Master's thesis

NTNU
Norwegian University of Science and Technology
Faculty of Engineering
Department of Civil and Environmental Engineering

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Chitosan and zirconium as coagulants for NOM-removal

Master's thesis in Civil and Environmental Engineering
Supervisor: Tor Håkonsen
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Abstract

The main research question for this thesis are:

> How does alternative coagulants, chitosan and zirconium, perform compared to traditional coagulants, especially in terms of removing NOM?

This thesis is based on experiments using Jar tests for different coagulation types. Two sources of raw water where utilized in the experiments, one from Vennatjønna in Malvik and the other from Stakkastadvatnet in Haugesund. The water from Malvik had high color of 56 mg Pt/l and the main fraction where humics at 79 %. The water from Haugesund had a color value of 31 mg Pt/l, and also humics as the largest fraction at 74 %.

The main intention where to evaluate for removal of Natural Organic Matter (NOM). NOM can lead to potential biological growth and reduce the impact of disinfection. Therefore, removing NOM are of high importance. Measurements of parameters color, turbidity, DOC, TOC and UV_{254} where conducted. For some selected samples, fractionation of the water where conducted using a LO-OCD measurements. The coagulants tested where chitosan and zirconium, and evaluated against the well studied polyaluminumchloride (PACl).

The tests were divided into four parts. The first part consisted of finding the optimum pH and dosage for the two coagulants. PACl is a well-studied and used coagulants, and further optimization test where not done. Another, new and little used polymer, microbial extracellular polymeric substances (EPS), where investigated as well. The second part consisted of evaluating for NOM removal. Calculated SUVA values where included here. In the third part, the water from Malvik were thinned out, in order to evaluate chitosan at lower raw water color values. Only chitosan was evaluated in this part. The last part contained the water from Haugesund, where chitosan and zirconium where tested on their own and then combined. Haugesund municipality utilize a combined coagulation of zirconium and chitosan as treatment today. A sample of this combination where given to be tested, and different dosage of this combination were investigated as well.

Optimum dosage for chitosan in Malvik where 7 – 12 mg/l with a pH of 5 -5.5 Zirconium had a optimum dosage range of 4- 10 with a pH of 4.5 – 5.5.The three coagulants all obtained NOM removal, where Zirconium and PACl achieved slightly higher removal than chitosan, but chitosan did obtain results indicating NOM removal within limit. EPS showed very little reduction in either color, turbidity and DOC. The coagulant are better suited for other water types. The test with water from Haugesund showed that zirconium and the combined coagulants performed better than chitosan alone, but chitosan obtained good results and proven its capabilities for treating the water.

Sammendrag

For denne oppgave var følgende forskerspørsmål stilt:

> Hvordan fungerer de alternative koagulantene, kitosan og zirkonium, sammenlignet med tradisjonelle koagulanter, spesielt når det gjelder å fjerne NOM?

Denne oppgaven er basert på eksperimenter med Jar-tester for forskjellige koagulasjonstyper. To råvannskilder ble brukt i forsøkene, den ene fra Vennatjønna i Malvik og den andre fra Stakkastadvatnet i Haugesund. Vannet fra Malvik hadde høy farge på 56 mg Pt / l og hovedfraksjonen var humus på 79%. Vannet fra Haugesund hadde en fargeverdi på 31 mg Pt / l, og også humus som den største fraksjonen på 74%.

Hovedintensjonen ved oppgaven er å evaluere for fjerning av naturlig organisk materiale (NOM). NOM kan føre til potensiell biologisk vekst og redusere virkningen av desinfeksjon. Derfor er det viktig å fjerne NOM. Målinger av parametere farge, turbiditet, DOC, TOC og UV_{254} har vært utført. For noen utvalgte prøver ble fraksjonering av vannet utført ved hjelp av en LO-OCD-måling. Koagulantene som ble testet var kitosan og zirkonium, som ble vurder opp mot den godt studerte polyaluminumklorid (PACI).

Testene ble delt inn i fire deler. Den første delen besto av å finne optimal pH og dosering for de to koagulantene. PACl er en godt studert og brukt koagulant, og videre optimaliseringstester for den ble ikke gjort. En annen, ny og lite brukt polymer, mikrobiell ekstracellulær polymere substanser (EPS), ble også undersøkt. Den andre delen besto av å evaluere for fjerning av NOM. Beregnede SUVA-verdier er inkludert her.. I tredje del ble vannet fra Malvik tynnet ut, for å evaluere kitosan ved lavere råvannsfargeverdier. Bare kitosan ble evaluert i denne delen. Den siste delen inneholdt vannet fra Haugesund, der kitosan og zirkonium ble testet på egen hånd og deretter kombinert. Haugesund kommune bruker en kombinert koagulering av zirkonium og kitosan som behandling i dag. En prøve av denne kombinasjonen ble gitt for å bli testet, og forskjellige doser av denne kombinasjonen ble også undersøkt.

Optimal dosering for kitosan i Malvik var 7 - 12 mg / l med en pH på 5 -5.5. Zirkonium hadde et optimalt doseringsområde på 4 - 10 med en pH på 4.5 – 5.5. De tre koagulantene oppnådde alle NOM-fjerning, hvor Zirconium og PACl oppnådde litt høyere fjerning enn kitosan, men kitosan oppnådde resultater som indikerte fjerning av NOM innenfor grensen. EPS viste veldig liten reduksjon i både farge, turbiditet og DOC. Koagulanten egner seg bedre for andre vanntyper. Testen med vann fra Haugesund viste at zirkonium og de kombinerte koagulantene presterte bedre enn kitosan alene, men kitosan oppnådde gode resultater og beviste sine evner for å behandle vannet.

Preface

This master is written during the spring of 2020 in the Master program Civil and Environmental Engineering at NTNU (Norwegian University of Science and Technology) for the subject of Water supply and Wastewater Systems. The thesis equals 30 ECTS credits. The lab work was executed in the Analytical lab at NTNU.

I would like to thank my supervisor Tor Håkonsen for guidance and support during this work and Thomas Meyn for additional guidance. I would also like to thank Trine Margrete Hårberg Ness with helping me with analysis in the lab and driving to Malvik to collect raw water for my tests.

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At last, I would also thank Stine Bendigtsen from Teta vannrensing AS for supplying me with Kitoflokk^{TM} and Aquator^{TM} coagulants, Kemira for supplying me with PAX-18 and everyone at European Centre of Excellence for Sustainable Water Technology (WETSUS) for swift delivery of EPS so that I could finish my tests. In addition, I would thank Malvik municipality for helping me with collecting raw water at their station.

Bærum, 31st of July 2020

Elise S. Fjornes

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List of Abbreviations (or Symbols)

NTNU	The Norwegian University of Science and Technology
NOM	Natural organic matter
TOC	Total organic carbon
DOC	Dissolved organic carbon
UV	Ultraviolet
LO-OCD	Liquid Chromatography- Organic Carbon Detection
PACl	Polyaluminum Chloride
SUVA	Specific UV absorbance
EPS	Extracellular Polymeric Substances
LMW	Low molecular wheight
CDOC	Chromatographic DOC

1 Introduction

Securing good and safe drinking water is elemental in our society today where the presence of harmful microorganisms and chemicals pose a risk to public health. Thus, good and stable treatment of drinking water that efficiently remove harmful agents is necessary. Climate change have led to increase in intensity and occurrences of rainfall. Several water sources have register higher values of color and somewhat more acid waters due to acid rains. Climate changes are expected to continue to develop and further changes in the water biology should be expected. Stronger rainfall may lead to more pollutants drained into the surface waters used as water sources, thus increasing vulnerability of the water sources. Utilizing water treatment capable of handling these changes is of great importance for further development and research should be conducted in order to prepare for the future.

1.1 NOM in drinking water

The main purpose for water treatment is to remove pollutants from the water source before serving it to the population. Bacterial, viruses, heavy metals and organic matter are examples of the most problematic occurrences in water. Technology have been researched and created in order to safely and efficiently remove such pollutants. One of these pollutans are natural organic matter (Crittenden, 2012).

NOM are organic chemicals, that originate from natural sources present in the water. High values of NOM in water may increase biological growth in the water if not treated and produce smell and odor. In addition, NOM may react with the disinfection of the water treatment and thus decrease the efficiency of these (Crittenden, 2012). Climate changes have shown increasing values of NOM in surface water in Norway, and is expected to continue increasing in the future. Coagulation is one of the well used treatment methods to remove NOM from water(Eikebrokk et al., 2004).

1.2 Alternative coagulants

With coagulation comes the choice of coagulants. The availability of different types of coagulants are wide and choosing may depend on different factors. Traditional coagulants include aluminum- and iron chloride. These have ben research and developed for decades and have been utilized ad optimized for water treatment worldwide. Despite their scientifically proven efficiency, there are drawbacks with these coagulants. Possible harmful waste, increasing values of metals released in nature and high sludge production are some. Therefore, alternative coagulants with different nature and science have been researched and produced in order to pose as alternative choices (Crittenden, 2012). Chitosan and zirconium are some examples of such choices. Some are natural organic coagulants that are 100 % biodegradable, in addition to lower sludge production that can reduce cost of production. These coagulants have shown treatment capabilities able to adapt for the future (Christensen, 2018).

1.3 Research question

The aim of this thesis is to investigate the performance of coagulants chitosan and zirconium for NOM removal compared to a more conventional coagulant, such as Polyaluminumchloride (PACl). During this thesis the following research question will be answered:

How does alternative coagulants, chitosan and zirconium, perform compared to traditional coagulants, especially in terms of removing NOM?

In order to answer the question, several supplementary questions are to be answered:

1. How does each of the coagulants perform in treatment efficiency compared to each other?
2. How well do the coagulants remove NOM?
3. In what way does chitosan perform with different color of the raw water?
4. With an industry perspective, how will the coagulants perform on their own, and combined together?

1.4 Limitations

During the work on the thesis several limitations have occurred:

- Not all dosages and pH values were tested for NOM parameters such as DOC, TOC and UV.
- Fractionation were only executed for the one apparent best sample of each coagulant
- For the raw water from Haugesund, the water had to be shipped to Trondheim, and a limited amount were only available for the tests. Therefore, one part of the tests for Haugesund were not as comprehensive as the other parts, since the water ran out at the end.

2 Theory

This chapter present the theory relevant for the work done in this thesis. Topics are divided into sub chapters below.

Over the course of history, the natural way to determine clean water was by visual observation. Without analytic chemistry the only way to treat water was by improving taste and the appearance of water. Selecting the best water source instead of purifying the water was a way to secure healthy water to the population. The romans build extensive systems to transport clean appearing water from sources long distances away from the cities. Only in the last 200 years have there been a rapid development in water treatment(Hall and Dietrich, 2000).

During the 17th century the British philosopher and scientist Sir Francis Bacon published his experiments on water purification, which included filtration, boiling, distillation, coagulating and percolation. In 1804 the first site facility to deliver filtrated water to a town was Paisley in Scotland. During the 1854 – 1855 cholera outbreak in London British Sir John Snow discovered the source of the outbreak was due to a contamination from sewage in one of the public pumping well and became known as the Broad Street Pump Affair. Further development, research and innovation have increased the knowledge and possibilities of the field until today and the available technological treatment methods today include several different treating methods within different treating goals (Hall and Dietrich, 2000).

2.1 NOM in water

NOM stands for Natural Organic Matter and is the term used to describe the organic chemical that originate from natural sources present in the water. The presence of these natural sources often comes from biological activity in the water, such as secretions from the metabolic activity of algae, protozoa and microorganisms. NOM can also occur in the water by landmass being washed into the water (Crittenden, 2012).

NOM consist of hydrophobic and hydrophilic components, where hydrophobic acids are the largest fraction and make up about 50 % of the total organic carbon (TOC) in the water. One way to describe these hydrophobic acids, is as humic substance and can be divided into different parts: (1) humic acids (HA), (2) fulvic acids (FA) and (3) humins. Humic acids are soluble in alkali, but insoluble in acids, and both fulvic acids humins are soluble in both alkali and acids. These humic substance are comparable from a structural point but are varying in both molecular size and functional group content (Sillanpää, 2014).

The molecules of NOM in negatively charged, where some have multiple anionic functional groups, thus making them polyelectrolytic. There is a distribution of the molecular weight of NOM where 90 % lies between 500 to 3000 Da (Crittenden, 2012).

Methods to remove NOM include coagulation, adsorption, membranes and disinfection. The parameters to measure NOM are typically TOC (total organic carbon), DOC (Dissolved organic carbon) UV_{245} absorbance and SUVA (Specific UV absorbance) (Crittenden, 2012).

2.1.1 SUVA - Specific UV absorbance

SUVA is a measurement often used as a guide for the treatability of NOM. There have been shown a correlation of SUVA with the hydrophobic fractions of NOM. SUVA is calculated as the ration of UV_{254} absorbance with DOC, se equation (2.1) below (Crittenden, 2012):

$$SUVA = \frac{UV_{254}}{DOC} * 100 \tag{2.1}$$

where SUVA = Specific UV absorbance [l/mg m]
UV_{254} = UV absorbance at 254 nm [cm^{-1}]
DOC = dissolved organic carbon concentration [mg C/l]

There is a suggested relationship between SUVA and DOC, and Table 2.1 below present this. The ability of high SUVA values to express the organic compounds better ability to react with the coagulation are shown through the table.

Table 2.1 Outtake from the Matilainen et al. (2010) review, presenting the connection of SUVA with DOC removals.

SUVA	Composition	Coagulation	DOC removals
>4	Mostly aquatic humics, high hydrophobicity, high MM compounds	NOM controls, good DOC removals.	>50% for alum, little greater for ferric.
2-4	Mostly aquatic humics, high hydrophobicity, high MM compounds	NOM influences, DOC removals should be fair to good.	25–50% for alum, little greater for ferric
<2	Mostly non-humics, low hydrophobicity, low MM compounds	NOM has little influence, poor DOC removals.	<25% for alum, little greater for ferric.

2.2 Analysis- and characterisation methods

2.2.1 Water quality

The regulations for drinking water in Norway are determined by the department of health and care serviced. The Norwegian food and safety authority have the responsibility for the drinking water management and have developed a guide for the drinking water regulations. In the regulations, the purpose is written as (Folkehelseavdelingen, 2016):

"The purpose of the regulations is to protect human health by requiring the safe delivery of sufficient quantities of health-safe drinking water that is clear and without prominent odor, taste and color."

The drinking water regulation have strict requirement for the water delivered to the customers. In order to secure good drinking water quality to the customer the requirements of two hygienic barriers need to be met. Therefore, low quality of the raw water, demand more extensive treatment in order to meet the requirements.

For the removal of NOM the parameters of color, organic carbon and turbidity especially interesting. The drinking water regulations have set some maximum values for some of the parameters mentioned (Folkehelseavdelingen, 2016). Table 2.2 below present these requirements.

Table 2.2 Requirements from the Drinking water regulations for some parameters

Parameter	Unit	Requirements from the Drinking Water Regulations
Color	mg Pt/l	20,0
TOC	mg C /l	3,0
Turbidity	NTU	1,0

Color

Color in water are an indicator organic content in the water, such as humics and fulvic acids. True color is measured with filtrated samples with a 0.45 μm filter. The drinking water regulations have a maximum color of 20 mg Pt/l (Folkehelseavdelingen, 2016), this is due to esthetic reasons. Water with color above 15 mg Pt/l can have a characteristic yellow brownish color (Ødegaard et al., 2014).

Total organic carbon (TOC)

Total organic carbon indicates the carbon content and amount of organic matter in water. High content of TOC can indicate the content of organic pollutants and metals that can bind to organic matter. Organic matter can increase biological growth in the pipe network and lead to substances that are harmful to health during chlorination (Ødegaard et al., 2014). The Drinking Water Regulations state the limit value for TOC as «no abnormal change». The recommended limit off TOC is below 3 mg C / l for coagulation systems that are to function as hygienic barrier (Folkehelseavdelingen, 2016).

Dissolved organic carbon (DOC)

Dissolved organic carbon is the same method as with TOC, after being filtrated through a 0.45 μm filter. Normally the DOC concentration is 80 – 90 % of the TOC concentration (Crittenden, 2012).

Turbidity

Turbidity is a parameter that measures the amount of particles in the water and indicates how clear the water is. Clay, silt, microorganisms, glacial mud, plankton and algae are examples of particles that affect turbidity (Ødegaard et al., 2014). In the drinking water regulations, there is no limit value for turbidity beyond that the water should be «acceptable to the subscribers». The Norwegian Food Safety Authority recommends that the turbidity based on water treatment is not higher than 1 NTU water supply systems using surface water (Folkehelseavdelingen, 2016).

UV absorbance at 254 nm

UV absorption measures how much light that can penetrate the water. The analysis of UV uses light of 254 nm with a spectrophotometer. The presence of humics and particles in the water can reduce the UV transmission in the water. A high transmission are desired for the water in order to reduce the risk of affecting the removal of microorganisms in the water (Ødegaard et al., 2014).

2.2.2 NOM – caracterisation

In order to know how to remove NOM from water, it is important to understand the different components of NOM. There are different ways that have been constructed to do this, and one of this is LO-OCD (Liquid Chromatography- Organic Carbon Detection) (Huber et al., 2011).

LO-OCD characterize NOM by dividing them by size and chemical functions. The functions are quantified based on organic carbon. A water sample is pumped into a chromatographic column of a porous media and the molecule size are determined based on how fast the molecules travel through the column. After the column, two detectors measure the water, one for organic carbon and another for UV. By doing this, the organic compound can be divided into five fractions: biopolymers, humics, building blocks, LMW acids and LMW neutrals. Table 2.3 present the different fractions and their sizes (Huber et al., 2011).

Table 2.3 Size and composition of NOM fractions (Huber et al., 2011)

Fractions	Typical size [Da]	Typical composition
Biopolymers	>20 000	Polysaccharides, Proteins, Aminosugars
Humics	300 - 450	Humic acids and felvic acids
Building blocks	~1000	Mostly breakdown products of humics
LMW acids	<350	Summaric value for monoprotic organic acids
LMW neutrals	<350	mono-oligosaccharides, alcohols, aldehydes, ketones and amino sugars

2.3 Coagulation

Coagulation is defined as the addition of a chemical to water where the objective is to destabilize particles in order to aggregate or forming a precipitate that will sweep particles form a solution or adsorb dissolved constituents. During water treatment the purpose of coagulation is to produce conditions that allow the following removal of particulate and dissolved matter.

A charged particle in raw water is surrounded by an electrostatic potential known as *electric double layer* that consists of a fixed adsorbed layer known as *Stern layer* where cations binds to the negatively charged particle, and an outer *diffuse layer* containing cations and anions. The electrical potential of the shear plane which is at the outer layer of the Stern layer is known as zeta potential. Particles in raw water have a particle stability which balance between the repulsive electrostatic force and the attractive force known as van der Waals force. If the water contains a stable particle suspension, the repulsive forces overcomes the attractive forces, and prevent aggregation and settling on their own. By adding a coagulant, particle destabilization occurs due to one or several of the following mechanisms (Crittenden, 2012):

(1) *Charge neutralization:* Addition of opposite charged ions or polymers resulting in adsorption of the ions to the particle surface and thus a reduction of the repulsive forces. The particles become stable again.

(2) *Sweep floc coagulation:* A mechanism specific related to hydrolyzing metal salts coagulants where soluble precipitates and particular matter becomes entrapped in the amorphous precipitates.
(3) *Double layer compression:* When the electrical double layer is compressed, particles in water may come together due to Brownian motion, and due to the Wander wall forces stay attached.
(4) *Interparticle bridging:* Polymers that have not absorbed to other surfaces due too one or more of the mechanisms (1) – (3) above, the remaining polymers may extend into the solution and adsorb on available surface site of other particles and create a "bridge".

2.3.1 Flocculation

Flocculation is defined as aggregation of destabilized particles into larger participates that are easier to remove than the original particles. There are different mechanisms that can affect flocculation:

(1) *Brownian motion:* Aggregation of small particles, and larger particles are formed
(2) *Orthokinetic settling:* Mechanical mixing lead to flocculation due to velocity gradients that causes collisions between suspended particles.
(3) *Differential settling:* Aggregation and growth of particles occur due to difference in settling velocity. Particle of different size and/or density will collide and flocculate.

Flocculators are divided into two groups: mechanical and hydraulic. In the mechanical type, horizontal paddles and vertical turbines are causing the aggregation of particles. The hydraulic part forces the water through a specific geometry to induce turbulence, for example baffled channels or pipes.

A formula for the RMS velocity gradient was developed by Camp and Stein (1943) in order to quantify mixing in turbulent flocculation:

$$G = \sqrt{\frac{P}{\mu V}} \tag{2.2}$$

where: G = RMS velocity gradient [s^{-1}]
P = power of mixing input to flocculation basin
V = volume of flocculation basin [m^3]
μ = dynamic viscosity of water [kg/m s]

2.3.2 NOM removal – Enhanced coagulation

Enhanced coagulation is the term used for when excess coagulant are applied on order to obtain NOM removal. Normally coagulation are optimized for turbidity removal, but when more coagulant are used than strictly needed, the pH are also changed, TOC removal are increased and NOM are removed from the water (Matilainen et al., 2010). Enhanced coagulation can be met by the following parts: (a) selecting the best coagulation type, (b) applying the best coagulation dosage and/or (c) adjusting the pH where the best or adequate coagulation conditions are achieved. Lower pH can influence the metal complex formed and therefore reduce the charge density of the humic and fulvic acids, thus making them more hydrophobic and therefore more adsorbable (Bratby, 2006).

