



Norwegian University of
Science and Technology

Evaluation of a new natural coagulant for removal of color by coagulation/ceramic membrane filtration

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Project task description

The aim of the master project is to evaluate a new natural coagulant, based on extract from tree bark, as pre-treatment for ceramic microfiltration. Context of the project is treatment of surface water for production of potable water.

The project is going to use a membrane filtration pilot setup here at IVM, consisting of three independent treatment trains. Ceramic microfiltration will be applied, with membranes having a nominal pore size of 100 nm. Analogue raw water will be used, consisting of tap water and NOM concentrate.

The project should evaluate membrane performance and quality of the treated water in dependence on operating conditions, including both chemical factors (pH, coagulant dose etc.) as well as hydraulic parameters (retention time, mixing intensity etc.). In depth understanding of the dominant mechanisms, influencing the process performance is expected to be an outcome of the project. The student is further expected to orally present his work in a student seminar held at IVM.

Abstract

This master thesis is based on experiments on a pilot plant at the department of Hydraulic and Environmental Engineering at NTNU. The master thesis is written for the Norwegian company INRIGO AS. The purpose of this master thesis is to evaluate a natural, organic coagulant called Ecotan bio s03, and to evaluate if the coagulant can be used for NOM removal on typical Norwegian surface water. Typical Norwegian surface water has a low pH, turbidity and alkalinity, and high concentration of color and NOM.

The pilot plant consists of coagulation, flocculation and membrane filtration through a ceramic membrane with 100 nm pore size. The raw water is tap water with additional NOM concentrate to imitate typical Norwegian surface water.

18 experiments were in total conducted, where 18 different conditions was evaluated. pH 6, 7.5 and 9 was chosen on the basis of the project thesis written during fall 2015. 20, 30, 40, 50, 60 and 70 mg EB3/l was the coagulant dosages used. The results did not live up to the expectations. The best result considering color was 61% removal and 16,26 mg Pt/l. A color residual far above the required level, and much higher than the project thesis. The best result considering carbon removal was 26,5% removal and 3,62 mg C/l, accomplished with the second lowest dosage at pH 6. pH 7,5 and 60 mg EB3/l resulted in 115% increase in carbon. The results illustrate that high coagulant dosages causes high carbon residual. Ecotan bio s03 contain a high concentration of carbon, which can make it difficult to reach the requirement considering carbon.

The results in this master thesis have been varying, causing difficulties making any conclusions. The experiments were initially scheduled to last for 48 hours, but most of them stopped earlier because of membrane clogging. On that basis the results considering TMP are difficult to draw any conclusions from. The conclusion is that the experiment should be performed one more time.

Sammendrag

I denne master oppgaven er det gjort forsøk med et pilotanlegg på institutt for vann- og miljøteknikk på NTNU. Oppgaven er skrevet for firmaet INRIGO AS. Målet med oppgaven er å evaluere en naturlig, organisk koagulant Ecotan bio s03. For så å vurdere om koagulanten kan brukes til fjerning av NOM på typisk norsk overflatevann. Typisk norsk overflatevann har en lav pH, lav turbiditet og alkalinitet. Det har et høyt fargetall og et høyt innhold av NOM.

Pilotanlegget er satt sammen av prosessene koagulering, flokkulering og membranfiltrering gjennom en keramisk membran med porestørrelse 100nm. Råvannet som er brukt er kranvann tilsatt humuskonsentrat for å etterligne typisk norsk overflatevann.

I alt er 18 forsøk gjennomført, der 18 forskjellige betingelser er undersøkt. Ut ifra resultatene fra prosjektoppgaven skrevet høsten 2015 valgte jeg å undersøke råvann med pH 6, 7.5 og 9. Ved disse pH verdiene testet jeg koagulantdosene 20, 30, 40, 50, 60 og 70 mg EB3/l. De oppnådde resultatene levde ikke opp til forventingene. Det beste resultatet for fargefjerning var 61% fjerning, med 16,26 mg Pt/l. Høyt over kravet, og mye høyere enn resultatene ved prosjektoppgaven i høst. Når det gjelder rest karbon var resultatene bedre, men fortsatt ikke bra nok. 26,5 % fjerning og 3,62 mg C/l var det beste resultatet, og oppnådd med den nest laveste dosen, 30 mg EB3/l. Ved høye koagulantdoser viser det seg at rest karbon øker. pH 7,5 og 60 mg EB3/l resulterte i en karbon økning på 115%. Ecotan bio s03 inneholder en høy konsentrasjon av karbon, noe som kan gjøre bruk av denne koagulanten svært vanskelig.

Resultatene har vært svært varierende gjennom forsøkene, noe som har gjort det vanskelig å trekke noen konklusjoner. I utgangspunktet skulle alle forsøkene vare i 48 timer, men på grunn av gjentetting av membranen, stoppet de fleste av forsøkene før. Dette gjorde at alle resultater som omhandler trykk ikke kan brukes. Konklusjonen er at forsøket bør kjøres igjen.

Preface

This master thesis is a part of the Master Program in Water and Wastewater Engineering at NTNU, Norwegian University of Science and Technology. The master thesis was written in collaboration with INRIGO AS, during the spring of 2016 in Trondheim, Norway.

It has been a technical challenge to run a pilot plant consisting of numerous pumps, pipelines and valves. In the beginning I used a lot of time adjusting valves and fixing leakages. I also had troubles with some of the analyzing machines. Because of problems with access and incorrect values, some of the analyzing machines and parameters had to be excluded from the master thesis. This delayed the experiments, the results was time limitations to be able to finish the master thesis.

I would like to thank my supervisor Thomas Meyn for guidance, help with installing and running the pilot plant and running LC-OCD analysis during this project. I would also thank Trine Hårberg Ness and Gøril Thorvaldsen for their help running analysis in the laboratory. At the end I want to thank my classmates for making this last semester a good one. For great conversations, help and encouragement through long days at the lab and office.

Trondheim, June 2016

Mari Helgestad

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List of terms and abbreviations

CEB	Chemically enhanced backwash
EB3	Ecotan bio s03 (the coagulant)
LMH	Liter/m ² *hour (flux)
MCL	Maximum contamination level
MF	Membrane filtration
NOM	Natural organic matter
RO	Reverse osmosis
SUVA	Specific ultraviolet absorbance
TMP	Trans membrane pressure

1. Introduction

All around the world you can find thousands of water treatment plants. Treatment plants with different size and with different tasks and issues. Norway is a country with a spread population and a lot of small chemical water treatment facilities. The benefits with chemical treatment are good and efficient treatment, and a process well known and easy to operate. But there are also disadvantages. One problem is the sludge handling. Sludge containing chemicals require further treatment before it can be discharged to the environment. Both treatment on site or transport to a sludge treatment facility are costly processes and unfavorable, especially for small treatment facilities. The risk that chemicals can infiltrate into the ground or worse into nearby water bodies, and pollute our environment is also a risk we want to avoid. This master thesis is based on results from a jar test in a project thesis, (Helgestad, 2015). In this master thesis a pilot plant containing coagulation, flocculation and filtration through a ceramic membrane with pore size 100nm is used. By using a membrane stricter regulations can be met, and the raw water less affects the effluent.

90% of Norwegian drinking water origin from surface water bodies. Typical Norwegian surface water is soft, acidic, has high concentration of humic substances, low turbidity and low alkalinity(Ødegaard, 2012). Humic is a collective term of non-degradable organics, which give color to the water, hereby called natural organic matter, NOM. Because of this, raw water often has to go through NOM removal for drinking water quality.

Raw water quality, either surface water, groundwater or river water is determinative for the treatment method. Coagulation/filtration are a good process for Norwegian waters, and are widely used in Norway. A conventional coagulation/filtration treatment plant consists of mechanical steps such as screens and sedimentation, but also more complex steps as mixing and flocculation with chemicals and polymers. Conventional coagulation/filtration plants is only used for raw water with high amount of turbidity, (Ødegaard, Østerhus, Melin, & Eikebrokk, 2010). In Norway, the most common combination is coagulation, flocculation and filtration due to the good quality of our surface water.

The objective of this project is to test a natural, organic coagulant extracted from tree bark, to evaluate if the coagulant is good enough for a direct membrane filtration plant on typically Norwegian surface water. By using an organic polymer we can avoid sludge with a high metal concentration.

2. Literature study and theory

2.1 Natural organic matter

NOM consist of compounds originated from either the soil or an upstream water body. The composition of NOM will vary from watershed to watershed depending on climate, vegetation, soil conditions and human activity (Crittenden, Trussel, Hand, Howe, & Tchobanoglous, 2012), and occur in a wide range of molar weight. NOM is present in most Norwegian water bodies, and because of climate changes, the amount of NOM have increased during the last 10-12 years (Eikebrokk, Juhna, & Osterhus, 2006), and is expected to increase further in the future.

The list of arguments why NOM should be removed from drinking water is long (Eikebrokk et al., 2006), (Zularisam, Ismail, & Salim, 2006):

- NOM affect the color, taste and odor of water.
- Reacts with most disinfectants, therefore decrease the disinfection power.
- Produces disinfection by-products that are carcinogens, and can under direct exposure lead to cancers, miscarriages and nervous system complications.
- Increases the demand of coagulant.
- Affects the biostability and increases the risk of biological growth within the network.
- Forms complexes with most chemical substances in the nature, and increase their mobility.
- Fouls membranes, and leads to shorter filter runs.

NOM is often illustrated as a vacuum cleaner because of its ability to absorb a large number of elements and substances. It contains a heterotrophic combination of hydro-tropic and hydrophilic organic compounds, based on their distribution. NOM can mainly be divided into two fractions, the hydrophobic and hydrophilic fraction. The third fraction is the transphilic fraction, which is a fraction between to two major fractions, figure 1. Thurman & Nijhoff (1985) explains the distribution of the different fractions of NOM. However, this may vary in dependence on season and source. The largest part of NOM is the hydrophobic fraction (49%), consisting of humic substances with high MW (1000-100 000). The hydrophilic, non-humic fraction (30%) con-

tribute with of 25-40% of the total DOC, and have a lower MW (polysaccharides, amino acids and protein) (Zularisam et al., 2006).

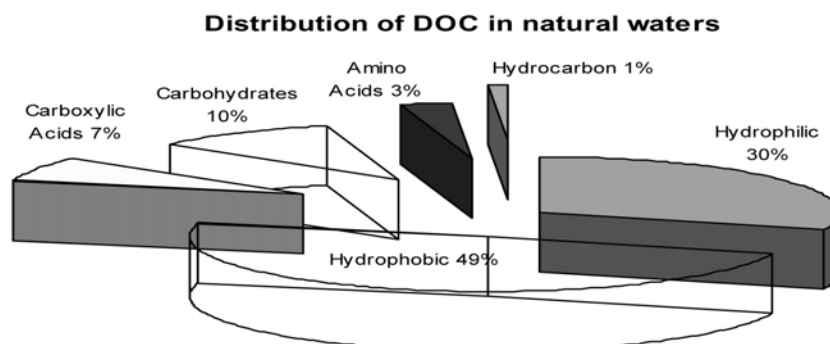


Figure 1 - An example on DOC distribution in natural waters (Thurman & Nijhoff, 1985)

There are different methods to measure the amount of humic substances. Color measurements [mg Pt/l] are the most common. pH 7 is set as a standard pH. This is because a high pH values increase color because of larger molecules (Halle, 1983).

2.1.1 How to remove NOM

It is possible to remove humic substances by several methods:

- By nano filtration, because of the large size of humic molecules (1000-100 000 MW) compared to the membrane pores (0,001 μ m). Approximately 100 plants in Norway today use membrane processes based on nanofiltration using a spiral wound module configuration.
- By coagulation. Enhanced coagulation is the most widely used process. Because of the humic substances negative charge they can be coagulated, adsorbed to a metal hydroxide and subsequently removed by floc separation.
- By ion exchange. But the use of ion exchange is limited because of disposal of the high TDS regeneration brine.
- By oxidation with strong oxidants. Since the color of humic substances is associated with its aromatic content and C=C bonds, the color can be removed by breaking these bonds through the addition of a strong oxidant.

- By oxidation and biological filtration, where ozone, a strong oxidant can break down the humic substances to smaller biodegradable components and subsequent removal in the biological filter (Ødegaard et al., 2010).

In this master thesis removal of NOM is done by coagulation. A deeper description of the method is given in chapter 2.2.

2.2 NOM removal by coagulation and flocculation

2.2.1 Introduction

Conventional NOM removal consists of coagulation, flocculation and separation. Coagulation is defined as the process that involves addition of a coagulant, for the purpose to destabilize particles in a solution. Once the destabilization is done, flocculation takes place where particles can aggregate and form flocs, as shown in figure 2.

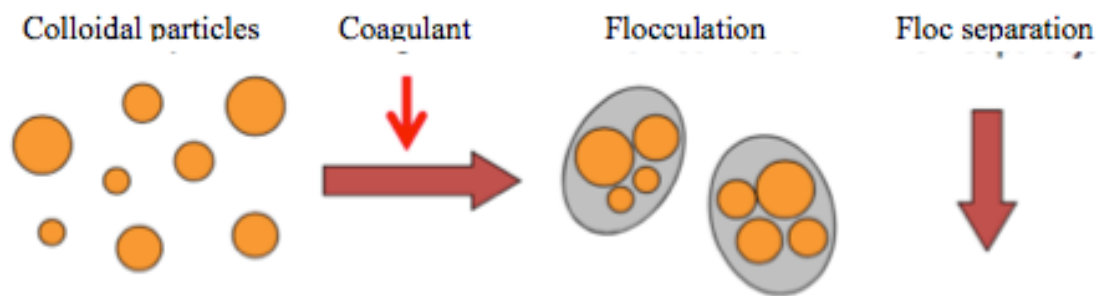


Figure 2 - Illustration of coagulation and flocculation of NOM (Ødegaard, 2010)

The size of particles in water differs from small colloidal ($1\text{nm} < d < 1\mu\text{m}$) particles to bigger suspended solids ($> 0,45\mu\text{m}$). Colloidal particles have a large surface area compared to their molecular weight, causing them to remain floating (Bratby, 2006). NOM molecules will also remain floating because of their small size, and their negative charge makes them stable without coagulation.

Coagulation

The main purpose of coagulation is particle destabilization. In a stable solution, repulsive forces prevent floc formation. Destabilization is done in order to neutralize the charge of the colloidal particles. Surface charge attracts ions of opposite charge,

which also attracts new counterions. This creates an ion cloud around the colloidal particle. The layer of cations and anions, that extends from the negative particle surface via the fixed Stern layer to the end of the diffuse layer, where the charge is zero and electroneutrality is satisfied, is called the electric double layer (figure 3). The electrical potential between the surface and a bit outside the Stern layer is called Zeta potential. Zeta potential is the electrical potential that causes interparticle repulsion. Zeta potential close to zero means that the conditions for aggregation of contaminants are maximized (Morfesis et al., 2009).

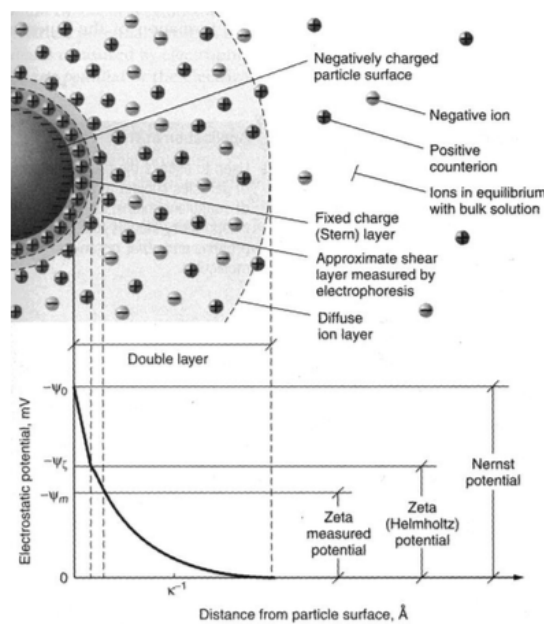


Figure 3 - Electric double layer (Crittenden, Trussel et al. 2012)

There are three main coagulation mechanisms:

1. Adsorption and charge neutralization

Particles can be destabilized by adsorption by oppositely charged ions or polymers. Most particulate matter in natural waters is negatively charged in a neutral pH-range (pH 6 to 8). Polymers of high charge density and low to moderate molecular weight (10 000- 100 000) are believed to be adsorbed on negatively charged particles as a patch on the surface and do not extend much from the surface (Crittenden et al., 2012).

