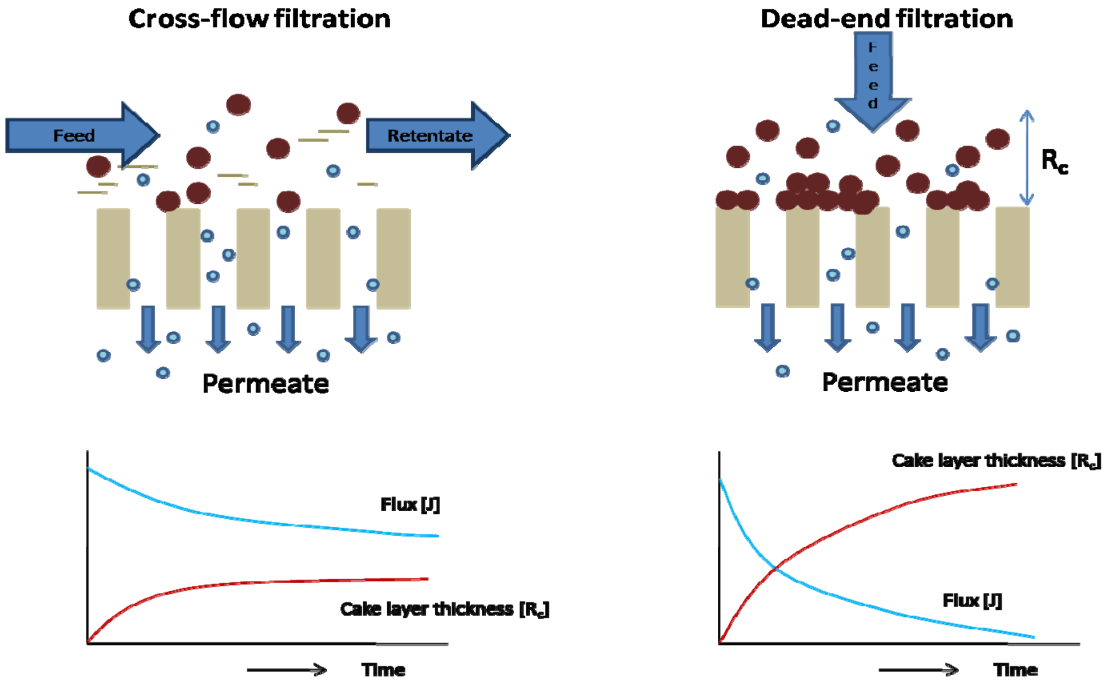


Figure 10: Difference between cross-flow and dead-end hydraulic configuration in membrane filtration. The accumulation of particles at the membrane surface is higher in dead-end mode than cross-flow mode and gives rise to a more rapid flux decline during filtration

2.4 Membrane fouling by NOM

Natural waters contain to some extent natural organic matter originating from vegetation, soil, wastewater, agricultural return etc. The content and composition in natural waters is hence very site-specific and dependent on the external environment. It has a tendency to affect the water quality negatively which makes its presence and relevance very important to water treatment operators (Fabris et al. 2008). Some of the concerns associated with NOM is listed by Eikebrokk et al. (2006):

1) Affects organoleptic properties of water (colour, taste and odour)

2) Reacts with disinfectants used in water treatment, thus reducing their disinfection power and forming disinfection by-products such as thrihalomethanes

3) May control the disinfectant demand and disinfection process design, operation and maintenance

4) Affects stability and removal of inorganic particles

5) May control the coagulant demand, - conditions and - performance

6) Affects corrosion processes

7) Can act as a substrate for microbial regrowth and hence affect the biostability in the distribution systems

8) Forms complexes with and increases mobility of chemical substances found in nature

9) Fouls membranes

10) Reduces the absorption capacity of activated carbon by pore blocking and competes with taste and odour compounds for available adsorption sites

The material referred to as NOM represents a diversity of particulate and soluble compounds of different molecular weight (MW) and functional groups (Zularisam et al. 2006).

Depending on their chemical properties NOM is commonly divided into two groups consisting of substances of different character: humic- and non-humic substances (Fabris et al. 2008; Fan et al. 2001).

2.4.1 Humic substances

Humic substances are a complex mixture of hydrophobic fractions of higher MW. The hydrophobic fractions are humic acid (HA), fulvic acid (FA) and humin. They are aromatic and aliphatic components with mainly carboxylic ($COOH^-$) and phenolic (OH^-) functional groups

(Fan et al. 2001). HA is the part of the humics that precipitates in acidic environment (pH 2 or less), FA remains in solution at acidic pH (pH 2 or less), whereas humin is insoluble in water at any pH (Thurman 1985). The high number of charged groups associated with humic substances gives rise to strong intramolecular repulsion.

Humic substances are the parts of NOM mainly responsible for the colour in natural waters (Fan et al. 2001). The colour is a result of the aromatic content and C=C bonds associated with the compounds. They are large, negatively charged molecules which makes them act like negatively charged colloids in water. They also tend to bind heavy metals and inorganic micro pollutants.

NOM is typically dominated by humic substances which constitutes up to 50% of the dissolved organic carbon (DOC) in natural waters. However, the amount of HA may increase to 90% in coloured surface waters (Thurman 1985). Further, the majority of HA in coloured surface waters is represented by FA (approximately 85-90%) The latter is probably due to its high solubility, caused by a high carboxyl and hydroxyl content and also because of its low MW compared to the other humic species. Both indicated in Figure 11 below.

Thorsen (1999) claims fulvic and humic acid has an average MW in the range of 300 – 10000 and 25 – 50000, respectively. Thurman (1985) however, states FA is associated with dissolved humic substances with an average MW in the range of 500 -2000, while HA is in the colloidal size range of 2000 – 5000, although sometimes higher than 100 000. FA is by Machenbach (2007) reported to be less than 2 nm in size, while HA has a much wider size distribution.

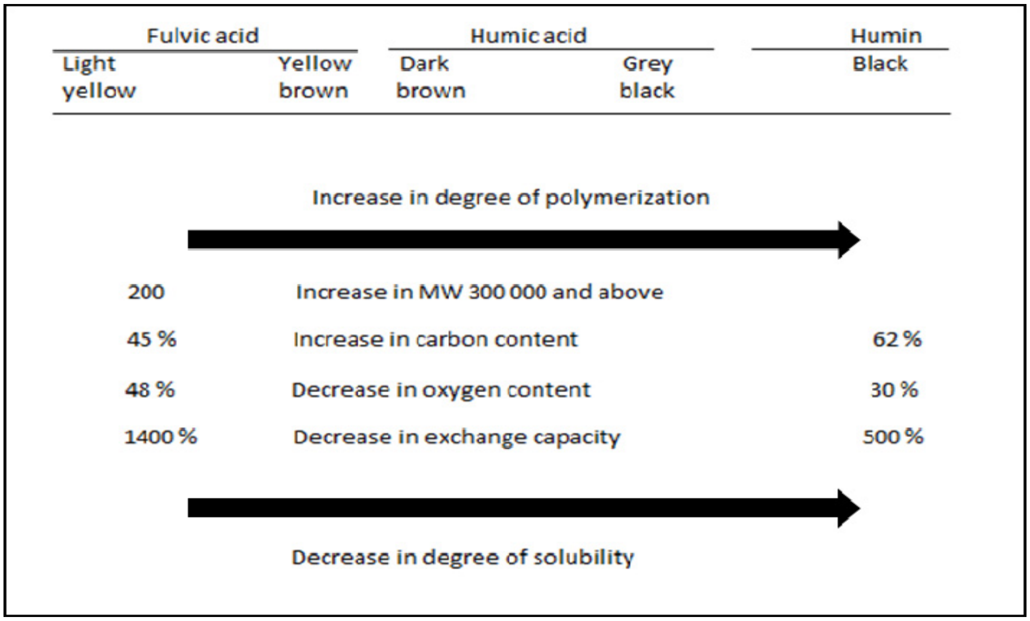


Figure 11: Chemical and physical characteristics of humic substances (Zularisam et al. 2006).

Table 1 summarizes the general properties of humic substances.

Table 1: General properties of humic substances.

Properties	Characterization
MW	High
Structure	Aromatic, double bonding
Charge	Negative at normal pH
Adsorbance	High
Complexation	Complexes with many compounds

2.4.2 Non-humic substances

Non-humic substances comprise hydrophilic and transphilic fractions of relatively low MW including transphilic acids, proteins, amino acids, carbohydrates etc (Fan et al. 2001).

The hydrophilic and transphilic compounds count for approximately 25-40% and 25% of the DOC in natural waters, respectively. The hydrophilic compounds are of low molecular weight compared to both transphilic and hydrophobic (humic substances) fractions, whereas the transphilic fraction has a MW in between hydrophilic and hydrophobic (Zularisam et al. 2006). Although non- humic substances seem to include smaller molecules than humic substances, they are also associated with very big molecules of polysaccharides and proteins with MW above 50000 (Thorsen 1999).

2.4.3 Solution chemistry

pH, ionic strength and NOM bulk concentration has an impact on the observed charge, molecular weight distribution and apparent size of natural organic substances in natural waters (Braghetta et al. 1997; Thorsen 1999). This is related to the high numbers of charged groups of the humic part of NOM, of which the most important are carboxyl (COOH), and, at higher pH, phenol (OH).

The density of ionized COOH and OH increases with pH and gives rise to strong intramolecular repulsion in the water. Opposite is a decrease in pH in general, synonymous with a change towards less negative charge and therefore less repulsion (Thorsen 1999).

These observed changes associated with pH in the water leads to more or less compact molecular configurations.

Braghetta et al. (1997) presents two hypothetical endpoints for humic NOM macromolecular configuration which depends on pH, ionic strength and organic bulk concentration. These are:

a) A rigid, compact, spherocolloidal macromolecule which is a result of high ionic strength, low pH and high bulk concentration. Cations distribute along the molecule and neutralize functional groups by intramolecular charge shielding which makes the organic molecule curl (Figure 12 (b)).

b) A flexible linear macromolecule which is a result of very low ionic strength, high pH (6,5 -9,5 (Aoustin et al. 2001)), low bulk concentration and hence high intramolecular repulsion (Figure 12 (a)) and

The more compact molecular configuration of humic substances at high ionic strength gives rise to a higher molecular weight distribution compared to the more linear configuration at low ionic strength (Aoustin et al. 2001). The charge densities of the different NOM fractions also tend to affect the coagulant demand when coagulation is applied as pre-treatment of the feedwater (Eikebrokk et al. 1996).

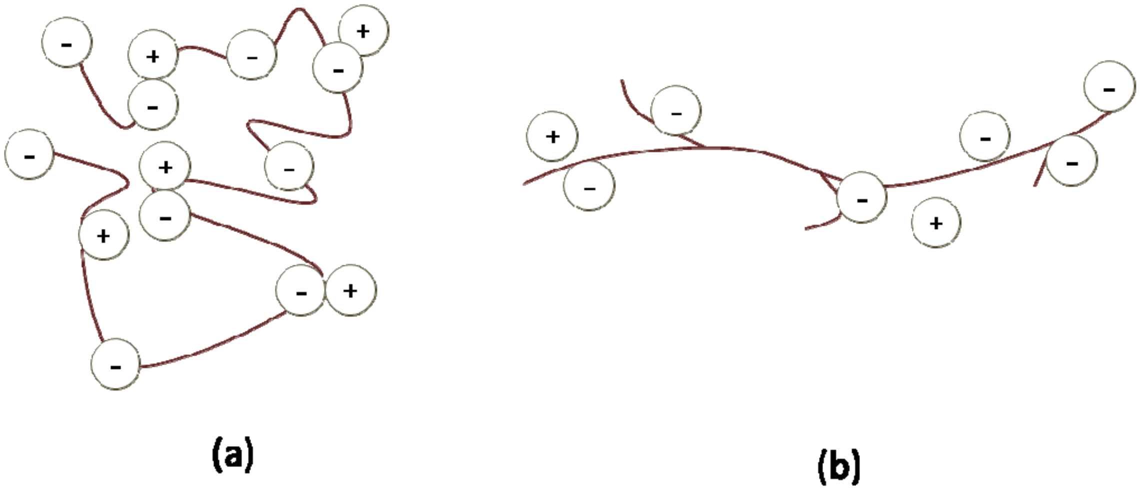


Figure 12: Sketch of hypothetical macromolecular configuration endpoints of NOM. (a), is the result of high intramolecular repulsion, while, (b), is the result of charge shielding and thereby low intramolecular repulsion.

2. 5 MF and UF pre-treatment

2.5.1 Pretreatment options

Drinking water treatment with respect to NOM by UF and MF membranes requires a certain level of pre-treatment of the feed water. Pre-treatment enables fouling control and thus a more economical sustainable operation of the system (Li 2008). Norman presents a variety of pre-treatment methods in use for low pressure membranes:

- coagulation
- PAC treatment
- coagulation+sedimentation
- coagulation+PAC
- preflocculation
- magnetic ion exchange (MIEX)

Coagulation is well suited for NOM removal due to the charge and colloidal properties associated with NOM (Ødegaard et al. 2010). Conventional coagulation followed by floc separation by granular media is probably the most common method for NOM removal. The use of MF and UF membranes as a replacement for granular media, however, is a process which has been studied less thoroughly (Li 2008). It was therefore in the interest for these studies to get a better understanding of coagulation as pre-treatment for NOM removal in low-pressure membrane systems. Due to the high NOM content (> 50 mg Pt/L), flotation was included in the pre-treatment as a pre-separation step (Ødegaard et al. 2010).

2.5.2 Coagulation/flotation

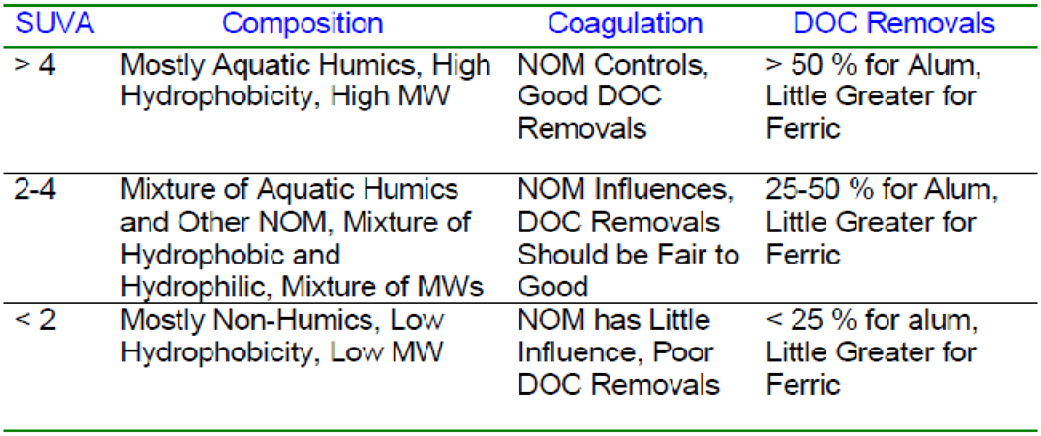
The large number of carboxylic groups associated with the humic part of NOM enables complexation reactions by addition of metal-ion-based coagulants. The complexation is followed by a phase change which reduces the NOM concentration of the feed water by forming a solid or adsorbing onto a solid (Eikebrokk et al. 2006). Flotation separates the precipitated complexes and the water containing less organic material is fed to the membrane for filtration (Maartens et al. 1999).