The coagulation dosage is influenced by the nature of NOM. High molecular weight NOM require lower dosage, due to the removal mechanism being charge neutralization. In comparison, if low molecular sized or non-humic substances are present, the mechanism will be adsorption to metal hydroxide surfaces, and the dosage need to be larger. The high molecular sized is more easily removed than the smaller sized due to them being hydrophobic in nature, and thus consisting of more aromatic compounds (Matilainen et al., 2010).

2.3.3 Metal salt coagulants

Inorganic coagulants used in water treatment are hydrolyzed salts of aluminum and ferric ions. The most extensive used coagulant is aluminum sulfate [$Al_2\ (SO_4)_3 \cdot n\ H_2O$] due to it being less expensive. Ferric species is suitable to aid destabilization in lime-softening process due to the ferric species being more insoluble over a wider pH range that the aluminum species (Crittenden, 2012). The sequence below illustrates how metal salts in aqueous solutions reacts with alkalinity species to soluble hydrolysis species.

$$Me^{3+} \longrightarrow Me(OH)^{2+} \longrightarrow Me(OH)_2^{+} \longrightarrow Me(OH)_3 \longrightarrow Me(OH)_4^{-}$$

Such a reaction will consume alkalinity. Due to the alkalinity being the buffer against changes of pH in water, the change in pH flowing the coagulation addition will depend on the initial alkalinity value. If the aim of the treatment process is to remove turbidity, NOM and color, the pH range during coagulation is 6 – 8. pH values lower than 6 can result in accelerated corrosion rates (Crittenden, 2012). Table 2.4 below present the common inorganic coagulants used in water treatment.

Table 2.4 Overview over the most common inorganic coagulants (Crittenden, 2012)

Coagulant	Chemical formula	Molecular Weight g/mol
Aluminum Sulfate	$Al_2(SO_4)_3 \cdot 14H_2O$	594.4
Sodium aluminate	$Na_2Al_2O_4$	163.9
Aluminum chloride	$AlCl_3$	160.3
Polyaluminum chloride (PACl)	$Al_a(OH)_b(Cl)c(SO_4)_d$	Variable
Polyaluminum sulfate (PAS)	$Al_a(OH)_b(Cl)c(SO_4)_d$	Variable
Polyiron chloride	$Fe_a(OH)_b(Cl)_c(SO_4)_d$	Variable
Ferric chloride	F_eCl_3	162.2
Ferric sulfate	$Fe_2(SO_4)^3$	400.0

Advantages and disadvantages related to metal salt coagulants

Aluminum salts is stable, easy to handle and readably soluble. Compared to ferric species, aluminum has a better turbidity removal, a higher color removal efficiency and more effective at low dosages. On the other hand, ferric species is reported to have a better NOM removal, even the middle size NOM fractions. In addition, ferric species is less sensitive to temperature compared to aluminum species (Matilainen et al., 2010).

Both species increase corrosivity due to sulphate and/or chlorine residuals in the treated water and have a high alkalinity consumption. The ferric species produce water of less buffer capacity which require a greater chemical addition for stabilization and corrosion control (Matilainen et al., 2010). The alum species can have a relatively high coagulant residual in the treated water and are temperature dependent (Haarhoff and Cleasby, 1988). Although it is not yet fully characterized, it argued that aluminum could have harmful effect on human health in relation to development of neuropathic diseases such as Alzheimer’s disease (Flaten, 2001).

2.3.4 Polymers

Polymers are long-chain molecules containing repeating chemical units where the structure provides distinctive physiochemical properties. In water treatment the use of polymers is due to two reasons: (1) coagulation to destabilize particles and (2) an aid to the formation of stronger and more shear-resistance flocs. The main mechanism for destabilization is charge neutralization. In addition, nonionic and anionic polymers can form bridges between particles (Crittenden et al., 2012). Compared to metal-based coagulants, polymers have a lower optimal dosage, no consumption of alkalinity, less sludge production and a less pH dependent process (Machenbach, 2007). According to Bolto (1995) the main benefits from using polymers are (1) an increase of the rate of separation of the solids and the water phase due to larger agglomerate sizes; and (2) a dramatically decrease in sludge volume, with as low as a third to what would normally be obtained. There are two classification groups of polymers: synthetic and natural.

Synthetic polymers

Synthetic polymers can be made from homopolymerization of the monomer or by copolymerization of two monomers. One benefit of polymer synthesis is that they can be manipulated into producing polymers of varying size, charge groups, number of charge groups per polymer chain and varying structure (Crittenden et al., 2012). Treatment performance is considered to be more consistent with synthetic polymers due to a more relatively insensitivity of the polymer characteristics to changes in raw water pH (Graham et al., 2008).

Despite the positive affects related to synthetic polymers, there are several drawbacks. Higher production cost and low degree of biodegradability are some issues mentioned. There is a potential toxicity issue related to the main polyelectrolyte monomer due to substances acquiring impurities such as acrylamide monomer during manufacturing and thus cause health problems. This has resulted in countries implementing dosage limitations in drinking water standards. Countries such as Japan and Switzerland have implemented strict restrictions to the use of synthetic polymers (polyelectrolytes) due to the uncertain long-term effects on human health (Graham et al., 2008). An overview of typical synthetic polymers used in water treatment are presented in table X below

Table 2.5: An overview over the different types of synthetic polymers (Crittenden, 2012)

Type	Charge	Molecular weight g/mole	Common application	Example
Anionic	Negative	10^4-10^7	Coagulant aid, filter aid, flocculant aid, sludge conditioning	Hydrolyzed polyacrylamides
Cationic	Positive	10^4-10^6	Primary coagulant, turbidity and color removal	Epichlorohydrin dimethylamine (epi-DMA) Polydiallyldimethyl ammonium chloride (poly-DADMAC)
Nonionic	Neutral	10^5-107	Sludge conditioning	Polyacrylamides
Others	Variable	Variable	-	Sodium alginate

Natural polymers

Natural polymers are polymers extracted from natural compounds, with biopolymers as a type of natural polymer derived from living organisms. Due to their natural origin, natural polymers are a sustainable solution when choosing coagulant. Sodium alginate is a natural polymer extracted from seaweed. Natural starches are another natural polymers and can be obtained from several sources such as potatoes, tapioca or plant seed. Another natural polymer is Chitosan, obtained from chitin shells (Crittenden et al., 2012). This is a compound investigated in several studies and applied to different fields.

Table 2.6 Presentation of possible natural polymers (Crittenden, 2012)

Coagulant	Chemical formula	Molecular weight Da
Sodium alginate	$NaC_6H_7O_6$	10^4- $2.0{\cdot}10^5$
Chitosan	$(C_6H_{11}NO_4)_n$	$3.8{\cdot}10^3$ – $2.0{\cdot}10^4$
Natural starch	$(C_6H_{10}O_5)_n$	Variable

2.4 Utilized coagulants

In this subchapter the theoretical background of each of the coagulants utilized are presented and discussed. A more in depth description of the operating pH and dosages for each of the coagulants are presented in chapter 3 later.

2.4.1 Chitosan

Chitosan is a cationic polyelectrolyte of D-glucosamine and N-acetyl-D-glucosamine and is a partially deacetylated chitin which is a linear polymer of chitobiose and virtually insoluble in water and organic solvents. A source of chitin is the organic substance of the shells from crabs, lobsters and shrimp (Domard and Rinaudo, 1983, Kawamura, 1991, Kurita, 2006)

The solubility of chitosan is pH dependent and is not soluble of a pH above 6,5. Thus, chitosan is dissolved in an acid solution, such as acetic acid. Normally a 1 percent solutions of chitosan are prepared in 1 percent acetic acid. (Kawamura, 1991).

The use of chitosan in water treatment have been extensively reviewed in addition to other applications such as in the medical, pharmaceutical, cosmetic, agricultural, photographic, biomedical and biotechnical fields (Kawamura, 1991). Due to several underlying properties of chitosan such as its non-toxicity, its biodegradability and chelation behavior, it is an attractive choice as coagulant compared to metal salts and synthetic polymers (Renault et al., 2009).

In drinking water treatment chitosan have obtained very good results and shown positive removal on different contamination types. Vogelsang et al. (2004) showed that chitosan is an effective remover of high molecular weight humic substances. In addition, Kvinnesland (2002) and Bratskaya et al. (2002) also reported good removal of humic substances, while Roussy et al. (2005a) and Roussy et al. (2005b) obtained positive results for inorganic suspensions with chitosan. Roussy et al. (2005a) report large and stable flocs with a fast settling of particles, and that scaling up the process will require smaller settling plants. Guibal et al. (2006) reported a very good efficiency at removal of particulate and dissolved contaminants in a coagulation flocculation process using chitosan and argued for the competitiveness of the process. Strand et al. (2002) and Strand et al. (2003) demonstrated positive results in efficiency of chitosan to flocculate bacteria suspensions. Compared to PACl during coagulation on synthetic turbid waters, Ruhsing Pan et al. (1999) showed that the optimal dosage of chitosan was less with larger floc sizes and faster settling rate. The authors argue for the cost effectiveness of replacing chitosan with PACl in water treatment processes.

One of the main advantages with chitosan is its natural origin. Chitosan is considered biodegradable, non – toxic and biological available (Kean and Thanou, 2010), thus making it an attractive alternative for sustainable solutions in treatment plants. In addition, chitosan can operate in a wider pH and dosage range (Vogelsang et al., 2004). Another advantages with chitosan is less sludge production, several studies have shown lower sludge production with the use of chitosan (Håkonsen, 2005), (Eikebrokk et al., 2001) (Liltved, 2001).

Despite the benefits of using chitosan in water treatment there are some concerns to be considered. Some studies have reported a lower ability to remove NOM compared to other coagulants (Eikebrokk et al., 2001) (Eikebrokk and Saltnes, 2002), The authors conclude that chitosan does meet the requirement for removal for NOM, but the Al coagulant performed better.

2.4.2 Zirconium

Zirconium is a non-toxic metal salt, and with a compound of about 0.023 % of the earth's crust zirconium is an economic and biological available alternative for the water industry for choice as a coagulant (Ayukawa, 1978). Several studies have shown that zirconium is an attractive alternative to the conventional coagulants with several positive traits.

Studies have shown that zirconium allows a higher NOM removal than conventional coagulants. Jarvis et al. (2008a) obtained results where zirconium showed a significant improved removal of NOM compared to Fe^{3+}, with a DOC removal above 90 %. The same results was obtained by Jarvis et al. (2012), where the removal of NOM was improved by zirconium compared to the conventional coagulants when operating in conditions that allows for optimized DOC removal and strong floc properties. Hussain et al. (2014) showed that zirconium is more efficient at removing low to medium range molecular weight organic compounds compared to Al coagulants. Aftab and Hur (2017) concludes that zirconium showed higher removal rates for DOM than Al at the same dosages. In addition, the results showed that Zirconium obtained highest DOM removal at a lower pH range, and the authors argue that zirconium ions can yield a larger amount of positive charges to a solution at very low pH conditions.

Another attractive trait of zirconium is the ability to form larger and more robust flocs. Jarvis et al. (2008a) obtained results where zirconium produced 27 % larger flocs than the conventional coagulant Fe. The same was shown by (Jarvis et al., 2012) with flocs of greater strength and robustness, with a greater resistance to shear stress.

Despite the positive attributes of zirconium there are some issues related to the compound. Zirconium is an un-regulated compound as a coagulant (Jarvis et al., 2008a), thus resulting in limited large scale and authentic experiments. In order to further investigate the ability of zirconium for water treatment, further studies are needed.

2.4.3 Polyaluminumchloride (PACl)

Polyaluminumchloride (PACl) is a prehydrolyzed metal salts, that are prepared by reacting alum with salts, chloride, and water under controlled mixing conditions. The chemical formula of PACl is $Al_a(OH)_b(Cl)c(SO_4)_d$. Note that not all formulas contain sulfate, but sulfate dos help to stabilize the aluminum polymers, and hinder them from precipitating (Crittenden, 2012).

When metal salts hydrolyze, hydrogen ions are released, and react with the alkalinity in the water. For PACl, the acids that would have been released during the formulation, are instead neutralized with the base (OH^-) during the manufacturing of the coagulants. Basicity is the term used for the degree of which the hydrogen ions that would be released by hydrolysis that instead are preneutralized. It is the ratio of hydroxide bound metal ions divided by charge of metal species (Crittenden, 2012).

There are several advantages with using preformed aluminum salts. Lower dosage use, when NOM does not influence the coagulant dosage at neutral or slightly acid conditions. Flocs are often stronger and denser and as the polymers gets larger, these characteristics also increases. It is less temperature dependent compared to unmodified alum salts. In addition, the polymer composition can increase effectiveness, due to larger cationic polymers that can be formed due to the increasing hydroxide – to aluminum ratio, that lead to enhanced charge neutralization (Crittenden, 2012, Matilainen et al., 2010).

2.4.4 Microbial extracellular polymeric substances (EPS)

Extracellular polymeric substances (EPS) is a microbial, natural flocculant. Due to it being considered eco-friendly, cost effective and sustainable, it can be an attractive alternative to synthetic polymers and mineral salts. EPS are a biopolymer, formed by different biochemicals secreted by microbes, and can represent about 50 to 90 % of the organic matter in a biofilm (More et al., 2014).

Due to the nature of EPS, the use is mostly related to waste water treatment. There have been some studies on the use of EPS for drinking water treatment. Li et al. (2009) obtained removal rates of 61.2 % and 95. % for COD and turbidity respectively with EPS synthesized by *Bacillus licheniformis* from drinking water. Buthelezi et al. (2009) was able to obtain removal rates for turbidity from 84.1 % to 93.6 % from river water with EPS produced by several bacterial strains. The potential use of EPS for NOM removal is argued due to its biosorption and bioflocculation capabilities (More et al., 2014). Wang et al. (2012) showed that EPS synthetized by *Pseudomonas aeruginosa* and *Pseudomonas putida* where able to remove NOM from aqueous environment. EPS are non-toxic and biodegradable, and is a sustainable alternative for coagulant in drinking water treatment.

Despite the positive arguments from several studies for application to water treatment, there are some problems with acceptance. Due to the nature of biological treatment, the risk of contamination by microbes may increase and can require additional unit operations for safety reasons. Therefore, before EPS can be considered for drinking water treatment, further studies are required.

3 Background

This chapter present the theoretical background for the methods and results presented in the following chapter. This chapter present and discuss the necessary theory that are used to determine material and values for the tests. The general theory for each of the coagulants are presented in chapter 2.4.

3.1 Coagulants

Chitosan is a coagulant of main interest for this thesis. Zirconium is also investigated due to the good results shown to removing NOM. There have also been shown promising results when these coagulants are combined together. PACl is a metal salt coagulant shown good NOM removal capabilities and also included in the testing. This way, the alternative coagulants can be compared to a more conventional coagulant well known and utilized in the field. Another alternative coagulant EPS are also included to investigate newer coagulants available. This coagulant is used more for investigating newer available coagulants, and thus not included in the main comparison for the coagulants. The different types of coagulant utilized for the tests in this report are presented in Table 3.1 below with their connecting features in addition to the positive and negative sides. EPS is not included here.

Table 3.1 Overview of the different coagulations, their features and positive and negative sides. (Matilainen et al., 2010) (Jarvis et al., 2008b) (Jarvis et al., 2012)

Coagulant	Chemical formula	Features	Positive	Negative
Chitosan	$(C_6H_{11}NO_4)_n$	Charge neutralization are the removal mechanisms of NOM molecules	Produce smaller amounts of sludge	Require higher dosage that lead to higher cost Formation of smaller flocs because of chagre neutralization
Zirconium	$H_{16}Cl_2O_9Zr$	Positive charge	Increased positive charge compared to traditional metal coagulants Larger and more stable flocs	Lesser tested and utilized.
PACl (Aluminium)	$Al_2(OH)_xCl_{6-x}$ $0<x>6$	Enhance amount of high- charged moderate -molar - mass hyrdoloysis species, e.g. Al_{13}	Lower dosage requirements and less sludge production. Lower aluminum residual in treated water Better NOM removal capacity than alum	Might not be as efficient at removing HMM and highly hydrophobic NOM The effectiveness are affected by coagulant hydrolysis species speciation

3.2 Bench scale tests

The selected method for testing coagulant conditions are "Jar test". This is often the standard bench scale testing procedure for determining coagulant dosages and types. The technology consists of 4 – 6 batch reactors equipped with a paddle mixer. Shapes of the jar are often square or circular, where the Square shaped jars can avoid the vortex flow sometimes happening when using the circular one. Jar test are able to simulate the conditions of a coagulation-flocculation process, to the degree possible (Crittenden, 2012). There have been some discussion on the preciseness of jar tests to full scale procedures. Christensen (2018) argue that jar tests are more appropriate for conventional treatments due to the appropriate large dosages and formation of bigger flocs that settle easier. The author further argue that conditions determined by jar tests for direct filtration may lead to filter clogging due to the need for less coagulant and the filtration producing smaller and more compact flocs. In addition, the strength and deposition of flocs are not notable by jar tests. These are properties important for the use of membrane filtration.

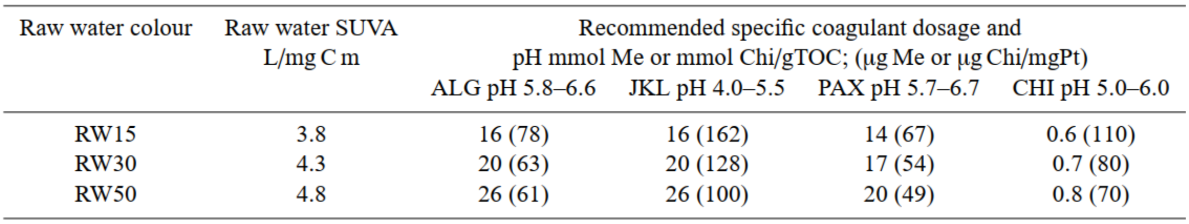
3.3 Dosage and pH values

This sub chapter present the theoretical background for dosage and pH for each of the coagulants utilized for this thesis.

Chitosan

In order to determine the dosages optimum for NOM removal, several reports and articles have been of interest. Ødegaard et al. (2010) have presented a recommended pH and dosage range of 0.11 – 0.07 mg Ch/mg Pt at pH 5.0 – 6.0 where the dosage levels need to obtain > 60 % reduction of color and 20 – 35 % reduction of TOC. Table 3.2 below present the recommended values from Ødegaard et al. (2010)

Table 3.2 Recommended values of coagulants suggested by (Ødegaard et al., 2010)



Raw water colour	Raw water SUVA L/mg C m	Recommended specific coagulant dosage and pH mmol Me or mmol Chi/gTOC; (µg Me or µg Chi/mgPt)			
		ALG pH 5.8–6.6	JKL pH 4.0–5.5	PAX pH 5.7–6.7	CHI pH 5.0–6.0
RW15	3.8	16 (78)	16 (162)	14 (67)	0.6 (110)
RW30	4.3	20 (63)	20 (128)	17 (54)	0.7 (80)
RW50	4.8	26 (61)	26 (100)	20 (49)	0.8 (70)

ALG-aluminium sulphate, JKL-ferric chloride; PAX-poly aluminium chloride; Chi-Chitosan.
For Me-coagulants: Dosage levels needed to obtain <0.1 mg residual Me/L, >90% and 50–60% colour and TOC reduction Absolute minimum dosages are 25% lower than the given practical minimum dosages.
For Chitosan: Dosage levels needed to obtain >60% and 20–35% colour and TOC reduction, resp

Christensen (2018)presented optimal treatment conditions for chitosan as 2- 6 mg /l with pH 4.0 – 7.0. The raw water used in the tests were of varying colors from 14 – 29 mg Pt/l. These reports and articles have been the fundaments for choosing pH and dosage values to test based on the raw water color and TOC values registered for the raw water used in this thesis.

Zirconium

Several studies have been conducted with zirconium, where it have been compared to other traditional coagulants. In order to determine the optimum conditions, these studies where used as guidelines for choosing dosage and pH. Christensen (2018) reported optimum conditions for zirconium as dosage 5 – 12 mg/l and pH 4.5 – 6,3 for raw water color of 14 – 29 mg Pt/l. Jarvis et al. (2012)presented optimum dosage as 5 – 15 mg/l at pH 5 – 6. Hussain et al. (2014) presented optimum conditions for DOC removal as pH 4.5 and dosage < 12 mg/l. Therefore, the tested dosages and pH values are chosen within these ranges for this thesis.

Polyaluminiumchloride (PACl)

The use of aluminum in water treatment have been extensively researched and investigated. Therefore, the dosage and pH values used in this thesis is based on previous research. Christensen (2018)reported optimum treatment conditions for Al as 1 - 5 mg/l at pH 5 - 6. In addition, Ødegaard et al. (2010)have presented a guide for recommended pH and dosage for the use of PACl in water treatment based on the raw water color value. based on this guide, a theoretical optimum dosage has been calculated for PAX, 3.39 mg/l at pH 5.7 – 6.7.

Equation given by (Ødegaard et al., 2010) for minimum required dosage for metal coagulants:

$$Dose\left(\frac{mgMe}{l}\right) = A * Raw\ water\ color\left(\frac{mg}{Pt}\right) + B \qquad (3.1)$$

Where A = 0.43
B = 0.30

EPS

The producer of EPS has given a recommended range for testing surface waters. For a concentration of 0.1 g/ l solution a range of 1 – 100 mg/g TSS are recommended. Choices of dosage will be based on this.