2. Adsorption and interparticle bridging

Polymer chains adsorb on particle surfaces at one or more sites along the polymer chain. This is a result of charge-charge interactions, dipole interactions, hydrogen bonding and van der Waals forces interactions. The rest of the polymer chain remains in the solution and adsorb on the surface of available particles. This creates a bridge between particle surfaces. This mechanism will occur with polymers with high molecular weight and low surface charge, (Crittenden et al., 2012).

3. Precipitation and Enmeshment (Sweep coagulation)

When dosing high doses of metal coagulants, aluminum and iron can create insoluble precipitants. These precipitants can catch other particles and NOM-molecules and make flocs, (Crittenden et al., 2012).

Flocculation

Flocculation is defined as the process where destabilized particles from coagulation are promoted to come together and make contact, forming larger aggregates, called flocs (figure 2). Flocs are heavier, bigger and easier to remove by separation, (Ødegaard, 2012).

It can be distinguished between two types of flocculation; microflocculation and macroflocculation. Microflocculation occurs due to the natural movements of particles in water, known as Brownian motion. This flocculation type takes long time and can be neglected for all larger particles (larger than $0,5\mu$). In macroflocculation you add energy to promote particle collision to create flocs. The velocity gradient is defined as G:

$$G = \sqrt{\frac{P}{\mu V}} \quad [T^{-1}]$$

P is the net power in the fluid, μ is the fluids dynamic viscosity and V is the volume (Crittenden et al., 2012). In the beginning of coagulation, it is normal to use a fast ve-

locity gradient, a high G (400 s^{-1}) to mix the coagulant completely. After short time, approximately 1 minute of high velocity gradient, the gradient G are lowered to let the particles connect and to not break them a part again. This part lasts longer, and the G -values varies from $10\text{-}100 \text{ s}^{-1}$, and retention time varies from $15\text{-}45 \text{ min}$ (Wenseth, 2013).

2.2.2 Coagulation of NOM

The presence of NOM in natural water greatly affects coagulation process. Coagulants remove dissolved NOM by complexation reactions followed by a phase change. An example is NOM removal from a solution ether by forming a solid or adsorbing onto a solid. There are three primary NOM-coagulation mechanisms:

- 1) Complexation of NOM with a dissolved metal coagulant specie, as Al or Fe, leading to precipitation of a Me-NOM solid.
- 2) Complexation of NOM with dissolved coagulant species leading to adsorption of this complexed material onto precipitated $\text{Me}(\text{OH})_3$.
- 3) Direct adsorption of NOM onto the surface of precipitated $\text{Me}(\text{OH})_3$ solids. In addition, NOM can coat inorganic particles, altering their coagulation behavior (Eikebrokk et al., 2006).

Susceptibility to coagulation is depending strongly on the type of NOM. Specific UV-absorbance (SUVA) is a parameter that gives information about that. SUVA correlates with the aromaticity and the hydrophobicity of organic carbon where high hydrophobicity is associated with good removal by coagulation (Eikebrokk et al., 2006). SUVA is defined as the linear relationship between the nonabsorbable fraction of DOC and UV absorbance in water (Crittenden et al., 2012).

$$SUVA = 100 * \frac{UV254}{DOC}$$

Edzwald and Tobiason (1999) developed a method where SUVA was an indication on the coagulation success, in terms of DOC removal by the coagulation step (table 1)

Table 1 – SUVA, (Edzwald & Tobiason, 1999)

SUVA	Composition	Coagulation	DOC removal
>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

2.2.3 Coagulant types

Metal coagulants

Metal coagulants based on aluminum and iron is traditionally used for NOM removal in Norway. Metals go through a hydrolysis and create complexes when they are dissolved in water. Hydrolysis consumes alkalinity, so pH and coagulant dosage are critical parameters for the metal state in and the amount of metals dissolved in water. Pre-polymerized aluminum chloride (PAX) has as an advantage of consuming less alkalinity than alum and is preferred in soft, low alkalinity waters in Norway. Iron coagulants, especially iron chloride (JKL) are extensively used because of a lower metal residual after filtration. Metal residual is the primary parameter when choosing pH, type and amount of coagulant.

Coagulation with organic coagulants

Cationic, synthetic polymers as Chitosan have also been used for NOM removal in Norway. Chitosan is a natural, cationic biopolymer created by deacetylation of chitin. Chitosan remove color reasonably well, but is not comparable to metal coagulant with

respect to DOC removal (Ødegaard et al., 2010). An advantage with chitosan is the low sludge production, and an environmentally friendly sludge without metals. Since chitosan is not a metal, there are no restrictions regarding metal residual.

Tannins are large molecule weight organic compounds, with mole weight ranging from 500 to 3000. They are acidic and formed through decomposition of plants. Different studies regarding coagulation with tanine have been carried out during the last decade. One study states that a coagulant from acacia trees can remove 91% turbidity and 57,3% TDS using a optimal dosage of 3 ml/l (Thakur & Choubey, 2014). Another study showed a 2,5 log removal of *E.coli* after stirring 10 g/l of acaia bark for 24 hours (Fayyad, 2014). However, these studies show as well that tanine is not suitable as a primary coagulant due too high residuals of turbidity, color and coagulant. Drinking water with a high tanine residual can be toxic in large amounts (Fayyad, 2014). Tanine can instead be used as a coagulant aid to reduce the amount of conventional coagulant. This has been tested using a jar test and synthetic water with various turbidity values, and 0,01-1 mg tannin/ml as the coagulant concentration. The jar test gave good results and turbidity concentrations under 0,02 FNU(Özacar & Şengil, 2002).

ECOTAN bio S03 (EB3) is a tannin based organic coagulant, that is approved for application in water treatment. It is a brownish fluid that is extracted from tree bark. EB3 is cationic and thus has a positive surface charge. Charge neutralization is the primary coagulation method because NOM has the opposite surface charge (Crittenden et al., 2012).

2.2.4 Optimization of coagulation

Sub-optimal operation of water treatment facilities is relatively widespread (Eikebrokk et al., 2006). The three most important factors to archive optimal coagulation and floc creation are operational pH, type of coagulant and coagulant dosage. Traditional water treatment facilities have as a goal to remove turbidity. The difference between coagulation for NOM removal and turbidity removal are that NOM removal requires a higher coagulant dose, a stricter choice of coagulant and a more exact pH adjustment (Eikebrokk et al., 2006). This type of coagulation is called en-

hanced coagulation and is predominantly controlled by NOM rather than turbidity or other substances.

The benefit of increasing coagulant dose is easier operation of the plant by a wider pH range (figure 4). There is a minimum critical dose to manage the required effluent quality (MCL). A decreasing dose minimizes this pH range, which makes it harder to operate a successful coagulation process (Ødegaard, 2012). But the dose can also get too high. A too high, not optimum coagulant dose causes increased amount of sludge, a possible higher coagulant residual if the pH is not correct, increased operational cost and short filter runs. Color and TOC removal may also decrease (Eikebrokk et al., 2006).

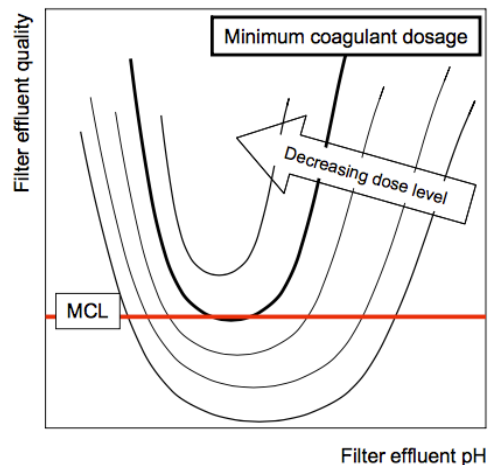


Figure 4 - Coagulation vs pH filter effluent (Eikebrokk, Juhna et al. 2006)

In theory, turbidity is often removed by sweep coagulation at a higher pH, while NOM removal require a lower pH for removal to occur. This is because low pH values affect the formation of metal complexes, which neutralizes the charge of NOM.

The previous section is mainly addressed to metal coagulants. There is not much information regarding optimization of organic coagulants.

2.3 Separation – Membrane filtration

2.3.1 Separation

Separation is the third step of the conventional coagulation-process, but not normal in the coagulation process in Norway because of low turbidity of surface water. There are two different methods to separate, by sedimentation or flotation. Sedimentation is a method where flocs settle and sinks to the bottom, and a clear phase appears at the top of the basin. In a flotation process air is pumped in, and a clear phase appears on the bottom of the basin.

Filtration is the last step of the coagulation-process, and can be used instead or in addition to sedimentation or flotation. In Norway it is normal to use filtration instead of other separation methods. Filtration can be done by different methods; through a membrane filter or through a granular filter. Granular filters consist of one, two or three types of media with different size and density. Sand and anthracite is the most common. Membrane filters have different pore openings depended on how large particles you want to let through.

2.3.2 Membrane filtration

Membrane filtration is used to meet stricter water treatment regulations due its good removal properties. Through membrane filtration biological, physical and chemical aspects can be removed. The influent water affects less the effluent, and the process is less space demanding than granular filtration and sedimentation (Li, Wu, Guan, & Zhang, 2011). Li, Wu et al. 2011 also concluded that a hybrid system containing coagulation and ceramic membrane filtration could remove DOC more efficient than coagulation and ceramic membrane filtration alone. Ceramic membrane filtration also results in lower chemical consumption (Rakruam & Wattanachira, 2014).

Membrane processes are a physiochemical separation technique where the difference in permeability of water constituents is the separation method (Crittenden et al., 2012). Membranes are classified after pore size and material properties. Four membrane types are currently used; microfiltration (MF) is the membrane that let through

the largest components, and reverse osmosis (RO) is the membrane that only let through ions (figure 5).

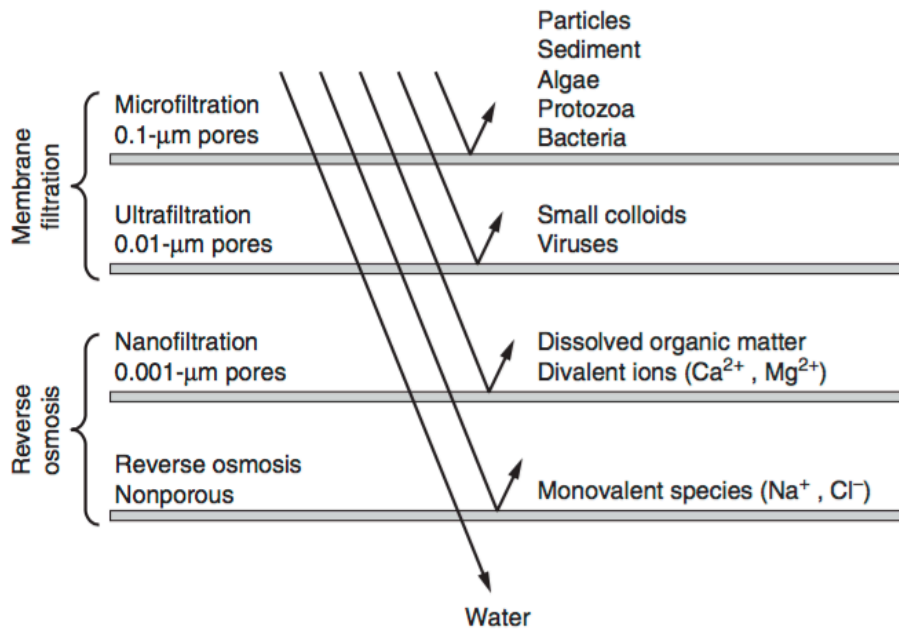


Figure 5 - Membrane specifications, (Crittenden et al., 2012)

Membrane systems are driven by pressure, when the pore size is small, during RO, more pressure has to be added for the raw water to go through the membrane. Typically 5-85 bar for RO, while MF uses pressure between 0,2-5 bar (Crittenden et al., 2012). Because of this RO is rarely used for NOM removal because of the cost of such high pressure. RO is more frequently used for desalination and to remove specific dissolved contaminants as arsenic, which is not a major concern in Norway.

There are different configurations for membranes. Outside-in (figure 6a) is a configuration where you can treat a large amount of water at the same flux because the outside of the fiber has a larger surface area than the inside. Inside-out is a configuration which can be accomplished under two different modes, dead-end and cross-flow depending on the flow regimes in the membrane. Dead-end (figure 6b) is a mode where the feed water flows perpendicular into the membrane, and is a less expensive way to treat water. The disadvantage is that large solids can clog the membrane and that it can treat less water at the same flux because the inside of the fiber has smaller surface area than outside of the fiber. Cross-flow (figure 6c) is the mode where the feed water flows parallel into the membrane. During this mode it is possible to operate at a high-

er flux because the cross-flow velocity flushes large solids and reduces impact of particles fouling the membrane. But there are also disadvantages with this modus. Particles can still foul the membrane, less water can be treated because of the reduced surface area and pumping cost associated with recycling the feed water through the membrane.

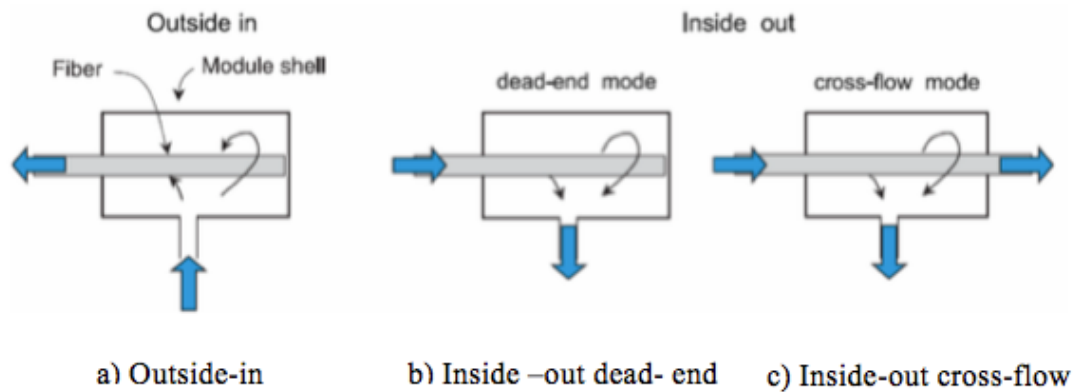


Figure 6 - Membrane configurations, (Crittenden et al., 2012)

Polymeric membranes are widely used in full-scale installations today. This is mainly due to the cost of ceramic membranes (Meyn, 2011), but also because they are available in a large range of pore sizes and because they are easy to obtain. But because of the reduced cost for producing membranes, ceramic membranes have lately been investigated as an alternative to polymeric membranes (Li et al., 2011). Ceramic membranes are able to operate at a higher flux, they experience higher feedwater recovery and backwash under higher pressure than polymeric membranes. Ceramic membranes also have low chemical cleaning requirements and have a longer lifetime than polymeric membranes (Lehman, Adham, & Liu, 2008). Ceramic membrane is therefore a good competitor to polymeric membranes.

2.3.3 Membrane fouling

The biggest challenge for operating a membrane filtration plant is membrane fouling. Fouling can be characterized by pore blocking, pore constriction and cake formation by whether it can be removed and by which material causing it (Crittenden et al., 2012). Membrane fouling causes shorter filtration cycles and a higher energy demand.