The properties and composition of NOM influences the treatability by coagulation. The coagulation of NOM by iron- and aluminum based coagulants, the latter being used in the filtration experiments in this study, has shown good removal efficiencies of higher molecular weight humic substance, while smaller sized hydrophilic NOM has been more difficult to remove. Low removal efficiency of the neutrals is claimed to be a result of its negligible charge density (Eikebrokk et al. 2006). The removal tendencies when using aluminum-based coagulants are in general hydrophobic rather than hydrophilic, charged rather than neutral and larger rather than smaller sized (Carroll et al. 2000).

Solution chemistry , coagulant dosage and the presence of particles other than NOM are also important for the treatment result. Optimum pH and coagulant dose is determined by a Jar-test (Eikebrokk et al. 2006).

Specific UV-absorption (SUVA) is a characterization method for raw water and is defined as "UV absorbance at 254 nm (1/m) divided by the concentration of dissolved organic carbon (mg C/L)" by Eikebrokk et al. (2006, p. 8). It correlates well with the aromaticity and the hydrophobicity of NOM and is therefore a method for estimating the removal efficiency of NOM by coagulation. As indicated in Table 2, high SUVA means high aromaticity or hydrophobicity of samples in the limited DOC and good removal efficiency with respect to NOM is expected. The Table is generated by Edzwald and Tobiason (1999) and shows the anticipated correlation between SUVA number and treatability of NOM.

Table 2: SUVA number and NOM treatability.



SUVA	Composition	Coagulation	DOC Removals
> 4	Mostly Aquatic Humics, High Hydrophobicity, High MW	NOM Controls, Good DOC Removals	> 50 % for Alum, Little Greater for Ferric
2-4	Mixture of Aquatic Humics and Other NOM, Mixture of Hydrophobic and Hydrophilic, Mixture of MWs	NOM Influences, DOC Removals Should be Fair to Good	25-50 % for Alum, Little Greater for Ferric
< 2	Mostly Non-Humics, Low Hydrophobicity, Low MW	NOM has Little Influence, Poor DOC Removals	< 25 % for alum, Little Greater for Ferric

2.6 Previous work and observations

2.6.1 NOM foulants

Low pressure membranes applied in drinking water treatment are known to experience a rapid flux decline due to fouling by NOM. Several studies have tried to identify the NOM components being mainly responsible for the fouling during membrane filtration. The results however are very confusing and conflicting.

Many researchers have identified the humic part of NOM as the major foulant during membrane filtration. Nilson and DiGiano (1996) reported the hydrophobic fraction of NOM as the main reason for the permeate flux decline compared to hydrophilic NOM during nanofiltration of a hydrophilic membrane. Filtration experiments conducted by Jucker and

Clark (1994) using hydrophobic UF membranes showed irreversible fouling was caused by HA rather than FA. This was claimed to be caused by the lower solubility of humic acid and also its higher binding affinity to the membrane because of more attachment sites.

Other researchers have found that low UV absorbing, higher molecular weight hydrophilic neutrals are the major NOM foulants (Lee et al. 2004; Carroll et al. 2000). Studies were conducted on hydrophobic low pressure MF and UF membranes and they showed the same results. Cho et al. (2000) and Fan et al. (2001) reported the order of fouling potential of the different NOM fractions as hydrophilic neutrals>hydrophobic acids>transphilic acids/slightly hydrophobic acids>charged hydrophilics. Fan et al. (2001) claimed the mechanisms which caused favorable fouling by the neutral fraction were a combination of adsorption of small molecules on the membrane porewall and pore blockage by larger colloidal organics (>30 kDa) within the membrane pore structure. The favorable fouling of hydrophilic neutrals was by Cho et al. (2000) concluded to be a result of its bulky macromolecular shape and neutral character, which allows it to adsorb onto negatively charged membranes.

Howe and Clark (2002) identified organic and inorganic colloids in the size range of 3-20nm as being the main foulants during low pressure membrane filtration. They stated that the physical dimension of the water components is the decisive factor for their tendency to foul the membranes. Molecular matter less than 3kDa was recognized as being too small to cause significant fouling, whereas particulate matter bigger than 0,20µm was too big to penetrate the pores and will therefore form a reversible cake on the membrane surface.

Other studies have revealed that the presence of inorganic particles to a great extent affect the fouling tendency of membranes. An increased concentration of calcium gave rise to an increased fouling rate in experiments conducted by Hong and Elimelech (1997) and Gosh and Schnitzer (1980). This phenomenon has been explained by a decrease in the electrostatic repulsion between the charged humic acids and the membrane when calcium is present, a phenomenon that becomes even more evident at decreasing pH and high ionic strength. Calcium is considered to act as bridge between the negatively charged membrane surface and the negatively charged functional groups of the humic part of NOM; hence an increased adsorption takes place on the membrane surface and causes fouling (Combe et al. 1998).

Several authors have reported relatively good results with respect to membrane performance after coagulation pre-treatment. Lahoussine-Turcaud et al. (1990) found that coagulation pre-treatment of river water using a hydrophobic polysulfone UF membrane reduced the short-term reversible fouling, while the rate of irreversible fouling was unchanged. They claimed the irreversible fouling was caused by "the hard to remove low MW polysaccharides", while the higher MW NOM often associated with reversible fouling was removed by pre-treatment. Carroll et al. (2000) applied coagulation pre-treatment before filtration through a MF membrane which resulted in a significant decrease in the rate of fouling. Pre-treatment by adsorption however did not give any remarkable results, and is the reason why colloidal NOM rather than dissolved NOM was claimed to be determining for the rate of fouling.

On the basis of previous studies by several researchers, it can be concluded that the influence of the properties of NOM and submicron particles on fouling is not well understood.

2.6.2 Models to predict membrane fouling

It is evident that the phenomenon of fouling is very complex, depending on both the physical and chemical characterization of the feed water and the membrane, but also the hydraulic configuration applied. Several models to predict membrane fouling has been proposed the last thirty years applied to different situations, among them are: Concentration polarization models, hydraulic models and blocking models (Hwang and Chen 2009).

Huang et al. (2007) developed a unified model expression based on the blocking model by Hermia (1982) presented in section 2.3.1.2 (Equation 5). The researchers modified the blocking model to be applicable to low pressure, constant flux filtration. They arrived at the expression seen in Equation 6:

$$\frac{dP'}{dV_s} = k_v P'^{n} \quad \left[\frac{Pa}{\frac{L}{m^2}} \right] \qquad [6]$$

In Equation 6, V_s is the unit permeate throughput (L/m^2), P' [Pa] is the normalized transmembrane pressure, and k_v is a fouling parameter which depends on the foulant concentration in the feedwater.

When having feed water dominated by particles hydrodynamic forces are expected to dominate over diffusive effects (Broeckmann et al. 2006). Concentration polarization control through back diffusion and osmotic effects may in those cases therefore be neglected and the fouling observed during filtration is represented by the blocking models. However, as NOM is a mixture of compounds ranging from ~1nm to more than 1000nm in hydraulic diameter (Thorsen 1999), diffusive effects may become significant during MF and UF filtration of NOM. The equation for concentration polarisation has been presented earlier in section 2.3.1.1, Equation 4.

3. Methodology

3.1 Experimental setup

3.1.1 Raw water

Raw water utilized in the membrane filtration experiments was prepared using NOM concentrate from a local full-scale ion exchange treatment plant by mixing the concentrate into tap water. The raw-water was constructed to represent typical Norwegian surface water. The composition of the raw water is shown in Table 3.

Table 3: Raw water characteristics.

Parameter	Unit	Value
pH	-	6*
Colour	mg Pt/L	42,7 ± 0,5
UV_{254}	m^{-1}	1,42 ± 0,02
DOC	mg C/L	6,78 ± 0,48
TOC	mg C/L	6,90 ± 0,45
SUVA	$m^{-1}mg^{-1}L$	0,209

* The pH of the raw water was 8,75 in the MF raw water experiments

3.1.2 Coagulant

Aluminum sulfate (ALS) was used as coagulant throughout the study. A 0,5% stock solution of the coagulant was prepared by adding 89,45 ml ALS to one liter of milli-Q water. See appendix A and B for coagulant specifications and calculations.

3.1.3 Jar –test protocol

Optimum coagulant dose necessary for NOM removal was determined using a Aztec flotation 4-jar test unit. Different doses of coagulant were added to 1-L jar-test beakers at optimum pH to determine the colour removal and the zeta potential of the formed particles. pH 6 was chosen as optimum pH for ALS coagulation in this study (Vik et al. 1985). Acid (1 M HCl) or base (1 M NaOH) were added to keep the pH sTable during the jar test since the effectiveness of the coagulation process is known to be highly dependent on the pH (Chow et al. 2004).

The paddle speed program was set to 200rpm in 60s for rapid mixing followed by a 10 min slow mixing at 80rpm. The flocculation speed was determined in terms of its G-value which was ~105sec and ~47sec for the rapid and slow mixing respectively (Severn Trent Services 2000). This gives Gt values for the rapid and slow mixing in the range of what has been recommended by Droste (1997). Coagulant was added by a dosing bar in the early phase of the rapid mixing to ensure rapid dispersion of the chemical. This is in accordance with the operator and technical manual for the flotation jar test unit (Severn Trent Services, 2000). A flotation step with 10% of recycling and pressure of 5,5 bar was subsequently provided, and samples were finally withdrawn for colour analysis and zeta potential measurements to determine optimum coagulant dose.

3.1.4 Membranes (MF and UF)

Three types of low pressure flatsheet membranes of different characteristics were evaluated in the experiments. These were a hydrophilic MF membrane and two hydrophobic UF membranes. The membrane specifications are shown in Table 4. The pore size of the membranes was found from the manufactures (Millipore and KOCH membrane systems) while the contact angle of the UF and MF membranes were adopted from Shon et al. (2009) and Clarke et al. (2002), respectively.

Table 4: Membrane specifications.

Membrane type **Membrane code**	**UF** **HFM-100**	**UF** **HFM-180**	**MF** **MF-Millipore**
Pore size/MWCO	50kDa	100kDa	0,1 µm
Membrane material	PVDF	PVDF	Mixed Cellulose Esthers
Hydrophilicity	Hydrophobic	Hydrophobic	Hydrophilic
Contact angle	94,2	92,4	38,9

3.1.5 Filtration protocol

-*Start-up considerations:* In order to operate the filtration experiments at a flux above which fouling occurred, critical flux, J_c, of the MF and UF membranes was determined prior to a filtration experiment. Critical flux has already been defined as “the flux below which a decline of flux does not occur; above it fouling is observed” (Field et al. 1995).

There are different methods available for determination of critical flux (Gugliemi et al. 2007; Le-Clech et al. 2003). In this work the flux step method proposed by LeClech in which critical flux is taken as the maximum flux at which the permeability decreases below 90% of the permeability for the first time step was applied. A step duration of 15 minutes and incremental flux increases from 5 - 105 $lm^{-2}h^{-1}$(lmh) and 20 – 190 lmh where applied to determine the critical flux of the MF and UF membranes respectively.

- *Membrane module:* The membrane module was build as a plate-and-frame module system with a total effective membrane surface area of 0,013 m^2.

- *Filtration configuration:* A flat sheet configuration was utilized in the experiments. The schematics of the filtration setups are shown in Figure 13. Submerged filtrations were performed in a membrane reactor tank of approximately 40 L.

The MF filtration experiments were run at two different fluxes when applied to raw water, whereas one flux, 110 lmh, was applied for the flotated raw water. The UF filtration experiments were run at 80 lmh when applied to both raw water and flotated raw water. The idea was to run the filtration experiments at different fluxes in order to observe its effect on fouling. However due to time constraints, this was only done for the MF raw water filtration experiments .

The filtration experiments were conducted at constant flux maintained by a peristaltic effluent pump (Masterflex L/S) and were run for 24 hours. The pump was set to operate at a maximum TMP of 0,8 bar. Raw water or flotated raw water (depending on the experiment) was fed to the membrane reactor by a raw water pump (Heidolph Pumpdrive 5201). The TMP and temperature were monitored during the experiments using a pressure transucer and a temperature transducer both connected to a computer. Lab view 8.2 was used for data acquisition and monitoring, whereas Win Link 2.0 was used for effluent pump control. Samples of the permeate were collected approximately every 6th hour during each experiment, while one raw water sample was collected prior to each experiment. Depending on the filtration experiment (with or without pre-treatment), a 6th sample was collected from the pretreated raw water.

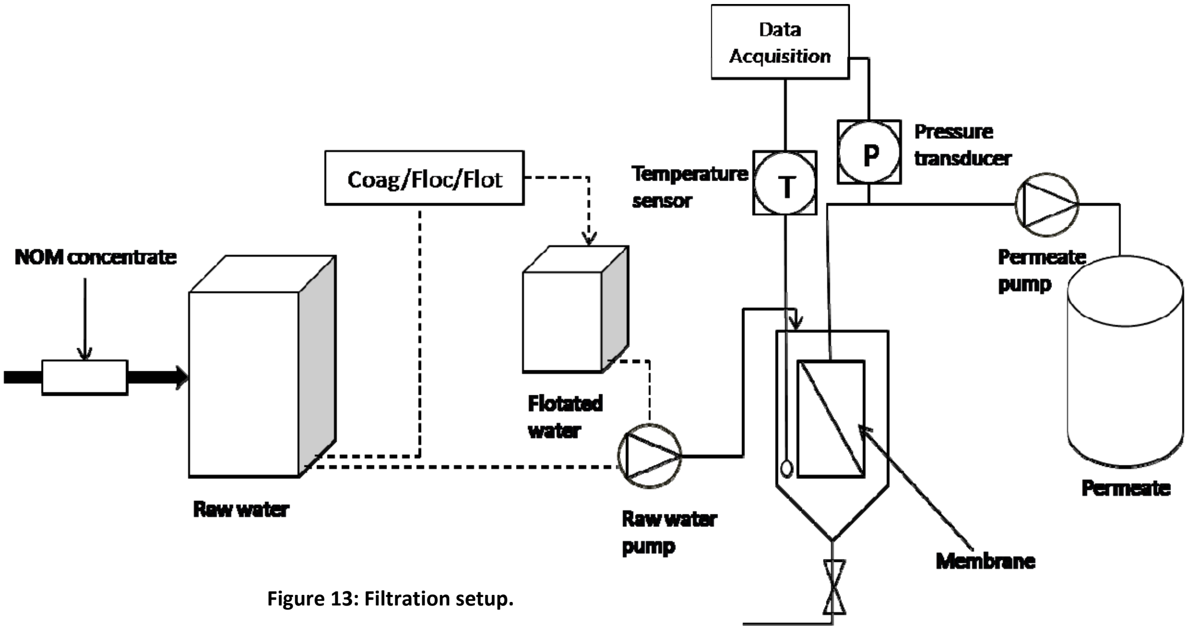


Figure 13: Filtration setup.