4 Materials and methods

In this chapter the first part presents the material used for the tests. The second part present the test plan which include an overview of the different parts of the tests and what were included. The last part presents the procedures for the different parts that are to be executed.

4.1 Materials

In this subchapter the different materials utilized for the tests are presented. First the raw water utilized are presented with connecting raw water quality parameters and the fractionation of the raw water. The second part include the different coagulants utilized for the test, which type and the distributer.

4.1.1 Raw water Vennatjønna in Malvik

Water for the tests was obtained from a feed pipe in the lake Vennatjønna in Malvik municipality. The water was stored in a dark and cold room between the tests. Table 4.1 below present the water quality of the raw water from Malvik.

Table 4.1 Water quality parameters of the raw water from Vennatjønna in Malvik

Parameter	Unit	Value
Color	mg Pt/l	56.4
Turbidity	NTU	0.810
TOC	mg C/l	6.8618 std 0.1679
DOC	mg C/l	6.4588 std 0.2139
pH	-	6.7

Fractionation

Figure 4.1 below present the fractionation of the raw water from Vennatjønna in Malvik.

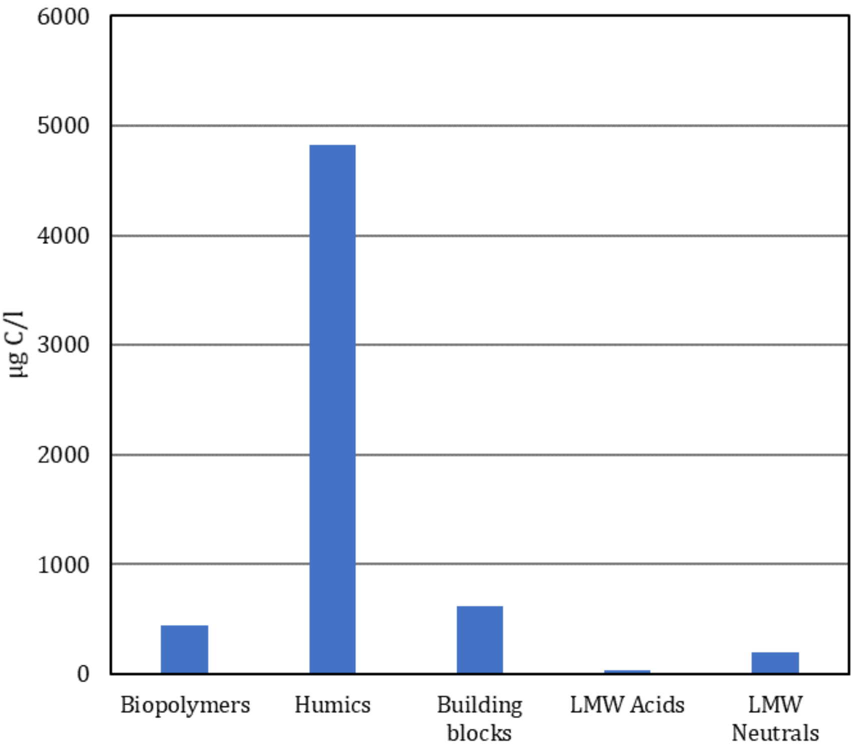


Figure 4.1 Fractionation of the raw water from Vennatjønna in Malvik.

Of the total CDOC present biopolymers 7 %, humics 79 %, building blocks 10 %, LMW acids 1 % and LMW neutrals 3 %. Humics is the part were color is presented and the high percentage of humics fits with the high color value of 56 mg Pt/l.

4.1.2 Water from Haugesund municipitality

Water for the tests from Haugesund were raw water from their drinking water source Stakkastadvatnet. As with the water from Malvik, the water was stored in a cold and dark place between tests. Table 4.2 below present water quality parameters from Stakkastadvatnet in Haugesund.

Table 4.2 Water quality parameters of the raw water from Stakkastadvatnet in Haugesund

Parameter	Unit	Value
Color	mg Pt/l	31.4
Turbidity	NTU	0.5
TOC	mg C/l	3.6
DOC	mg C/l	3.4
pH	-	7.1

Fractionation

Figure 4.2 below present the fractionation of the raw water from Stakkastadvatnet in Haugesund.

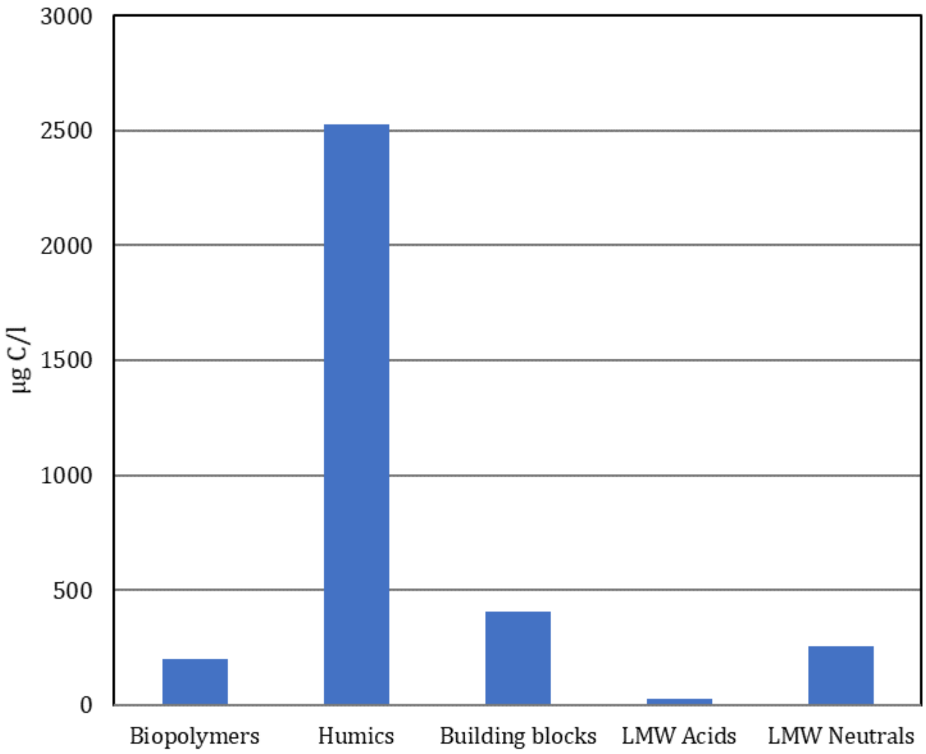


Figure 4.2 Fractionation of the raw water from Stakkastadvatnet in Haugesund

Of the total CDOC of the raw water present biopolymers are 6 %, humics 74 %, building blocks 12 %, LMW Acids 1% and LMW neutral 7 %.

4.1.3 Coagulants

Chitosan

The chitosan utilized in the tests, KitoFlokk^{TM}, was obtained from Teta Vannrensing Ltd (Norway) and was of low molecular weight (100 kDa). The powder has a low acetylation degree (Fa) close to 0.2.

Zirconium

Zirconium was utilized by using a zirconium (IV) oxychloride octahydrate powder, Aquator^{TM}, obtained from Teta Vannrensing Ltd (Norway). The powder contains 27 % (w/w) of pure Zirconium

PACl

Polyaluminumchloride was utilized by using PAX-18 obtained from Kemira. PAX-18 is of medium basisity with highly charged aluminum. PAX-18 contains 9 ± 0.3 % of Aluminum (Al^{3+}).

EPS

The coagulant microbial extracellular polymeric substances (EPS), were deliverd by WETSUS, European Centre of Excellence for Sustainable Water Technology, EPS are produced in a membrane bioreactor treating synthetic wastewater from biodiesel and (bio)ethanol industries. From the reactor, bound EPS are extracted

Chitosan and zirconium mix

The coagulant utilized in Haugesund municipitality is combined mix of KitoFlokk^{TM} and Aquator^{TM}. The mxing ratio is KitoFlokk^{TM} represent 12 % of Aquator^{TM}:

0.12 kg KitoFlokk^{TM} for 1 kg of Aquator^{TM} in a total of 7.1 l of liquid where 0.1 l acid.

4.2 Overview tests

In the parts below a short summary and overview of the tests are presented.

1. Optimation tests
    - Execute a number of tests for each coagulant in order to find the optimum dosage and pH, so called "matrix" format.
    - Include analysis parameters: color, turbidity and pH
2. Validation and repetition
    - Repeat the best dosage and pH 4 times for each coagulant. Total 4 runs
    - Make sure color value is the same as previous tests: 56 mg Pt/l
    - Include addition analysis parameters: UV, TOC and DOC.
3. Different raw water color
    - Decide on 3 different values of color to test; 25, 40 and 56 mg Pt/l.
    - Decide appropriate dosage and pH values to test for each of the coagulants. The same dosage of the same coagulant might work differently for different color value
    - Decide amount of test to be executed for each coagulant
    - Parameters to be tested: Color, turbidity and pH
    - For each of the color value (25 and 40), test the analyzing parameters from 4. above.
4. Haugesund muicipitality
    - Test the dosage used today for different pH values
    - Test 4 dosages of chitosan
    - Test 4 dosages of zirconium
    - Test 4 dosages below the dosage of today
    - Test 4 dosage above the doage of today
    - Mix a new combination of zirconium and chitosan and test
    - Include parameters for al tests; color, turbidity, UV, DOC and TOC

4.3 Proceduers

In this sub chapter the different procedures for testing are presented and explained.

4.3.1 Preparation

Chitosan

A solution of chitosan was prepared. Since chitosan is presented in powder, the solution must contain acid. A 2 % (w/v) chitosan solution was prepared by adding chitosan powder in 1 M HCl.

Procedure for preparation of the solution

1. Prepare the amount of water
2. Mix in the amount of powdered coagulant in the water. Insert the powder piece by piece while mixing the water
3. Make sure all the powder is evenly mixed before next step
4. Add the amount of acid in the solution
5. Mix until the solution is even. Should be a clear, yellow color.

Zirconium

Zirconium (IV) oxychloride octahydrate powder is highly soluble in water. therefore, a solution of 15 % (w/w) was prepared by dissolving the powder in distilled water.

Procedure for preparation of the solution:

1. Prepare the amount of water
2. Mix in the amount of powdered coagulant in the water. Insert the powder piece by piece while mixing the water
3. Make sure all the powder in evenly mixed

PAX

PACl 18 is a prepeard substance and no further preperations was needed before use.

EPS

EPS was prepared by measuring 0.1 g EPS / l in distilled water. A 100 ml solution was prepared with 0.01 g powder EPS. The procedure for the preparation of the solution is:

1. Prepare the amount of water
2. Measure the amount of EPS
3. Mix in the amount if EPS with a magnet stirrer. Let the water stir when the powder is added
4. Let the solution mix for 24 hours.
5. If the solution is not mixed after the mixing time. Add a couple of drops 1 M NaOH

4.3.2 Implementation

Procedure for the jar tests

The procedure for the jar test were as following:

1. pH was adjusted to the correct value before adding the coagulant
2. Addition of coagulant and fast mixing for 30 s
3. Slow mixing for 20 minutes and pH measurements
4. Sedimentation for 30 minutes
5. Collection 10 ml of water 2 – 3 cm below the surface for testing
6. Another sample of the water was filtrated through a 0.45 μm filter

4.3.3 Analysis

The following tests were executed for analysis of the performed jar tests.

Color

Color was measured by Perkin Elmer Lambda 650 machine. Prior to the tests, the water utilized was filtrated through a 0,45 μm filter.

Turbidity
Turbidity was measured using Hach 2100 AN IS turbiditimeter.

pH
pH was measured using a Hach sension+ H31 with the electrode PHC2701-8. The technology was calibrated using two points, pH 4 and pH 7 prior to use.

UV
UV was measured by using a Perkin Elmer Lambda 650 machine. For the test all the samples were filtrated beforehand using a 0,45 μm filter.

DOC and TOC
DOC and TOC was measured using Tekmar Dohrmann Apollo 9000 at high temperatures. Prior to the DOC test, the water was filtrated using a 0,45 μm filter.

TSS

TSS were measured using 100 ml water samples. First, the bowls used for testing were weighted, then filled with 100 ml of water. The samples were then dried at 105 °C for 24 hours. The bowls were then weighted again. TSS were then calculated by subtracting before and after.

Fractionation
Fractionation procedure were conducted as explained in chapter 2.2.2 using a LC-OCD fractiometer

5 Results and discussion

This chapter presents the results obtained from the tests and the discussion related.

5.1 Comparing coagulants

The results from the matrix tests will be presented in this chapter. For chitosan and zirconium, a significant number of tests were conducted for different pH and dosages, while PAX-18 was pre-determines both pH and dosage based on theory obtained.

5.1.1 Chitosan

Figure 5.1 below presents the results from the "matrix" tests for chitosan. Between the pH 4.5 – 6.5 several dosages were tested for each pH increasing with 0.5. Figure 5.2 presents these results by showing how pH influence the efficiency for each dosage tested in the matrix.

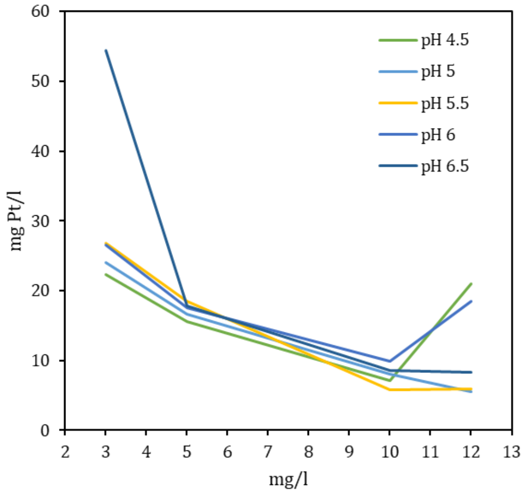


Figure 5.1 illustrates the efficiency for different chitosan dosages

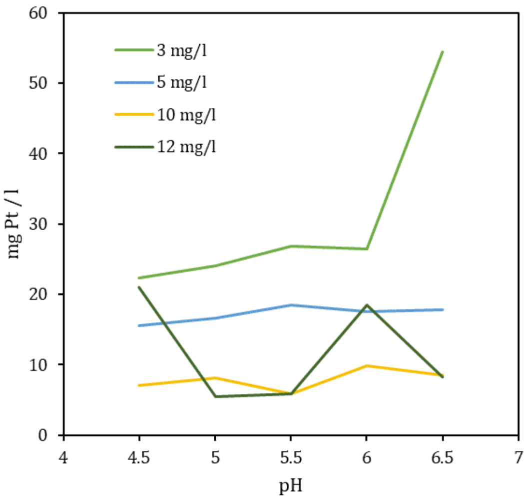


Figure 5.2 illustrates how pH effects the efficiency of each dosages on the treatment

Based on the results from the tests a 10 mg/l dosage obtained most destabilization and reduction in color for all pH values. Figure 5.1 illustrates a parabola effect from the results, where a stage of optimum dosage is reached, and destabilization occurs and is then followed by a stage where the water is stabilized again often due to surplus of coagulant.

Comparing results from both Figure 5.1 and Figure 5.2 the optimum pH would be 5 - 5.5. Notably, dosage 12 mg/l at pH 6 have an irregular value compared to the same dosage at pH 5.5 and 6.5. This test could be repeated in order to investigate whether or not the result were irregular measurement. Note, all color values below 5 mg Pt/l should be written as < 5 mg Pt/l, but are included with whole numbers due to arguments sake.

These results are consistent with previous studies (Christensen, 2018). Although, the raw water utilized here have greater color value, and therefore obtain best results at higher dosages.

5.1.2 Zirconium

As with chitosan, zirconium was tested on the raw water in a matrix format. For pH values between 4 – 6.5 several zirconium dosages were tested with an increasing pH value of 0.5 for each run. Figure 5.3 present the result from the matrix test for zirconium and Figure 5.4 present the results by showing the influence of pH.

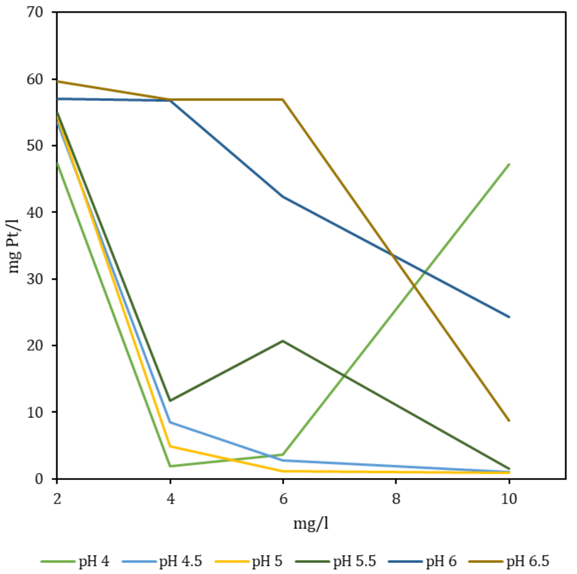


Figure 5.3 illustrates the efficiency for different zirconium dosages

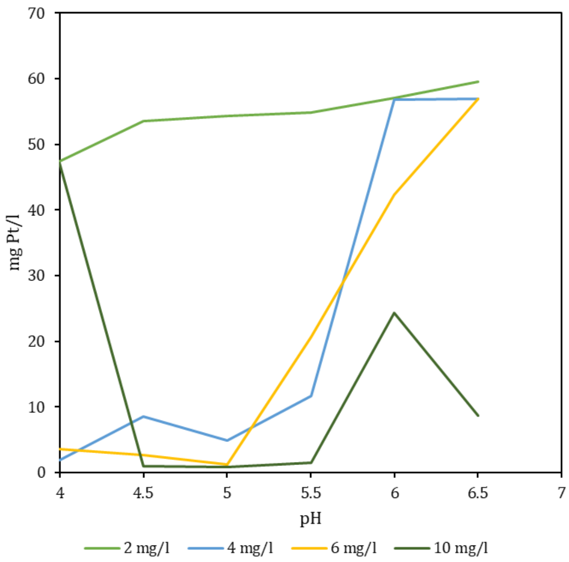


Figure 5.4 illustrates how pH effects the efficiency of each dosages of the coagulant

Figure 5.3 show an optimum minimum dosage between 4 – 6 mg/l for some of the pH values. The higher pH values require higher dosage than the lower pH. The lowest results obtained were 0.9 mg Pt/l at dosage 10 mg/l for pH 5. For all pH values, the low dosage of 2 mg/l obtain little reduction in color. Figure 5.4 illustrates how at pH 5.5 a distinctive peak is reached, and higher pH values are less efficiency at lower dosages. A pH between 4.5 – 5.5 seems to be optimum.

Some of the dosages obtain significantly low result, less than 5 mg Pt/l. Notably, these results should be presented as < 5 mg Pt/l, but for arguments sake are included here. Therefore, the difference between the dosages might be insignificant for these low results, and are therefore difficult to place the "most optimum" dosage if it is below 5 mg Pt/l.

The results obtained here are corresponding with conditions presented in other studies. With an optimum range of 4 – 10 mg/l for pH 4.5 – 5.5 found here this corresponds with Christensen (2018) results of 5 – 12 mg/l pH 4.5 – 6.3 and Jarvis et al. (2012) 5 – 15 mg/l pH 5 -6, with a slight difference.

5.1.3 PAX-18

PAX-18 was tested in order to investigate the other coagulants performance compared to a more well tested and investigated coagulant well used in the industry and research. Due to the significant and comprehensive research available, the dosages and pH was predetermined and not tested in the "matrix" format. The dosages chosen was 1, 3, 5 and 7 mg /l with PAX- 18. The pH was set to 6. Figure 5.5 below present the results obtained from these tests.

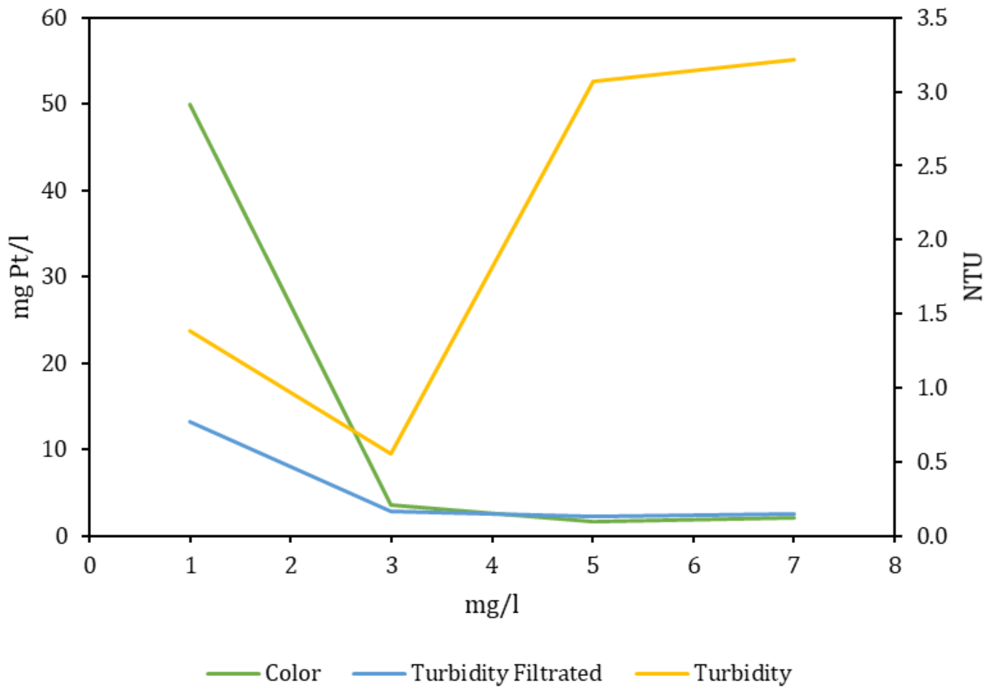


Figure 5.5 illustrates the performance of PAX- 18 in removal of color and turbidity. The left axis represents color mg Pt/l and the right axis represent turbidity NTU. Both filtrated and un-filtrated turbidity are included in the figure.