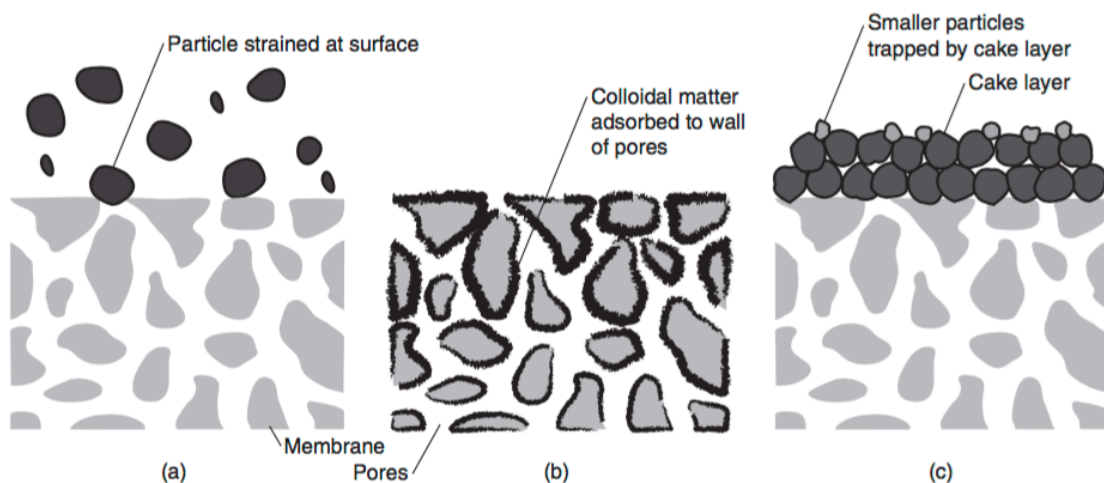


Figure 7 - Mechanisms for rejection in membrane filtration, (Crittenden et al., 2012)

Pore blocking (a) in figure 7, occurs when particles completely blocks the entrance to a pore. Pore constrictions (b) occur when the material smaller than the pores get transported to the pore walls by diffusion or hydrodynamic conditions. A necessity for this mechanism to happen is that the particles must have affinity for attaching the pore walls, if not they will flow right through the membrane. The third mechanism is cake formation (c). Cake formation happens when particles too large to enter the pores creates a cake on the membranes surface. The cake layer acts as a dynamic layer filter and can retain smaller particles, but the layer also generates hydraulic flow resistance. The mechanism depend water characteristics, particle size, stability, porosity and compression ability. It is difficult to understand which mechanisms that occur because several mechanisms often occur simultaneously (Crittenden et al., 2012).

After operating over time, the membrane will gradually be clogged with particles, which will decrease the flux. Full-scale facilities generally operate with constant flux, so it is important to cleanse the membrane regularly. To cleanse the membrane, compressed air and water runs through the membrane. This backwash normally last for one to three minutes and removes the cake layer on the membranes surface. The interval between every backwash is called filter run, and is normally between 30 min and 90 min (Crittenden et al., 2012). It is desirable to have as long backwash interval as possible, to increase the amount of produced water in comparison with loss of water, which is backwashed water. This type of fouling, which can be removed with

normal backwash, is called reversible fouling (figure 8), and is the desirable fouling because it is a easy way to remove solids.

Permanent flux loss, which will not be removed by normal backwash, is called irreversible fouling. To remove this part it is necessary to use chemicals, and this method is called chemically enhanced backwash (CHB). Chemicals used for backwash is acids for inorganic material and bases for organic material (Lerch et al., 2005). How often and for how long CHB is done depends on the amount of fouling, but CHB is normally done after 8-12 filter runs. One to four times a year the membrane goes through a comprehensive cleaning called a CIP process (cleaning in place). CIP is done to cleanse the membrane completely clean, and this is done with chemicals (Crittenden et al., 2012).

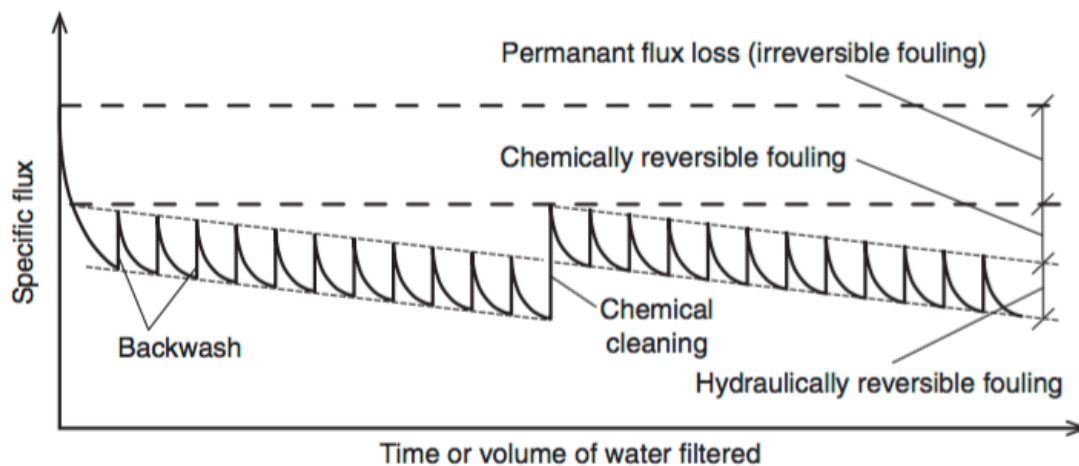


Figure 8 - Variation in specific flux during filtration of natural waters, (Crittenden et al., 2012)

By measuring the pressure loss through the membrane, it is possible to determine the amount of fouling. The idea is to measure the pressure before and after the membrane to see how much pressure is added to push the water through the membrane. This is given through trans membrane pressure (TMP), which is the pressure decay. TMP will increase over time during the filter run, because of continuously fouling. TMP is therefore an important operational parameter on a membrane filtration plant, and tells

the amount of reversible fouling and cake formation. Too high reversible fouling on the other hand causes short filter runs, which is not desirable.

How NOM affects membrane fouling

NOM has been identified as a major membrane foulant for drinking water treatment by low-pressure membranes (LPM) as micro filtration (MF) and nano-filtration (NF), both for polymeric membranes and ceramic membranes. In Norway nanofiltration is the most commonly used membrane, but during the last years coagulation together with MF and UF have been studied for NOM removal (Wenseth, 2013).

The largest component in NOM is hydrophobic fractions, this is also the component which gives color, and therefore desirable to remove. Hydrophobic fractions have a negatively surface charge and can easily be removed by adding a cationic coagulant, which together will create a cake layer on the membrane surface. This means that NOM contribute to reversible fouling, and cake formation. Neutral and hydrophilic parts of NOM as polysaccharides, protein and amino acids are more difficult to remove, and contributes to irreversible fouling. The neutral part is difficult to remove because of its lack of charge, and can therefore not be removed by charge neutralization (Wenseth, 2013).

NOM fouling is a complex phenomenon. This is because of the complexity and different types of NOM that exists in natural sources and NOM-membrane interactions (Raspati, 2015). LMP fouling after coagulation differs from fouling without coagulation, because of the particles surface charge. As told in section 2.2, to archive good coagulation or destabilization is the desirable surface charge is neutral. It is therefore possible to reduce NOM attachment to the membrane by using membranes with higher negatively charged zeta potential, to reduce the attraction force (Raspati, 2015). Konieczny, Bodzek, and Rajca (2006) concluded that coagulation affects membrane fouling in a positive way, and that coagulation should be applied ahead of ceramic membranes to extend the membranes lifetime.

2.3.4 Coagulation – MF filtration versus Coagulation - sandfilter or UF

There are multiple benefits with coagulation – MF-filtration. Metal membranes can be operated with fluxes up to 200 LMH over longer time resulting good result (Leiknes, Ødegaard, & Myklebust, 2004). Ceramic membranes can operate at a higher flux, 250 LMH giving the same good result. Ceramic MF membranes combined with coagulation gives good NOM-removal and have good resistance against chemical cleaning (Meyn, 2011).

Compared with a conventional coagulation - sand filter, coagulation -MF-filter has several benefits. The hygienic barrier is raised, the process is less space demanding, a constant permeate mix, they are lighter and easier to handle and the process is more automatically.

If coagulation – MF –filtration is compared to coagulation – NF-filtration, MF looks like the best choice. MF can operate at a higher flux causing a smaller membrane area, the process is less energy demanding, less fouling and waste less water and chemicals in the cleaning process (Meyn, 2011).

2.4 Water quality requirements

To determine drinking water quality, it has to be set required parameters. In Norway the Norwegian Food Safety Authority, ”Mattilsynet” is responsible for the approval of waterworks and requirement guidelines.

§ 12 in The Norwegian Drinking Water Standard says:

“The drinking water shall, when received by the costumer, according § 5, be hygienic, clear, without any marked taste, odor, or color. It should not contain physical, chemical or biological compounds that may be harmful at normal use.”

(NorwegianFoodSafetyAuthority, 2011)

For a coagulation process considering NOM removal, the required limiting values are listed below, in table 2. The most important parameters are color, total organic carbon (TOC) and coagulant residual.

Table 2 - Water quality requirements, “Drikkevannsforskriften”, (Norwegian Food Safety Authority, 2011)

Parameter	Requirement in Norwegian Water Standard	The Indication for good operation	for Preferable value
Color [mg Pt/l]	<20	<10	<5
TOC [mg C/l]	<5	<3	
Turbidity [FNU]	<1	<0,2	

NOM can create both taste and odor in drinking water, and cause problems for disinfection and corrosion. This is why there are color requirements. Raw water over 20 mg Pt/l must be treated considering color. For raw water below that value treatment is not required but recommended.

If water is treated in order to remove color, and if the process used is to be considered as a hygienic barrier, the water needs to be treated to a color level below 10 mg Pt/l, preferred under 5 mg Pt/l.

Total organic carbon, TOC, is a measurement of the total carbon concentration in water. The requirement is set to 5 mg C/l. A high carbon concentration leads to growth in the network. Because of this we want a lower carbon concentration, and the recommended value is set to 3 mg C/l after a coagulation process.

Since carbon is added to remove carbon in this master thesis, it is interesting to see the final concentration of TOC.

Turbidity in water is caused by the presence of suspended particles that reduce the clarity of water (Crittenden et al., 2012). Norwegian surface water has normally low turbidity, below 1.0 FNU. For that reason treatment regarding turbidity removal is not

normal in Norway. The requirement set by the Norwegian Food Safety Authority is 1.0 FNU out of plant without treatment and $<0,2$ out of each filter after coagulation. At the consumers tap the limit is <4 FNU (NorwegianFoodSafetyAuthority, 2011). Too high levels of turbidity can cause contaminants as viruses and bacteria to attach the suspended solids. It can also increase the growth in the network.

3. Project thesis experiences

ECOTAN bio s03 is the coagulant that is used in this master thesis, and from now on called EB3. EB3 is tannin based, organic coagulant extracted from tree bark. EB3 is a thick and sticky liquid with brownish color and a wood-like smell.

Table 3 - Information regarding ECOTAN bio S03

Parameter	Values
pH sol. aqueous	2,4
Working pH	4,5-8
Specific gravity	1,11 g/cm ³
Viscosity	0-50 cps
TOC	145787 mg C/l

In the project thesis I ran a F-EEM analysis to get some information regarding the coagulant. The result is given in figure 9.

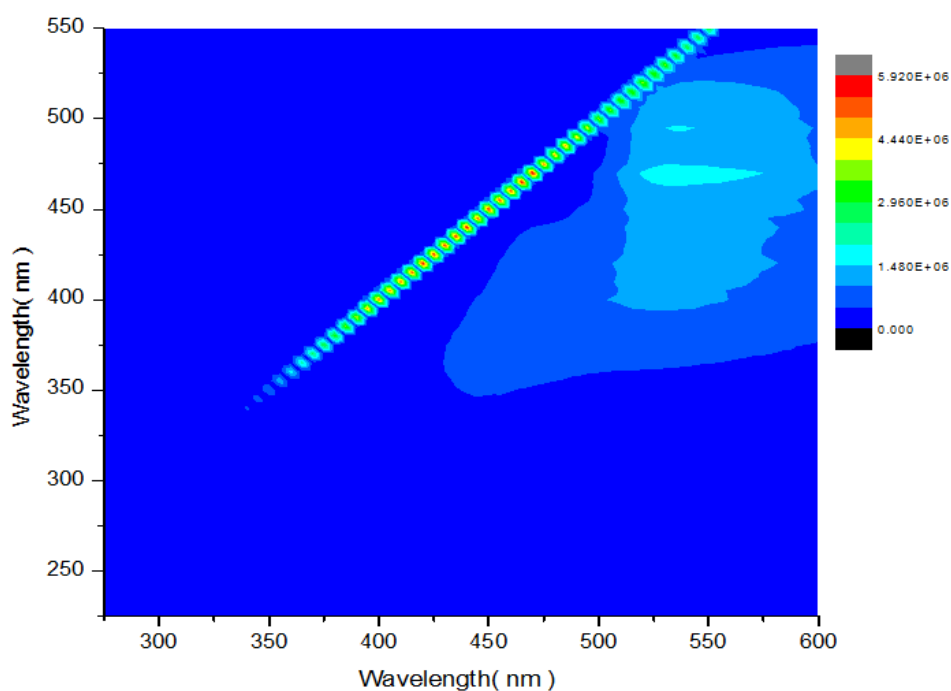


Figure 9 - F-EEM analysis of EB3, diluted 100 times, (Helgestad, 2015)

The figure shows fluorescence signals at an emission wavelength on 500-600nm and 375-500nm as the excitation wavelength. There are little information about these areas in literature, because of that the only conclusion I could draw was that the wavelengths were within the humic specter.

Because of lack of information I ran a LC-OCD analysis to understand what kind of carbon existed in EB3. Figure 10 shows a carbon fractionation of the coagulant.

EB3 mainly consist of low-molecular weight neutrals (83%), which have low ion density. The second largest fraction is building blocks (7,10%), which represents the breakdown of humic substances. Acids are the smallest fraction with 1,80%. EB3 is an cationic coagulant with a positive surface charge (Crittenden et al., 2012).

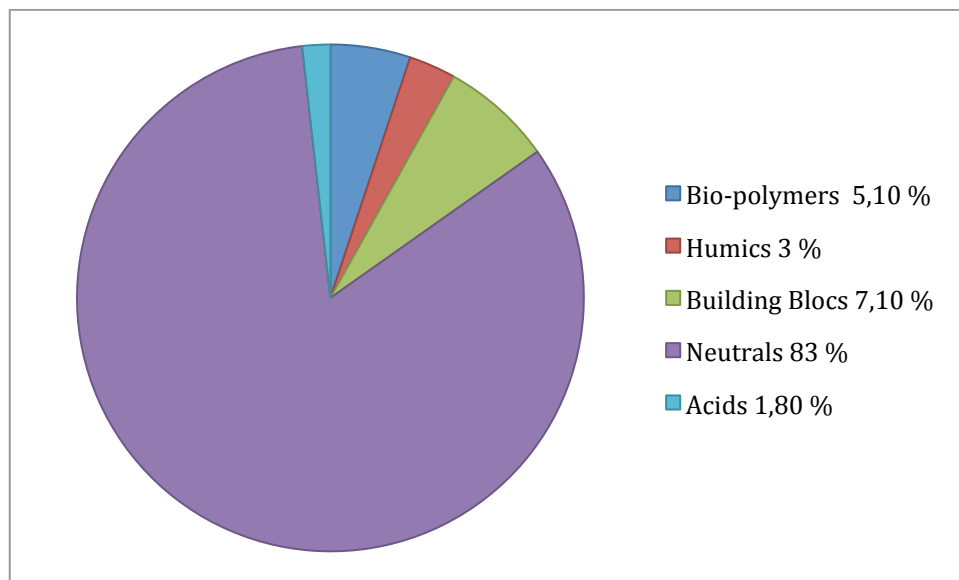


Figure 10 - Carbon characterization, EB3, (Helgestad, 2015)

EB3 was evaluated as a water treatment coagulant in my project thesis. The results are given in figure 11, 12 and 13. The dose was diluted 100 times, which means that the amount of EB3 added is 40-80 mg/l.