3.2 Analytical tools

3.2.1 Treatment efficiency

Due to the polydispersity, heterogeneity, spatial and temporal variability of NOM described earlier, it is essential to use several analytical tools to characterize the water with respect to NOM. This reveal much information about NOM as possible as well as ensuring reliable results.

The treatment efficiency and major foulants during filtration of typical Norwegian surface waters by low pressure submerged membranes has been identified. This was done by measuring colour removal, UV_{254}-absorbance, charge, size and hydrophobic/hydrophilic NOM content of the samples collected during the filtration experiments. Analysises were conducted on samples from the feed water, the desorbed membrane and the permeates, all at pH 6, unless otherwise stated by the protocols. Analysises with respect to UV_{254}-absorbance, charge and size were only conducted on samples collected from the UF experiments, whereas analysises with respect to hydrophobic/hydrophilic NOM content were conducted on samples from all experiments.

3.2.2 Colour and UV_{254}-absorbance

NOM has, in contrast to inorganic material, properties which enable adsorption of visible light and UV light over a wide range of wavelengths. This correlation makes colour and absorbance of UV light a good method for identification of the concentration of NOM in natural waters (Eikebrokk et al. 2006). True colour and UV-absorption were determined by a Hitachi U-3000 UV–vis spectrophotometer and according to Norwegian standards (NS 4787 and NS9462, respectively).

The true colour of a sample is a measure of its DOC content. By comparing the DOC content in the feed water and the permeate, valuable information about the treatment efficiency with respect to DOC is obtained. The sample was passed through a 0,45µm filter prior to analysis and the colour was determined by measuring the absorbance at 410nm using a 50mm quarts cuvette. The results are given in Mg Pt/l.

The UV absorbance of NOM at 254nm is sensitive to aromatic content, properties subscribed to the humic- and fulvic part of NOM as discussed earlier. By measuring the UV_{254}-absorbance it is therefore possible to identify whether or not the hydrophobics are part of the major foulants. The UV_{254}-absorbance was measured using 50mm a quarts cyvette. The results are given in absorbance/5 cm which is converted to absorbance/m for the reporting. Specific ultraviolet absorbance (SUVA) has been defined in previous chapters as the ratio of UV at a wavelength of 254nm and DOC and has been used to determine the hydrophobicity of the samples.

3.2.3 Charge

Various NOM fractions exert different charge densities. Therefore, by measuring the zeta potential of the water prior to and after a filtration experiment, information about the fouling mechanisms taking place is obtained. Zeta-potential was analyzed by Coulter DelsaNano HC.

3.2.5 Hydrophobic/hydrophilic NOM content

A fractionation technique to characterize the water with respect to NOM has been conducted. Rapid fractionation is one technique which has been developed to enable a better understanding of the types of organic compounds present before and after treatment of water. It gives a characterization of NOM by grouping the NOM into a limited set of categories (fractions) (Croue et al. 2004). Although NOM comprises thousands of distinct chemical components, sub-groups of NOM tend to share some common features as indicated earlier with the classification of NOM into humic and non-humic substances.

The separation mechanisms involved in the fractionation may explain certain aspects of the physical and chemical properties of NOM. The technique distinguish four different NOM fractions, i.e. very hydrophobic acids (VHA), transphilic acids/ slightly hydrophobic acids (SHA), hydrophilic charged (CHA) and hydrophilic neutral (NEU) (Chow et al. 2004).

CHA is a mixture of proteins, amino acids and anionic polysaccharides, whereas the NEU are ascribed to low molecular weight carbohydrates, aldehydes, ketones and alcohols. The VHA and SHA however are attributed to higher MW humic and fulvic acids (Eikebrokk et al. 2006).

Non-functionalised resins adsorb the different fractions depending on the degree of hydrophobicity and charge of the fractions (Carroll et al. 2000). The actual organic carbon concentration of each fraction (mg/l) is determined by measuring the DOC concentrations before and after contact with the different adsorbent resins (Chow et al. 2004). DOC was determined by catalytic wet oxidation (Tekmar Dohrmann Apollo 9000), and the calculations to quantify the concentration of each fractions are:

VHA = Raw – (DAX-8 effluent)
SHA = (DAX-8 effluent) – (XAD-4 effluent)
CHA = (XAD-4 effluent) – (IRA-958 effluent)
NEU = (IRA-958 effluent)

The technique was conducted on both feed water (raw water + pre-treated raw water), permeates and on the desorbed membrane water. The results give a good indication of what particles that: a) are present in the feed water; b) are retained by the membrane; c) are the main foulants; d) passes the membrane without being entrapped. The feed water and the desorbed membrane water were filtered by a 0.45 µm filter prior to the fractionation in order to remove particulate organic carbon (PAC) from the water. The methodology of the technique has been described by Chow et al (2004).

Method

The sample to be fractionated was acidified to pH 2 and fed onto a DAX-8 resin in which VHA are retained. Acidification of the sample ensures complete adsorbance of organic acids. This is because the most efficient adsorbance takes place two pH units below the pKa, which is between 4-5 for organic acids (Thurmann 1985).

Further the unadsorbed concentrate from the DAX-8 resin was fed onto an XAD-4 resin in order to adsorb the SHA (or transphilic acids). The unadsorbed sample from the XAD-4 resin consisting of hydrophilic organics was then adjusted to pH 8 before the sample finally was fed onto an IRA-958 anion exchange resin. The IRA resin retains hydrophilic charged material whereas the unadsorbed, remaining sample consists of hydrophilic neutrals.

The resins were eluted with NaOH or a mix of NaOH and NaCl as part of the cleaning procedure, and the desorbed VHA, SHA and CHA was collected for further analysis. The samples were acidified to pH 2 for storage. A schematic description of the technique is provided in Figure 14 below.

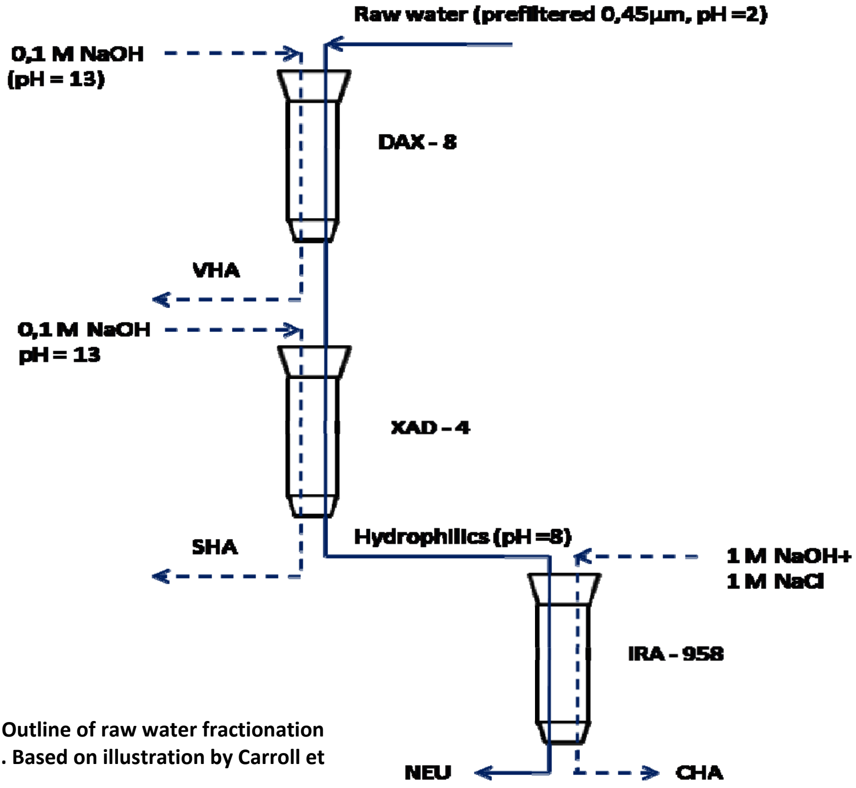


Figure 14: Outline of raw water fractionation procedure. Based on illustration by Carroll et al. (2000).

3.2.6 Fouling rate and fouling mechanisms

The curvefit-tool in matlab was used to calculate the 1st derivative of the TMP as a function of V_s (unit permeate throughput = (time*flux/3600)) to arrive at the best fit line of the TMP plot. The shape of the curve may also tell something about the fouling mechanisms taking place.

4 Results and discussion

4.2 Identification of main NOM foulants and the effect of various operating conditions

Different operating conditions have been applied to the filtration experiments in order to arrive at more sustainable operational modes of membrane filtration of surface water for drinking water production. Time constraint and the great complexness of NOM and membranes have made it difficult to include all aspects. The focus has therefore been on the effect of applying different fluxes, pre-treatment by coagulation/flocculation followed by flotation, and the effect of having membranes of different characteristics (hydrophobicity and pore size).

4.2.1 Effect of flux variations in MF filtration experiments

Figures 15 and 16 show the percentage of DOC removal of the different NOM fractions relative to the raw water during MF experiments operated at flux 110 and 140 lmh, respectively. The Figures also include the relative content of the different NOM fractions to the total DOC in the desorbed membrane. Equation 1 presented in the literature review was applied in the calculations. Negative values are equivalent with no rejection.

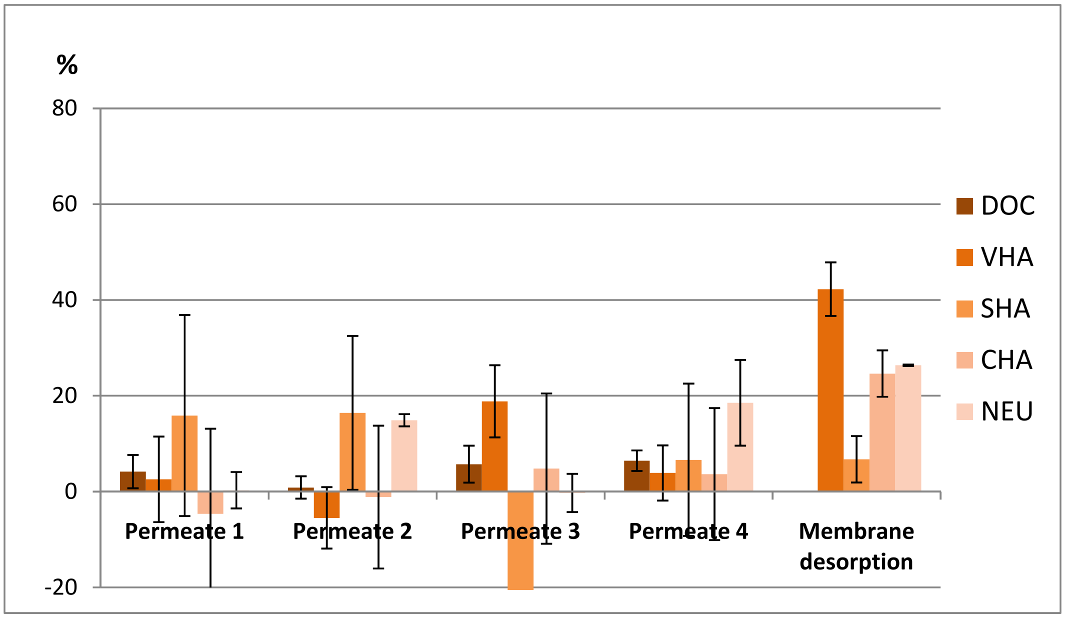


Figure 15: Results of raw water filtration experiment applied to MF membrane operated at flux 110. It shows the NOM fraction rejection in permeate 1, 2, 3 and 4 collected at different time intervals, and the NOM fraction content of the membrane desorption.

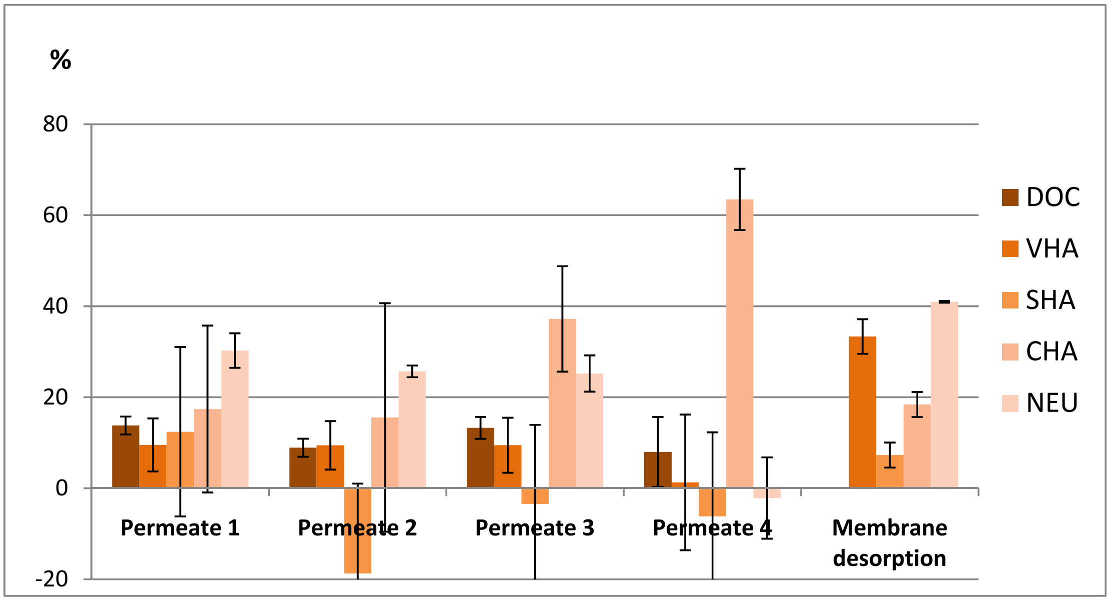


Figure 16: Results of raw water filtration experiment applied to MF membrane operated at flux 140. It shows the NOM fraction rejection in permeate 1, 2, 3 and 4 collected at different time intervals, and the NOM fraction content of the membrane desorption.