Figure 5.5 illustrates how dosages above 3 mg/l obtain significant result of reduction in color and turbidity. Dosage 5 mg/l obtain the lowest result of color with 1.6 mg Pt/l while dosage of 3 mg /l obtain lowest turbidity un-filtrated, indicating a significant forming of flocs and sedimentation.

Calculated optimum minimum dosage where 3.4 mg/l at pH 6 and this corresponds with the results obtained here. Despite the higher dosages obtaining higher reduction in color and filtrated turbidity, a dosage around 3 mg/l would be both safe and economically due to lower use of dosage. Christensen reported optimum conditions for PAX-18 1 – 5 mg/l at pH 5-6 which is shown in these results as well. Despite not obtaining a clear parabolic effect as would be expected, higher dosage of 7 mg/l were not tested, due to the amount of existing data available on the subject.

5.1.4 Comparison of the results

In Figure 5.6 below all three coagulants are presented together in order to show the different efficiency for each of the coagulant. Based on the results obtained from the "matrix" tests of chitosan and zirconium, the best dosages and pH values are included in the figure. For PAX-18 all the tested dosages were included.

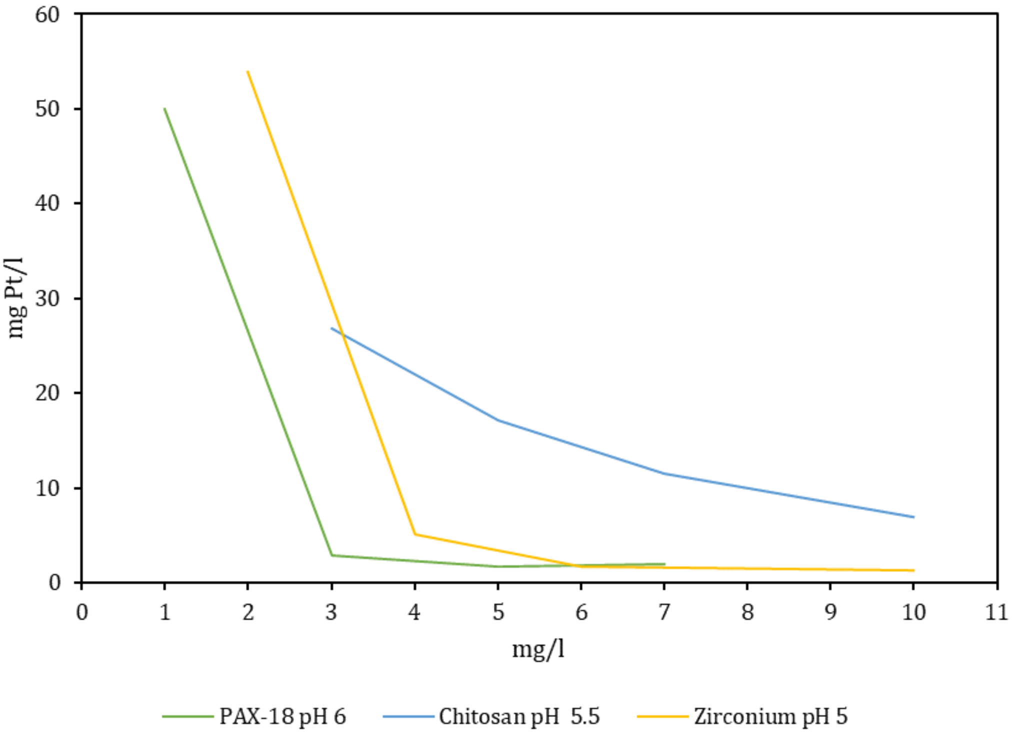


Figure 5.6 present the performance for color removal of each of the coagulants compared to each other.

Comparing all three coagulants with each other, they all are capable of obtaining results within the need range below 20 mg Pt/l and all obtain results below 10 mg Pt/l for some dosages. PAX-18 have the lowest minimum optimum dosage of all three coagulants, at 3 mg/l. While Zirconium obtain the most reduction in color. Zirconium does have a relatively low minimum optimal dosage at 4 mg/l. PAX and Zirconium obtain color values below 5 mg Pt/L, while chitosan obtains color values below 10 mg Pt/l. This show all three coagulants ability to perform and remove sufficiently. Chitosan does require higher dosage in order to obtain acceptable result. Due to the environmentally nature of chitosan, there are less risk related to higher dosage use of chitosan, say compared to PACl, where the higher aluminum content could pose a risk.

5.1.5 EPS

In addition to the other coagulants tested, some initial testing was conducted for another alternative coagulant, Extracellular polymeric substances (EPS). These tests were only preliminary for the coagulant and not part of the main comparison between the other coagulants. There are always interesting and important to investigate new and less known coagulants, in order to further develop the science.

The dosages were determine based on TSS. TSS were measured for the raw water in Malvik where:

$$TSS = 0.2 \text{ g TSS / l}$$

The dosage range recommended for surface water were 1 – 100 mg / g TSS.

For the test, the lower range were choses for testing. The results are presented in Table 5.1 below.

Table 5.1 Results of EPS for color, turbidity and DOC.

Dosage mg / g TSS	Color mg Pt/l	Reduction in color	Turbidity F NTU	Reduction in Turbidity	DOC mg C/l	Reduction in DOC
1	52.0	7 %	0.20	-9 %	6.01	7 %
4	52.4	6 %	0.14	25 %	6.32	2 %
8	52.1	7 %	0.20	-9 %	6.27	3 %
12	53.8	4 %	0.17	8 %	6.58	-2 %
16	54.5	3 %	0.17	7 %	6.12	5 %
20	54.4	3 %	0.21	-13 %	6.41	1 %
24	54.5	3 %	0.14	24 %	6.07	6 %
28	54.1	3 %	0.23	-24 %	6.20	4 %

The results here show that EPS have very little impact on reduction of color, filtrated turbidity and DOC. Highest reduction are observed at dosage 1 mg/ g TSS with a reduction of 7 %. A DOC reduction of 7 % where observed for the same dosage. This coagulant is therefore not suited for removing NOM from water.

Based on data for the coagulants, the coagulant is more efficient for removing suspended solids in the water. The raw water utilized in the test hade relatively low turbidity and very little TSS. This is common for most Norwegian surface waters. Thus, making EPS not suitable as coagulant in Norway for drinking water treatment.

On the other hand, water with NOM and high particle content could be of interest. Possible combination with other coagulants more suited for NOM removal could be interesting and further investigated. Another application is wastewater. Tests have been executed for this coagulant on wastewater, and further test would be of interest.

5.2 NOM removal

Based on the “matrix” tests for zirconium and chitosan, a number of dosages and pH values was selected and repeated in order to obtain statistical and additional performance data. In this chapter the statistical values are presented in one part, and the other part include the results from the additional parameters tested in order to evaluate NOM removal. The last part of this chapter includes the result from the fractionation for these chosen dosages.

5.2.1 Statistical results

After the “matrix” tests for chitosan and zirconium, a number of dosages were repeated several times in order to validate their statistical values. The performance for both color and turbidity removal are presented.

Color removal

In Figure 5.7 below, a selection of the best performing dosages and pH for each of the coagulants are presented with their statistical variables included for color removal.

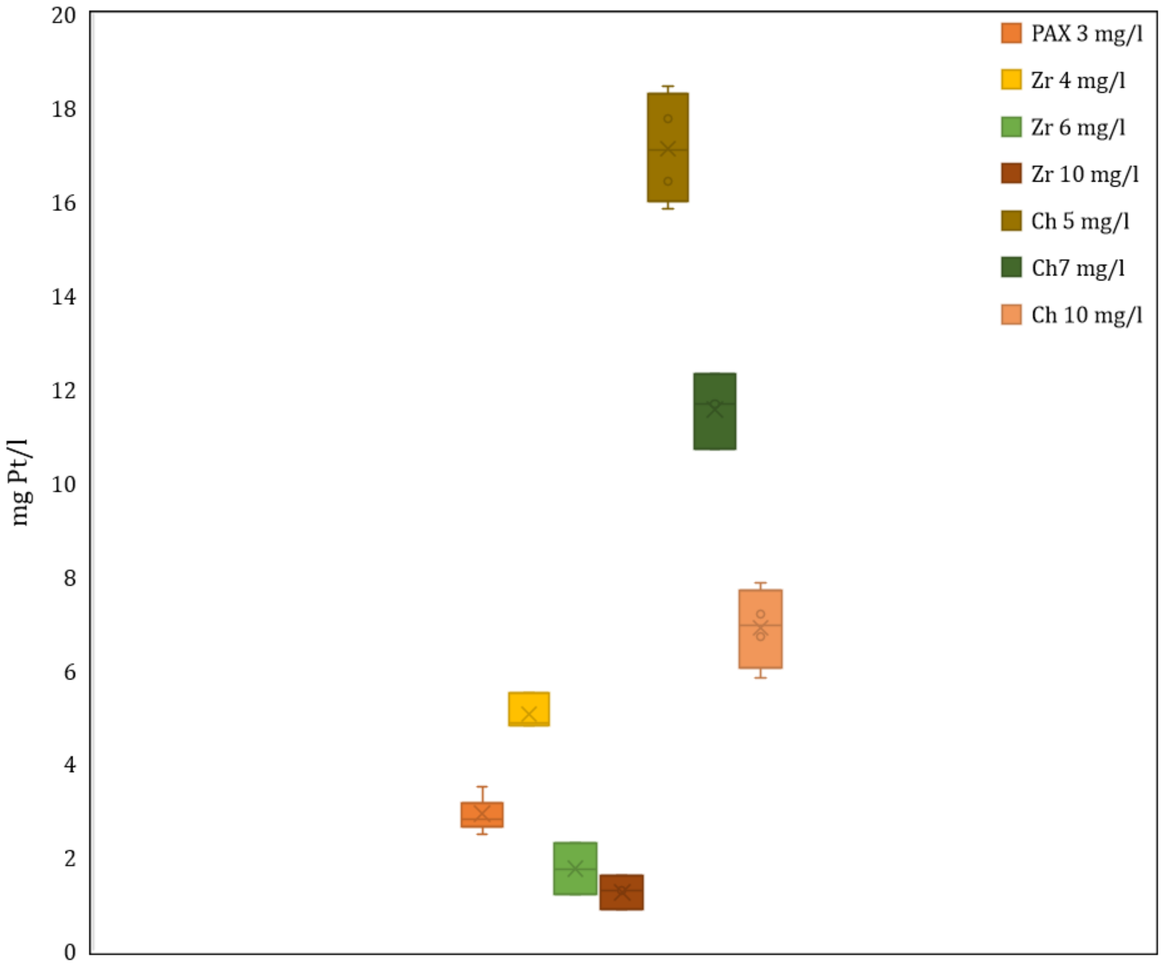


Figure 5.7 The statistical results for each of the coagulants and their chosen dosages for color removal.

All the dosages are presented in a box diagram where the top line outside the bars shows the highest measured value. The bottom line outside the bars shows the lowest measured value. The upper part of the columns shows the upper quartile and the lower part shows the lower quartile. The cross inside the pillars shows the mean values of the measurements and the line inside the bar shows the median value.

For all the dosages of the three coagulants, the results are all under 20 mg Pt/L, which is the needed limit. Overall chitosan has somewhat higher values than PAX and Zirconium, but did obtain values around 7 mg Pt/l for dosage 10 mg/l.

Zirconium obtain the lowest values with values as low as 1 mg Pt/l, and PAX at dosage 3 mg/l obtain color value of 3 mg Pt/l. Note that all values under 5 mg Pt/l would normally be "written" as < 5 mg Pt/l, but due to the necessary for argument, all values are presented here. Due to the inaccuracy of the measurement analysis, the statistical comparison for these values may be ineffective, and not correct. Nevertheless, they are included here.

Chitosan is the coagulant that achieve the largest spread of results for the same dosage. Chitosan dosage 5 mg/l have over 2 mg Pt/l difference from the largest to the lowest results color value. Both PAX and zirconium obtain the results closer in values.

Turbidity removal

As with color removal, the same dosages and pH values are presented in Figure 5.8 below for turbidity removal. These tests are for filtrated turbidity. There where to many differences on the infiltrated turbidity samples and where not included here.

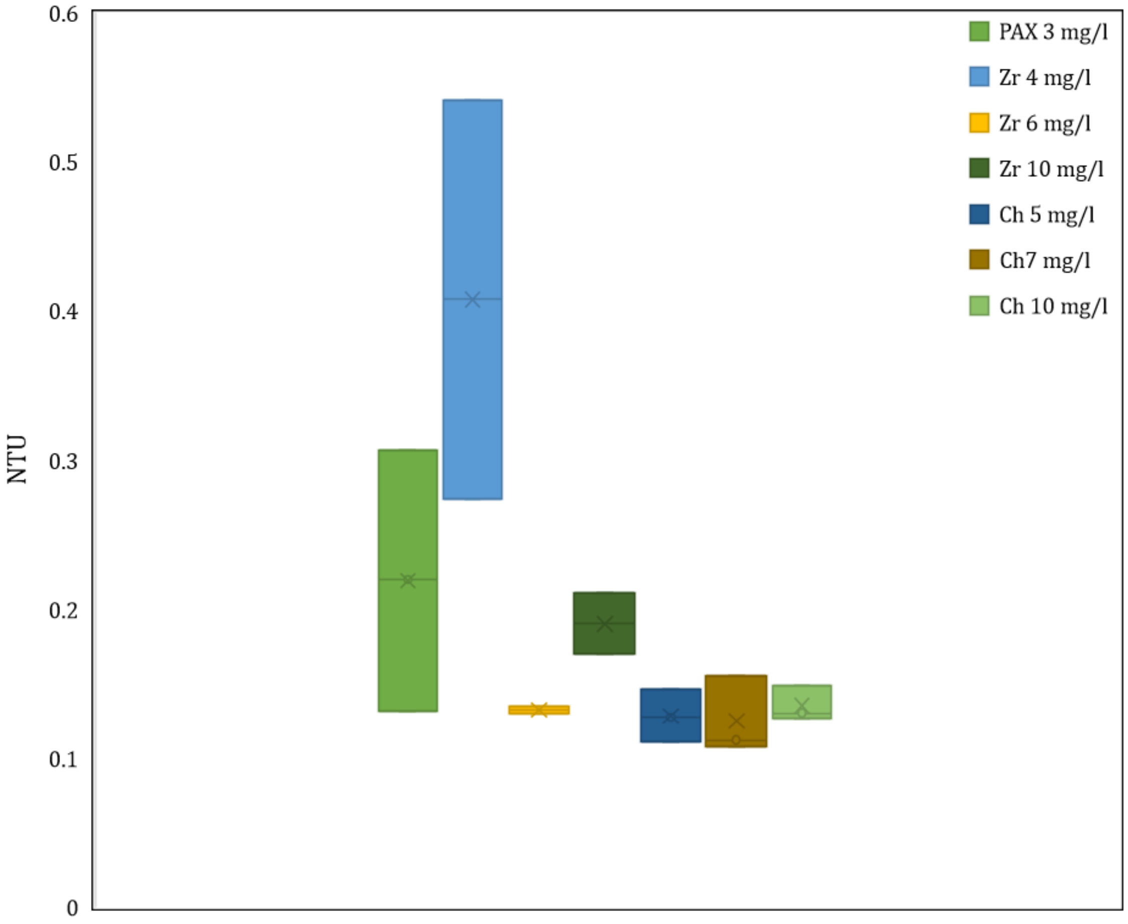


Figure 5.8 The statistical results for each of the coagulants and their chosen dosages for turbidity removal. Includes filtrated turbidity.

All the dosages are presented in a box diagram where the top line outside the bars shows the highest measured value. The bottom line outside the bars shows the lowest measured value. The upper part of the columns shows the upper quartile and the lower part shows the lower quartile. The cross inside the pillars shows the mean values of the measurements and the line inside the bar shows the median value.

Beside one zirconium dosage, all results for filtrated turbidity are below 0.4 NTU. Most of the coagulant dosages are mostly between 0.1 – and 0.21 NTU. Two dosages, PAX 3 mg/l and Zirconium 4 mg/l, have a relatively high spread of date. Zirconium 4 mg/l have results as low as 0.27 up to 0.54 NTU. An important note, due to adjustment during the testing period, this dosage was not tested for filtrated turbidity as many times as the other coagulants. Therefore, the statistical data may be less accurate for zirconium. PAX 3 mg/l had results varying from 0.131 NTU up to 0.29 NTU. Due to the low turbidity values and inaccuracy of the analysis technology, these statistical variations may be insignificant.

5.2.2 NOM removal

For the chosen dosages and pH values for each of the coagulants, NOM removal was evaluated. Several additional parameters were tested for the chosen dosages. these parameters were UV, DOC and TOC. SUVA was calculated after the test and are presented below.

Chitosan

To evaluate the performance of chitosan for NOM removal, three dosages at pH 5.5, 5 mg/l, 7 mg/l and 10 mg/l was included for testing. The results for these dosages are presented in Table 5.2 below.

Table 5.2 The results of the chitosan dosages for UV, DOC and TOC after treatment.

Dosage mg/l	pH	UV cm^{-1}	DOC mg C /l	TOC mg C/l
5	5.5	0.14	4.35	4.36
7	5.5	0.08	3.29	-[a]
10	5.5	0.10	2.92	4.55

[a] *Missing data – not tested.*

Zirconium

In the same way as for chitosan, three zirconium dosages and pH values were tested for UV, DOC and TOC. The dosages included 2 mg/l, 4 mg/l and 10 mg/l at a pH of 5. The results are presented in Table 5.3 below.

Table 5.3 The results of the zirconium dosages for UV, DOC and TOC after treatment.

Dosage mg/l	pH	UV cm^{-1}	DOC mg C /l	TOC mg C/l
4	5	0.04	2.04	2.57
6	5	0.02	1.47	1.75
10	5	0.02	1.08	6.32

PAX-18

As earlier mentioned, PAX-18 was not tested extensively due to already comprehensive studies in the field. Therefore, only three of the four tested dosages were tested for UV, DOC and TOC during the repetition for statistical analysis. The dosages of PAX-18 at pH 6 was 1 mg/l, 3 mg/l and 5 mg/l. The results are presented in Table 5.4 below.

Table 5.4 The results of the PAX-18 dosages for UV, DOC and TOC after treatment.

Dosage mg/l	pH	UV cm^{-1}	DOC mg C /l	TOC mg C/l
1	6	0.25	5.81	6.15
3	6	0.04	1.97	2.11
5	6	0.03	1.40	6.36

All the coagulants were able to obtain TOC value below 5 mg C/l. Only zirconium and PAX obtain TOC values below 3 mg C/l. Chitosan where not able to obtain TOC values below 3 mg C/l but did obtain less than 5 mg C/l for two. TOC for 7 mg/l where not usable and could not be used in this analysis. DOC values were below 3 mg C/l for dosage 10 mg/l. A relatively high reduction of DOC were observed by chitosan with maximum reduction of 55 % at dosage 10 mg/l. Ødegaard et al. (2010) have provided an estimate of minimum 20 -

35 % TOC reduction for chitosan dosages. Dosage 5 mg/l obtained a TOC reduction of 36.4 % which are within recommended limit.

Zirconium obtained TOC values below 3 mg C/l for dosage 4 mg/l and 6 mg/l. All DOC values were below 3 mg/l. A maximum reduction in DOC were observed for dosage 10 mg/l as 83 %. PAX obtained TOC values below 3 mg/l for dosage 3 mg/l. Dosage 3 mg/l and 5 mg/l obtained DOC dosage under 3 mg/l. PAX observed a reduction of DOC as 78 % for dosage 5 mg/l. Ødegaard et al. (2010) recommended a reduction of 50 – 60 % for TOC, which dosage 3 m g/l obtain with a 69 % reduction.

SUVA

Figure 5.9 below present the calculated SUVA values for the three coagulants and the tested dosages and pH for each. SUVA is calculated by UV- 254 cm and DOC values. SUVA for the raw water was calculated to be 4.53 l/mg m.