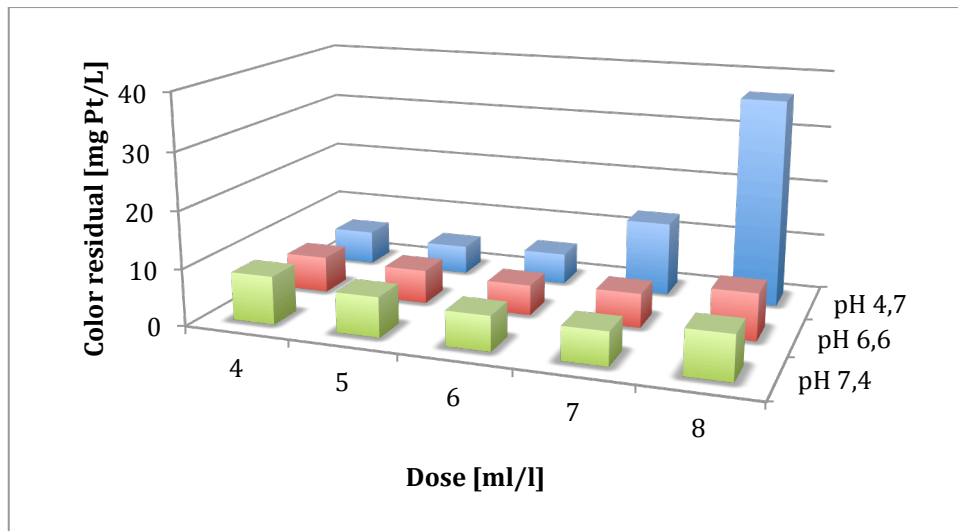


Figure 11 - Color residual from project thesis, (Helgestad, 2015)

The result was that the recommended value given in the Norwegian drinking water standard considering color was reached in most cases. But the preferable value, color < 5 mg Pt/l, was not met.

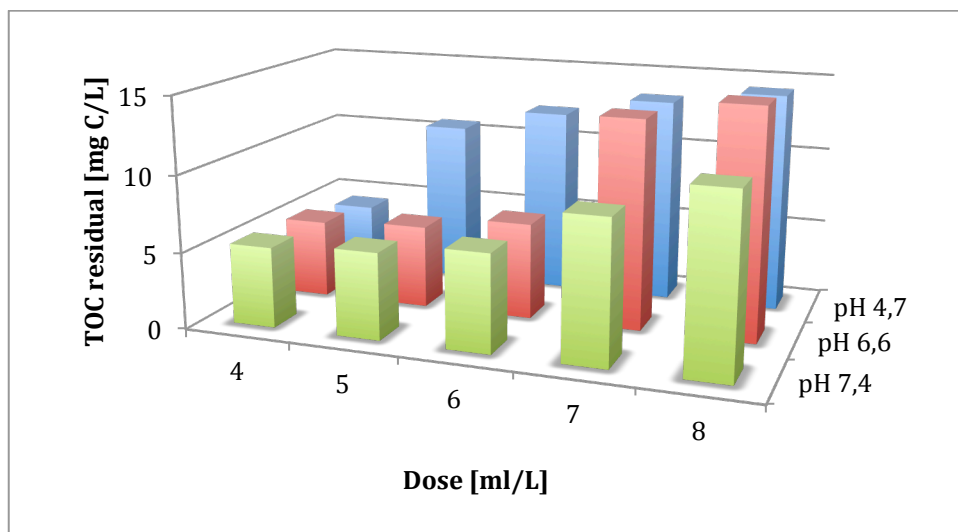


Figure 12 - Carbon residual from project thesis, (Helgestad, 2015)

The biggest problem in the project thesis was to remove enough carbon to reach the Norwegian drinking water quality standard, when such amounts of carbon were added in the coagulation step. I managed to remove most of the humic substances, but because EB3 contained such high amount of neutrals, the carbon concentration was too high in the end.

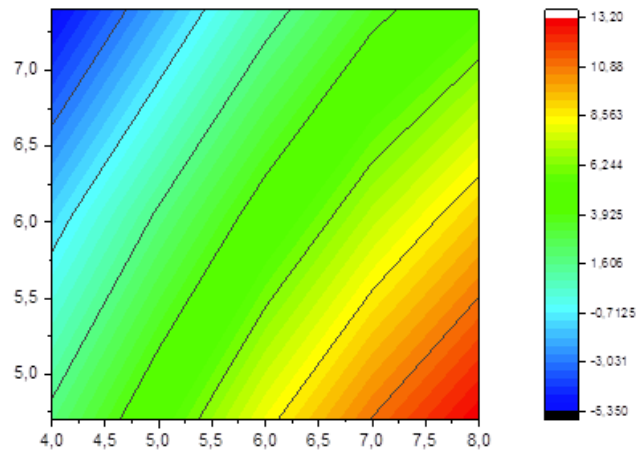


Figure 13 - Relationship between zeta potential, pH (Y-axis) and dose (X-axis)

An evaluation of the various zeta potentials was also carried out (figure 13). But it was difficult to use the information when it was little correlation between zeta potential, color and carbon removal.

EB3 was therefore not recommended for NOM-removal under Norwegian conditions using coagulation, flocculation and sedimentation as a method (Helgestad, 2015).

4. Questions to answer

1. Is it possible to remove enough carbon?

On background on my project thesis the biggest question is if it is possible to reach the Norwegian drinking water standard considering carbon concentration. EB3 contains 145787 mg C/l and that was the biggest issue during the project thesis (Helgestad, 2015).

2. How will EB3 affect membrane fouling

Fouling is the biggest challenge in a membrane treatment facility. Coagulation normally benefits the resistance for fouling; my question is whether that applies with EB3 too.

5. Methods

5.1 Process configuration – the pilot plant

The experiments were done in a membrane filtration pilot plant containing coagulation and flocculation as pretreatment, as shown in figure 14. The goal is to obtain good NOM-removal and remove efficient amount of color and carbon.

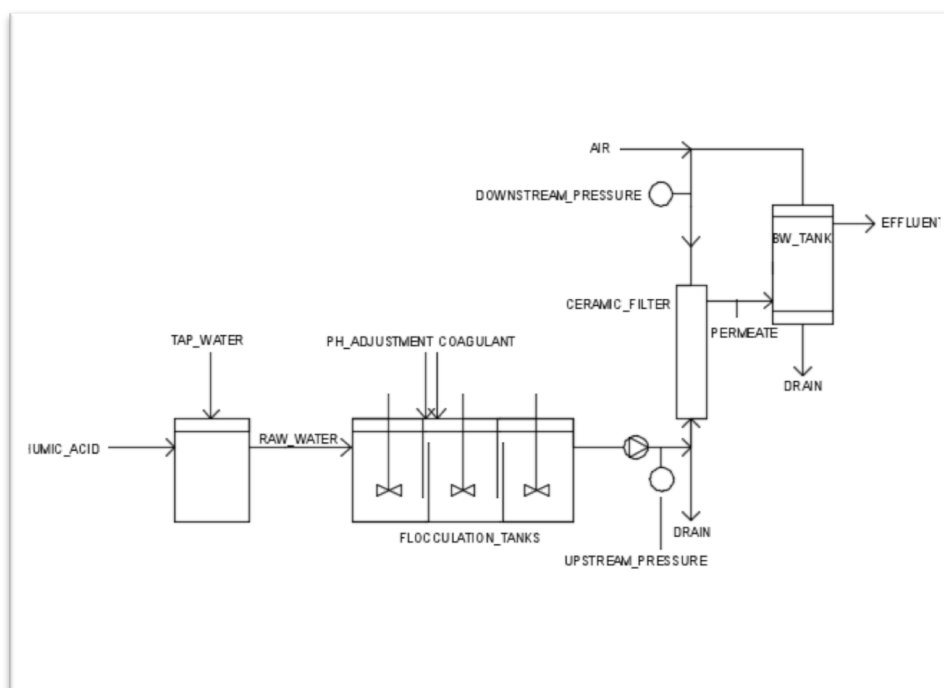


Figure 14 - Pilot plant setup

Under the master thesis three identical, parallel lines have been used, running under different conditions. Tap water was first mixed with organic matter concentrate, before entering the mixing tanks. More information regarding that procedure is given in chapter 5.3. First acid was added to adjust the pH to the desired value, and then the desired amount of coagulant was added. Total retention time after adding acid and coagulant was 20 minutes. Operational parameters are given below in table 4.

Table 4 - Operational parameters coagulation and flocculation

	G-value [s ⁻¹]	Retention time [min]	Volume [L]
Rapid mixing	118,7	13,3	168
Slow mixing	12,2	6,7	334

The next step was membrane filtration. Pretreated water got pumped into the membranes at a constant flux of $139,5 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, which is equal to 1 L/min. The pilot plant was equipped with three identical ceramic membranes, operated in dead-end, outside-in mode with a nominal pore size of $0,1 \mu\text{m}$. Each membrane module was 1m long with an effective area of $0,43\text{m}^2$, consisting of 55 channels. All membrane specifications are given in table 4. Regular cleaning with water and high pressure was performed each hour. The backwash pressure was initially 5 bar then decreased to 2 bar at the end of the regular cleaning. The regular cleaning lasted in total for 10 seconds. Between each experiment the membranes got soaked with chemicals at $40\text{-}45^\circ\text{C}$. First over night by citric acid solution ($w=1\%$ and $1,9 < \text{pH} < 2$), and then by sodium hypochlorite ($c = 3 \text{ g/kg}$) for approximately six hours.



Figure 15 - Photo of the ceramic membrane, taken of T. Meyn

Table 5 - Test conditions

Membrane type	Ceramic membrane
Module length/diameter	1m/0,3m
Channels pr module	55
Channel diameter	2,5mm
Module area/nominal pore size	$0,43\text{m}^2 / 0,1\mu\text{m}$
Operational flux	$139,5 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$
Regular cleaning intervals/procedure	1 hr/backwash and air blow

5.2 Measured parameters

5.2.1 Color and UV₂₅₄

Visible and ultraviolet absorbance has extensively been used to characterize raw water, before and after treatment. UV₂₅₄ and color are also used as a surrogate parameter to DOC because of their good association to DOC (Eikebrokk et al., 2006). UV/VIS Spectrometer, Lambda 650, measures UV₂₅₄, UV₄₁₀ and color. The samples for color were measured in a 5 cm cuvette at 410nm wavelength. They were also filtered through a cellulose nitrate filter with pore size 0,45µm in advance. The formula to calculate color from absorbance is: Color = 369,14 *absorbance (410nm). UV₂₅₄ was also measured in a 5cm cuvette, but divided by five.

A curve that adjust color on the basis of pH was made to optimize color results. Hydrochloric acid was added raw water, to create raw water samples with different pH values. Then color was then measured and plotted into a correlation factor –curve (figure 16).

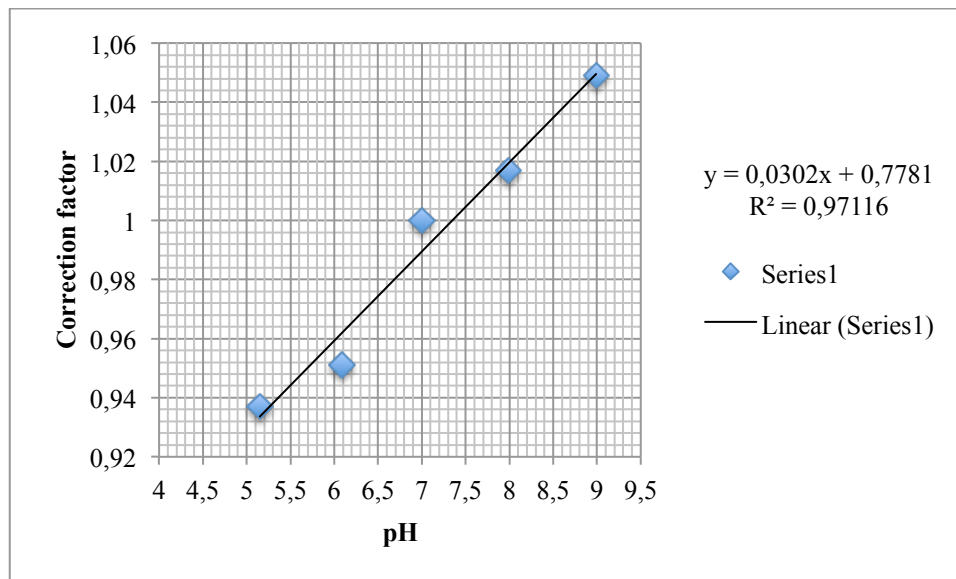


Figure 16 - Correlation factor for color measurements on the basis of pH

Table 6 - Color and correlataion factor including standard deviation

pH	Color	Corr.factor
5,15	34,638±0,043	0,937±0,0011
6,09	35,167±0,1858	0,9517±0,005
7	36,951±0,0977	1±0,0026
7,99	37,566±0,0213	1,0164±0,0006
8,99	38,735±0,0426	1,0483±0,0012

The correlation was done by dividing the color measurements from the pilot plant by the correlation factor in figure 16. The difference before and after correction was rather small, an increase in color for low pH values, and a decrease for high pH values. An example is a sample with pH 9,1. The samples original color number is 24,99 mg Pt/l, but after correction the color is 26,72 mg Pt/l.

5.2.2 TOC and DOC

Total organic carbon (TOC) and dissolved organic carbon (DOC) were measured with Fusion Total Organic Carbon (TOC) Analyzer TM. DOC was filtered through a cellulose nitrate filter with pore size 0,45µm in advance.

5.2.3 F-EEM

Fluorescence Excitation – Emission Matrix is a test widely used to characterize dissolved organic matter (DOM) in water. In this master thesis I will look at wavelengths and peaks at the emission/excitation spectra to characterize the raw water sample, (Chen, Westerhoff, Leenheer, & Booksh, 2003). To run this test, Horiba Fluoromax-4 will be used.

5.2.4 SUVA

SUVA means specific UV absorbance and is an indication on expected DOC removal. The relationship is given in the theory part. UV was measured by UV/VIS Spectrometer, Lambda 650. The sample was measured in a 50mm cuvette three times, and then I found the average and divided by five. DOC was measured with Fusion Total Organic

Carbon (TOC) Analyzer TM and was filtered through a cellulose nitrate filter with pore size 0,45µm in advance.

5.2.5 LC-OCD

LC-OCD is the concept of organic carbon fractionation. The method is used to separate the pool of NOM into major fractions of different sizes and chemical functions and to quantify these on the basis of organic carbon. The method is based on sending a sample through a size exclusion chromatography column and measure the time this sample use to the finish line. Larger fractions will use shorter time than small, and this way we can determine the different fractions of NOM in the solution. The method is further described elsewhere (Huber, Balz, Abert, & Pronk, 2011).

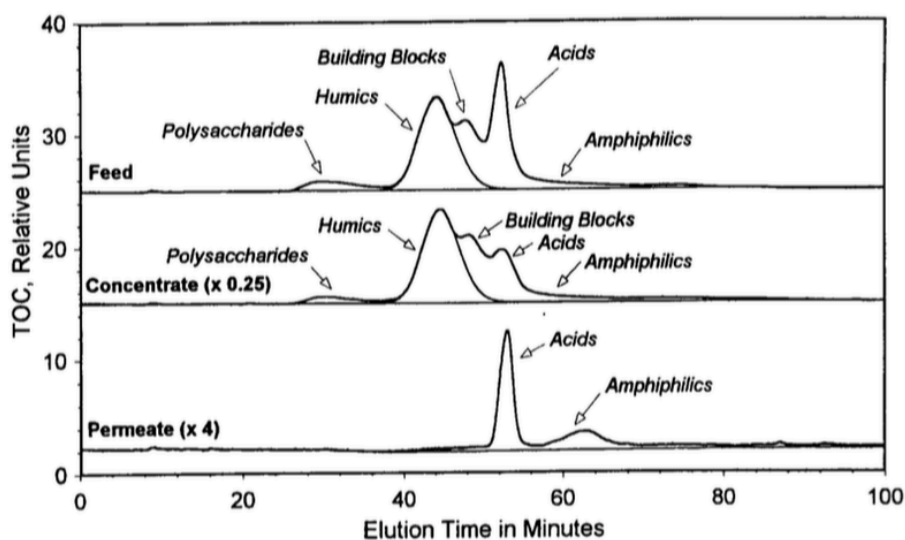


Figure 17 – Chromatogram (Huber 1998)

Figure 17 is an example on how liquids are acting in a chromatogram. This confirms that the largest particles use shorter time through the installation.

The results are graphically presented in the result part, while the background data is given in appendix 1.

5.2.6 Fouling

Fouling is clogging of the membrane, and is designated with Trans Membrane Pressure (TMP). TMP is an expression of the pressure difference before and after the membrane, and describes fouling over the membrane (figure 18). TMP was measured

and logged online in a text file by the pilot plant. This text file was then processed with a Matlab script and at the end in Excel to find the total increase in TMP per cycle and the total increase for the whole experiment. TMP is given in kPa.