The results indicate a more efficient removal of DOC when experiments are operated at 140 lmh rather than 110 lmh. At 110 lmh almost no DOC is being removed, whereas at 140 lmh a removal of roughly 10% DOC is observed during filtration. The increase in removal efficiency at higher flux might be a result of a more dominant concentration polarization mechanism which influences the membrane selectivity.

From what has been discussed in the literature review the applied flux is known to be of high importance with respect to concentration polarization. The higher the flux, the higher is the concentration of solutes accumulating at the membrane surface in accordance with Equation 4 presented earlier, and the effect of concentration polarization will increase. When applying feed water dominated by macromolecules to microfiltration one expects an increase in the membrane rejection to take place (Mulder 1996). That is because the macromolecules accumulating at the membrane surface will act as a second or dynamic membrane giving rise to an increased rejection of the lower molecular weight compounds. The experimental results shows a preferential rejection of the lower MW hydrophilic charged (CHA) and hydrophilic neutrals (NEU), thus confirming this statement. An exception to this statement is permeate 4 at flux 140lmh where no rejection of the NEU has been measured. The result is difficult to explain other than being due to the dynamics of the system or measurement errors.

The solubility of the retained solutes in the concentration polarization layer may be exceeded thereby forming a gel phase at the membrane surface. If that is the case it is expected that the gel layer will exert an additional resistance to the flow of water through the membrane and a higher TMP will be observed during the filtration experiment, especially at flux 140lmh. This is a theory supported by Chang and Benjamin (1996).

Nevertheless, the preferential removal of CHA and NEU is likely to be a consequence of the membrane characteristics.

4.2.2 Effect of membrane characteristics in MF and UF experiments

All samples collected during the filtration experiments were applied to the rapid fractionation technique, while analysis with respect to aromaticity and colour were only applied to the samples collected from the UF experiment. The standard deviation for UV-absorbance and colour was very low and is therefore not included in the graphs showing the results.

4.2.2.1 MF filtration experiments, flux 110 and 140

The results presented in Figures 15 and 16, show a preferential adsorption and fouling by the negatively charged hydrophobic fraction of NOM. This is indicated by the high percentage of VHA represented in the membrane desorption in the Figures. It is found to be the main foulant in the experiments conducted at 110 and the second main foulant in the experiments conducted at flux 140. The fact that VHA is the number one foulant in the filtration experiment operated at flux 110 is an opposing observation since the fraction was subjected to almost no rejection. This might represent a weakness of the fractionation technique, which is by Croue et al. (2000) claimed to never be 100% successful. The same authors mention this to be a consequence of the chemical and physical properties of the fractions which may hinder complete separation, e.g. humic and non-humic fractions forming complexes. In addition is NOM is subjected to extreme pH values that could change its properties. Presuming the results from the fractionation of the membrane desorption are correct, the favorable fouling by VHA may be reasoned by hydrophobic interactions being more dominant than electrostatic repulsion. This statement is reinforced by the fact that the hydrophobic fraction of NOM is the fraction associated with highest charge density (Eikebrokk et al. 2006).

Membranes applied in the industry are modified to carry a negative charge in order to prevent rapid fouling by NOM. That is also the case for the clean MF membranes applied in this study, thus electrostatic repulsion between the negatively charged membrane and the negatively charged NOM is expected. It is also characterized as being hydrophilic in character. However, due to its relatively low hydrophilicity (contact angle 38°) it is known to have hydrophobic spots which will interact with the hydrophobic NOM (Filtration Solutions, Inc. 2000). The membrane is anticipated to have a strong binding affinity to the hydrophobic NOM at these spots due to hydrophobic interactions which in this case seems to be the governing mechanisms that cause fouling.

If hydrophobic/hydrophilic interactions are more dominant than electrostatic repulsion, this may also explain the results showing preferential fouling by CHA compared to SHA, although SHA is more represented in the raw water. Hydrophilic interactions between the hydrophilic charged NOM and the membrane overcomes the electrostatic repulsion, thus, reflecting the importance of hydrophilic interactions.

The results from the rapid fractionation also show a preferential fouling by NEU in the experiment conducted at 140 lmh while it is the second main foulant in the experiment conducted at 110lmh. The hydrophilic neutrals govern the fouling at flux 140, and this corresponds to what was discussed previously, about the increased rejection of NEU due to concentration polarization. The accumulated particles at the membrane surface form a gel layer which is desorbed with the membrane during membrane desorption. The neutral character of the fraction is probably another factor that allows it to adsorb onto the negatively charged membranes.

4.2.2.2 UF filtration experiments, flux 80

It is interesting to observe the results from the UF experiments showing the extent of rejection of the different NOM fractions and which fractions are main responsible to the fouling of the membrane. The results of the HFM 180 filtration experiment, presented in Figure 17, show that a negligible part of the hydrophilic charged fraction fouls the membrane although being rejected by the membrane. This is a different observation from the hydrophilic MF membrane where CHA was a big part of the membrane foulants.

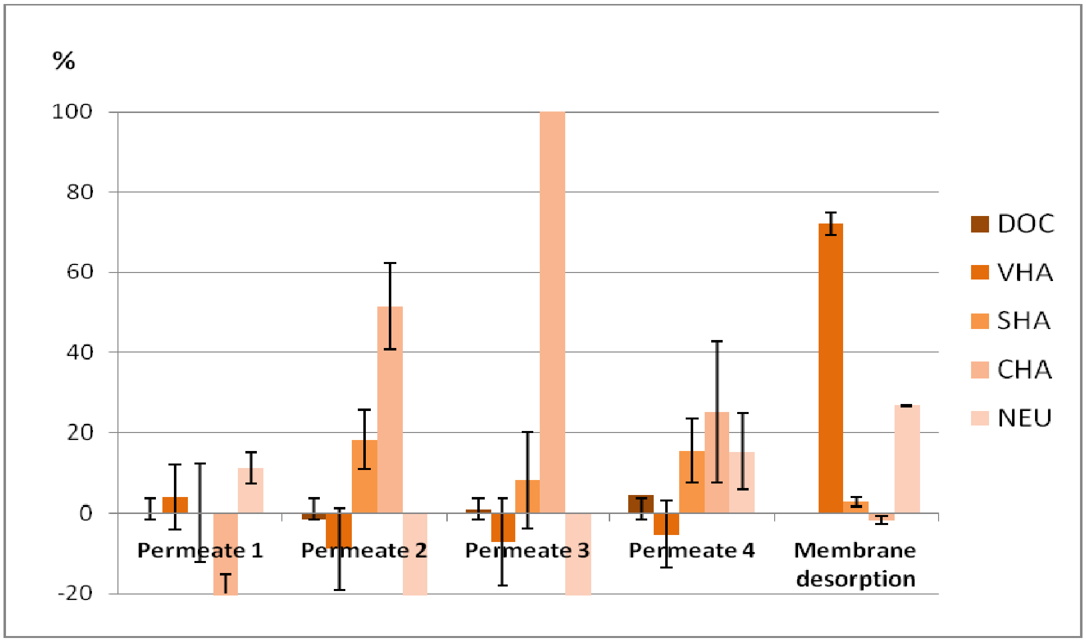


Figure 17: Results of raw water filtration experiment applied to the PVDF HFM 180 membrane. It shows the NOM fraction rejection in permeate 1, 2, 3 and 4 collected at different time intervals, and the NOM fraction content of the membrane desorption.

The UF membranes are hydrophobic in character, and therefore, it was not expected to observe any hydrophobic/hydrophilic interactions between the hydrophilic charged fraction of NOM and the membrane in the UF experiment. The rejection of the CHA observed by the PVDF HFM 180 in permeate 2, 3 and 4 is therefore most likely a result of electrostatic.

The experiment conducted on the HFM 100 membrane shows a different result. In contrast to the filtration experiment with the PVDF HFM180 membrane, almost no rejection of the CHA is observed and more CHA is part of the membrane foulants, although not very significant (~5%). The results are presented in Figure 18.

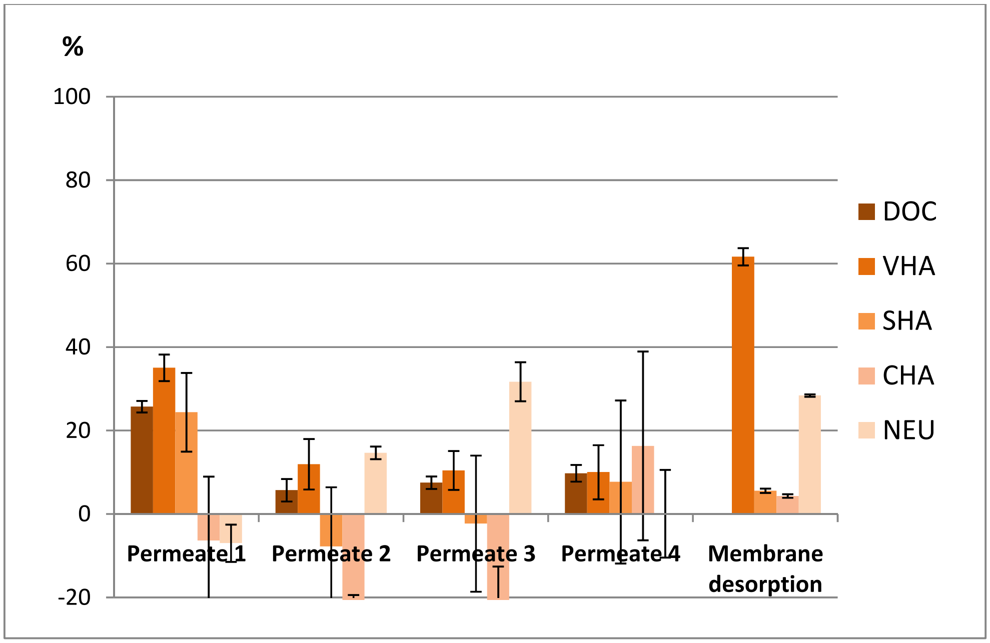


Figure 18: Results of raw water filtration experiment applied to the PVDF HFM 100 membrane. It shows the NOM fraction rejection in permeate 1, 2, 3 and 4 collected at different time intervals, and the NOM fraction content of the membrane desorption.

Such a difference might be related to their different pore sizes. The HFM 100 membrane has pores which are half the size of the HFM 180 membrane. The electrostatic repulsion during filtration by the HFM 100 membrane is, according to McDowell-Boyer (1986), therefore less significant. This may further give rise to a higher fouling potential of the CHA as observed in that more CHA is present in the desorbed membrane in Figure 18.

Both UF membranes is observed to be subjected to fouling in the order of VHA>NEU>SHA>CHA. This is as expected and in accordance with previous studies by Nilson and DiGiano (1996) who reported most of the fouling was caused by the hydrophobic NOM component. This is again most likely due to hydrophobic interactions between the hydrophobic NOM and the hydrophobic membrane. In addition, properties like high aromaticity, adsorbance and MW associated with hydrophobic NOM are probably important.

4.2.2.3 Total DOC removal in raw water experiments of MF and UF membranes

All the filtration experiments show low rejection/removal efficiency of DOC. This correspond with the fact that the membranes have a pore size which in general is much bigger than most of the NOM components, and the NOM may therefore pass the membrane without any size exclusion. Figure 19 below shows the total DOC removal obtained in the raw water filtration experiments. It is calculated based on the average DOC content of all samples collected during filtration.

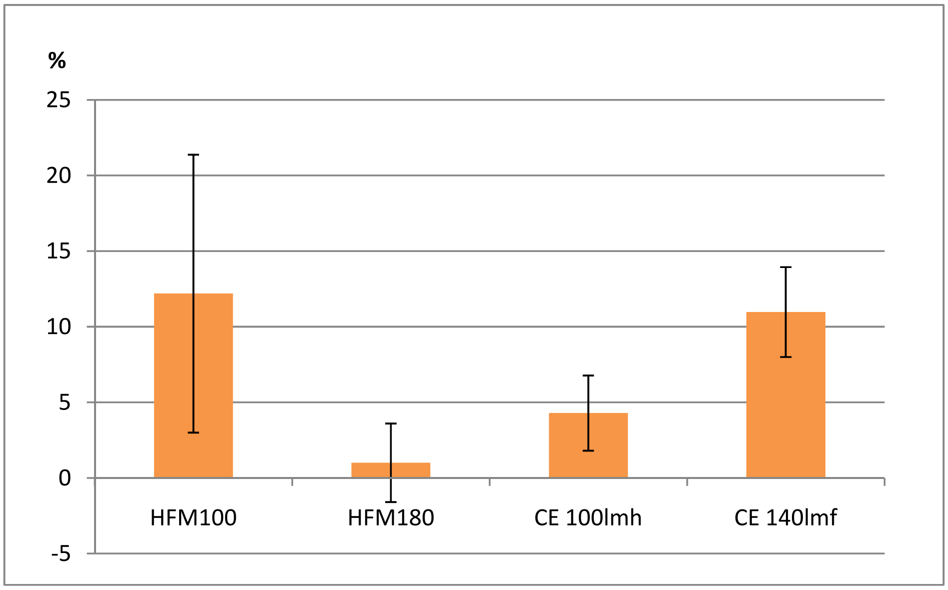


Figure 19: Total DOC removal, raw water filtration experiments.

The best performance is observed by the HFM 100 membrane (when the standard deviation is not considered) and is likely a result of its smaller pore size.

Figures 20 to 23 show the DOC content of the different fractions in the raw water and permeates during the different filtration experiments. The Figures demonstrate the low DOC removal attributed the membranes. The DOC content in the different permeates collected during filtration is approximately the same as for the raw water.