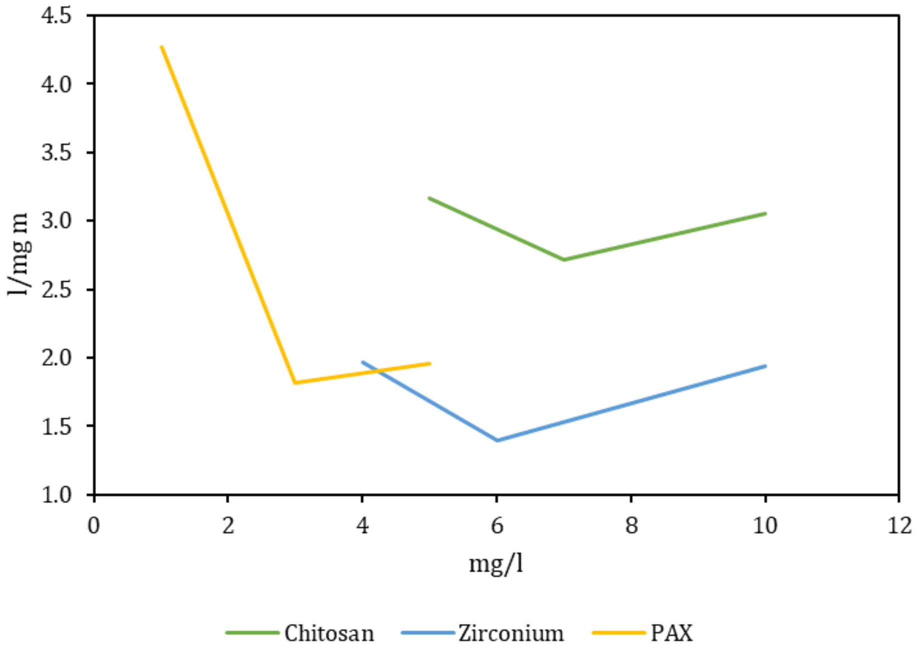


Figure 5.9 Present SUVA for each of the coagulants and their dosages and pH values found to most efficient for color and turbidity removal.

Chitosan obtain overall higher SUVA values than Zirconium and PAX, with Zirconium obtaining the lowest SUVA of all three, with 1.4 l/mg m at dosage 6 mg/l. Chitosan obtain the lowest SUVA value of 2.7 l/ml m at dosage 7 mg/l. PAX obtain the lowest SUVA value at 1.81 l/mg m. Normally SUVA lies between 1 – 6 l /ml. All coagulants obtain a significant reduction of SUVA that indicates NOM removal after coagulation.

While chitosan obtains less reduction than the others, this were expected due to chitosan’s slightly lower ability to remove NOM than PAX-18 or zirconium. Despite this, a 40 % of SUVA where reduced by chitosan at dosage 7 mg/l including a reduction of color to 11,3 mg Pt/l, a significant reduction of NOM may be assumed. Low SUVA and color values can indicate a removal of highly charged, large molecular weight and hydrophobic organic compounds (Hussain et al., 2014). Zirconium obtained 69% reduction in SUVA at dosage 6 mg/l. The high reduction of color at the same dosage does indicates a significant reduction in NOM. PAX obtained a 60 % reduction of SUVA that compared to the high reduction of color present relatively high NOM removal.

Jarvis et al. (2012) explain zirconium's higher NOM removal as zirconium have demonstrated higher zeta potential and argues that it delivers more charge than the other coagulants, and the better performance are related to the increased charge on precipitated Zr solids.

5.2.3 Fractionation

Based on the results from the "matrix" tests a number of samples was selected and tested using a fractionation method, LC-OCD. Mostly all of the tests repeated for the previous two parts from this chapter some tests were not tested for fractionation. The exclusion was based on the initial results of color and turbidity. The results are presented in Figure 5.10 below. The additional results are presented in Appendix 4.

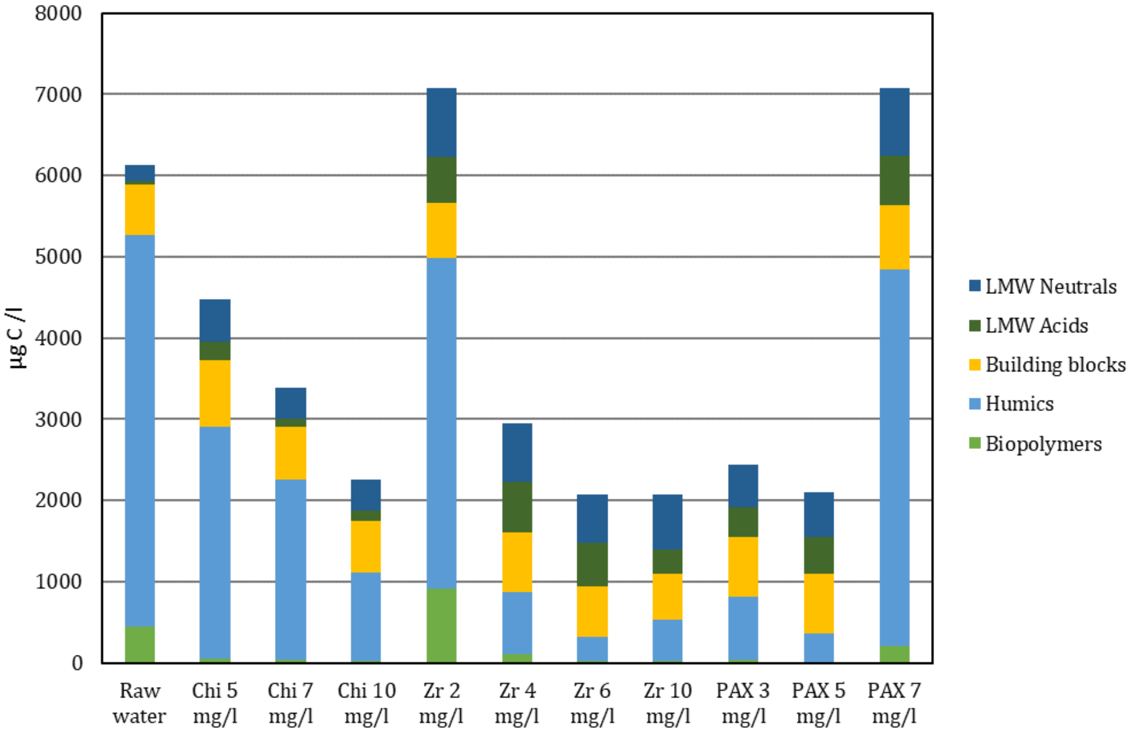
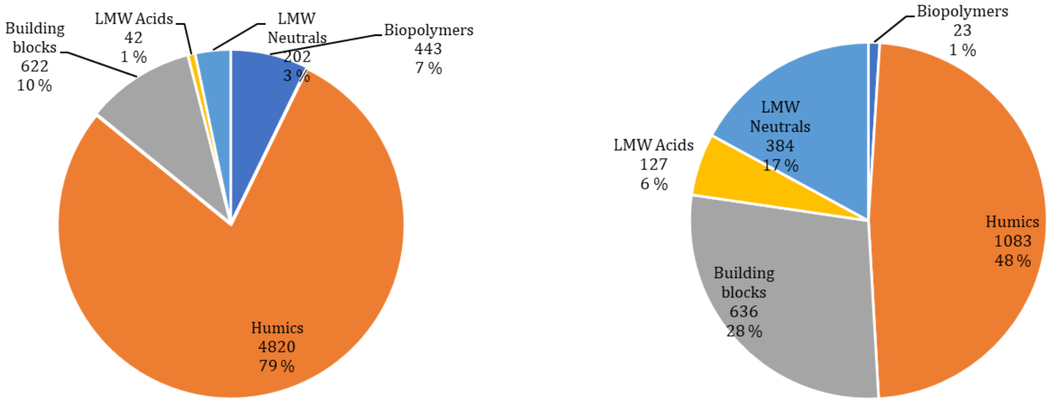
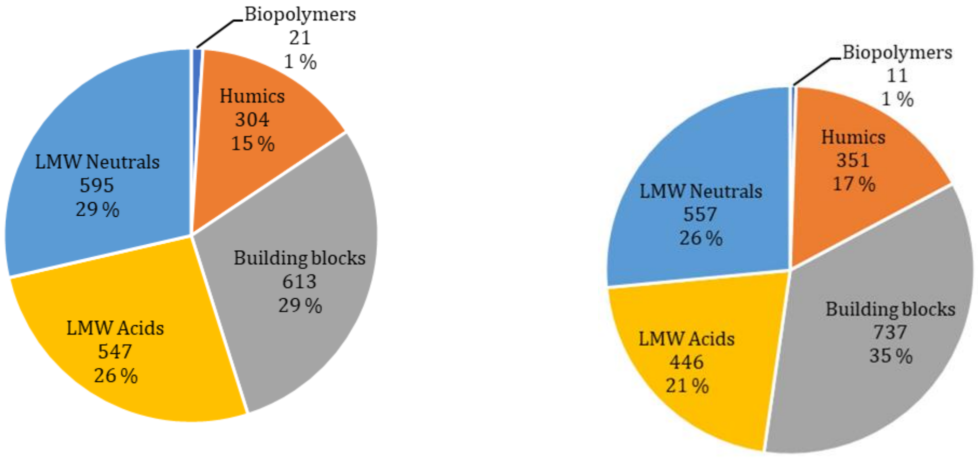


Figure 5.10 The fractionation results for the selected water samples of treated water from Malvik.

For their respectively optimum dosage observed and discussed earlier, all three coagulants obtain relatively removal of humics, as well as removal of biopolymers. Though for some dosages, an increase of building blocks and LMW neutrals and acids were observed. During coagulation, the part to be removed are humics. This is observed for near all coagulant and dosages, with exception of two, Zirconium 2 mg/l and PAX 7 mg/l. Figure 5.10 present the percentage of the fractionation results for four selected samples.



(a) Raw water (b) Chitosan 10 mg/l



(c) Zirconium 6 mg/l (d) PAX 5 mg/l

Figure 5.11 The percentage of the fractionation results for four selected samples. The value in the middle present the µg C/l of the fraction.

Zirconium and PAX had a larger reduction of humics than chitosan. All three coagulants had similar reduction of the largest molecular sized fractions, biopolymers. All coagulants observed an increase of the lower molecular sized fractions after treatment, but chitosan observed less increase than zirconium and PAX.

For chitosan, the highest dosage reduces the most amount of humics, while the lowest dosages removed the least. Chitosan consist of carbon bindings and therefore may contribute to some of the increase of building blocks. Some of the humics may also be converted to building blocks instead of being removed. The calculated SVUA values for chitosan were lowest for 7 mg/l, while dosage 10 mg/l observed most reduction in humics, and a significant reduction of the largest molecular size fractions, biopolymers. This previous studies have reported that increasing chitosan dosage, increases the low molecular sized fractions after treatment (Vogelsang et al., 2004).

For Zirconium, a dosage of 6 mg/l remove the most amount of humics. This correlates with the lowest SUVA value from chapter 5.2.2 which were for dosage 6 mg/l. A low zirconium dosage of 2 mg/l increases biopolymers, building blocks LWM acids and LWM neutrals, while a small amount of humics are reduced.

A PAX dosage of 5 mg/l obtained the lowest amount of humics, a dosage of 7 mg/l obtain a slight reduction of humics and biopolymers, while increasing building blocks and LMW neutrals and LMW acids. PAX observed the lowest SUVA value at dosage 3 mg/l, while dosage 5 mg/l obtain the highest reduction of humics.

5.3 Different rawwater color

The raw water obtained from Malivk is of a significant high color (56 mg Pt/l).Normally water of lower color is more suitable when utilizing chitosan as coagulant for treatment. Therefore, by thinning out the raw water with tap water from the lab, two additional raw water values were tested in addition to the raw water from Malvik. The tap water is from Trondheim municipality, with a color value of 14 mg Pt/l.

After initial some tests the new water samples were prepared. Table 5.5 below present the amount of water and tap water mixed and the color values for the new mixed water.

Table 5.5 New water samples prepared. Include amounts of raw water and tap water utilized and measured color values.

Water No	Parts tap water %	Parts raw water %	Color mg Pt/l
1	0	100	56
2	40	60	34
3	70	30	27

Color removal

Figure 5.12 below present the results from all three water samples. Dosages and pH were chosen based on the results obtained from chapter 5.1 tests for chitosan. Due to lower color in the water, a lower dosage was assumed while the optimal pH of 5.5 was still utilized.

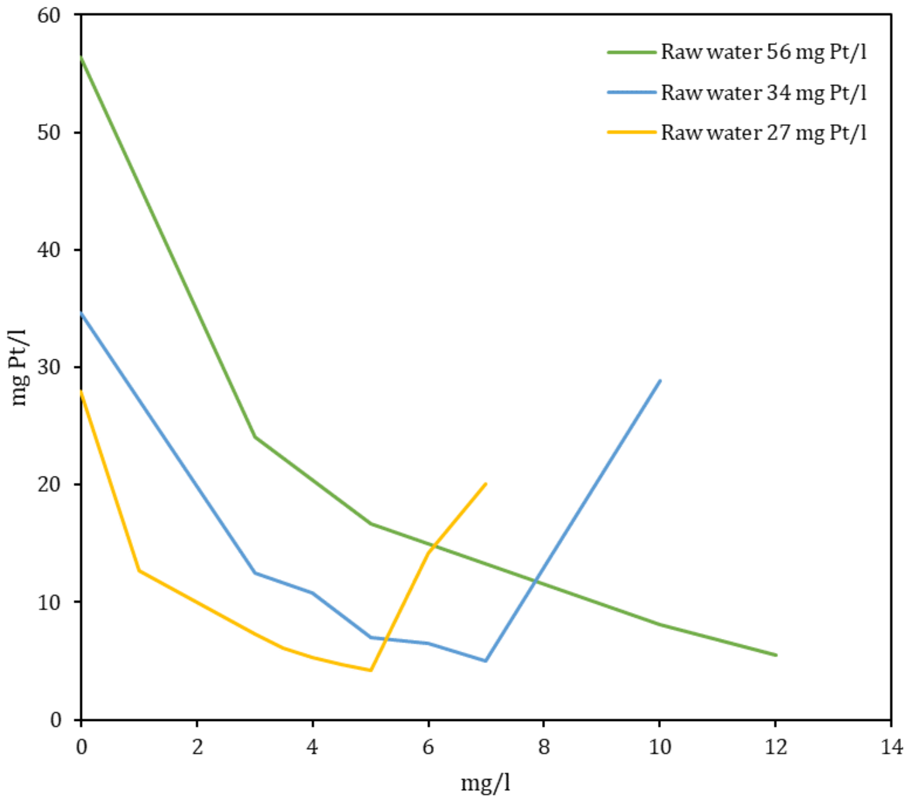


Figure 5.12 The results for color removal by chitosan for the three different raw water color values. A pH of 5.5 was chosen for all tests.

Figure 5.12 above show that for higher color values in the raw water, a higher dosage is needed. For the Raw water no 1 the lowest dosage appear to be at 12 mg/l, while the lowest is at 7mg/l and 5 mg/l for No 2 and 3 respectively. For no 2 and 3 a clear parabola tendency is observed, while for no 1 the graph is not going upwards yet. Due to ionic connections there is expected that at some point higher dosages will not obtain necessary destabilization due to abundance in many positive ionic bindings and therefore increase the color instead of decreasing. There is possible to assume that a higher dosage of 12 mg/l will present this tendency but were not tested her. A dosage of 12 mg/l obtained a color value of 5 mg Pt/l and therefore possible to assume that a lower color value is

The figure also show a clear correlation with the raw water color, and the minimum optimal dosage. As the raw water color decreases, so does the minimum optimal dosage. As earlier mentioned, a raw water color of 56 mg Pt/l is higher than what normally applied with chitosan as coagulant. These result confirm that lower raw water color are more appropriate in order to operate with a more acceptable dosage level. Nevertheless, the results show chitosan's ability to remove, despite the high raw water color. With a reduction of 90 % for dosage 12 mg/l, chitosan has proven its capability.

Turbidity removal

Figure 5.13 below present the results for turbidity removal by chitosan for each of the water samples.

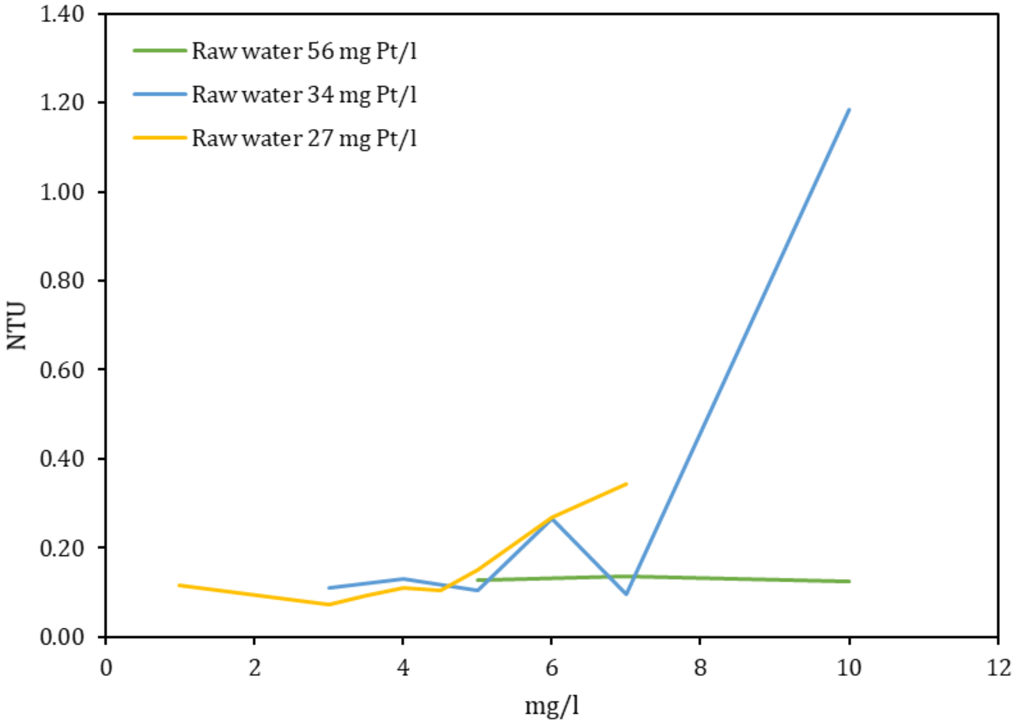


Figure 5.13 Presents the results for turbidity removal by chitosan for each of the water samples. The results are for filtrated turbidity.

Figure 5.13 show the filtrated turbidity levels after coagulation. Filtration with a 0.45 m filter could sometimes represent a sand filter for a treatment plant, and therefore the results could be comparable. All three water types obtain low turbidity levels for most of the dosages.

For water type no 2 the turbidity value is the highest with 1.18 NTU for dosage 10m g/l. this correlates with the high color value of 29 mg/l which is the highest off all the coagulants after the tests. There may be possible to assume that the high dosage results to many positive ions for the "levels in the water" Despite that one value, all their values are within the needed range.

5.4 Haugesund municipality

In this chapter the results of the test on the raw water from Haugseund are presented. Several coagulants have been tested. Chitosan, zirconium on their own, and then combined together with two different ratios. A fractionation on some of the samples are also presented at the end.

5.4.1 pH

The first tests that were conducted was to investigate the current dosage for the coagulation mix at different pH values. This is so the municipality can obtain information whether the pH that are used today is good, or if there might be of interest to evaluate other possibilities.

For these tests the dosage of 47 µl/l was used on pH values from 4 – 6, where the values 4, 4.5, 5 and 6 were tested. Due to somewhat limited amount of water, no further values were investigated beside these. Figure 5.14 below present the results for these tests.

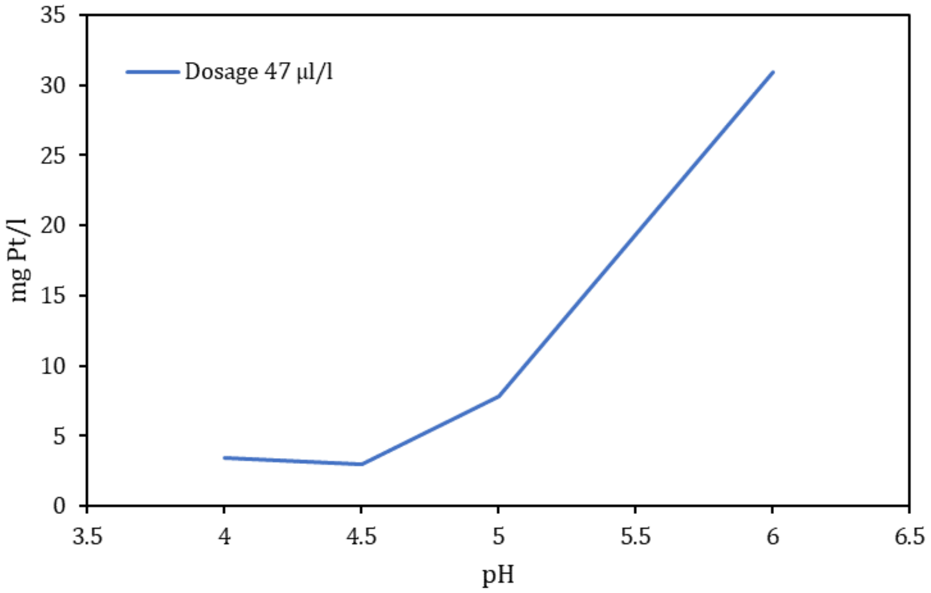


Figure 5.14 Illustrates how efficiency of pH for the current dosage of the coagulation mix utilized at the municipality today

Figure 5.14 above show how pH of 4 – 4.5 is optimum, with a pH of 4.5 showing the best result. Therefore, the pH of the current dosage for treatment at the municipality is based on the results obtained hare, at optimum range and that the current operation pH should be continued.

NOM removal

Three of the pH values tested with dosage 47 µl/l where tested for UV, DOC and TOC.
The results are presented in Table 5.6 below.