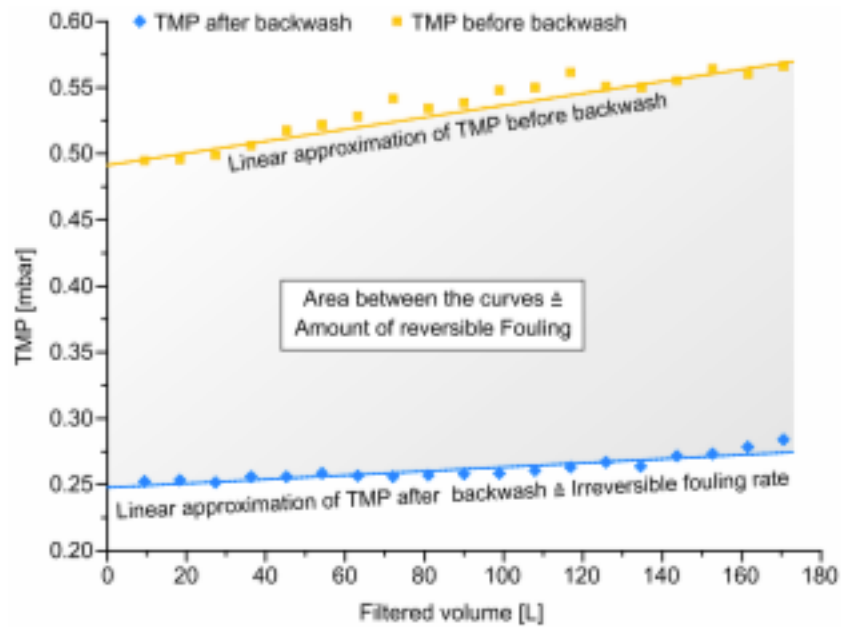


Figure 18 - Example calculation on reversible and irreversible fouling,(Meyn, 2011)

TMP were also used to calculate reversible and irreversible fouling. TMP before and after each backwash were plotted against filtered volume, as shown in figure 18. Then the best-fitted regression curve was added, representing the actual fouling rate during an experiment. Because some very short filter runs, it was difficult to make straight lines, so there are some uncertainties in the calculations. Then the area between the two curves was calculated, and divided by the total filtration time. That represents the reversible fouling rate, expressed as mbar/h. The irreversible fouling rate is the area under TMP after backwash divided by the total filtration time, expressed as mbar/h.

5.2.7 Jar test

Jar test is a good way to figure out the optimal pH and coagulant dose. The process is efficient and it is possible to use the same conditions as in full scale.

5.3 Raw water

In this study analogue water is used to archive stable raw water characteristics. Tap water is mixed with organic matter concentrate, obtained from a nearby ion exchange water treatment plant. Use of analogue water for pilot projects have been a success several times before (Meyn, 2011), (Leiknes et al., 2004). The raw water values in this master thesis will vary through the experiments because I manually had to adjust the amount of tap water.

5.3.1 Analogue water vs. natural water

Meyn (2011) did a study comparing analogue water and natural water as pretreatment in a coagulation tank and in inline coagulation. The results showed similar results, with the exception of alkalinity, pH, calcium and BDOC primary. The biggest contrast is irreversible fouling where analogue water gets 15-20% higher fouling than natural water. Analogue water has lower reversible fouling, which is nor beneficial. The results regarding color and DOC removal were comparable, with only 10% higher removal for natural water (Meyn, 2011). This study illustrates that analogue raw water can be used for coagulation - membrane filtration.

6. Results and discussions

6.1 Raw water characteristics

To archive the desired color and TOC values, NOM regenerate was added to tap water from Trondheim. The characteristics of the raw water used in this master thesis are listed below, in table 7. The values vary from experiment to experiment because I manually had to adjust the amount of tap water for every experiment.

Table 7 - Raw water characteristics

Parameters	Value
TOC	4,1384-6,6564±0,6463
DOC	4,8169 ± 0,1276
Color	37-44±0,21
SUVA	3,69

The raw water contains a great number of color that varies through the experiments and a grate amount of carbon. The small difference in DOC and TOC indicates that carbon mainly is dissolved.

The specific UV-absorbance analysis gave a SUVA on 3,69. According to table 1 that represents 25-50% DOC removal during coagulation. SUVA between 2 and 4 indicates that the raw water is a mixture of aquatic humic substances, hydrophobic and hydrophilic humic substances. The raw water contains humic substances with a diversity of molar weights. I did not calculate SUVA for every experiment, because an exact value is not that important when SUVA only gives an indication on the result of the coagulation.

To confirm the humic content in the SUVA analysis, a F-EEM analysis was performed. The result is given below in figure 19.

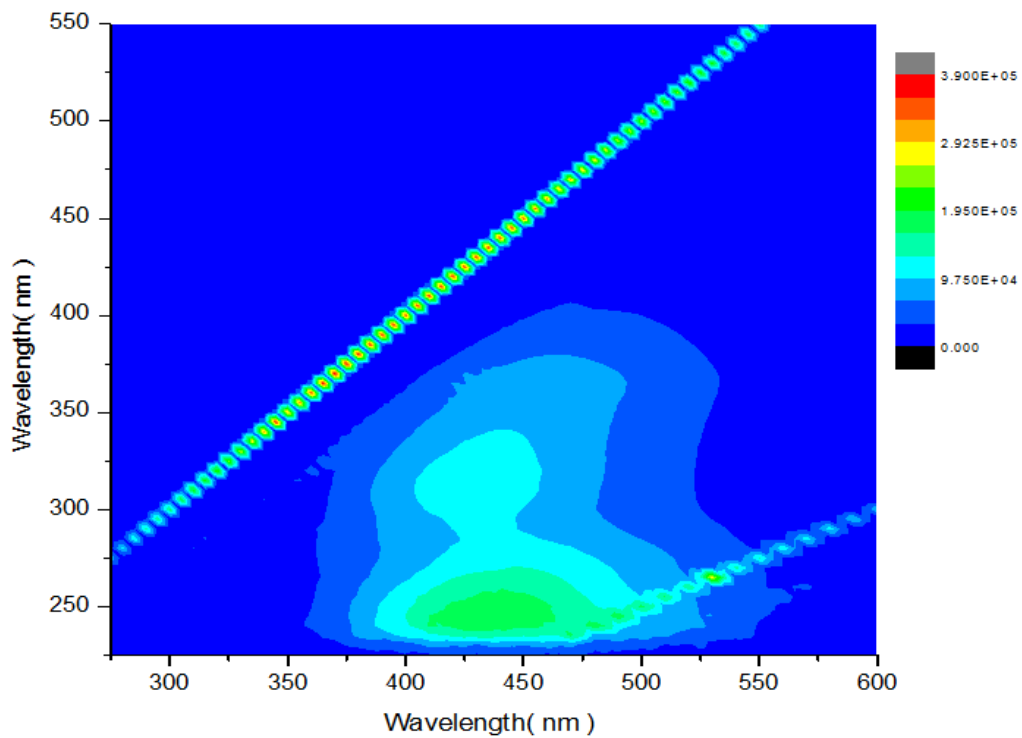


Figure 19 - Raw water F-EEM analysis

The raw water fingerprint had an emission wavelength between 400nm and 475nm, and an excitation wavelength between 230nm and 260nm. This wavelength fingerprint relates to the hydrophobic fraction given in (Chen et al., 2003). That concludes that the raw water used in this master thesis mainly consist of humic substances with high MW.

A LC-OCD analysis was also done to characterize carbon in the raw water. Figure 20 shows the results.

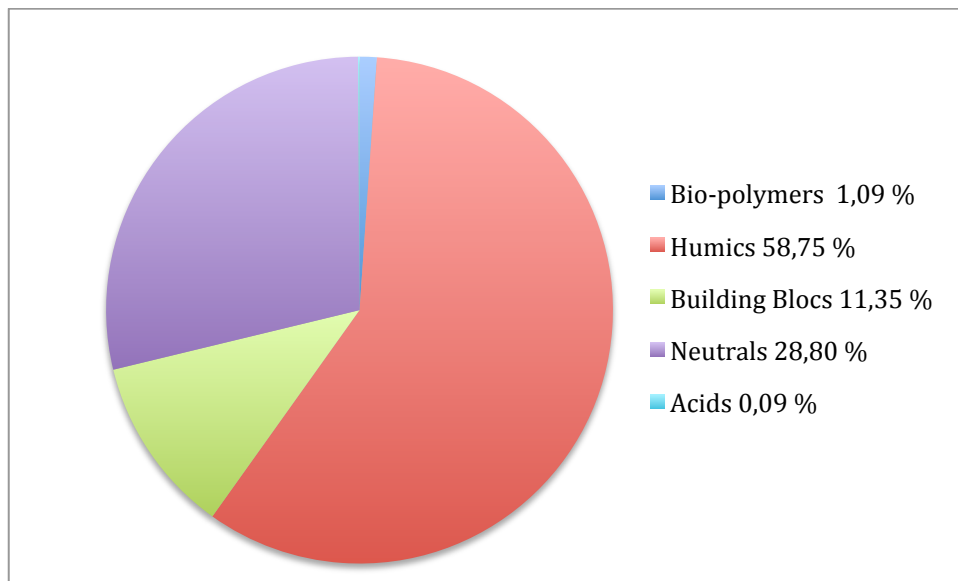


Figure 20 - Carbon characterization, the analogue raw water

The biggest share is not surprisingly humic substances by almost 60%, a little less than in Leirsjøen from the project thesis. The second largest share is neutrals by almost 30%. Leirsjøen only contained 10% neutrals, so this difference may contribute to a difference in coagulation efficiency.

6.2 Experiences with ECOTAN bio s03

Biological growth

For the pumps to deliver the right amount of coagulant, milli-Q water was in this experiment added to dilute the coagulant concentration. The dilution ratio was 1:50. This mix remained in the coagulation tank during each experiment, in the beginning a little bit longer. Over some time I registered some biological growth, molds or fungi in the coagulation tank (figure 21). The biological growth had a white, light yellow color and a gentle, fluttering consistency. This was not observed during the project thesis, even though the mix was in a bottle for several months. The only difference between the master thesis and the project thesis regarding the coagulant is the dilution ratio; in the project thesis ratio 1:100 was used. I do not think that the dilution ratio made the difference. I think the reason has to be a reaction with residuals from inside the tank. Since the coagulant is formed through decomposition of plants, there is likely to believe that this is a biological reaction.

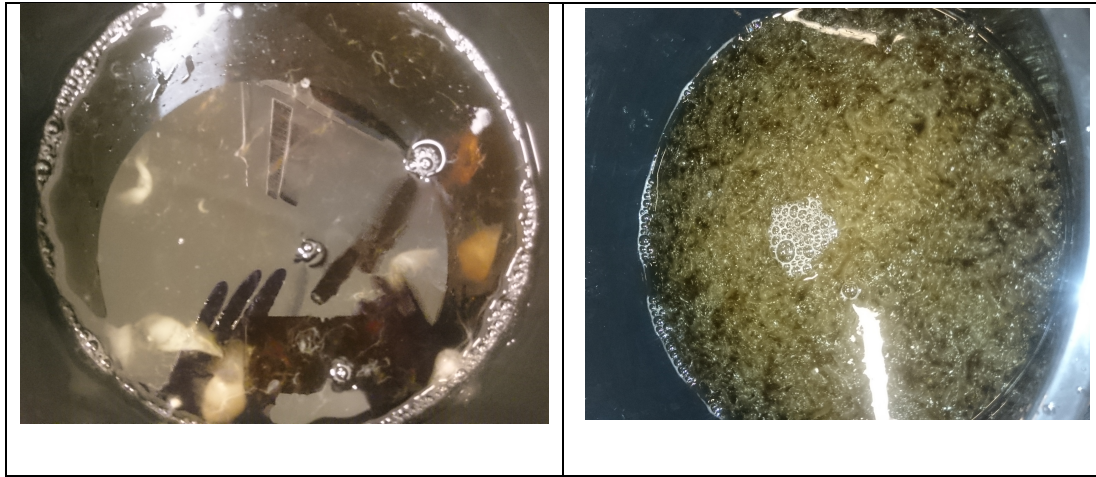


Figure 21 - Picture of the EB3 growth

To avoid this problem I added the coagulant to the coagulant tank containing milli-Q water right before starting each experiment. Because each experiment lasted up to 48 hours, molds or fungi still grew in the coagulation tank, and in the pipelines. Biological growth in the pipelines resulted in troubles for the pumps, which got clogged. I tried to clean both the pipelines, coagulation tank and the pumps with sodium hypochlorite (3000 ppm), but the growth continued.

6.3 The pilot plant

Six rounds of experiments were done in this master thesis, where in total 18 different conditions were used testing EB3. An overview is listed in table 8. Each experiment was scheduled for 48 hours, but as table 8 shows that did not happen. The experiments that did not run in 48 hours were stopped when the membranes were full, and when the pumps did not deliver the right amount of permeate. Or because of time limitations.

Table 8 - Conditions for each experiment

Nr	pH	Amount [mg/l]	EB3	Run time [hr]	Membrane/line [number]
1-1	6	20		48	1
1-2	6	30		24	4
1-3	6	40		48	3
2-1	6	50		8,5	1
2-2	6	60		3,5	2
2-3	6	70		8	3
3-1	7,5	20		47	4
3-2	7,5	30		1,5	2
3-3	7,5	40		1	3
4-1	7,5	50		4	4
4-2	7,5	60		0,5	2
4-3	7,5	70		0,5	3
5-1	9	20		24	2
5-2	9	30		10	2
5-3	9	40		1,5	3
6-1	9	50		15	4
6-2	9	60		2	2
6-3	9	70		2	3

The first obstacle was to adjust raw water to the desired pH value. On the basis of the project thesis (Helgestad, 2015) I chose 6, 7.5 and 9 as the pH conditions I wanted to test. Here hydrochloric acid was added to adjust the pH. During the optimization I have only focused on pH and dosage. If I had longer time I would have focused more on flocculation duration and speed, and operated under different fluxes.

6.4 Pilot plant results

All 18 experiments were scheduled for 48 hours, but some of them stopped earlier, because of clogged membranes and too high TMP, or because of time limitation. To examine how color and TOC varies over time, and if the results were trustworthy

even if the experiment only lasted for some hours, samples were taken evenly during 48 hours, as figure 22 shows.

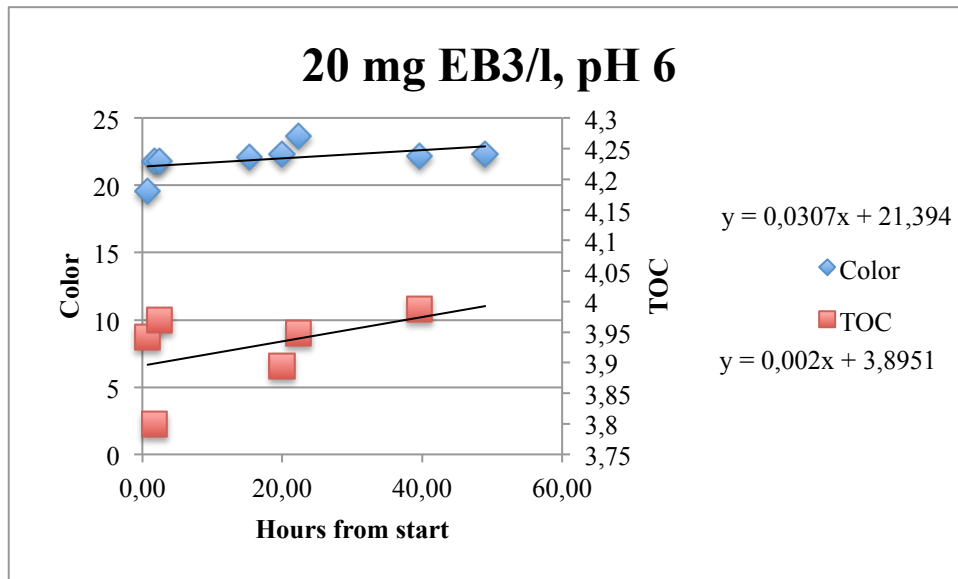


Figure 22 - Change in color and TOC concentrations over time

The trendlines shows that both the color and carbon residual increase over 48 hours. But the increase is so small that it is negligible, as the linear equations show. On the basis of figure 22, I assume that point measurements can be used as reliable results.

6.4.1 Color removal

On the basis of the project thesis I assumed good color removal and color residual between 5 mg Pt/l and 10 mg Pt/l. The figure below shows an overview over color residual through all the experiments.