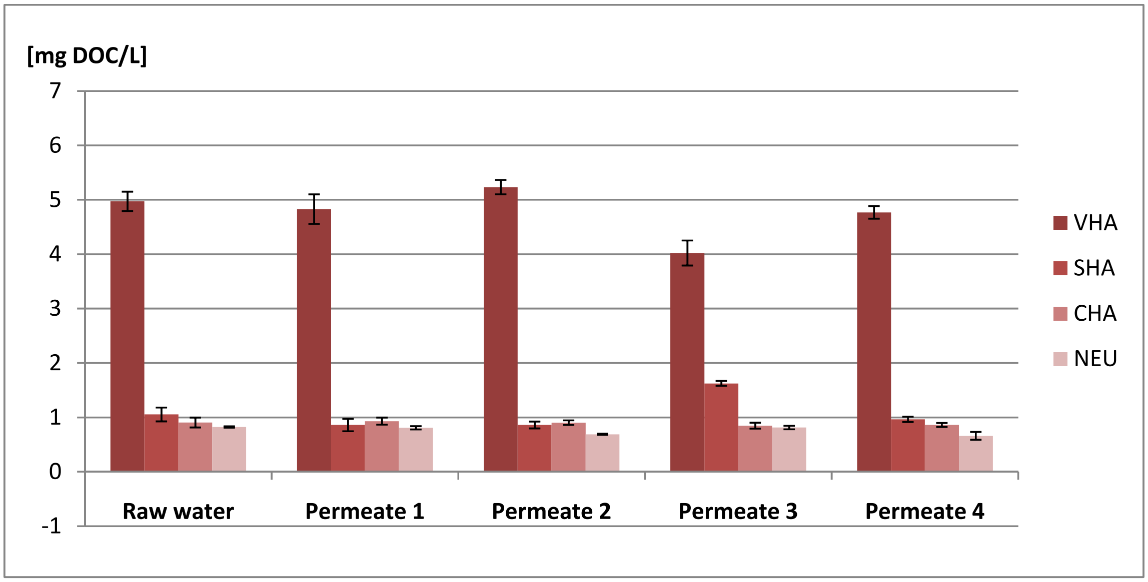


Figure 20: NOM fraction content. Results of raw water filtration experiment applied to MF membrane operated at flux 110.

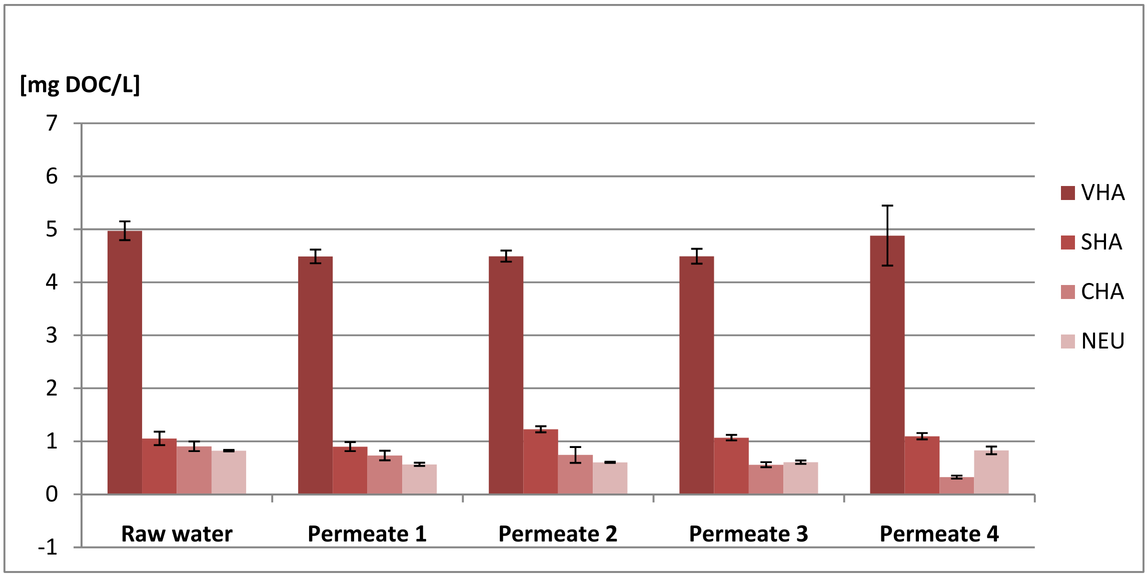


Figure 21: NOM fraction content. Results of raw water filtration experiment applied to MF membrane operated at flux 140.

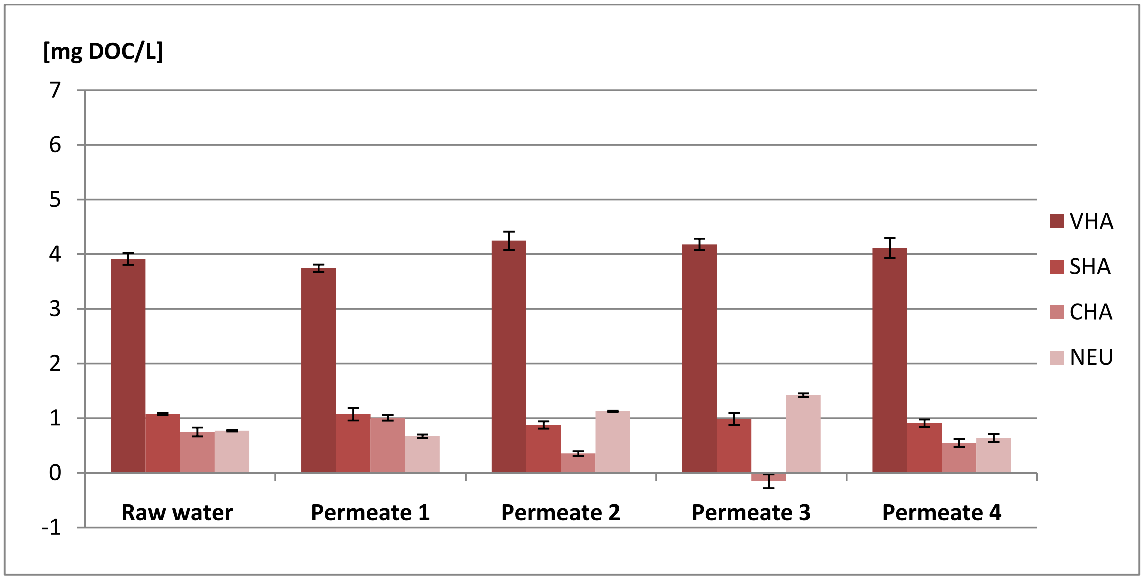


Figure 22: NOM fraction content. Results of raw water filtration experiment applied to PVDF HFM 180 membrane (UF).

Permeate 1 of the filtration experiment conducted on the HFM 100 UF membrane has a significant lower VHA content than what is observed elsewhere. The VHA content of permeate 2 jumps before it slightly increases in permeate 3 and 4. A similar, but weaker trend is observed for the HFM 180 UF membrane. This might reflect an adsorption process taking place. In that case, the good removal efficiency in the beginning of the filtration experiment is a result of the many available adsorption sites.

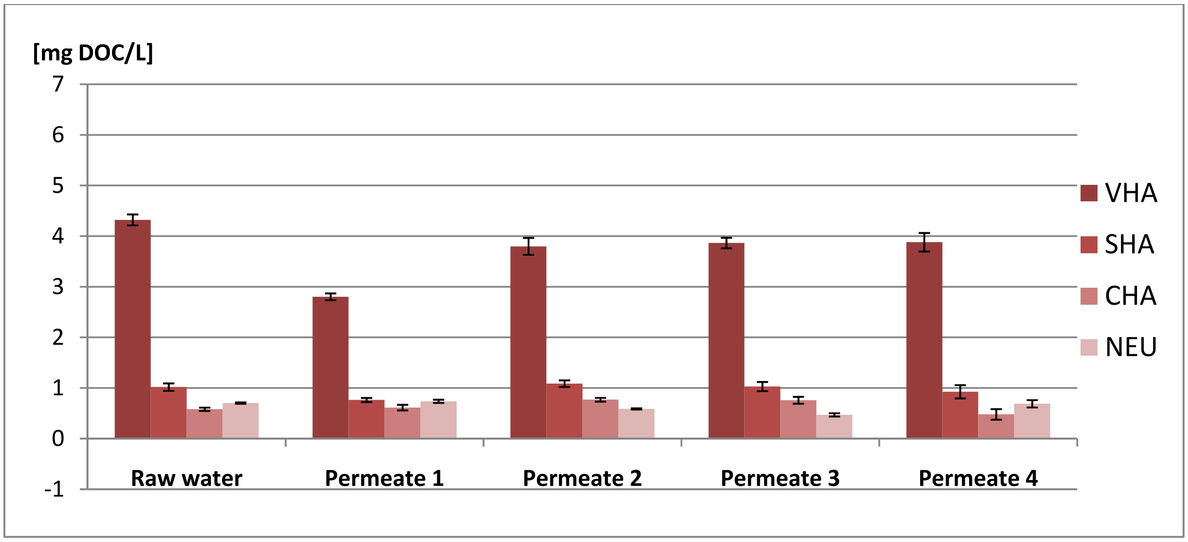


Figure 23: NOM fraction content. Results of raw water filtration experiment applied to PVDF HFM 100 membrane (UF).

The samples collected during the UF filtration experiments were in addition to NOM fractionation analysed with respect to colour, UV_{254}-absorbance and zeta potential. The methodology and background information about the characterization methods have been presented earlier, while the results and discussion regarding the results is the focus of this section. Figure 24 shows the same trend as the results obtained from the fractionation of the raw water and permeates. Colour and UV_{254}-absorbance is, as mentioned earlier, properties attributed the hydrophobic fraction of NOM, and the corresponding results from the independent analytical tools therefore indicate reliable results with respect to the VHA.

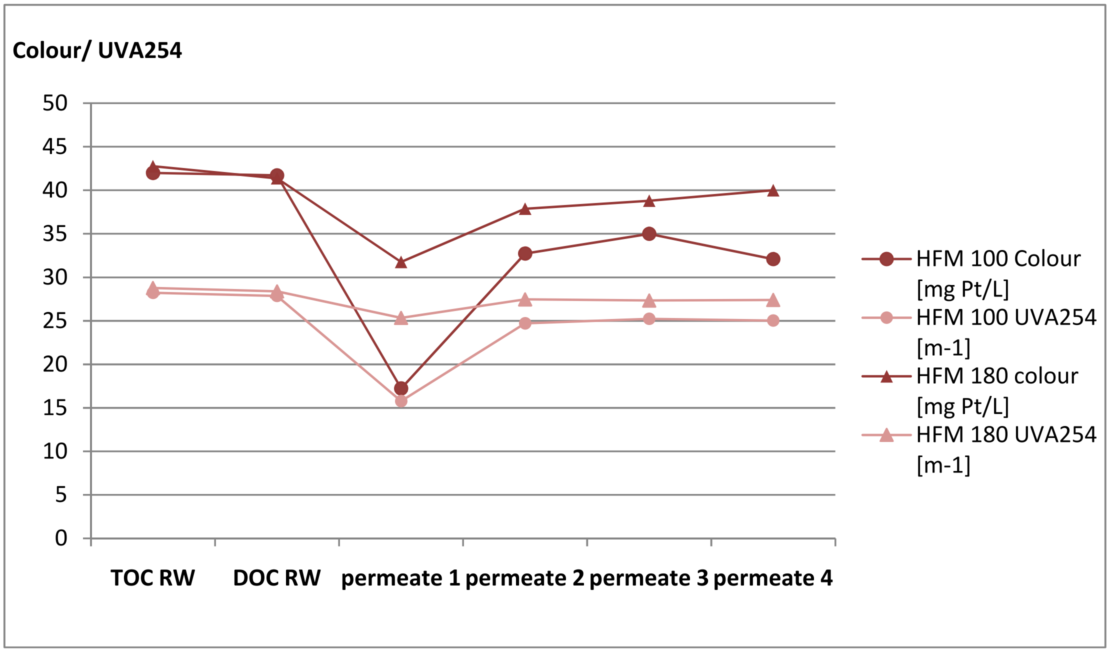


Figure 24: Colour and UV254-absorbance of UF filtration experiments conducted with raw water.

The results of the zeta potential measurements given in Figure 25 are different for the two UF membranes. Hydrophobic NOM is associated with high charge density, and it was therefore expected low zeta potential measurements of permeate 1 for both membranes corresponding to the low VHA content in the permeates.

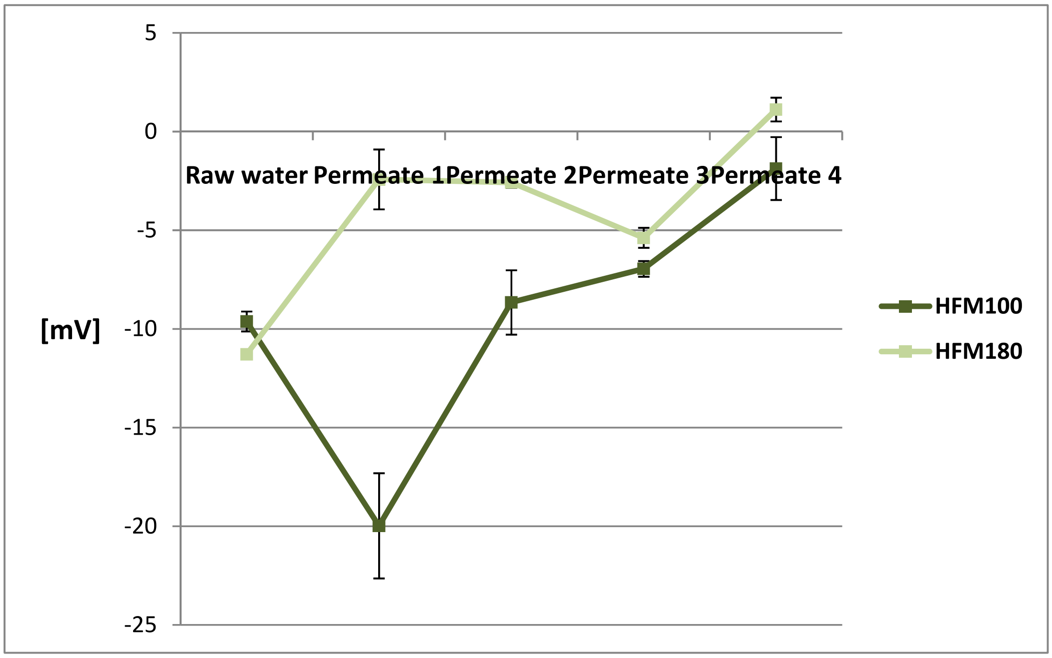


Figure 25: Zeta potential measurements of raw water and permeates from UF experiments.

The raw water fed to the MF membrane was not pH adjusted (pH=8,75) in contrast to the raw water fed to the UF membrane (pH=6) prior to the experiments. However, since NOM is known to exhibit a more negative charge at higher pH, the statement that hydrophobic/hydrophilic interactions are more dominant than charge interaction is still valid.

4.2.3 Effect of pre-treatment

Pre-treatment was applied in order to achieve a better membrane performance both with respect to fouling as well as rejection.

The large number of carboxylic groups associated with the humic part of NOM enables complexation reactions by addition of metal-ion-based coagulants. Pre-treatment by coagulation has shown good removal efficiency of higher MW humic substances in previous studies, while smaller sized hydrophilic NOM have been more difficult to remove. In this work, coagulation followed by flocculation and flotation was applied. This type of pre-treatment has not been investigated extensively as known by the author. Coagulation followed by sedimentation however, is a method which has showed very good treatment results with low fouling potential of the membrane applied after the pre-treatment (Li 2008). Similar results were expected in this study.