Table 5.6 The results of the current dosage of the coagulation mix utilized at the municipality today for UV, DOC, TOC and SUVA

Dosage µl/l	pH	SUVA l/ml m	UV cm^{-1}	DOC mg C /l	TOC mg C/l
47	4	1.43	0.03	2.30	4.08
47	4.5	3.87	0.06	1.44	3.72
47	5	1.56	0.03	1.96	4.30
47	6	-	-	-	-

No pH obtained a TOC below 3 mg C/l. Based on the results of DOC and TOC, pH 4.5 show most reduction of NOM. A DOC reduction of 57 % where obtained at this pH. In addition to the low color value, an optimum NOM reduction at pH 4.5 may be assumed.

5.4.2 Chitosan

Tests were conducted with only chitosan on the raw water from Haugesund. The pH was set to be of similar to the operating pH at the municipality of today, 4.5. If some results show significant promise, it would be easier for the municipality to implement this to the existing treatment. Figure 5.15 below present the result for chitosan.

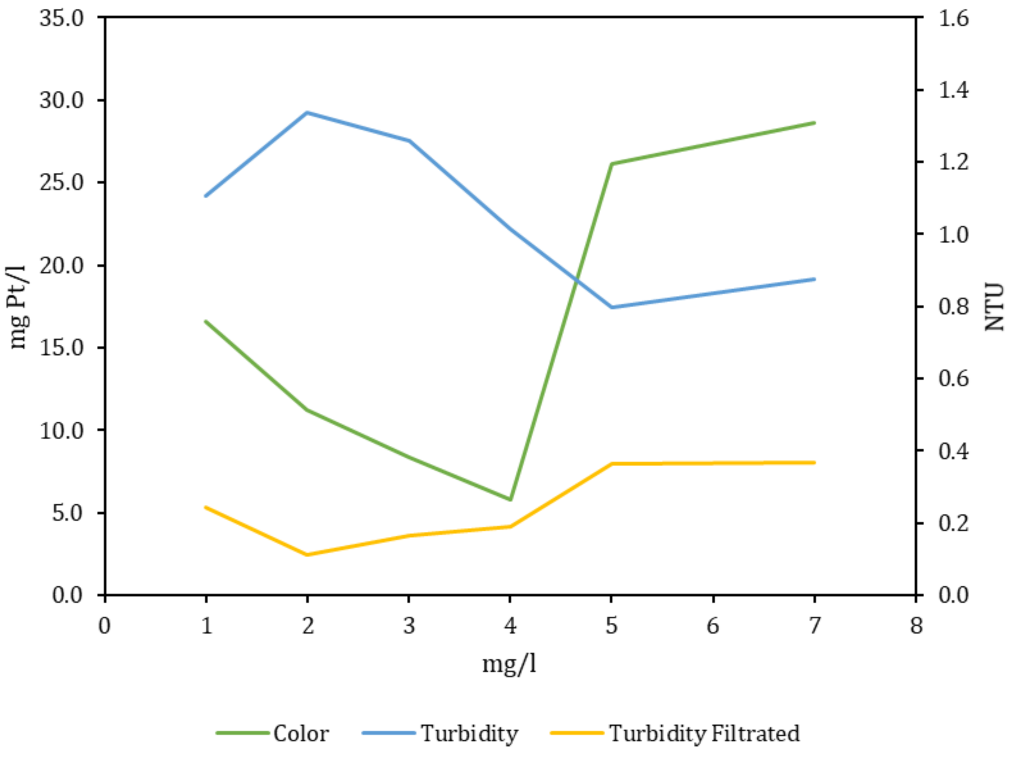


Figure 5.15 The result for chitosan on the raw water from Haugesund. Includes color on the y-axis and turbidity on the secondary axis

The results show that the lowest color value is obtained by the dosage of 3 mg/l where the value is 8.4 mg Pt/l. At the same dosage, filtrated turbidity is also lowest at 0.17 NTU. At the same time turbidity un-filtrated is highest at this dosage, that might suggest a higher amount of flocs formed.

At dosage 3 mg/l the results are of a low value that the coagulant itself obtain a significant result. Since the coagulant used at the facility today are a mixture of chitosan and zirconium, the results here indicate chitosan's ability to remove a significant amount of color and turbidity on its own. Ideally more chitosan and less zirconium would be better due to the less environmental impact and wider pH range with the use of chitosan in addition to the less sludge production connected with chitosan.

As previous tests have shown an ideal pH from 5 – 5,5 it could be argued that potential better results could be obtained with the same dosage at this pH.

NOM removal

All dosages of chitosan where analyzed for UV, DOC and TOC. The results are presented in Table 5.7 below

Table 5.7 the results of chitosan dosage on removal of UV, DOC and TOC for the raw water from Haugesund

Dosage Mg/l	pH	UV cm^{-1}	DOC mg C /l	TOC mg C/l
1	4.5	0.12	3.02	4.09
2	4.5	0.09	3.55	4.59
3	4.5	0.07	2.33	4.80
4	4.5	0.10	2.42	4.89
5	4.5	0.13	4.09	5.51
7	4.5	0.15	5.23	5.88

No dosage obtained TOC value below 3 mg/l. Dosage 1 mg/l and 3 mg/l obtained TOC values below 5 mg C/l. Only dosage 3 mg/l obtained a DOC value below 3 mg/l. For all dosage, an increase of TOC was observed. It is possible that the high TOC value for al dosages can be explained by the nature of chitosan. Chitosan is made of carbon bindings and may therefore contribute to the amount if carbon in the water. A reduction of 30 % DOC where observed for dosage 3 mg/l. Compared with the relative low color value of 8.4 mg Pt/l at this dosage, a relatively NOM reduction may be assumed.

5.4.3 Zirconium

Tests were also conducted with only zirconium with the raw water from Haugesund. In the same way as with chitosan, the pH was set to be 4.5. Figure 5.16 below present the results.

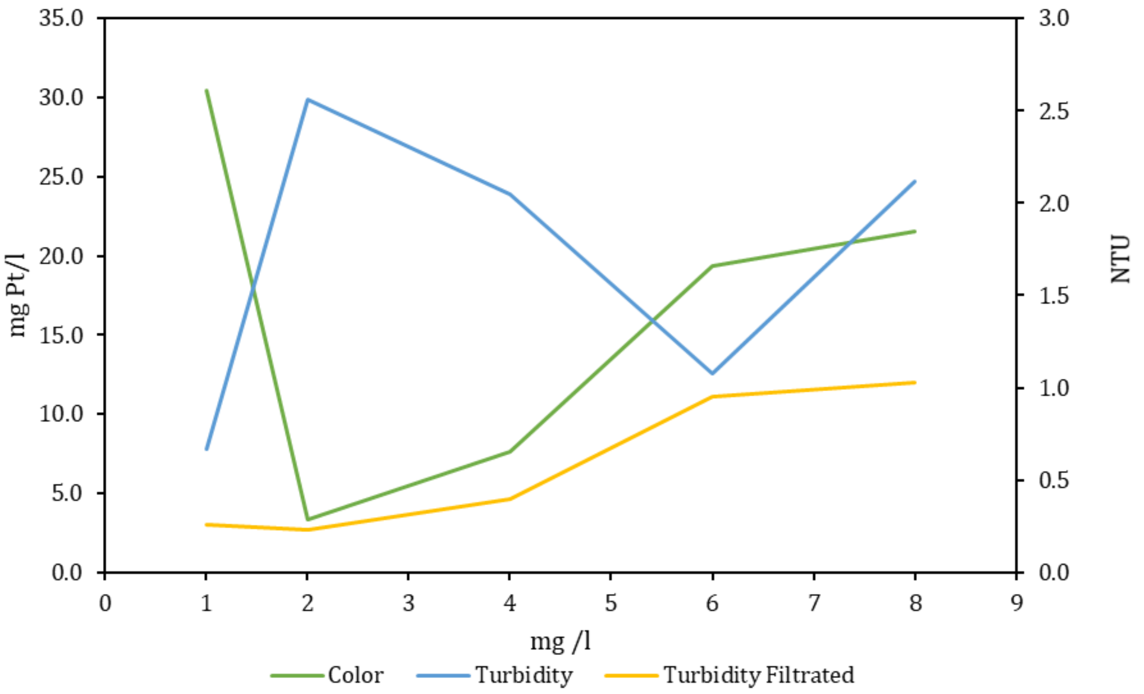


Figure 5.16 The result of zirconium on the raw water from Haugesund. Includes color on the y-axis and turbidity on the secondary axis

Zirconium obtain the best result at dosage 2 mg /l with a color value of 3.7 mg Pt/l after treatment. Filtrated turbidity is also lowest at this dosage while un filtrated turbidity is highest, indicating higher of number flocs formed.

Most of the dosages above 2 mg/l obtain color values below 10 mg Pt/l but the lowest is at 2 mg/l and are continuing to increase and the highest value is at 8 mg/l indicating the surplus of coagulant in the water. Therefore, a dosage higher than 2 mg/l might be unnecessary. Dosage of 1 mg/l have very little impact on the reduction of color.

NOM removal

All dosages of zirconium where analyzed for UV, DOC and TOC. The results are presented in Table 5.8 below.

Table 5.8 The results of zirconium on removal of UV, DOC and TOC for the raw water from Haugesund

Dosage mg/l	pH	UV cm^{-1}	DOC mg C /l	TOC mg C/l
1	4.5	0.16	3.85	3.91
2	4.5	0.03	1.85	1.78
4	4.5	0.03	1.01	3.94
6	4.5	0.09	2.46	3.89
8	4.5	0.10	2.56	3.83

Dosage 2 mg/l obtained TOC value below 3 mg/l. Al other dosages where below 5 mg/l. All dosages obtained DOC values below 3 mg/l. The highest reduction of DOC where obtained at dosage 4 mg/l with a 70 % reduction. In contrast with the water sample of treated from Haugesund, that had a DOC reduction of 68 %, this zirconium dosage performed even better. In addition to the low color value at 7.6 mg Pt/l obtained by this dosage, a relative reduction in NOM may be assumed. Dosage 2 mg/l had the lowest color value at 3.7 mg Pt/l, obtained a DOC reduction of 45 %.

5.4.4 Different dosages

Tests were also conducted with the same coagulation mix of zirconium and chitosan, but with different dosages. This way there are possible to evaluate the existing dosage and eventually adjust is the results indicate so. The pH for these tests were also set at 4.5. The results are presented in Figure 5.17 below.

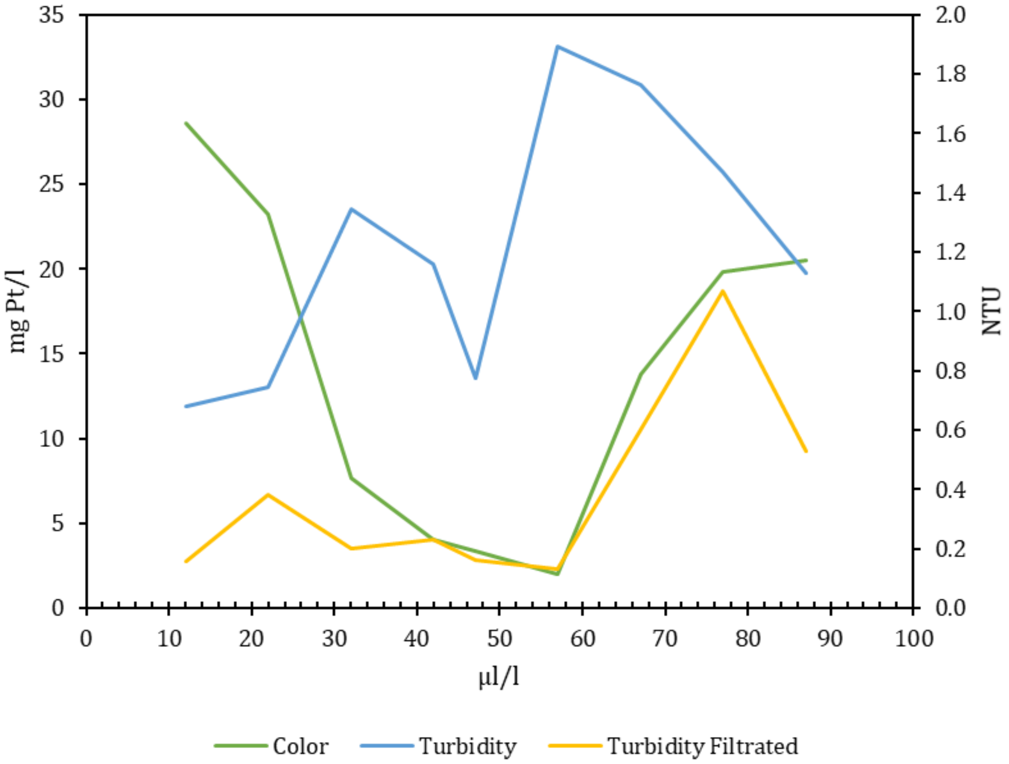


Figure 5.17 The results of different dosages of the existing coagulation combination on the raw water from Haugesund. Includes color on the y-axis and turbidity on the secondary axis

At dosages between 32 – 57 mg/l obtain color values below 10 mg Pt/l. While the original dosage of 47 µl/l obtain color value of 3,4 mg Pt/l, the lowest is obtained at 57 µl/l with 2.0 mg Pt/l. The lowest filtrated turbidity value is also observed at this dosage 0.13 NTU.

As observed earlier with chitosan in the thesis, a parabola effect are observed as with the results, where after a destabilization time, stabilization are observed again due to excess coagulant.

The dosage of today is at 47 µl/l. If the municipality wants to reevaluate the dosage of today, there are results that indicate a possibility for lower dosage use. Although it could be argued that a security range is included, and that the dosage today represents this. With the optimum dosage observed here to be slightly above the dosage of today, the municipality may already have decreased the dosage as far as safety allows.

NOM removal

All dosages of the existing coagulation combination where analyzed for UV, DOC and TOC. The results are presented in Table 5.9 below.

Table 5.9 Results for the existing coagulation combination on removal of UV, DOC and TOC for the raw water from Haugesund

Dosage µl/l	pH	UV cm^{-1}	DOC mg C /l	TOC mg C/l
12	4.5	0.16	3.33	3.88
22	4.5	0.13	2.97	4.01
32	4.5	0.04	1.82	3.29
42	4.5	0.04	1.45	2.78
47	4.5	0.03	2.30	4.08
57	4.5	0.03	1.18	4.44
67	4.5	0.06	1.61	3.80
77	4.5	0.08	1.94	3.79
87	4.5	0.10	2.49	3.69

Only dosage 42 µl/l one dosage obtain a TOC value below 3 mg C/l, while all dosages obtain TOC values below 5 mg C/l. Apart from dosage 12 µl/l, all dosages obtained DOC values below 3 mg/l. Dosage 57 µl/l obtained the highest reduction of DOC, with a 65 % reduction, which were only slightly lower than the water sample of treated water from Haugesund which had a reduction of 68 %. Dosage 42 µl/l had a reduction of DOC of 57 %.

5.4.5 New combination

For the last tests with the water obtained from Haugesund, one run where a new combination of zirconium and chitosan where attempted.

The focus of the new combination was to lower the amount of zirconium and increase chitosan. The combination of today is contain 12 % chitosan per zirconium. Therefore, the intention where to double the amount of chitosan and use 24 % of chitosan

For 10 g of zirconium in 10 ml water, 2.4 g of chitosan in 60 ml of water and 1 ml of acid. The results are presented in Figure 5.18 below.

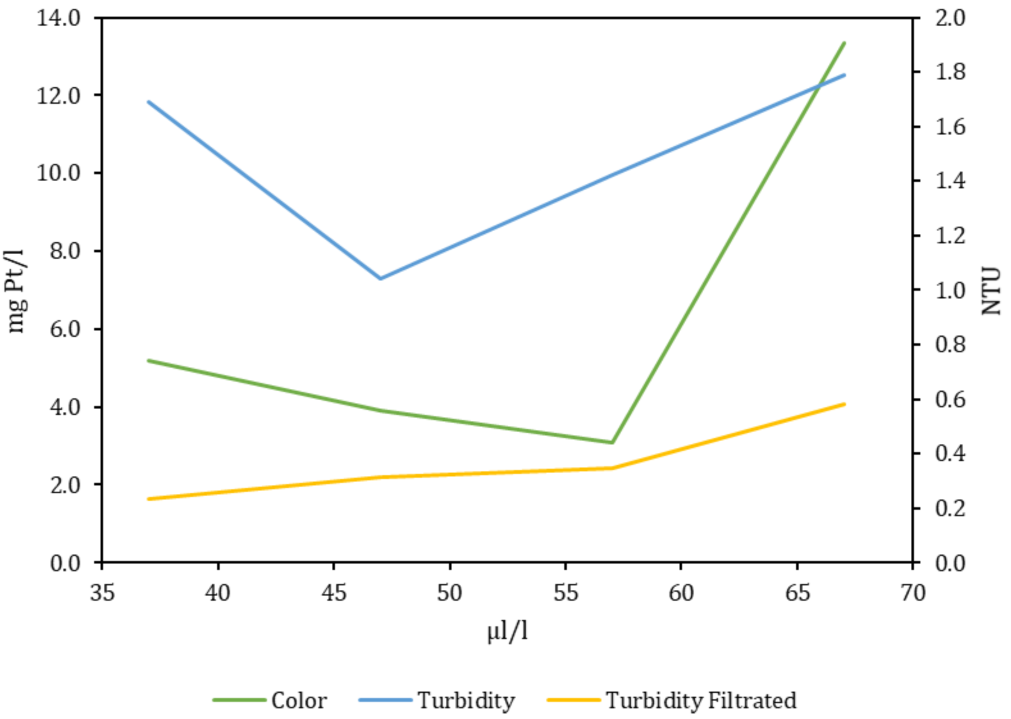


Figure 5.18 The results of the new combination of coagulation on the raw water from Haugesund. Includes color on the y-axis and turbidity on the secondary axis

All dosages obtain result below 15 mg Pt/l and most below 10 mg Pt/l. The lowest color value is observed at 57 µl/l with 3.1 mg Pt/l. Lowest filtrated turbidity value is observed at dosage 37 µl/l.

The amount of zirconium in the new combination of coagulants is notably the same as the original combination. Therefore, these dosages are not significantly less or with better results despite the higher chitosan content. This might be because the excess of coagulant doe not give a significant improvement of reduction.

The aim was to investigate whether a higher part of chitosan could be used in the coagulation mix. Due to the ratio tested, the same amount of zirconium were added to the water, but a higher amount of chitosan was also included. In order to lower coagulation use, a combination with less zirconium could have been tested. Due to limited amount of raw water left, there were not possible to adjust this combination, and therefore not possible to decide wether a higher amount of chitosan is possible.

NOM removal

All dosages of the new combination of coagulant where analyzed for UV, DOC and TOC. The results are presented in Table 5.10 below.

Table 5.10 The results of the new combination of coagulant on removal of UV, DOC and TOC for the raw water from Haugesund

Dosage µl/l	pH	UV cm^{-1}	DOC mg C /l	TOC mg C/l
37	4.5	0.05	2.04	4.04
47	4.5	0.04	1.66	4.10
57	4.5	0.04	1.34	4.16
67	4.5	0.07	1.81	4.31

No dosage obtained TOC under 3 mg C/l, but all obtained values below 5 mg C/l. All dosages obtained DOC values below 3 mg C/l. Dosage 57 µl/l obtained the most reduction of DOC, with a 60 % reduction. Dosage 37 µl/l obtained a reduction of DOC with 40 %.

5.4.6 Overall comparison

Table 5.11 below present the results of the analysis for several parameters. Included here, are the raw water, the treated water sample from Haugesund, apparent best dosage of chitosan and zirconium, and two selected dosages from the existing coagulation combination and the new combination each. That way an easier overall comparison of the different efficiency for the different coagulations are shown.

Table 5.11 Present an overview of the results for several parameters for the water from Haugesund. Some samples are selected

Sample	Color mg Pt/l	SUVA l/mg m	UV cm^{-1}	DOC mg C/l	TOC mg C/l
Raw water	31.4	4.8	0.16	3.4	3.6
Treated water	3.8	2.7	0.03	1.1	1.3
SB 47 µl/l	3.3	1.4	0.03	2.3	4.1
Chitosan 3 mg/l	8.4	3.2	0.07	2.3	4.8
Zirconium 2 mg/l	3.4	1.7	0.03	1.8	1.8
EC 42 µl/l	4.1	2.9	0.04	1.5	2.8
EC 57 µl/l	2.0	2.2	0.03	1.2	4.4
NC 37 µl/l	5.2	2.3	0.05	2.0	4.0
NC 57 µl/l	3.1	2.8	0.04	1.3	4.2

EC = Existing combination
NC = New combination

All results obtain color value below 10 mg Pt/l, and with the exception of two dosages, the rest also obtain result below 5 mg Pt/l. The lowest TOC values are obtained by the water sample from Haugesund and zirconium 2 mg/l. 57 µl/l of the existing combination obtained best result for color and SUVA, but had a relatively high TOC value. 47 µl/l of the same combination, had a color value of 4.1 mg Pt/l, and a TOC value of 2.8 mg C/l. The chitosan dosage had the highest SUVA and TOC after treatment, indicating less NOM reduction than the other coagulants. This would be expecting due to the slightly lower ability to remove NOM. Zirconium had generally low SUVA, DOC and TOC values, and confirming the coagulants effective NOM removal capabilities. The new combination had relatively low color values, but high TOC values.

Note, that the color results below 5 mg Pt/l should be expressed as < 5 instead of whole numbers. In order to obtain an image of efficiency they are included here, but the difference in may not be accurate since the measuring instrument are not able to measure these low values correctly. Therefore, concluding whether one dosage or coagulant is better than the other can not be done correctly and it will mostly be suggestions.