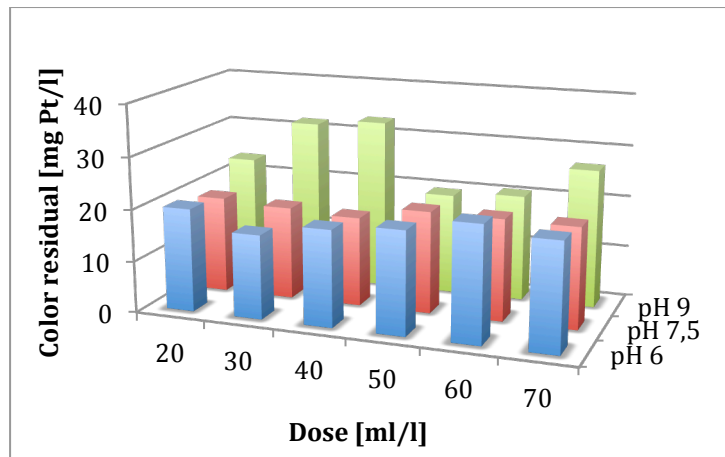


Figure 23 - Color residual dependence on pH and coagulant dose.

The recommended value for color residual in the Norwegian drinking water standard after coagulation is < 10 mg Pt/l, preferably < 5 mg Pt/l. As shown in figure 23, none of the values were within the expected range. Around 50% of the raw water color was removed during the treatment process. There were some initial raw water variations, but that should not affect the treatment efficiency. The best result was 61% color removal with 30 mg EB3/l at pH 6, but a color residual on 16,26 mg Pt/l is much higher than the recommended value. The removal rate is slightly decreasing while increasing dose at pH 6 and 7.5. On the basis of the project thesis and literature I had expected a U-formed figure (Fayyad, 2014). The removal rate at pH 9 had a decreasing slope when the dosage increased, opposite than for pH 6 and 7.5.

6.4.2 Carbon removal

In terms of carbon removal, concentrations between 5 mg C/l and 15 mg C/l were expected. The results are given below in figure 24.

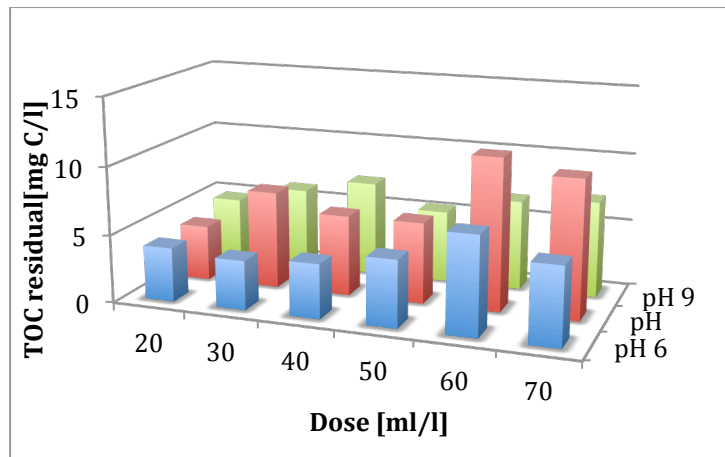


Figure 24 - Carbon residual in dependence on pH and coagulant dose.

The TOC requirement given in “Drikkevannsforskriften” is <3 mg C/l after coagulation. That requirement will not be met at pH 6, 7.5 or 9 with EB3. The lowest carbon residual concentration was 3,6 mg C/l, achieved at pH 6 with 30 mg EB3/l. The figure shows an increase in carbon residual when increase in dosage. The increasing amount of carbon is not unexpected because of the high concentration of carbon in EB3. This was also registered during the project thesis, and in other literature (Fayyad, 2014). In these experiments carbon is only removed with low coagulant concentrations, preferably at pH 6. With 60 and 70 mg EB3/l at pH 7.5 there is observed an over 100% increase of carbon.

6.4.3 Reversible and irreversible fouling

Reversible fouling is defined as the amount of fouling which can be annulled by normal backwash. In this thesis quantified as the area between the two TMP graphs, before and after backwash (figure 18). Because of the variety in filter run time, the average pressure build up per hour is plotted in the figures below (figure 26 and 27). Some of the experiments got their membrane clogged after so short time that there was not possible to calculate reversible or irreversible fouling. Those experiments were 3-2, 3-3, 4-2, 4-3 and 5-3, and illustrated in appendix 1. Experiment 2-2, 6-2 and 6-3 also had small amount of TMP-data. Reversible and irreversible fouling is calculated for these experiments, but the result is uncertain because of small amount of data.

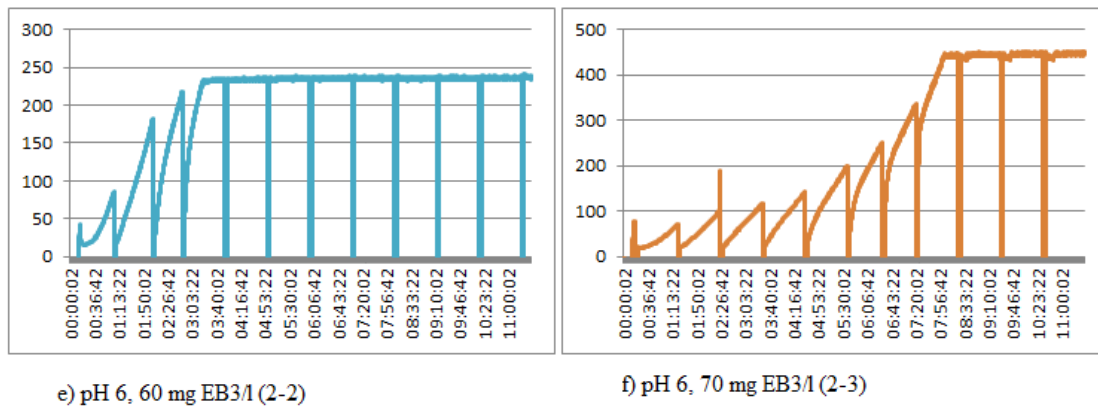


Figure 25 - Examples of TMP over time.

One parameter in calculating reversible and irreversible fouling is the membrane/lines maximum TMP potential. The maximum TMP the membrane can handle before it stops delivering the desired amount of permeate. The membrane is clogged and ready to get cleaned at approximately 150 kPa, but in these experiments the maximum measured stable kPa value varies from 250 kPa to 500 kPa. An example is given above in figure 25, the complete list is given in appendix 1. For membrane 1 the maximum is 500 kPa, and for membrane 2 the value is much lower, 250 kPa. For membrane 3 the value is 450 kPa and for membrane 4 the value is 250 kPa in the beginning and 500 kPa in the last run. This difference will contribute significantly to the result when fouling is calculated from the area under each graph.

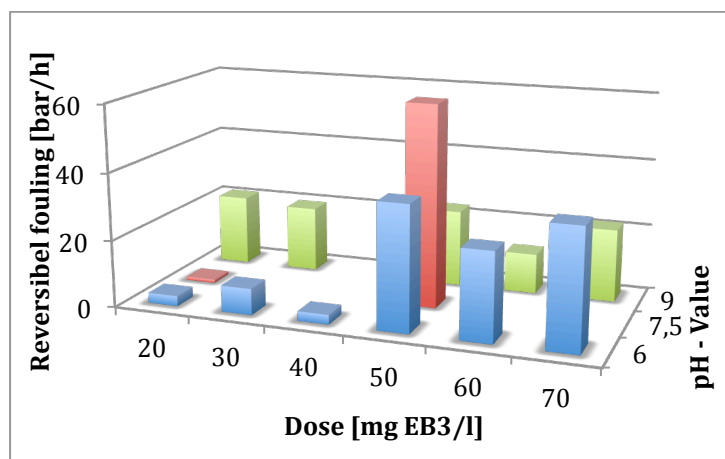


Figure 26 - Reversible fouling rate in dependence of pH and coagulant dose

Figure 26 shows a large variability in average reversible fouling from 0,96 bar/h to 62,7 bar/h. The highest value was reached at pH 7,5 with 50 mg EB3/l, an experiment with a steady, high increase for 4 hours before it reach the membranes maximum ca-

capacity. 62,7 bar/h is a very high pressure build up and indicates that something is not working as it should be working. 0,96 bar/h is the lowest value. This value was accomplished at pH 7,5 and with 20 mg EB3/l, and were one of the experiments ran for 22 hours without any significantly TMP increase.

Irreversible fouling, the fouling that is not removed by normal backwash is in this thesis quantified as the area under the linear TMP graph after backwash. In figure 27 is the irreversible fouling divided by the total filtration time to show the irreversible fouling rate.

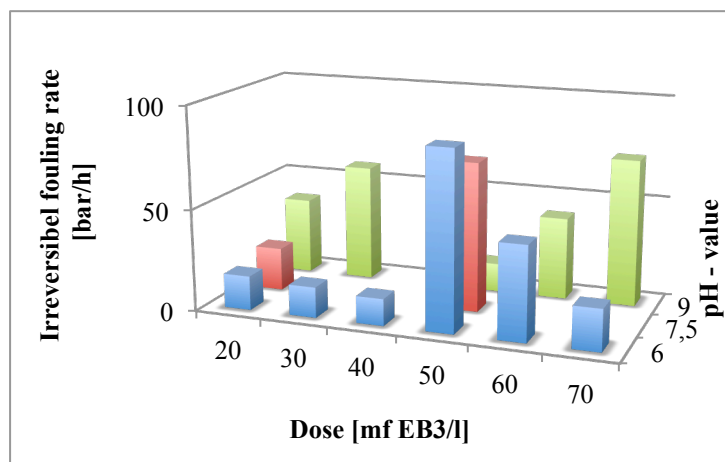


Figure 27 - Irreversible fouling rate depended on pH and coagulant dose

The tendency with large variations continues on figure 27. The irreversible fouling rate is highest at pH 6 with 50 mg EB3/l (2-1), when the fouling was 87,11 bar/h. That was an experiment that ran for eight hours before the membrane were completely clogged. Run 2-1 also had high average reversible fouling, 325,6 bar. The lowest irreversible fouling were archived at pH 6 with 40 mg EB3/l (1-3), 13 bar/h. Run 1-3 ran for 47 hours without any significant increase in pressure.

It is difficult to draw any conclusions from these results. Preferably these results could give information regarding floc creation, because high irreversible fouling indicates poor floc creation. High dosages may give higher reversible fouling because the higher amount of sludge produced will increase the load on the membranes. The fouling is too high, and the results vary too much that it is difficult to draw any conclusion. The problem may be the analogue water because the use of analogue instead of

natural water affects fouling negatively. Irreversible fouling is higher and reversible fouling are lower using analogue water compared to lake water (Meyn, 2011).

It is also difficult to see any connections between the different parameters. At pH 7,5 the lack of data makes it hard to find connections between fouling, color and carbon removal. At pH 6 and pH 9 there is enough data, but no clear correlations between the different parameters.

6.4.4 Jar test

The high color residual in the pilot plant experiments was a surprised. The color residual was much higher than during the jar test in the project thesis. One possible solution could be that the membrane feeding pump broke the flocs. That incident has been observed several times before. The re-growth potential is high if a metal coagulant is used and if charge neutralization is the dominating coagulation mechanism (Meyn, 2011). But breakage of flocs could be a greater problem using an organic coagulant. On that basis a jar test was established using analogue water and the same conditions as in the project thesis. First by adding the coagulant, then rapid mixing for one minute. Slow mixing for 20 minutes and 20 minutes sedimentations at the end. The results are shown in the figure below.

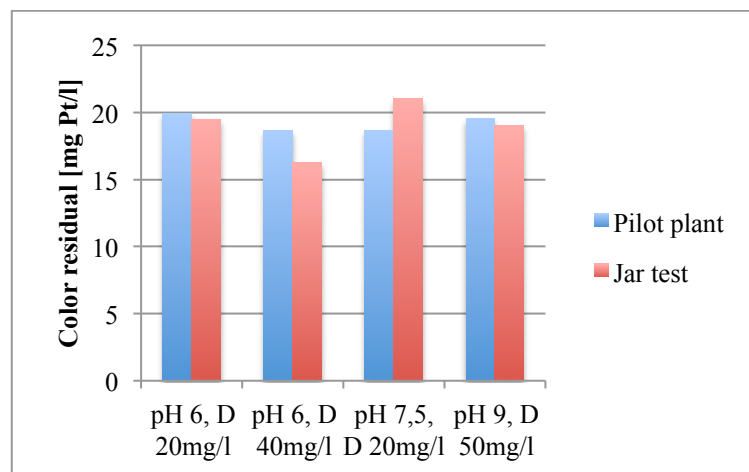


Figure 28 - Comparison between the pilot plant result and jar test on the basis of color residual

Figure 28 shows that the results considering color residual are approximately the same for the pilot plant and the jar test. The only difference between this jar test and

the jar test in the project thesis is the raw water. Raw water from a lake in Trondheim, Norway was used in the project thesis, while analogue water is used in the master thesis. On the basis of the LC-OCD analysis (figure 20), there were some differences in carbon composition between water from Leirsjøen and the analogue water. The analogue water is very basic and adjusted with a great amount of acid to reach pH 6, 7.5 and 9. That may be a difficult combination for the coagulant. The only conclusion that can be drawn is that flocs are created and that they partly settle after 20 minutes of sedimentation. But that do not change the fact that color is not removed.

6.4.5 Carbon characterization

To get more information about what kind of carbon that was removed and added, a LC-OCD analysis were completed. A complete overview is given in appendix 2. One of the main objectives in this master thesis was to remove color and hereby NOM which is causing the color. In the figure below (figure 29), NOM removal and color residual are plotted on the basis of added coagulant dosage.

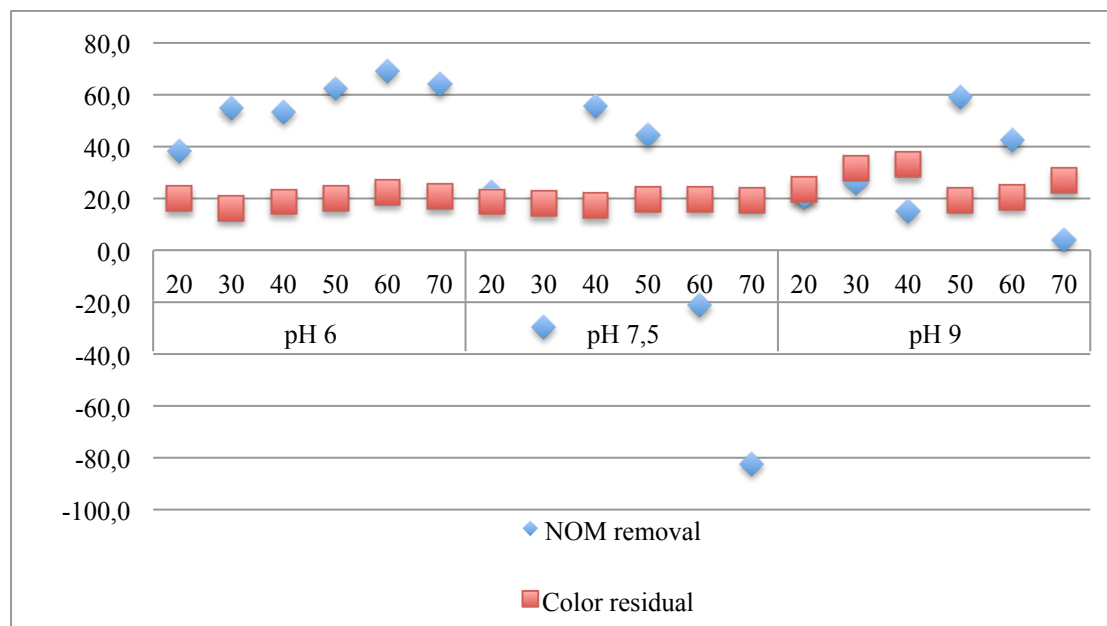


Figure 29 - Removal of NOM and color on the basis of coagulant dose.