The effect of feed water pre-treatment was investigated for *all membranes* at *one flux* and the samples collected during the experiments were analysed in a similar manner as for the raw water presented in the previous paragraph, except for excluding zeta potential measurements and including SUVA measurements. The Specific UV-absorption (SUVA) was in addition measured for the UF membranes to estimate the removal efficiency of NOM by coagulation and too see whether it corresponds with the obtained results. The standard deviations for UV-absorbance, SUVA and colour were very low and are therefore not included in the graphs showing the results.

4.2.3.1 Coagulant dose determination

The performance result of ALS in the jar test is presented in Table 5. It shows that a coagulant dose of 28 mg Al/L was most efficient at removing colour and it also gave a zeta potential relatively close to zero.

Colour removal is the determining factor in finding optimum coagulant dosage (Machenbach 2007), a dosage of 28 mg Al/L was therefore chosen to produce pretreated raw water for the filtration experiments.

Table 5: Optimum coagulant dose.

Dose [mg/L]	Colour [mg Pt/L]	Zeta potential [mV]
0	39,646	-0,873
10	29,107	6,82 - 7,49
20	5,659	4,77 - 4,8
30	3,134	1,9 - 1,98
25	3,102	0,444
28	2,81	0,837 - 0,837
33	3,431	0,458 - 0,332
36	2,866	0,369 - 0,596

4.2.3.2 MF experiment, flux 110

The removal of the DOC and the respective fractions during the MF experiment are shown in Figure 26 below. The Figures also include the relative content of the different NOM fractions to the total DOC in the desorbed membrane

The effect of pre-treatment is illustrated by “Pre-treatment”, while the effect of the membrane filtration with time is illustrated by “permeate 1, 2 etc.”, the latter being relative to the concentration of the different fractions of the pretreated water.

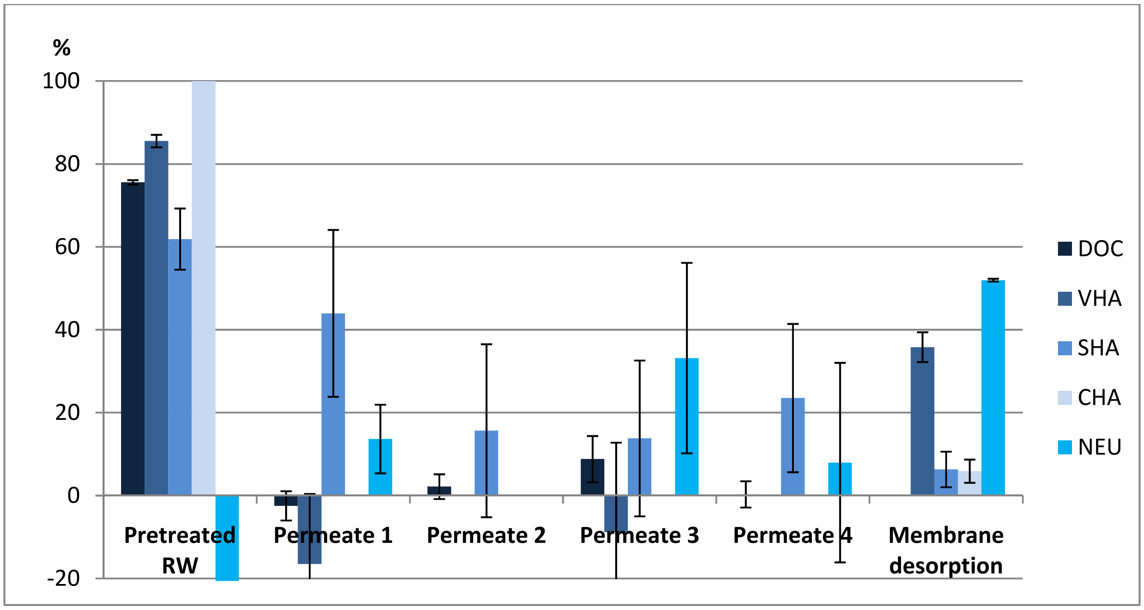


Figure 26: Results of pretreated water filtration experiment applied to the MF membrane at flux 110. It shows the pre-treatment efficiency of the raw water, the rejection of NOM fractions in permeate 1, 2, 3 and 4 collected at different time intervals, and the NOM fraction content of the membrane desorption.

The water was treated with ALS at optimum dose for DOC removal (≈75%, Figure 29 presented later in the report) before it was fed to the membrane. The membrane filtration shows low additional removal of the remaining DOC after pre-treatment. This is similar to what was observed in the MF filtration conducted on raw water, and may also here be reasoned by its relatively large pore size compared to the size of the remaining DOC.

The DOC removal during pre-treatment is attributed to the hydrophobic and the hydrophilic charged fraction of NOM, whereas the hydrophilic neutrals are not removed to any extent. This is illustrated in Figure 26, where the relative content of VHA, SHA and CHA in the flotated/pretreated raw water has decreased significantly while the relative content of NEU has increased. The efficient removal of hydrophobic NOM and the hydrophilic charged fraction of NOM is probably a result of its negative charge and colloidal properties (Ødegaard et al. 2010).

Figure 26 reflects a very dynamic system with a change in the water composition with time. Although the pre-treatment of the water is observed to remove all the hydrophilic charged fractions of the water (CHA is not present in the flotated raw water), CHA is still present in the membrane desorption and permeate 3. In addition to reflect a dynamic system, this might again represent a weakness of the rapid fractionation technique.

The most apparent trend is associated with the neutral fraction which is observed not to be removed by the pre-treatment. However, it is rejected to some extent by the membrane during the filtration experiment, which further correlates with its presence in the membrane desorption. In this case it is the neutral fraction of NOM which is the major foulant. That is different from what was observed in the raw water filtration experiment of the same membrane at flux 110lmh where the hydrophobic fraction of NOM was the dominating foulant.

By plotting the data of the TMP collected during the experiment of both the raw water and the pretreated water, one might be able to understand to what extent the different NOM fractions (VHA versus NEU) contribute to the fouling of the membrane. The TMP plot is presented in the next subchapter.

4.2.3.3 UF filtration of pretreated water, flux 80

The UF filtration experiments of pretreated water show quite similar tendencies to what was observed for the MF experiment. This is reflected in Figures 27 and 28.

The pre-treatment is efficient in removing hydrophobic and hydrophilic charged NOM, while the hydrophilic neutrals are much more difficult to remove. The neutrals are, however, removed to some extent during filtration which corresponds with its present in the desorbed membrane. In addition, a substantial part of the VHA observed is to be removed during filtration of pretreated water through the tightest UF membrane (HFM100).

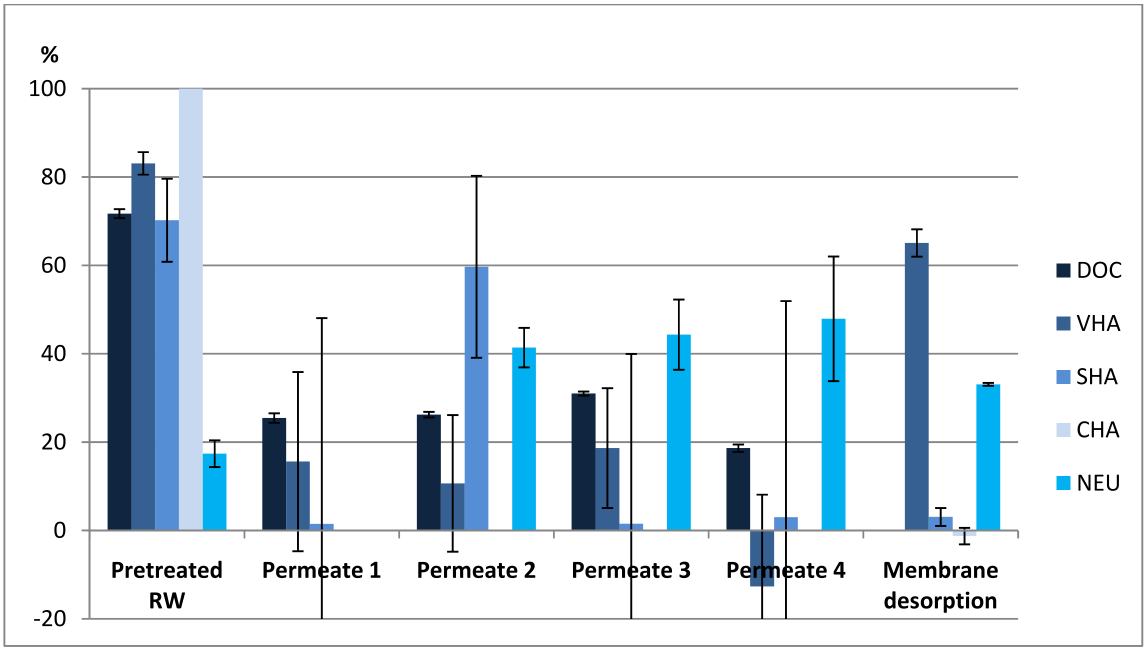


Figure 27: Results of pretreated water filtration experiment applied to the UF PVDF HFM 100 membrane at flux 80. It shows the pre-treatment efficiency of the raw water, the rejection of NOM fractions in permeate 1, 2, 3 and 4 collected at different time intervals, and the NOM fraction content of the membrane desorption.

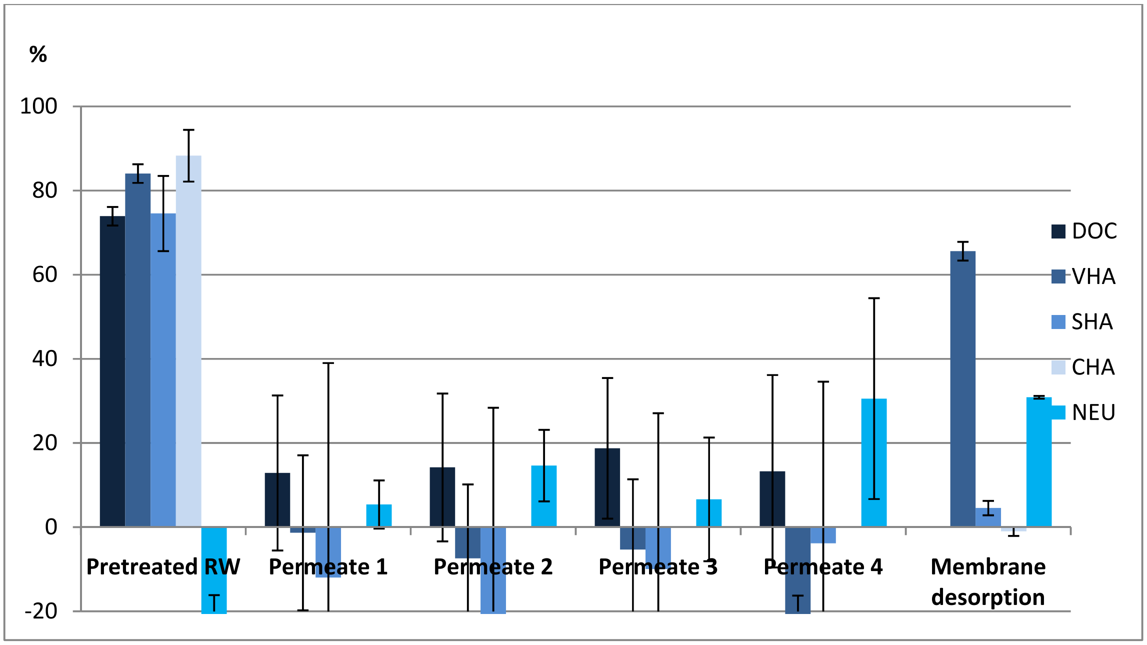


Figure 28: Results of pretreated water filtration experiment applied to the UF PVDF HFM 180 membrane at flux 80. It shows the pre-treatment efficiency of the raw water, the rejection of NOM fractions in permeate 1, 2, 3 and 4 collected at different time interval.

Severe standard deviations of the data makes it difficult to draw any further conclusions.

4.2.3.4 Total DOC removal in pretreated water filtration experiments by MF and UF membranes

Figure 29 illustrates the total DOC removal of the pre-treatment and the different filtration experiments.

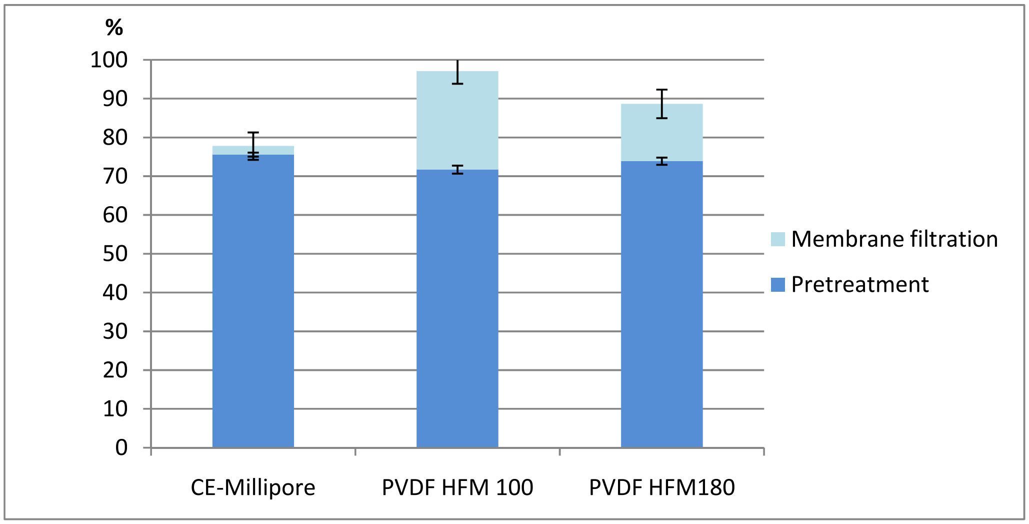


Figure 29: Total DOC removal, pretreated raw water filtration experiments.

The results indicate a better removal efficiency of DOC in connection with UF filtration compared to MF filtration, while the pre-treatment gives similar results. It is not very surprising to observe that the most efficient removal of DOC during the filtration is associated with the tightest UF membrane, although the additional removal is quite small.

Figures 30 to 32 show the DOC content of the different fractions in the raw water, flotated raw water and permeates during the different filtration experiments. The figures again demonstrate the low DOC removal attributed the membranes.