SUVA

SUVA for Chitosan and Zirconium

SUVA were calculated for all dosages of chitosan and zirconium. The results are presented in Figure 5.19 below. SUVA is the ratio of UV_{254} and DOC, and the SUVA value for the raw water in Haugesund were calculated at 4.78 l/mg m. The SUVA value for the treated water in Haugesund were calculated at 2.74 l/mg m.

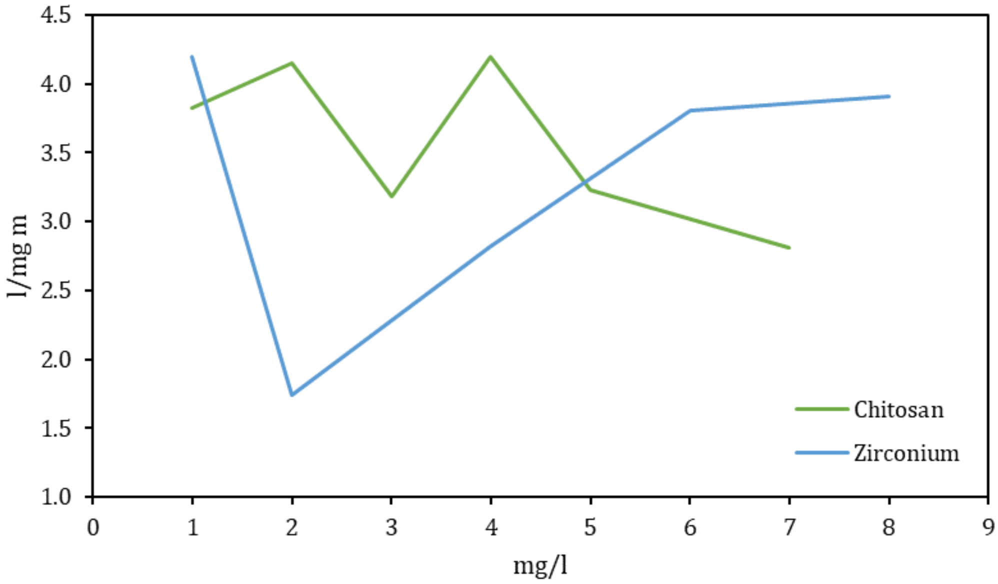


Figure 5.19 The SUVA results for chitosan and zirconium on the raw water from Haugesund

Zirconium obtain the lowest SUVA value 1.74 l/mg m at dosage 2 mg/l, and obtained a SUVA reduction of 64 %. Chitosan obtain overall higher SUVA values than zirconium. This were also observed with the water from Malvik. The lowest SUVA for chitosan is observed at dosage 7 mg/l with a value of 3.18 l/mg and a SUVA reduction of 34 %, almost half of the zirconium one. This would be expected, as chitosan has lower ability to remove NOM.

SUVA existing and new coagulant combination

SUVA were calculated for the test of both the existing and new zirconium / chitosan coagulant. The results are presented in Figure 5.20 below.

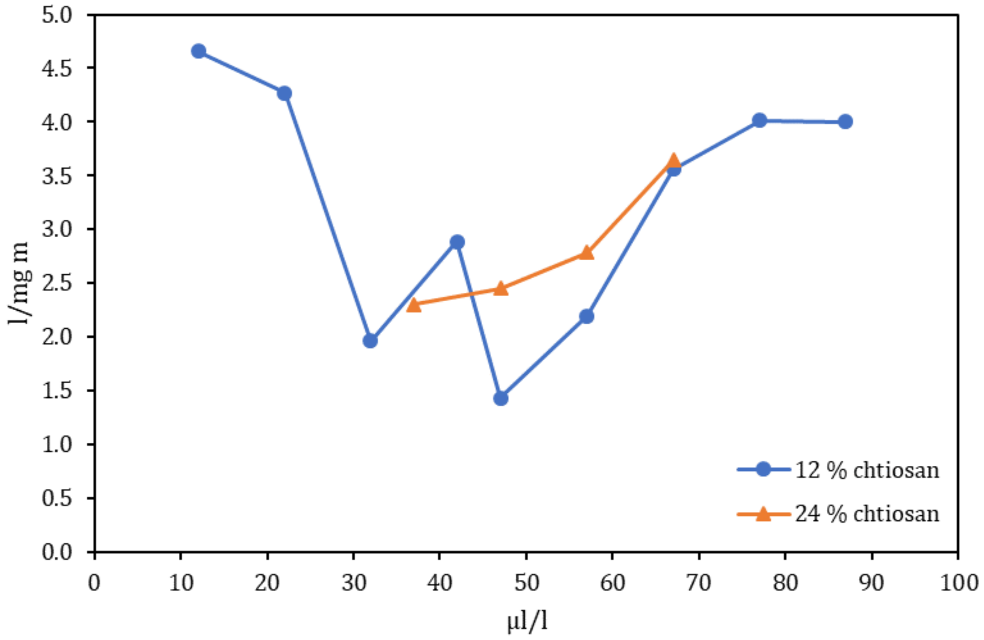


Figure 5.20 The SUVA results for the existing and new coagulation combination on the raw water from Haugesund

The lowest SUVA value of 1.4 l/mg m where obtained by the existing coagulation combination at47 µl/l, which is the dosage the municipality utilize today. While the color value where not lowest at this dosage, it where below 5 mg Pt/l, indicating a relatively high NOM removal. Only one dosage of the new coagulant combination where lower than the existing combination, with a SUVA value 0f 2.3 l/mg m. This where also lowest of the dosages for the new combination. Combined with the low color value of 5.2 mg Pt/l, a relative NOM reduction may be assumed.

Fractionation results

Some of the tests of the water from Haugesund were tested using a fractionation method, LC-OCD. One chitosan dosage was tested, 3 mg/l and four dosages of the chitosan zirconium mix, 37 µl/l, 42 µl/l, 57 µl/l and 67 µl/l. The results are presented in Figure 5.21 below. The additional results are presented in Appendix 8.

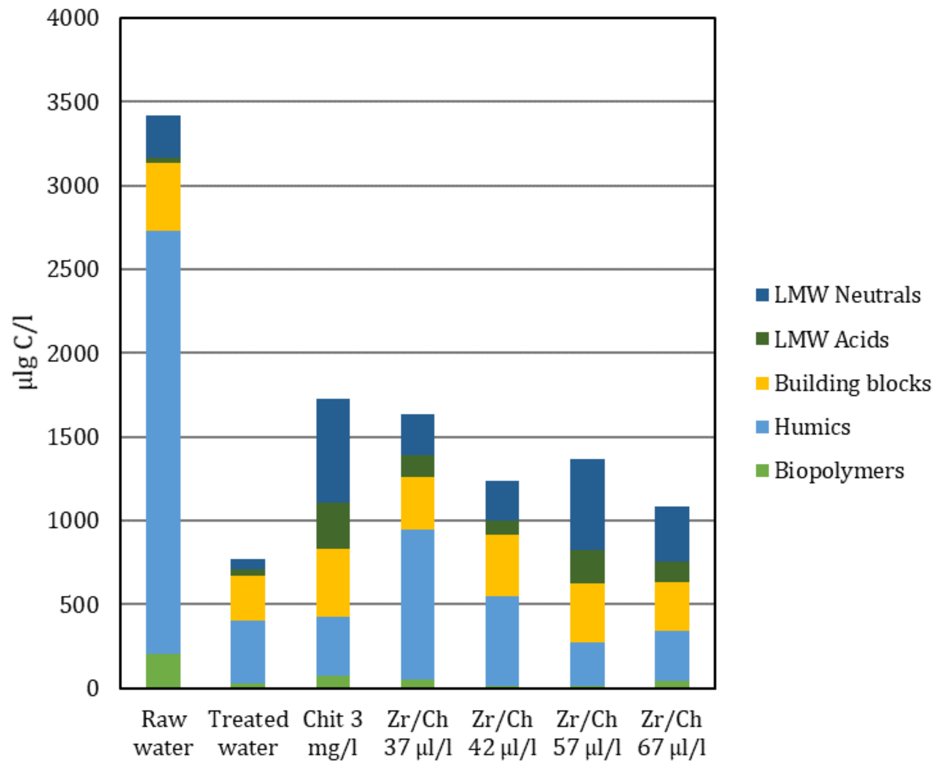
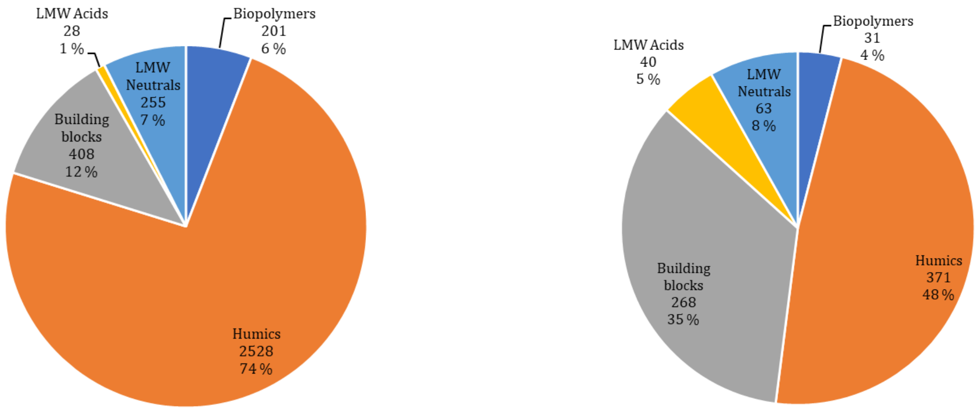


Figure 5.21 The fractionation results for the selected samples for different coagulations and dosages on the raw water from Haugesund, the raw water and the water sample of treated water from Haugesund.

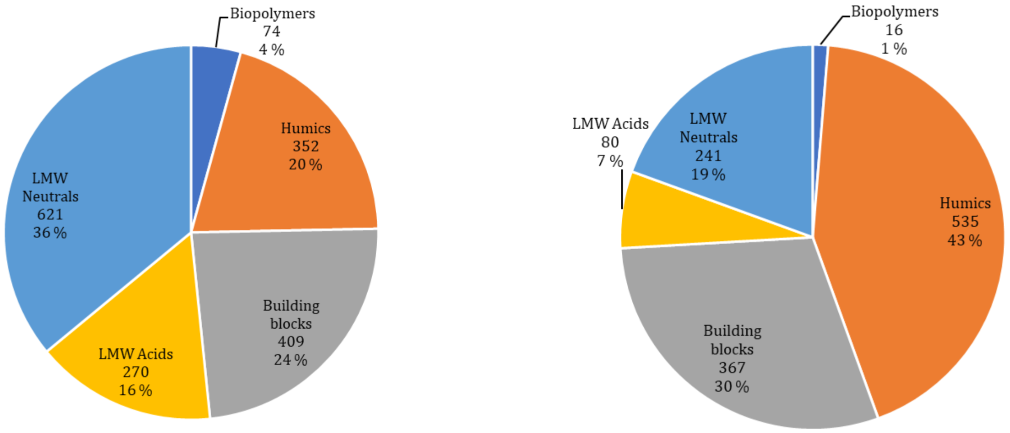
All coagulant and dosages tested achieve relatively high reduction of humics and biopolymers. The water sample of treated water from Haugesund achieved overall most reduction of total CDOC, compared to the other dosages tested. Dosage 57 µl/l achieve the most reduction of the larger molecular size fractions, biopolymers and humics. This dosage also observed an increase of LWM neutrals after treatment compared to the raw water. It is possible that some of the larger sized molecules have been dissolved to smaller particles instead of being removed and register as lower molecular size instead. The chitosan sample obtained more reduction of humics than the treated water from Haugesund, while dosage 57 and 67 achieved more reduction than the other two.

Figure 5.22 below show the difference of the fractions for the raw water, treated water, chitosan dosage 3 mg/l and zirconium + chitosan dosage 42 µl/l.



(a) Raw water

(b) Treated water



(c) Chitosan 3 mg/l

(d) Zirconium + Chitosan EC 42 μl/l

Figure 5.22 The percentage for the fractionation results for a selected four samples

All three samples show a significant reduction of humics and biopolymers. It is clear that the only sample, showing significant reduction of the lower particle sizes are the water sample of treater water from Haugesund.

The chitosan dosage had a relative high increase of low molecular size acid and neutrals compared to the raw water. Vogelsang et al. (2004) reported that when chitosan dosage increased, so did the low molecular sized fractions. The same is sown by the results obtained here.

Similar for all samples, are a significant reduction of the larger molecule sized fractions, biopolymers and humics. No samples of the water run with obtained reduction of the lower molecular sized fractions. One reason for this might be insufficient separation, where only the larger molecular sizes where removed, while the treated water from Haugesund achieved this. In addition, the larger particles could have been dissolved and registered as lower molecular size instead of being removed. Another reason could be failure in the testing. The tests might not have been correctly done. If time had permitted it, these test could have been repeated in order to investigate the reason or determine if it is correctly measured.

6 Conclusion

The research question set in chapter 1.3 where following:

How does alternative coagulants perform compared to traditional coagulants, especially in terms of removing NOM?

The sub questions are answered separately below. At the end, the main conclusion for the research question are summarized

How does each of the coagulants perform in treatment efficiency compared to each other?

The result in this thesis show that zirconium and PAX-18 performed slightly better than chitosan in terms of color and turbidity, but chitosan performed well within limit.

- Chitosan, zirconium and PAX-18 were able to reduce color to values below 10 mg Pt/l.
- Higher dosage of chitosan where needed to achieve high reduction, but the results are well performing and able to "compete" with the two other coagulants in terms of achievement. A reduction of 90.3 % where achieved by chitosan for one dosage.
- PAX-18 obtained the minimum optimal dosage at lowest dosage, 3 mg/l. This were corresponding with previous studies in the field.
- Zirconium achieved the most reduction in color of 98,4 % for dosage 10 mg/l at pH 5. Minimum optimal dosage where only slightly higher than PAX-18, at 4 mg/l.
- EPS had little impact on neither color, turbidity, DOC, TOC or UV. The coagulant is more suited to water of high particle content. Water types that could be applied are waste water or water sources with high particle level.

How well do the coagulants remove NOM?

All coagulants achieved NOM removal for optimum dosage. Chitosan obtain slightly less reduction than the other two, but still within reasonable limit.

- After repeating some dosages and pH for the three coagulants, chitosan showed the most spread in results for all of the three dosages repeated. Only one dosage of PAX-18 where repeated, but the results had lower spread of data. Three dosages of zirconium where repeated, and showed lower spread than chitosan
- Chitosan did not obtain TOC below 3 mg/l, as were the limit, but did achieve a reduction of TOC of 36,4 %. A DOC reduction of 55 % were also achieved. Chitosan had overall higher SUVA values than the other two coagulants. NOM removal are suggested due to relatively low SUVA value and color value at dosage 10 mg/l.
- Zirconium obtained TOC values below 3 mg/l for two dosages and had a maximum reduction of DOC of 83 %. Zirconium achieved the lowest SUVA value for all three coagulants. Coupled with very low color value indicated high NON reduction.
- PAX-18 obtained TOC values below 3 mg/l and a TOC reduction of 69 % which were above recommended amount. In addition, PAX-18 had a DOC reduction of 78 %. A low SUVA value was achieved and coupled with low color value relative high NOM removal were achieved.
- Fractionation results show that zirconium achieved the most reduction of larger molecular sized fractions. Chitosan where able to reduce the larger molecular sized

fractions for several dosages, while the smaller sized increased. PAX-18 had a relative high reduction of biopolymers and humics, while the smaller particle sized increased.

In what way does chitosan perform with different color of the raw water?

Chitosan have shown greater application for water of lower color but were able to perform with higher dosage on the highest color value.

- A correlation of the raw water color and the minimum optimal dosage were obtained. For decreasing raw water color, the minimum optimal dosages decreases.
- Shown that chitosan operates more appropriately for lower raw water colors, but did obtain sufficient removal for the highest value of raw water
- Turbidity reduction were sufficient for most dosages of chitosan for the different water samples.

With an industry perspective, how will the coagulants perform on their own, and combined together?

Zirconium and the combined coagulation showed better removal capabilities than chitosan alone, but chitosan alone obtained result confirming its ability to treat the water at Haugesund.

- Results showed that the pH utilized today are optimum for the combined zirconium and chitosan coagulant.
- A color reduction of 81.5 % where achieved for chitosan dosage 4 mg/l. Chitosan are able to efficiently treat the raw water in Haugesund. Relatively high TOC values were reported for all chitosan dosages but a 30 % reduction of DOC where obtained.
- Zirconium obtained a high reduction of color, and the minimum optimum dosage achieved the most reduction. TOC value below 3 mg/l were achieved, and a reduction of DOC of 70 %.
- A slightly higher dosage of 57 µl/l than the dosage of today, 47 µl/l, achieved most reduction of color, but several lower dosages where able to obtain color values below 5 mg Pt/l.
- Fractionation results showed that all of the dosages and coagulants achieved a reduction of the larger molecular sized fractions, and the treated water sample from Haugesund achieved most reduction of the smaller particle sized fractions.

Overall conclusion

Both chitosan and zirconium performed adequate comparison with PAX-18. All coagulants showed ability to remove NOM from water, where chitosan removed somewhat less than the two others, as expected. Even though chitosan performed lower, the results were within limit.

7 Recommendations for future assessment

There are several recommendations for future work and research apparent from the work done here. Some of the recommendations based on the tests on the water from Malvik are:

- Investigate the dosage and pH values that appeared optimum here with a separating step after in order to obtain a more comprehensive study.
- Execute more test for NOM removal with different pH values. pH was not investigated within the parameters DOC, TOC and UV.
- Investigate these results of dosage and pH with direct filtration. The fractionation result of the treated water from Haugesund indicated better removal of humics, than the samples with only coagulation.
- Separating with membranes. The theoretical studies showed less sludge production with chitosan. This is a trait that could prove beneficial for membrane filtration

There are some recommendations apparent based on the tests on the water from Haugesund:

- Based on the results obtained for chitosan with the water from Haugesund, there are possibilities of increasing amount of chitosan in their existing dosage. Further investigation and extensive tests of chitosan could be done
- Trying another combination where the amount of zirconium is reduced, and chitosan increased.

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Appendices

Appendix 1

Data Chitosan tests

Table A1.1: Color removal chitosan; mg Pt/l

Dosage mg/l	pH 4.5	pH 5	pH 5.5	pH 6	pH 6.5
3	22.4	24.1	26.8	26.5	54.5
5	15.6	16.6	18.5	17.6	17.9
10	7.1	8.1	5.8	9.9	8.6
12	21.0	5.5	6.0	18.5	8.3

Table A1.2: Turbidity removal chitosan; NTU

Dosage mg/l	pH 4.5	pH 5	pH 5.5	pH 6	pH 6.5
3	2.163	0.466	1.313	1.317	1.37
5	3.293	0.441	0.394	9.553	0.447
10	2.377	1.27	2.71	0.628	0.427
12	1.813	2.453	2.64	3.24	0.407

Table A1.3: Results chitosan on SUVA, UV, DOC and TOC. pH for the test were 5.5.

Dosage mg/l	SUVA l/mg m	UV cm^{-1}	DOC mg C/l	TOC mg C/l
5	3.2	0.14	4.35	4.363
7	2.7	0.08	3.29	-
10	3.1	0.10	2.92	4.554

Appendix 2

Data Zirconium tests

Table A2.1: Color removal zirconium; mg Pt/l

Dosage mg/l	pH 4	pH 4.5	pH 5	pH 5.5	pH 6	pH 6.6
2	47.38	53.53	54.352	54.87	57.01	59.57
4	1.87	8.55	4.856	11.73	56.80	56.93
6	3.66	2.73	1.218	20.70	42.32	56.93
10	47.13	1.02	0.885	1.55	24.36	8.72

Table A2.2: Turbidity removal zirconium; NTU

Dosage mg/l	pH 4	pH 4.5	pH 5	pH 5.5	pH 6	pH 6.6
2	1.03	1.00	0.98	0.77	0.62	0.82
4	1.72	1.06	0.60	2.54	1.39	1.96
6	2.80	0.36	0.31	3.63	3.21	1.96
10	1.20	0.53	0.55	0.23	4.78	1.62

Table A2.3: Results for zirconium for SUVA, DOC, UV and TOC. pH for the tests were 5.