The figure shows occasionally correlations between NOM and color removal on the basis of coagulant dosage. At pH 6 with dosage 50, 60 and 70 mg EB3/l the NOM removal are efficient, but the color residual are still high. That means that the pilot plant is removing NOM, and that color is a result of coagulant residual. EB3 has a brown, yellow color so it is not a surprise if some of that color infects the sample. The

most successful experiments are those with high NOM removal and low color residual. Low color residual has not been observed during this master thesis, and there are small differences between the results as figure 29 shows. The best example on high NOM removal and low color residual are at pH 6, with 30 mg EB3/l.

During a handful of the experiments listed in figure 29, the NOM removal is negative. That means that NOM is added. The coagulant contains only 3% humic substances, so it is unexpected that NOM is added. During experiments with pH 9 and 20, 30, 40 and 70 mg EB3/l the NOM removal is low, and color residual high. That means that the used conditions are not unsuccessful.

Since EB3 contains humic substances, the relationship between added coagulant and NOM removal is plotted in the figure below (figure 30). This is done to understand how the amount of EB3 affects NOM removal.

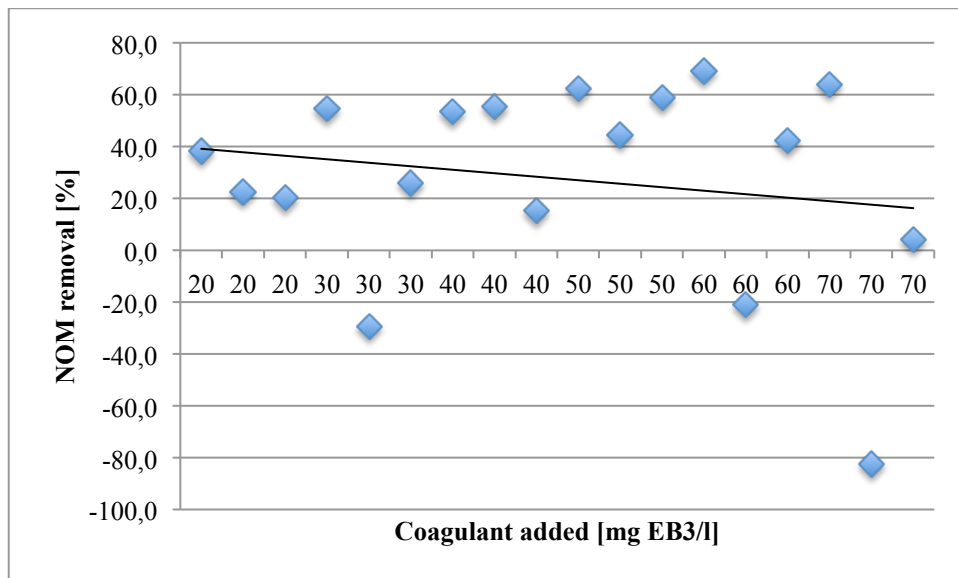


Figure 30 -NOM removal depending on added coagulant

Figure 30 show that the NOM removals have a slight decrease when the amount of EB3 increases. That confirms that the share of humic substances in the coagulant contribute to a less effective treatment considering NOM removal.

The amount of humic substances is reduced for all samples but three. At the same time the amount of neutrals is increased for all samples. That is the reason why the total amount of carbon in this master thesis in many cases increases.

6.5 Uncertainties

Since this master thesis is based on several experimental tests, uncertainties will always be an issue. The pilot plant is an advanced plant that combines several elements, which mostly are connected together via a control board. Through the whole test period I have tried to follow a test plan, and do the things in the same order, but I can not exclude that something have been done differently through the period.

All three membranes got cleaned before starting the test rounds with the same cleaning procedure as between each test round, with citric acid and sodium hypochlorite. After the first cleaning I started the pilot plant with only tap water, to insure that the cleaning procedure was working. I also did this procedure two times between the test rounds. Beside that I have assumed that the membranes were cleaned after the cleaning procedure. This an possible error source, and it may be that some of the membranes were cleaned better than the rest, even though all three of them went through the same procedure.

Before running the experiments I also insured that the coagulant pump gave the same amount of EB3 as I added to the control board. But during one experiment one of the pumps stopped delivering coagulant because of some biological growth inside the pump. This was a one-time episode, and the experiment was repeated once again, but it may be some difference between the planned dose and the actual dose for rest of the experiments.

The raw water characteristic varies during the test period because the amount of tap water was manually adjusted, as mentioned earlier in the thesis. The pH is supposed to be stabile through the experiment, but here the pH varies a little bit. I ignore these

variations because it will always be changes in raw water, because of seasonal variations etc.

This are the main error sources in this master thesis. There will also be propagation of errors, uncertainties of variables when doing laboratory testing's. In this thesis standard derivations are included in most of the cases, to eliminate errors. If something else can have affected the experiments, that information is given when the result are presented.

7. Revisiting questions

1. Is it possible to remove enough carbon?

One of the goals in this master thesis was to remove enough carbon to reach the Norwegian Drinking Water Standard considering TOC residual. That goal was not met at any conditions during this master thesis. The LC-OCD showed that the amount of humic substances was removed for most of the experiments, but the high concentration of neutrals in EB3 increased the amount of neutrals in all of the effluent samples. The lowest concentration of carbon were archived at pH 6 with 30 mg C/l. Because of the high concentration of carbon in EB3, a low dosage is necessary to accomplish low carbon residuals.

2. How will EB3 affect the membrane fouling?

Question number 2 was how EB3 would affect membrane fouling. That question is not possible to answer because of the variations in pressure measurements over the membranes. There are no clear correlations between filter run time, fouling and the results on color and carbon residual. The only thing noticed is that the time before clogging decreases according to usage of the membranes. Low coagulant dosage also affects the filter run time positively.

8. Conclusion

In this master thesis it is difficult to understand the result of the coagulation, and the dominating coagulation mechanism. From the jar test I know that flocs are created, but the final color residual shows that there is still a lot of color left. The LC-OCD analysis showed that some of the experiments removed a large part of humic substances, but still had a high color residual. That means that some of the color residual is color from the coagulant itself. The LC- OCD analysis also showed that the increase in carbon residual is a result of increase in neutrals from the coagulant. On that basis low dosages of EB3 are necessary to reach the Norwegian Drinking Water Standard considering carbon.

TMP and fouling are main reason why the results are not usable. It was difficult getting the membranes cleaned between each experiment, which resulted in short filter runs and results that were not comparable. Some indications of rapid clogging of membranes were that the membranes got faster clogged when they were used several times before. A high coagulant dosage also indicates of shorter filtration time.

The results in this master thesis can unfortunately not conclude whether Ecotan bios03 can be used as a coagulant in pretreatment before ceramic microfiltration. The results are not coherent and do not show well defined correlations between the different parameters measured. Each experiment is also completed only one time, and you cannot with safety insure that the measurements are correct when they only are completed once.

9. Further work on this subject

As stated in the conclusion, the results from this master thesis cannot conclude whether Ecotan bio s03 work as a coagulant for pretreatment for ceramic microfiltration. On that basis, these experiments should be completed and evaluated for a second time. As I also mentioned in the conclusion part, an experiment should be completed three times before a final conclusion is made. By further work some additional parameters should be tested to get a better understanding on the coagulants behavior, some of these were planned and described in appendix 3:

- Continuous measurements regarding pH, color residual, TOC and DOC residual and turbidity.
- Zeta potential should be measured to get more info regarding the coagulation mechanism.
- Flocculation index should be measured to get more information regarding the floc creation and the success of the coagulation.

It would also benefit the thesis and give more trustworthy results by:

- Finding a better cleaning procedure to ensure that the membranes are completely clean between every experiment.
- Finding a better way to adjust the raw water so the raw water characteristics vary less than they have during this master thesis. The best solution would have been to use natural lake water for all the experiments, but that will be difficult to implement.
- Optimize the flocculation setup by trying different retention times and velocity gradients.
- Vary the flux.

10. References

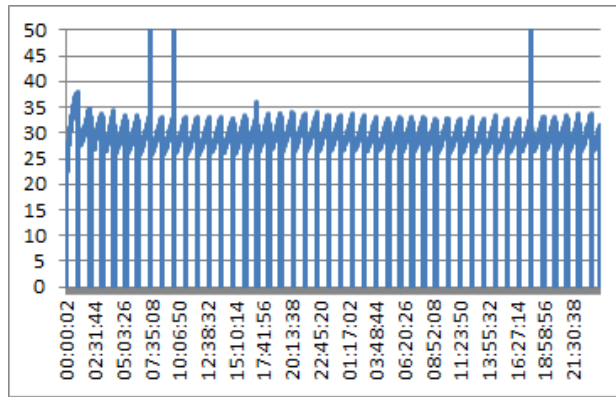
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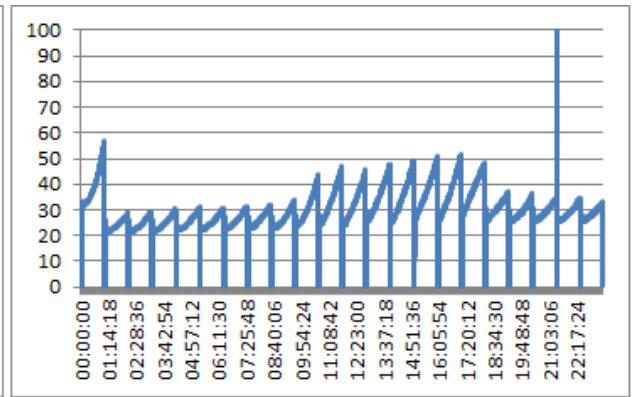
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Appendix 1 – Trans membrane pressure over time.

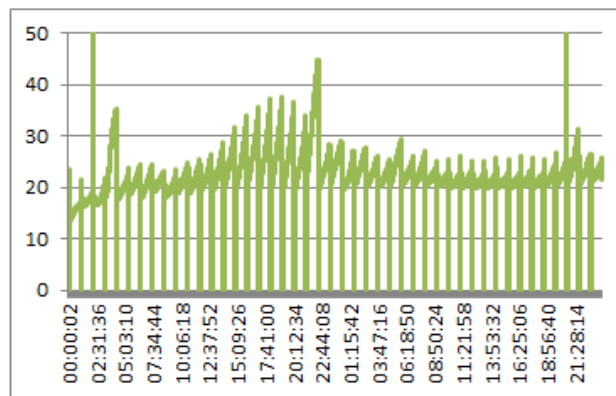
The pilot plant continuously logged the pressure difference before and after the membrane. That pressure difference is called the trans membrane pressure (TMP) and is in the figures below designated by kPa. TMP is in the figures below plotted against filter run time.



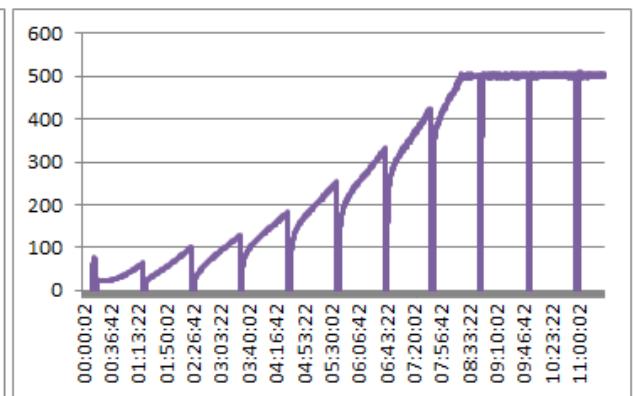
a) pH 6, 20 mg EB3/1 (1-1)



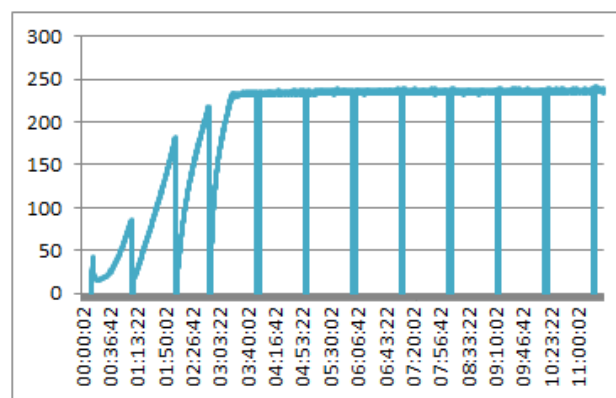
b) pH 6, 30 mg EB3/1 (1-2)



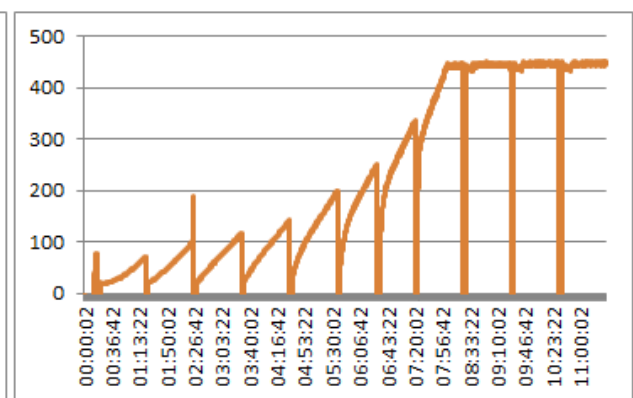
c) pH 6, 40 mg EB3/1 (1-3)



d) pH 6, 50 mg EB3/1 (2-1)



e) pH 6, 60 mg EB3/1 (2-2)

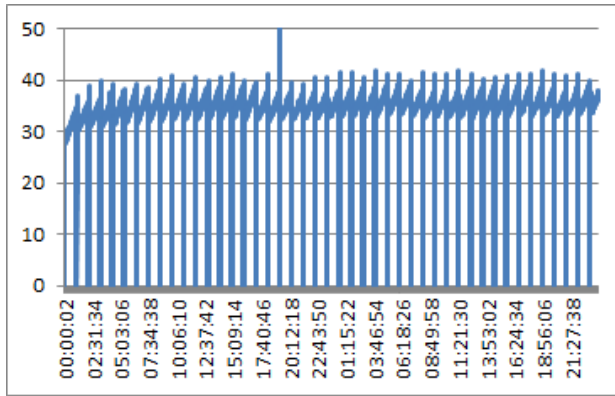


f) pH 6, 70 mg EB3/1 (2-3)

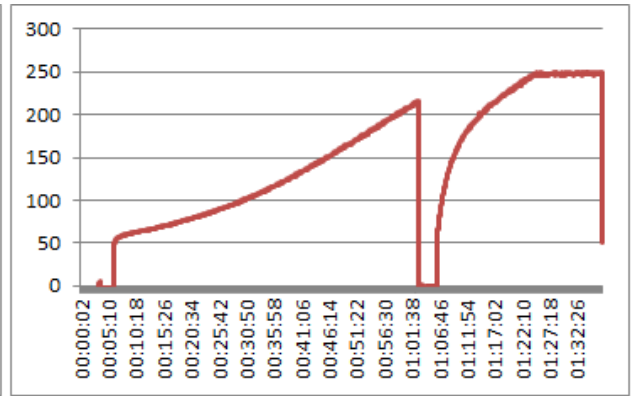
The duration and filter run time for each condition are shown in the figures above. The first run with 1-1 and 1-3 lasted without problems for 48 hours. Run 1-1 with a stable TMP on 35 kPa, while 1-3 had a top after around 15 hours. Run 1-2 had stable TMP values over 24 hours, but got stopped because of time limitations. I think an important factor for the stable results are that this was the first run, so the membranes were completely clean ahead of the start. Run 2-1 to 2-3 was after the membranes had been used once before and cleaned according to the cleaning procedure given in chapter 5.1, and the TMP graphs look completely different. Instead of a stable TMP, the membranes got clogged after 8.5, 3.5 and 8 hours. If that is because of a less successful coagulation or if it is something wrong with the membranes or the line is impossible to state after only one test.

There are small differences in color at pH 6 for run 1-1 to 1-3 and 2-1 to 2-3. That means that runtime do not affect the quality of color residual. Carbon residual for pH 6 increases for the runs with short filter run time, but that is truly because increased amount of carbon is added.