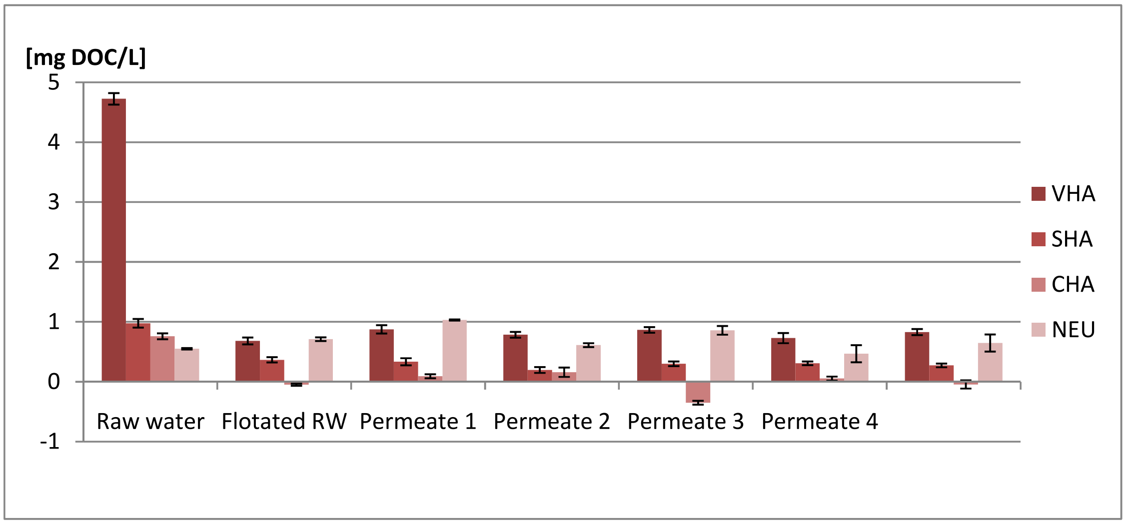


Figure 30: NOM fraction content. Results of raw water filtration experiment applied to MFmembrane at flux 110.

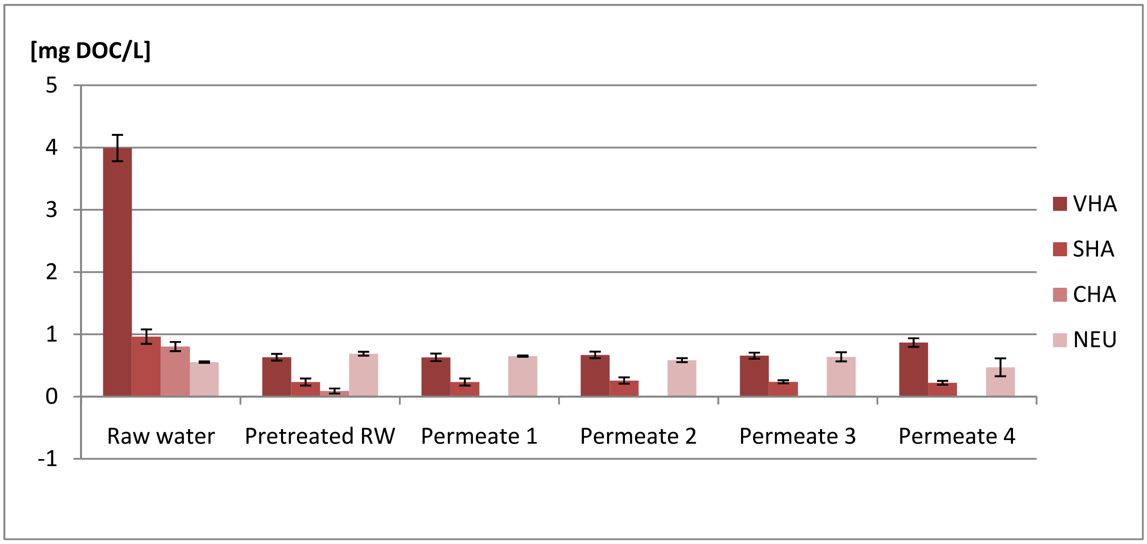


Figure 31: NOM fraction content. Results of raw water filtration experiment applied to PVDF HFM 180 membrane (UF).

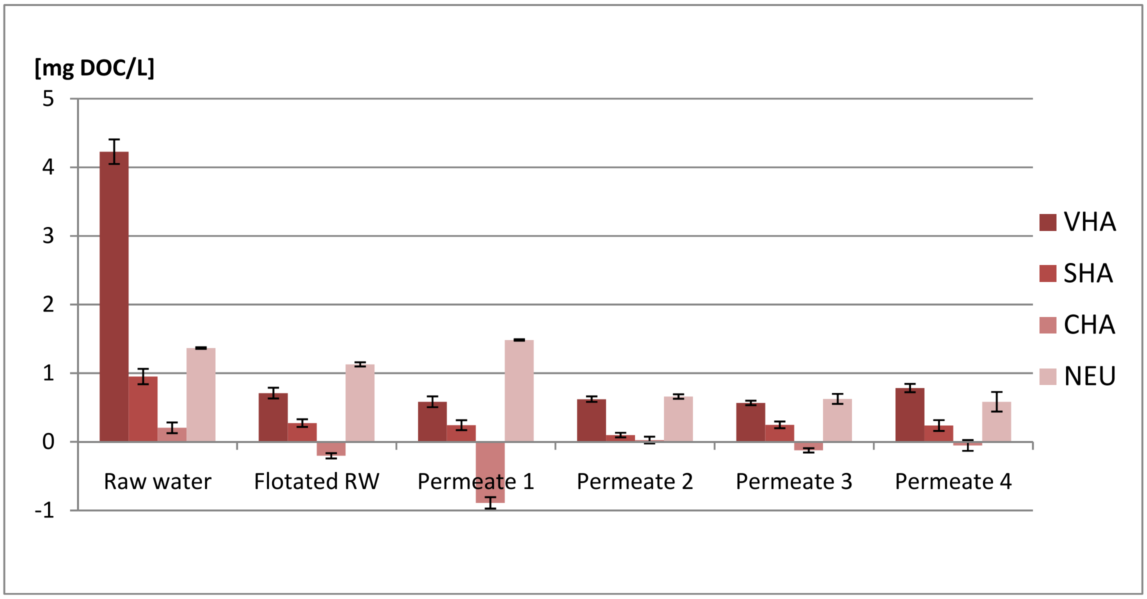


Figure 32: NOM fraction content. Results of raw water filtration experiment applied to PVDF HFM 100 membrane (UF).

Good treatability of NOM (>50% DOC removal) by coagulation is according to Edzwald and Tobiason (1999) expected if you are having a raw water with SUVA number above 4, cf. Table 2 in the literature review. The SUVA number of the raw water utilized in the UF filtration experiments is presented in Figure 33.

The SUVA number, the colour and UV_{254}-absorbance is observed to stabilize after the pre-treatment (Figures 33 and 34), and a stable hydrophobic NOM content of the permeates collected during the filtration experiments was therefore also expected. Figures 31 and 32, showing the DOC content of the water samples, confirms this is true for both UF experiments, and is an indication of reliable results.

No backwash was included in this study. It is therefore not possible to separate between the irreversible fouling caused by adsorption of the fractions in the membrane pores, and the reversible fouling due to concentration polarization and gel cake formation at the surface of the membrane.

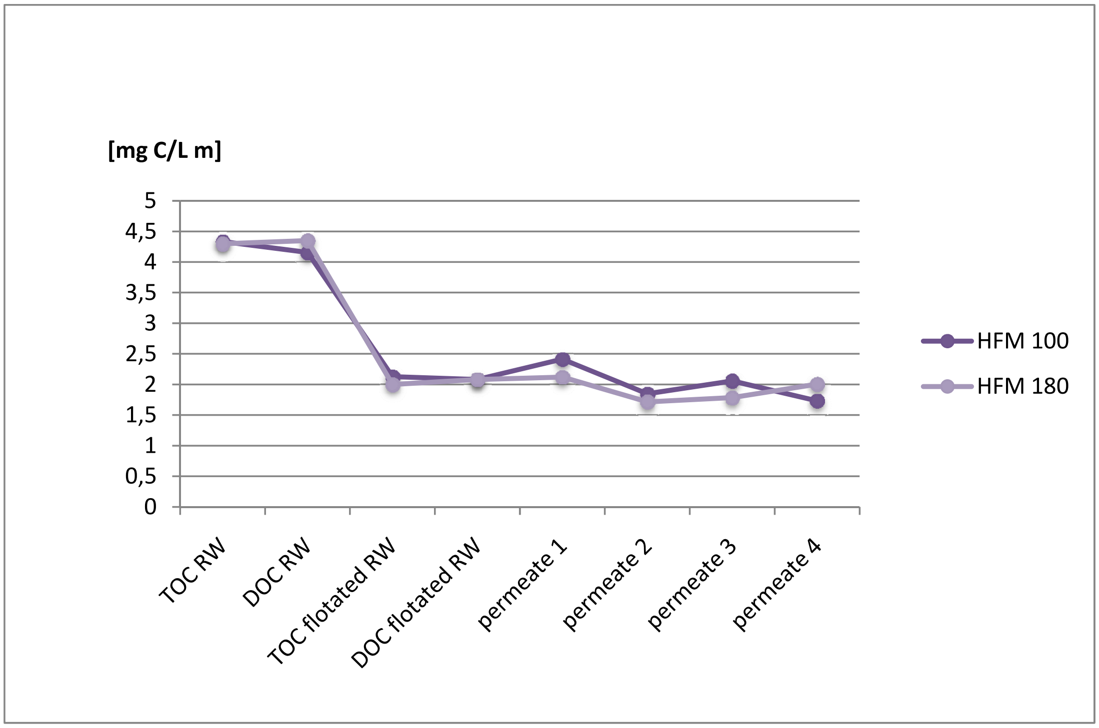


Figure 33: SUVA number, flotated water.

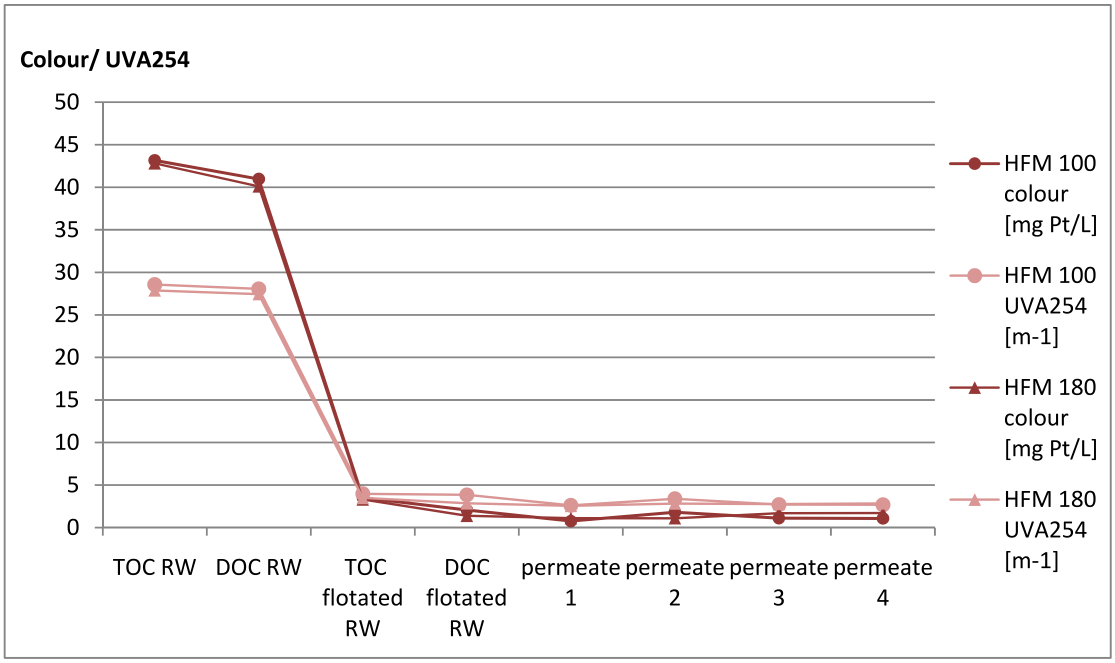


Figure 34: Colour and UV-254 absorbance, UF experiments conducted on flotated water.

4.2.4 Analysis of fouling mechanisms and fouling rate

The unified model expression for low pressure membrane filtration developed by Huang (2007) has been applied to the filtration experiments conducted in this study. This was done in order to get a better understanding of the fouling mechanisms taking place and to observe how the rate of fouling changes with different operating conditions. The model has been described and presented in previous chapters, while the plot obtained from the interpretation of the model is presented in Figure 35.

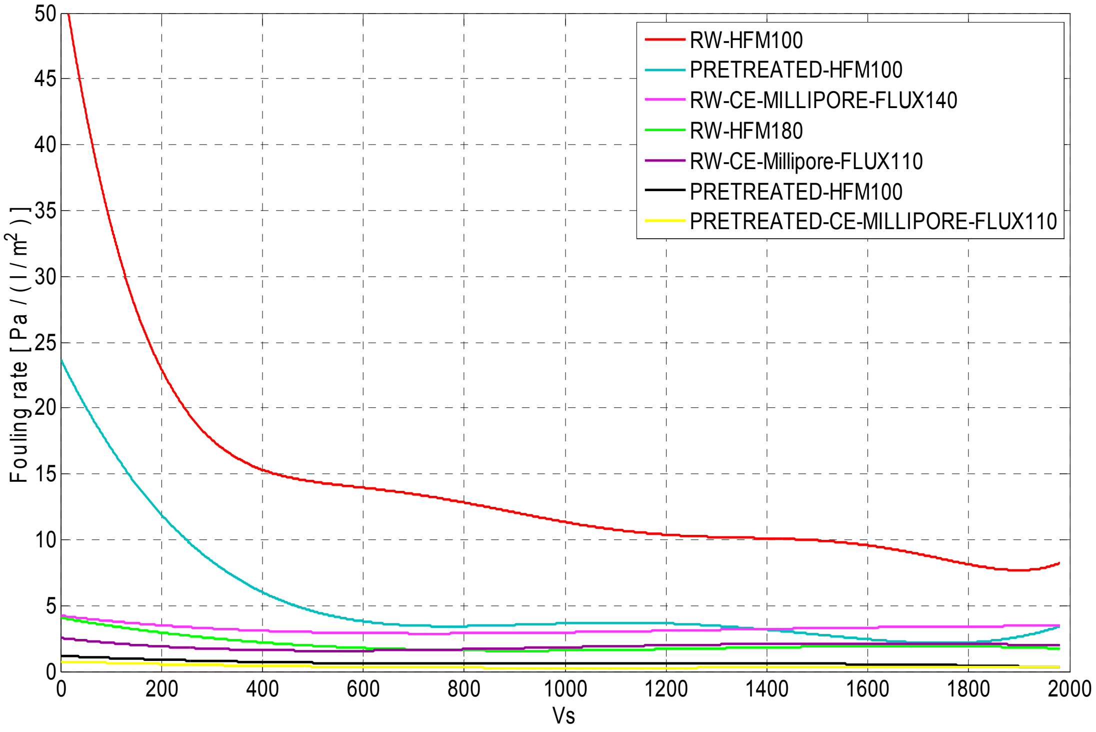


Figure 35: Fouling rate of the different filtration experiments.