Dosage mg/l	SUVA l/mg m	UV cm^{-1}	DOC mg C/l	TOC mg C/l
2	26.20	0.28	1.08	6.67
4	1.96	0.04	2.04	2.57
6	1.40	0.02	1.47	1.75
10	1.94	0.02	1.08	6.32

Appendix 3

Data PAX-18 tests

A3.1: Results for PAX -18 on ccolor , turbidity and filtrated turbidity

Dosage mg/l	Color mg Pt/l	Turbidity Filtrated NTU	Turbidity NTU
1	50	0.8	1.4
3	3	0.2	0.6
5	2	0.1	3.1
7	2	0.1	3.2

Table A3.2: Results for PAX -18 on SUVA, UV, DOC and TOC. pH 6

Dosage mg/l	SUVA l/mg m	UV cm^{-1}	DOC mg C/l	TOC mg C/l
1	4.27	0.25	5.81	6.15
3	1.82	0.04	1.97	2.11
5	1.96	0.03	1.40	6.36

Appendix 4

Table A4.1: Fractionation data from Malvik

	DOC															
		HOC	CDOC													
				Bio-polymers					Humic substances (HS)					Buildin g blocks	LMW Acids	LMW Neutrals incl. SOM
	Dissolved	Hydrophobic	Hydrophilic		DON (Norg.)	N/C	% proteins in bipol	cTEP		DON (Norg.)	N/C	Aromaticity SUVA-HS	Mol.-weight (Mn)			
	ppb-C % DOC	ppb-C % DOC	ppb-C % DOC	ppb-C % DOC	ppb-N	µg/µg	%		ppb-C % DOC	ppb-N	µg/µg	L/(mg*m)	g/mol	ppb-C % DOC	ppb-C % DOC	ppb-C % DOC
Raw water	6130	< 1	6130	443	84	0.19	57		4820	196	0.04	4.77	707	622	42	202
	100%	0 %	100 %	7 %					79 %					10 %	1 %	3 %
Ch 5 mg/l	4481	< 1	4481	53	1	0.02	7		2856	58	0.02	3.87	591	823	226	523
	100%	0 %	100 %	1 %					64 %					18 %	5 %	12 %
Ch 7 mg/l	3388	< 1	3388	36	< 1	-	-		2218	46	0.02	3.60	557	660	94	381
	100%	0 %	100 %	1 %					65 %					19 %	3 %	11 %
Ch 10 mg/l	2973	< 1	2973	23	< 1	-	-		1803	37	0.02	3.06	514	636	127	384
	100%	0 %	100 %	1 %					61 %					21 %	4 %	13 %
Zr 2 mg/l	7084	< 1	7084	918	149	0.16	49		4074	106	0.03	4.67	574	673	559	860
	100%	0 %	100 %	13 %					58 %					10 %	8 %	12 %
Zr 4 mg/l	2948	< 1	2948	108	14	0.13	40		765	13	0.02	2.68	462	731	622	722
	100%	0 %	100 %	4 %					26 %					25 %	21 %	24 %
Zr 6 mg/l	2079	< 1	2079	21	7	0.35	100		304	6	0.02	1.98	430	613	547	595
	100%	0 %	100 %	1 %					15 %					29 %	26 %	29 %
Zr 10 mg/L	2076	< 1	2076	21	6	0.26	79		515	4	< 0,01	0.40	401	563	291	685
	100%	0 %	100 %	1 %					25 %					27 %	14 %	33 %
PAX 3mg /l	2436	< 1	2436	43	13	0.31	93		770	12	0.02	2.06	436	733	375	516
	100%	0 %	100 %	2 %					32 %					30 %	15 %	21 %
PAX 5 mg/l	2102	< 1	2102	11	< 1	-	-		351	< 1	-	1.75	420	737	446	557
	100%	0 %	100 %	1 %					17 %					35 %	21 %	26 %
PAX 7 mg/l	7085	< 1	7085	205	22	0.11	32		4640	98	0.02	4.76	642	789	609	841
	100%	0 %	100 %	3 %					65 %					11 %	9 %	12 %

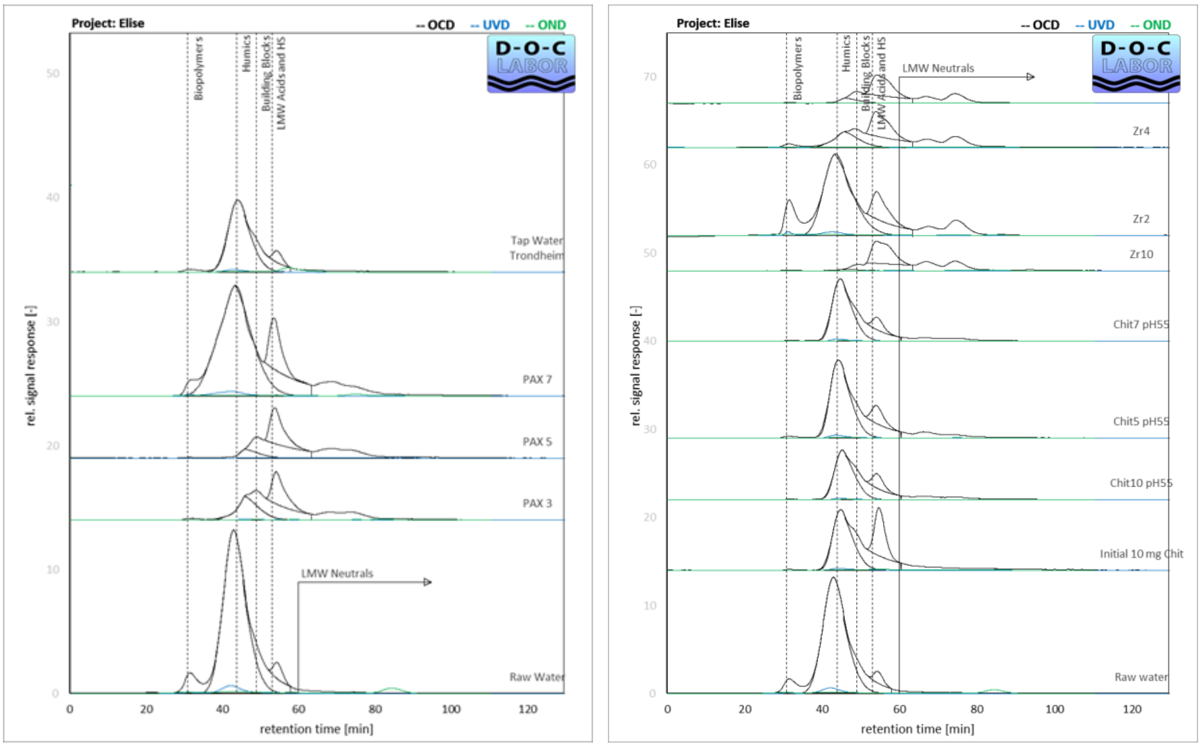

Figure A4.1: LC-OCD chromatograms from the fractionation from Malvik

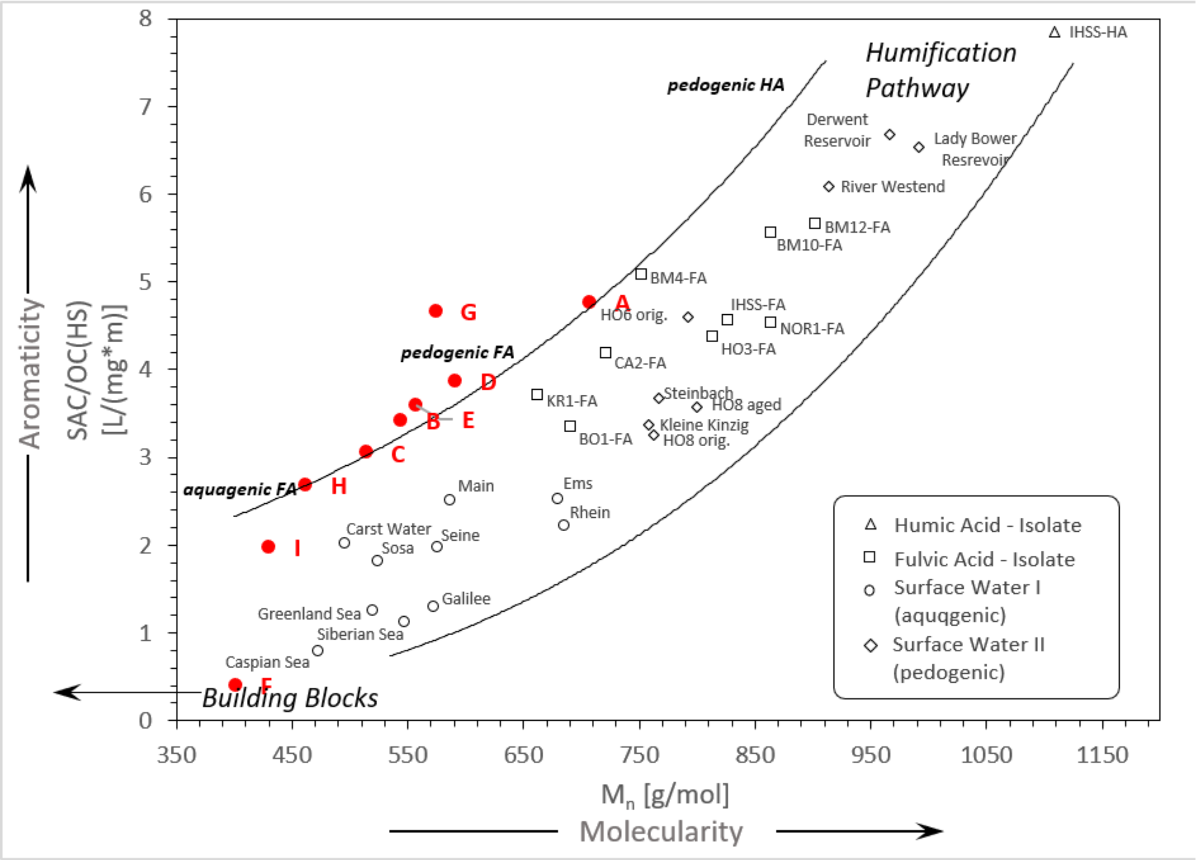

Figure A4.2: Humics diagram for the water from Malvik

Appendix 5

Chitosan for different raw water color Malvik

Table A5.1: Results for chitosan with raw water 27 mg Pt/l. pH 5.5

Dosage mg/l	Color mg Pt/l	Turbidity NTU
0	27.99	-
1	12.70	0.12
3	7.31	0.07
3.5	6.06	0.09
4	5.26	0.11
4.5	4.67	0.10
5	4.24	0.15
6	14.23	0.27
7	20.10	0.34

Table A5.2: Results for chitosan with raw water 34 mg Pt/l. pH 5.5

Dosage mg/l	Color mg Pt/l	Turbidity NTU
0	34.62	-
3	12.53	0.11
4	10.82	0.13
5	7.03	0.10
6	6.54	0.27
7	5.04	0.10
10	28.88	1.18

Table A5.3: Results for chitosan with raw water 56 mg Pt/l. pH 5.5

Dosage mg/l	Color mg Pt/l	Turbidity NTU
0	56.42	-
3	24.09	-
5	16.63	0.13
7	11.60	0.13
10	8.09	0.12
12	5.47	-

Appendix 6

Data for EPS results

Table A6.1: The results for EPS on color, turbidity and DOC

Dosage mg /l	Color mg C /l	Reduction in color	Turbidity NTU	Reduction in Turbidity	DOC mg C/l	Reduction in DOC
1	52.0	7 %	0.20	-9 %	6.01	7 %
4	52.4	6 %	0.14	25 %	6.32	2 %
8	52.1	7 %	0.20	-9 %	6.27	3 %
12	53.8	4 %	0.17	8 %	6.58	-2 %
16	54.5	3 %	0.17	7 %	6.12	5 %
20	54.4	3 %	0.21	-13 %	6.41	1 %
24	54.5	3 %	0.14	24 %	6.07	6 %
28	54.1	3 %	0.23	-24 %	6.20	4 %

Appendix 7

Data Haugesund

Table A7.1: Results for chitosan with the raw water from Haugesund. pH 4.5

Dosage mg/l	Color mg Pt/l	SUVA l/mg m	UV cm^{-1}	DOC mg C/l	TOC mg C/l	Turbidity NTU	Turbidity NTU F
1	16.6	3.8	0.12	3.02	4.09	1.1	0.2
2	11.2	4.1	0.09	3.55	4.59	1.3	0.1
3	8.4	3.2	0.07	2.33	4.80	1.3	0.2
4	5.80	4.2	0.10	2.42	4.89	1.01	0.19
5	26.1	3.2	0.13	4.09	5.51	0.8	0.4
7	28.7	2.8	0.15	5.23	5.88	0.9	0.4

Table A7.2: Results for zirconium with the raw water from Haugesund. pH 4.5

Dosage mg/l	Color mg Pt/l	SUVA l/mg m	UV cm^{-1}	DOC mg C/l	TOC mg C/l	Turbidity NTU	Turbidity NTU F
1	30.41	4.19	0.16	3.85	3.91	0.67	0.26
2	3.37	1.74	0.03	1.85	1.78	2.56	0.23
4	7.59	2.82	0.03	1.01	3.94	2.05	0.40
6	19.37	3.80	0.09	2.46	3.89	1.08	0.95
8	21.52	3.91	0.10	2.56	3.83	2.12	1.03

Table A7.3: Results for different dosages of the existing combination with the raw water from Haugesund. pH 4.5

Dosage mg/l	Color mg Pt/l	SUVA l/mg m	UV cm^{-1}	DOC mg C/l	TOC mg C/l	Turbidity NTU	Turbidity NTU F
12	28.58	4.7	0.16	3.33	3.88	0.7	0.2
22	23.21	4.3	0.13	2.97	4.01	0.7	0.4
32	7.64	2.0	0.04	1.82	3.29	1.3	0.2
42	4.07	2.9	0.04	1.45	2.78	1.2	0.2
47	3.40	1.4	0.03	2.30	4.08	0.8	0.2
57	2.03	2.2	0.03	1.18	4.44	1.9	0.1
67	13.82	3.6	0.06	1.61	3.80	1.8	0.6
77	19.85	4.0	0.08	1.94	3.79	1.5	1.1
87	20.49	4.0	0.10	2.49	3.69	1.1	0.5

Table A7.4: Results for the new coagulation combination with the raw water from Haugesund. pH 4.5

Dosage mg/l	Color mg Pt/l	SUVA l/mg m	UV cm^{-1}	DOC mg C/l	TOC mg C/l	Turbidity NTU	Turbidity NTU F
37	5.17	2.30	0.05	2.04	4.04	1.69	0.23
47	3.90	2.45	0.04	1.66	4.10	1.04	0.32
57	3.10	2.79	0.04	1.34	4.16	1.42	0.34
67	13.33	3.64	0.07	1.81	4.31	1.79	0.58

Appendix 8

Table A8.1: Fractionation results from Haugesund

	DOC															
		HOC	CDOC													
				Bio-polymers					Humic substances (HS)					Buildin g blocks	LMW Acids	LMW Neutrals incl. SOM
					DON (Norg.)	N/C	% proteins in biopol	cTEP		DON (Norg.)	N/C	Aromaticity SUVA-HS	Mol.-weight (Mn)			
	Dissolved	Hydrophobic	Hydrophilic													
	ppb-C % DOC	ppb-C % DOC	ppb-C % DOC	ppb-C % DOC	ppb-N	µg/µg	%		ppb-C % DOC	ppb-N	µg/µg	L/(mg*m)	g/mol	ppb-C % DOC	ppb-C % DOC	ppb-C % DOC
Raw water	3420	< 1	3420	201	16	0.08	23		2528	73	0.03	5.08	629	408	28	255
	100%	0 %	100 %	6 %					74 %					12 %	1 %	7 %
Trea. water	770	< 1	770	31.5	< 1	-	-		371	8	0.02	3.57	434	264	40	63
	100%	0 %	100 %	0					48 %					34 %	5 %	8 %
Ch 3 mg/l	1727	< 1	1727	74	< 1	-	-		352	< 1	-	3.44	448	409	270	621
	100%	0 %	100 %	4 %					20 %					24 %	16 %	36 %
Zr/Ch 37µl/l	1638	< 1	1638	50	< 1	-	-		899	< 1	-	4.23	461	314	129	246
	100%	0 %	100 %	3 %					55 %					19 %	8 %	15 %
Zr/Ch 42µl/l	1239	< 1	1239	16	< 1	-	-		535	< 1	-	3.01	441	367	80	241
	100%	0 %	100 %	1 %					43 %					30 %	6 %	19 %
Zr/Ch 57µl/l	1370	< 1	1370	15	< 1	-	-		261	< 1	-	2.62	432	351	197	547
	100%	0 %	100 %	1 %					19 %					26 %	14 %	40 %
Zr/Ch 67µl/l	1084	< 1	1084	42	< 1	-	-		297	< 1	-	4.54	473	297	119	329
	100%	0 %	100 %	4 %					27 %					27 %	11 %	30 %
Ch 3mg/l*	2974	< 1	2974	51	< 1	-	-		1937	56	0.03	4.64	594	481	154	351
	100%	0 %	100 %	2 %					65 %					16 %	5 %	12 %
Ch 3mg/l**	2529	< 1	2529	20	< 1	-	-		1256	27	0.02	4.44	535	508	294	451
	100%	0 %	100 %	1 %					50 %					20 %	12 %	18 %

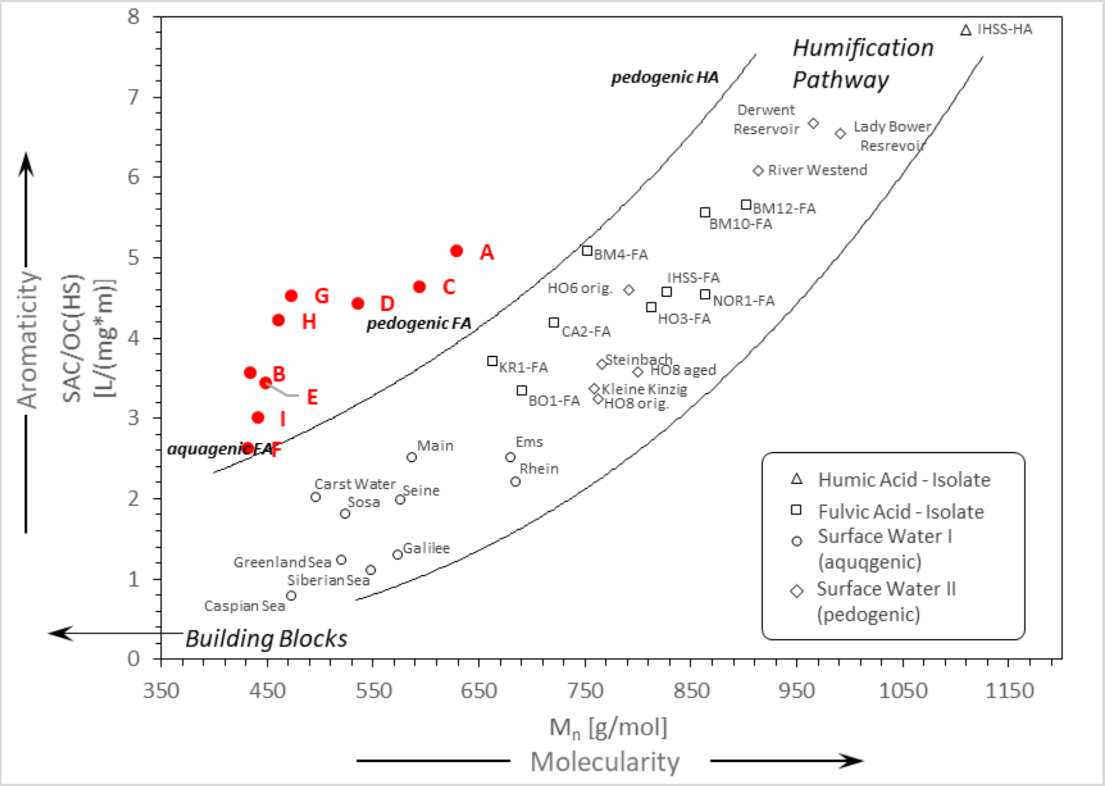

Figure A8.1: Humics diagram for the water from

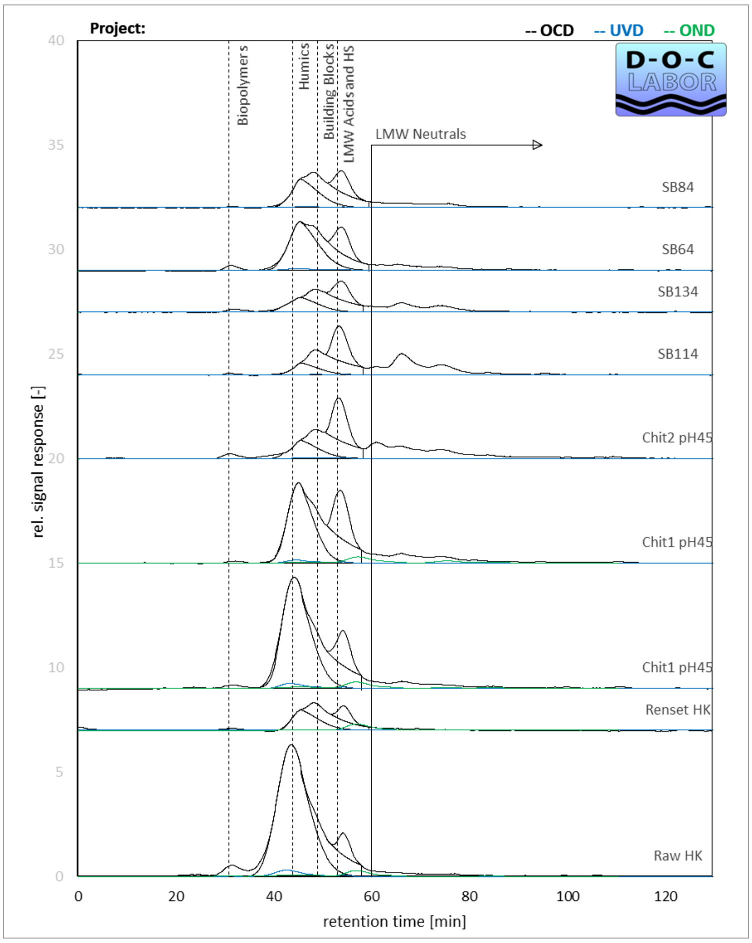

Figure A8.2: LC-OCD chromatograms from the fractionation from Haugesund

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