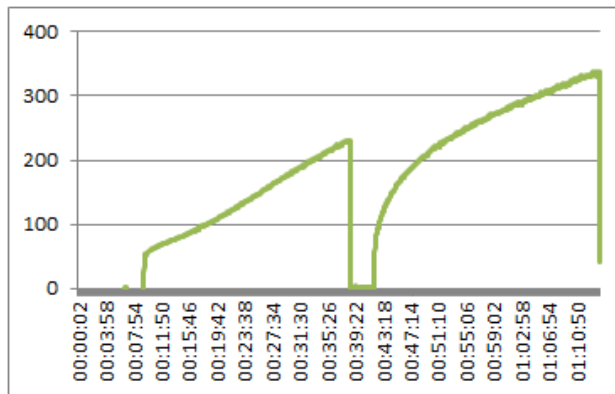
The differences in filter run time are even larger at pH 7,5 as shown in the figures below. pH 7,5 was the last pH tested. The membranes in line 2 and 3 had been used four times before, while the membrane in line 1 only had been used two times before run 3-1 to 3-3. That may be an explanation why the differences in filter run time is so significant.



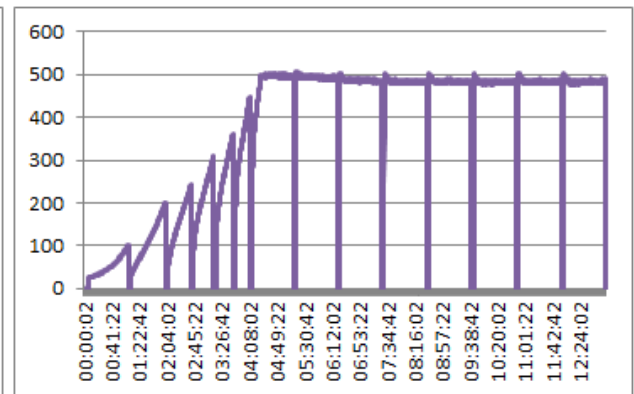
a) pH 7.5, 20 mg EB3I (3-1)



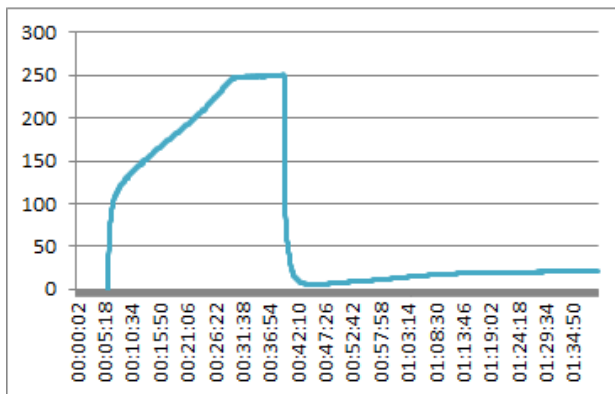
b) pH 7.5, 30 mg EB3I (3-2)



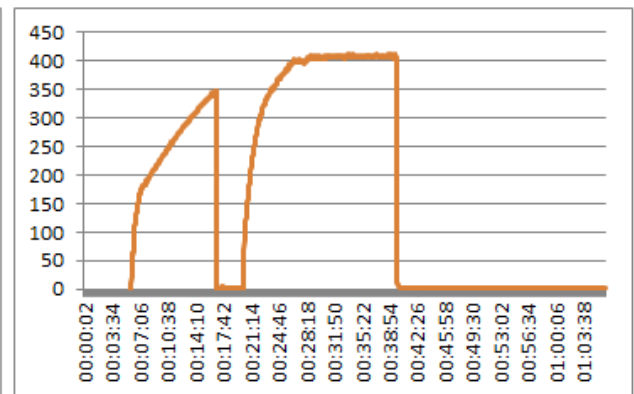
c) pH 7.5, 40 mg EB3I (3-3)



d) pH 7.5, 50 mg EB3I (4-1)



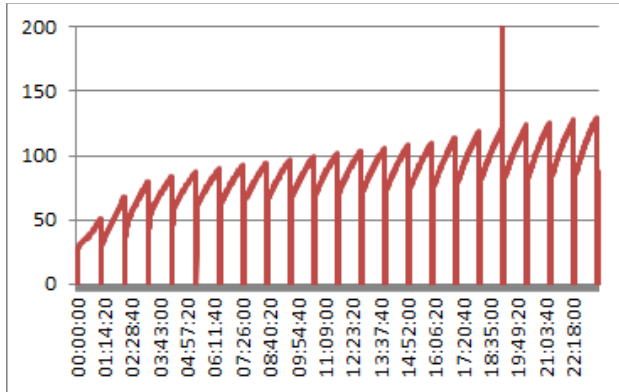
e) pH 7.5, 60 mg EB3I (4-2)



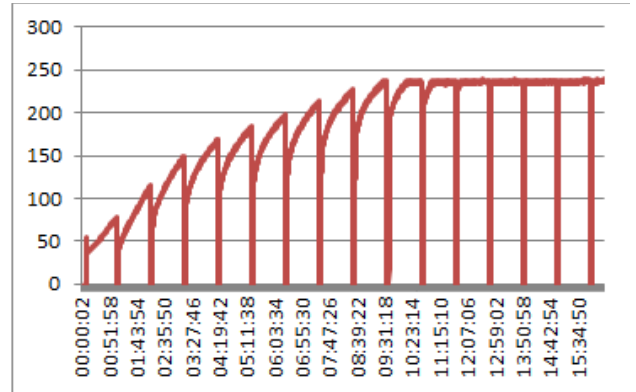
f) pH 7.5, 70 mg EB3I (4-3)

The differences in color residual were negligible at pH 7.5. Even though the run 3-2, 3-3, 4-2 and 4-3 were unsuccessful considering TMP and filter run time, the permeate color residual was roughly the same as 3-1, which ran for 47 hours without any distinct increase in TMP. Run 3-1 accomplished the best carbon removal. But I think the reason is the low dosage of coagulant and not the filter run time. I base this assumption on the project thesis and literature.

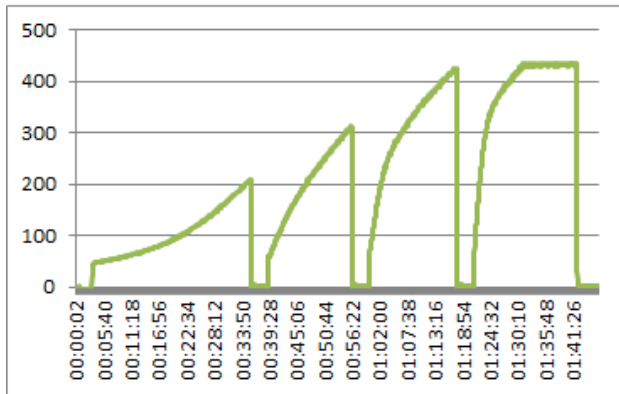
None of the TMP curves for pH 9 shows stable TMP over time, as shown in appendix 1. There is neither a clear correlation between carbon, color residual and TMP. All of the tests with pH 9 were done with membranes that were used less than for pH 7.5, and more used than with pH 6. The average filter run time for pH 9 is also between the average filter run time for pH 6 and pH 7.5.



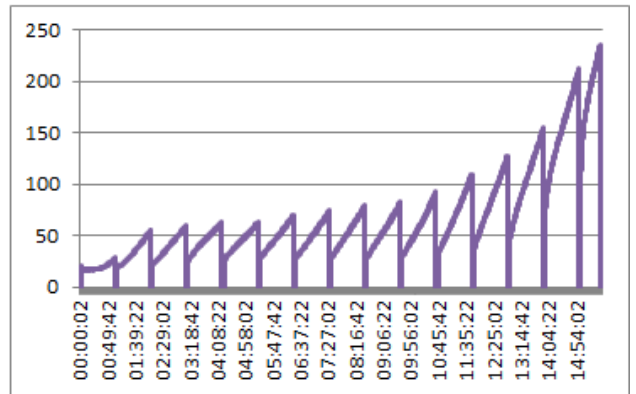
a) pH 9, 20 mg EB3/1 (5-1)



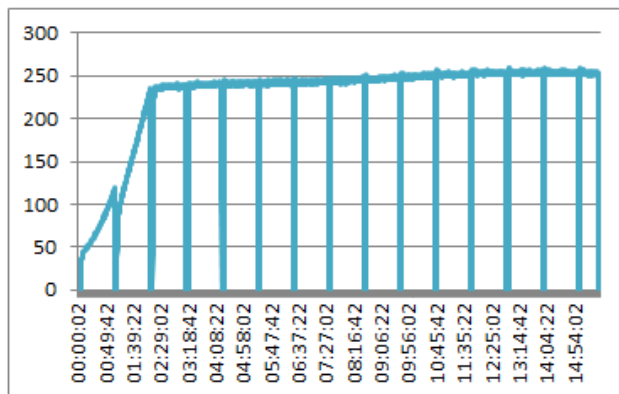
b) pH 9, 30 mg EB3/1 (5-2)



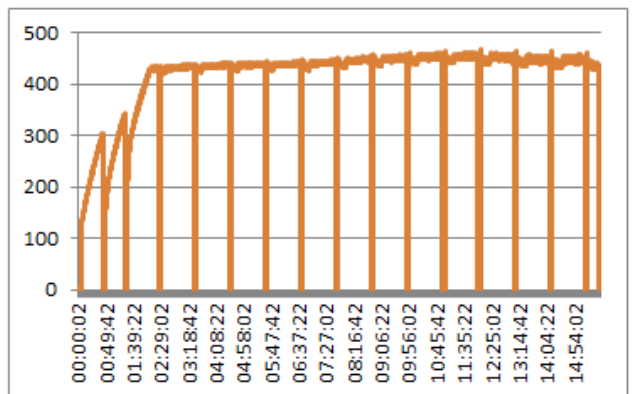
c) pH 9, 40 mg EB3/1 (5-3)



d) pH 9, 50 mg EB3/1 (6-1)



e) pH 9, 60 mg EB3/1 (6-2)



f) pH 9, 70 mg EB3/1 (6-3)

Ahead of some of the experiments, a cleaning procedure examination was done. Tap water without additives was used in the pilot plant and the result was that there were problems getting the membranes clean. The flocs were trapped hardest in membrane 2 and especially in membrane 3. This affects the clogging, and on that basis it is not a surprise that the average filter run time decreases over time. Through all these tests membrane 1 or 4 have normally had the lowest coagulant concentration, 20 mg EB3/l, but also 50 mg EB3/l. I can therefore not state that the amount of EB3 used is a direct correlation with the problem getting the membranes clean. But a high amount of coagulant can contribute to an unsuccessful cleaning process.

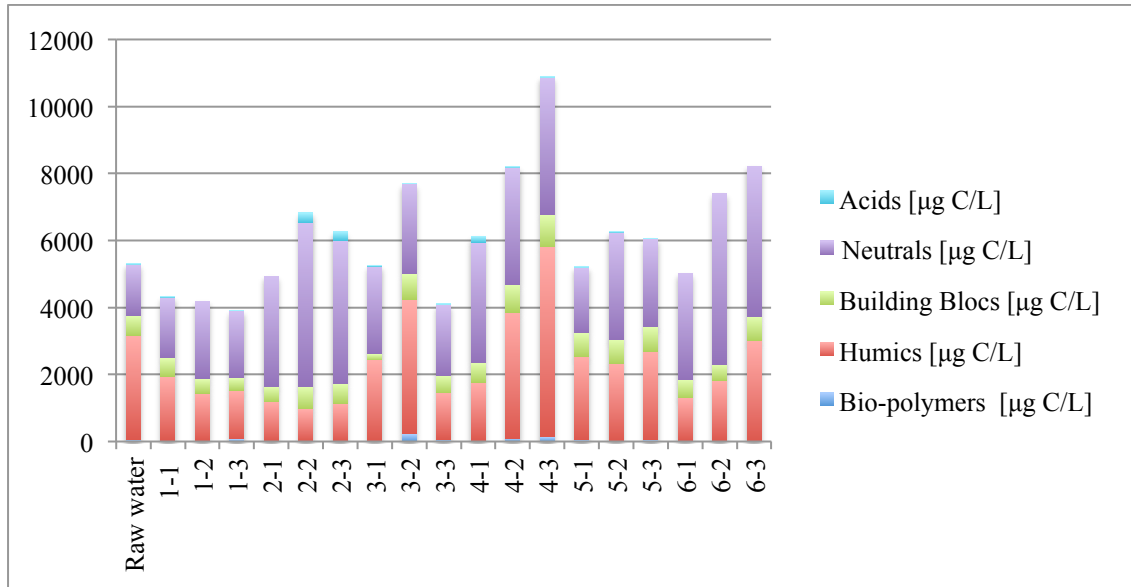
The filtration did not work as they were planned as the figures above show. The membranes reached their maximum capacity too fast. That resulted in difficulties calculating irreversible and reversible fouling.

Appendix 2 - Carbon characterization

To characterize both the raw water and the permeate samples, a LC-OCD analysis was carried out. The result is listed below and is foundation behind the graphs in chapter 6.1 and 6.4.7.

Experiments	Conditions	Bio-polymers	Humics	Building Blocs	Neutrals	Acids	C-DOC
		[$\mu\text{g C/L}$]	[$\mu\text{g C/L}$]	[$\mu\text{g C/L}$]	[$\mu\text{g C/L}$]	[$\mu\text{g C/L}$]	[$\mu\text{g C/L}$]
Raw water		58	3110	601	1518	5	5293
1-1	pH 6, D 20	31	1915	554	1807	3	4311
1-2	pH 6, D 30	29	1411	432	2314	0	4187
1-3	pH 6, D 40	78	1448	371	2002	2	3901
2-1	pH 6, D 50	18	1171	454	3296	0	4937
2-2	pH 6, D 60	17	959	668	4900	286	6830
2-3	pH 6, D 70	19	1118	597	4273	267	6275
3-1	pH 7.5, D 20	30	2407	182	2616	2	5237
3-2	pH 7.5, D 30	227	4024	757	2683	6	7698
3-3	pH 7.5, D 40	65	1385	528	2111	3	4091
4-1	pH 7.5, D 50	36	1727	602	3583	184	6132
4-2	pH 7.5, D 60	102	3763	834	3486	2	8187
4-3	pH 7.5, D 70	138	5670	977	4082	6	10873
5-1	pH 9, D 20	55	2475	719	1937	30	5216
5-2	pH 9, D 30	32	2300	727	3188	7	6254
5-3	pH 9, D 40	51	2635	742	2622	1	6051
6-1	pH 9, D 50	34	1279	547	3170	0	5030
6-2	pH 9, D 60	24	1793	496	5087	0	7400
6-3	pH 9, D 70	22	2980	735	4479	0	8216

The graph below shows that the concentration of humics decreases in half of the samples, but that the concentration of neutrals increases. The total concentration of dissolved, organic carbon are both increasing and decreasing after treatment.



Appendix 3 – Not measured parameters

To give a trustworthy and good evaluation, numerous parameters should have been tested. Some of the parameters I think should have been included are listed below. If this evaluation were carried out one more time, these parameters would benefit the result.

Online TOC, DOC, color and turbidity

To archive good, reliable data over time, an online TOC, DOC, color and turbidity meter was installed, Spectro::lyser™ from Scan Messtechnik. The samples were not filtered in advance, but calibration algorithms used turbidity to differ TOC from DOC, and to calculate the correct color number. Spectro::lyser™ is a spectrometric probe with a path length of 10 cm, which measures wavelengths between 220nm and 720nm (Meyn, 2011). Because of some authorization problems, Spectro::lyser™ was not used in this master thesis, samples were taken manually instead.

Turbidity

Turbidity describes the presence of suspended particles that reduce the clarity of water. Because turbidity is a requirement in the Norwegian Drinking Water standard, turbidity should have been measured in this master thesis. But because the turbidity machine was not accurate for low values as I had, I decided to exclude turbidity. Also the fact that DOC and TOC is approximately the same indicates that there are no particles.

Flocculation Index

Flocculation index is a measurement that gives information regarding the size of flocs. Flocculation index does not give an exact size, but compare the sizes and gives an idea on how the coagulation turned out. This is information I should have had, especially because the treatment happens inside tanks, which makes it hard to see the operation and eventual errors. Because of time limitations I have not had time for flocculation index.

Zeta potential

To achieve a good coagulation it is necessary to reduce the surface charge of NOM by destabilize them with an opposite charged solution. Zeta potential is a measure of the electrical potential that causes interparticle repulsion (Morfesis et al., 2009). Zeta potential can be found on the outer side of Stern layer in the electric double layer (figure 3). This value is widely used to determine coagulant dosages. In this study Delsa™ Nano HC is used to measure zeta potential. Zeta potential was not measured because of time limitations and samples with high degree of uncertainty.