4.2.4.1 Fouling mechanisms

The model is a revision of Hermia's blocking model, and the different fouling rates observed in Figure 35 is therefore claimed to be a result of blocking mechanisms.

Some trends may be identified in Figure 35. Each curve can more or less be divided into two line segments; the first segment being a concave curve, while the other segment is more linear. This observation is subtle for some of the curves due to the scale of the Figure, it is however very significant for the filtration experiments conducted on the HFM100 membrane. The same observation was found by Hwang and Chen (2009) when analyzing particle fouling in a submerged system. They identified the initial and most severe fouling as a result of membrane blocking mechanisms (n>0), while cake filtration was identified as the dominating fouling mechanism when the curve depicted a straight line (n =0). This explanation may also be adopted in this study, although the trend is not that apparent (except for the PVDF HFM 100 membrane). The membrane filtration system is most likely dynamic with the surface cake characteristics changing over time. The resistance of the cake may change with time due mechanisms like cake compression and depending on the size distribution of the feed water compounds (Lee et al. 2005). This can explain why the second line segment deviates from the straight line observed during filtration.

It is important to keep in mind that the blocking model by Hermia (1985) was derived based on fouling by particles. The literature study during this work has revealed a great complexity attributed to NOM, including the size of its constituents. The fouling mechanisms taking place during filtration may therefore rather be a result of concentration polarization and gel layer formation than blocking mechanisms.

A concentration polarization layer most likely develops in the beginning of the filtratrion experiment due to concentration build-up of retained solutes. If the water contains compounds having a significant diffusion coefficient, a diffusive back transport of the compounds will take place. At some point during filtration, the convective solute transport to the membrane surface may balance the permeate flow and the diffusive backtransport (Mulder 1996). This in, turn gives rise to a steady state situation which might be identified as the straight line segment in Figure 35.

4.2.4.2 Fouling rate

It is observed that the rate of fouling at flux 140lmh is bigger than at flux 110 lmh. This result corresponds to a more severe gel layer formation when the experiment is operated at flux 140 lmh. The hypothesis that more low MW compounds are being rejected as a result of the more severe concentration polarization and gel layer formation at higher flux is therefore strengthened.

The pre-treatment of the raw water showed good removal efficiency of the hydrophobic and the hydrophilic charged fraction of NOM. The main foulant of all membranes after pre-treatment was attributed the hydrophilic neutrals while the main foulant when raw water without pre-treatment was applied was attributed the hydrophobic NOM fraction (except for the MF membrane operated at flux 140 lmh).

Figure 35, which shows the fouling rate, may give an indication of to what extent the different NOM fractions (VHA versus NEU) contribute to the fouling of the membrane before and after pre-treatment.

It is observed that the rate of fouling of pretreated water in any case is lower than for the raw water. This is an indication of lower concentration of potential foulants in the feed water after pre-treatment and that the pre-treatment has been successful in removing the main fraction responsible in fouling of the membranes. Meaning, although NEU is found in the desorbed membrane it does not necessarily contribute severely to fouling which gives an increase in TMP with time.

5 Conclusions

The results of this study show that characterization of NOM composition, membrane properties, a good understanding of the NOM-membrane interactions and how the interaction is affected by different operating conditions are critical in predicting fouling behavior of low pressure submerged membranes.

Different NOM foulants were identified and the rate of fouling changed depending on the operating conditions applied to the filtration experiments. The differences in fouling mechanisms were not very significant:

- *Effect of flux variations*: The MF membrane operated at flux 140 gave a better NOM removal than the same membrane operated at flux 110. This is a result which was hypothesized with the formation of a more severe concentration polarization layer at the membrane surface at higher flux which influences the membrane selectivity. The accumulated particles at the membrane surface will act as a second or dynamic membrane which enhances the separation. The effect was most severe for the lower MW hydrophilic part of NOM. Higher flux also resulted in an increase in the fouling rate which correspond with the concentration polarization and further a gel-layer formation which exerts an additional resistance to the flux.
- *Effect of membrane characteristics*: Hydrophobic and hydrophilic interactions between the membranes and the different NOM fractions seemed to govern the membrane fouling in the experiments, while electrostatic repulsion was proven to be less significant for the NOM-membrane interaction. With one exception (MF flux 140), the main foulant in the filtration experiments were attributed to VHA. Low DOC removal was observed in all experiments most likely due to inadequate membrane pore size relative to the size of the NOM.
- *Effect of pre-treatment*: Pre-treatment showed good removal efficiency of CHA, VHA and SHA and it significantly reduced the rate of fouling of the membranes. A bigger part of the membrane foulants was associated with NEU, although VHA still was the main foulant. This may imply that the increase in TMP and fouling is related to other NOM fractions than the hydrophilic neutrals and the very hydrophobic acids.
- *Fouling mechanisms*: When considering NOM as a mixture of small particles, the fouling mechanisms taking place during filtration is identified as blocking mechanisms in the beginning of the filtration before it changes to cake filtration with time. The blocking mechanism was most severe for the HFM 100 membrane.

In summary, strategies to reduce fouling may include careful membrane selection and pre-treatment of the raw water. Sufficient knowledge about the composition of raw water is also important.

6 Suggestions for further research

First, it must be stated that due to time limitations, no repetitions have been carried out to verify the results which lead to the recommendations given in the Conclusion. This research should therefore be followed up by further investigations.

Even though the study revealed interesting and important points about membrane fouling there are some uncertainties attributed these results. This is due to the great complexity associated with membrane filtration of surface water of high NOM content and the dynamic behavior of the filtration system applied (membrane + feed water). Further research should therefore implement a smaller scale pilot unit to provide better control. It should also include studies on how the relative concentration of each NOM fraction in the raw water, solution chemistry (pH, ionic strength and hardness), and the change in membrane surface characteristics (pore size and charge) during filtration affects the rejection and fouling observed.

Backwash and relaxation which is proven to be a determining aspect in membrane filtration, has not been investigated thoroughly in this study. It is therefore recommended to investigate the effect of such operational conditions to the fouling propensity of membranes in future research.

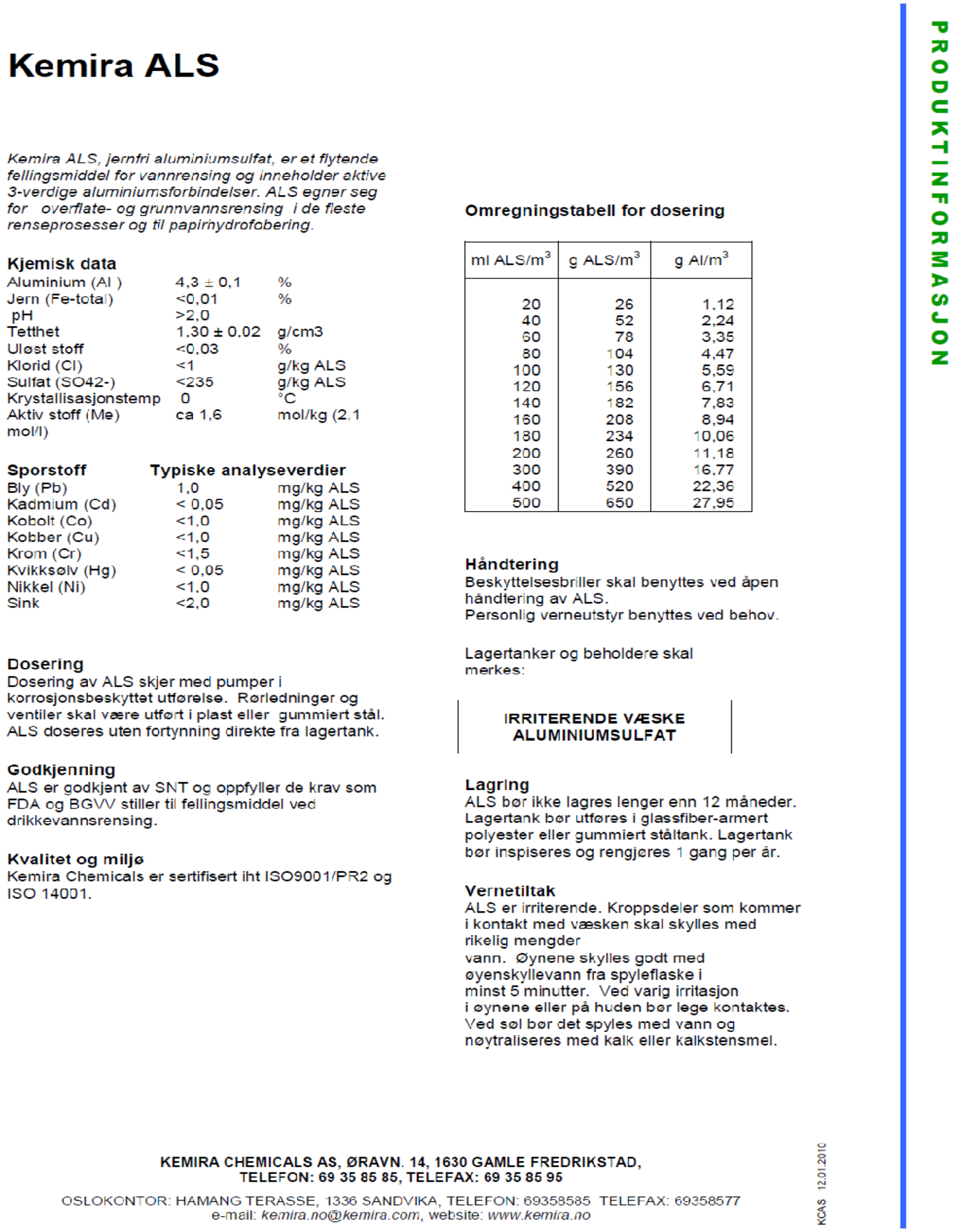
Pre-treatment by flotation in membrane filtration as applied in this study is a new configuration which showed relatively good treatment results throughout this work. It would have been interesting to include an investigation of its economy and energy demand in order to evaluate its competitiveness to other conventional membrane configurations.

The coagulant dosage applied in the pre-treatment was high, (28 mg Al/L), to arrive at the optimum treatment result. Further optimization of the pre-treatment process should therefore be carried out.

The rapid fractionation technique for NOM characterization appeared to be the bottleneck of this study. The author would therefore recommend to couple or substitute the technique with other established methods for NOM characterization in future work.

Appendices

Appendix A



PRODUKTINFORMASJON

Kemira ALS

Kemira ALS, jernfri aluminiumsulfat, er et flytende fellingsmiddel for vannrensing og inneholder aktive 3-verdige aluminiumsforbindelser. ALS egner seg for overflate- og grunnvannsrensing i de fleste renseprosesser og til papirhydrofobering.

Kjemisk data

Aluminium (Al)	4,3 ± 0,1	%
Jern (Fe-total)	<0,01	%
pH	>2,0	
Tetthet	1,30 ± 0,02	g/cm3
Uløst stoff	<0,03	%
Klorid (Cl)	<1	g/kg ALS
Sulfat (SO42-)	<235	g/kg ALS
Krystallisasjonstemp	0	°C
Aktiv stoff (Me)	ca 1,6	mol/kg (2,1 mol/l)

Sporstoff	Typiske analyseverdier	
Bly (Pb)	1,0	mg/kg ALS
Kadmium (Cd)	< 0,05	mg/kg ALS
Kobolt (Co)	<1,0	mg/kg ALS
Kobber (Cu)	<1,0	mg/kg ALS
Krom (Cr)	<1,5	mg/kg ALS
Kvikksølv (Hg)	< 0,05	mg/kg ALS
Nikkel (Ni)	<1,0	mg/kg ALS
Sink	<2,0	mg/kg ALS

Dosering
Dosering av ALS skjer med pumper i korrosjonsbeskyttet utførelse. Rørledninger og ventiler skal være utført i plast eller gummiert stål. ALS doseres uten fortynning direkte fra lagertank.

Godkjenning
ALS er godkjent av SNT og oppfyller de krav som FDA og BGVV stiller til fellingsmiddel ved drikkevannsrensing.

Kvalitet og miljø
Kemira Chemicals er sertifisert iht ISO9001/PR2 og ISO 14001.

Omregningstabell for dosering

ml ALS/m^3	g ALS/m^3	g Al/m^3
20	26	1,12
40	52	2,24
60	78	3,35
80	104	4,47
100	130	5,59
120	156	6,71
140	182	7,83
160	208	8,94
180	234	10,06
200	260	11,18
300	390	16,77
400	520	22,36
500	650	27,95

Håndtering
Beskyttelsesbriller skal benyttes ved åpen håndtering av ALS.
Personlig verneutstyr benyttes ved behov.

Lagertanker og beholdere skal merkes:

IRRITERENDE VÆSKE
ALUMINIUMSULFAT

Lagring
ALS bør ikke lagres lenger enn 12 måneder. Lagertank bør utføres i glassfiber-armert polyester eller gummiert ståltank. Lagertank bør inspiseres og rengjøres 1 gang per år.

Vernetiltak
ALS er irriterende. Kroppsdeler som kommer i kontakt med væsken skal skylles med rikelig mengder vann. Øynene skylles godt med øyenskyllevann fra spyleflaske i minst 5 minutter. Ved varig irritasjon i øynene eller på huden bør lege kontaktes. Ved søl bør det spyles med vann og nøytraliseres med kalk eller kalkstensmel.

KEMIRA CHEMICALS AS, ØRAVN. 14, 1630 GAMLE FREDRIKSTAD,
TELEFON: 69 35 85 85, TELEFAX: 69 35 85 95
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KCAS 12.01.2010

Appendix B

Preparation of 0,5 % Al stock solution, calculations:

Appendix A gives the specifications of ALS needed for the calculations.

0,5 % Al solution = 5 g Al/L

Al content in ALS = 4,3 %

P_{ALS} =1 ,3 g/ml

$$\frac{5\text{gAl}}{\text{L}} = \frac{4{,}3\text{gAl}}{100\text{gALS}} * \text{X}$$

$$\text{X} = \frac{5\text{gAl}}{\text{L}} * \frac{100\ \text{gALS}}{4{,}3\text{gAl}} = \frac{116{,}28\text{gALS}}{\text{L}}$$

$$\frac{\frac{116{,}28\text{gALS}}{\text{L}}}{\frac{1{,}3\text{g ALS}}{\text{ml}}} = \frac{89{,}44\text{ml}}{\text{L}}$$

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