# Treatment of cooling tower blowdown water. The effect of biodispersant on the ultrafiltration membrane



Raluca Olariu

August, 2015



**Challenge the future** 

## Treatment of cooling tower blowdown water – The effect of biodispersant on the ultrafiltration membrane

Raluca Olariu

Sanitary Engineering Section, Department of Water Management Faculty of Civil Engineering and Geosciences Delft University of Technology, Delft

#### for the degree of: *Master of Science in Civil Engineering*

Date of defense: 27 August 2015

Committee: Prof.dr.ir. L. C. Rietveld

Dr.ir. S.G.J. Heijman

Dr. S. Pande

Delft University of Technology Sanitary Engineering Section

Delft University of Technology Sanitary Engineering Section

Delft University of Technology Hydrology Section

#### I. Summary

Taking into account the growing population, water scarcity is a relevant problem which needs to be addressed. Wastewater needs to be assured by quality, ecosystems protected and the wastewater reuse in industry should be a more common approach that would also assure the reduction of fresh water intake. Dow Chemicals decided to reduce the fresh water consumption by reusing the wastewater streams. Evides built a pilot plant in Terneuzen that will treat 3 water sources: rainwater, wastewater treatment plant effluent and cooling tower blowdown (CTBD) water. The biggest stream and the most difficult to treat is the CTBD water due to its high salinity and composition resulting after the evaporation process.

Since the performance of the pilot was not very efficient and the ultrafiltration (UF) membrane suffered from rapid fouling during operation with CTBD, a solution to reduce the fouling was researched. First, the coagulation/flocculation step was evaluated. It is known that iron chloride used as coagulant will decrease the pH of solution, which will result in smaller and more difficult to settle flocs. For the improvement of the coagulation step a base was added together with the coagulant in order to keep the pH in the sweep coagulation zone.

Since the focus of the research was on improving the UF operation, more attention was put into what could be the cause of it. It is known that in the cooling tower many chemicals are added to prevent corrosion, scaling or microbial growth. Of all chemicals, the biodispersant was the unknown solution which prevents microorganisms attaching to surfaces. The assumption made was that the biodispersant will form a layer on the membrane's surfaces which causes the pressure increase after continuous operation.

The nature of the biodispersant was investigated through surface tension and electrical-conductivity measurements and it was concluded that the biodispersant is a non-ionic surfactant. The critical micelle concentration was established to be 0.03 mg/l.

CMC is the concentration above which the biodispersant is not only present as molecules, but it start forming micelles. The higher the concentration, the higher the number of micelles will be. When the concentration is equal with the CMC the solution is saturated with surfactant molecules which form a layer on the surfaces.



Figure 0-1 Biodispersant molecules behaviou

Furthermore, the operation of the UF was observed in experiments with different biodispersant concentrations. Solutions of demiwater and Schie canal water with and without biodispersant were filtrated in order to observe the fouling behavior. It was indeed seen that the biodispersant is causing the fouling of the UF membrane and the backwashes did not help restore the initial membrane resistance. Experiments with powdered activated carbon (PAC) and clay were also performed to see if the adsorption of biodispersant was possible, but the results were not promising. For clay the adsorption area was too small and not much was adsorbed. For PAC, besides the biodispersant there are present other organics that will compete for adsorption.

Because the surfactant concentration in the blowdown water was much higher than the CMC concentration (assumed 4 mg/l) experiment with solutions with surfactant concentration closer to the CMC were performed. It was observed that at a concentration of 0.1 mg/l biodispersant the fouling was much lower than the fouling increase recorded with solutions at 4 mg/l biodispersant and the backwashes were more efficient.

At a biodispersant concentration of 0.1 mg/l the system is supposed to still be saturated. Therefore, it is assumed that the microbial growth should not be increased and the system's behavior will not be affected by the decrease of biodispersant dosage. This statement should be further researched, but it a decrease in biodispersant dosage would not only result in a stable efficient operation of the pilot, but also lower operational cost, since less surfactant would be added in the cooling tower.

### II. Preface

After about one year of extensive research and experimental work, the thesis necessary for completing the Master Track Water Management, within the department of Sanitary Engineering of the Faculty of Civil Engineering and Geosciences at Delft University of Technology was completed. At the beginning of the research there were many things unknown, but by the end I got a better understanding of the issues I have started with and managed to come up with a solution. It was not an easy process, since I began with one theory and in the end got a better insight into surfactant action, determination and removal. Many experiments were performed, cooperated with different partners involved in the project and the individual research resulted in this report and valuable knowledge gained for the future.

The result of all this work could not have been completed without the help of many people. Hence, I would like to avail myself of the opportunity to thank some of them;

First of all I would like to thank all the members of my committee; Luuk Rietveld thank you for all the support and all the guidance you showed me throughout my study. You gave me the opportunity to go to Mozambique for one of your projects. Thank you for proposing to work on the E4Water project! I have gained so much experience and knowledge that will be of great value in the future.

Bas Heijman, thank you for always being available for discussions, for the supervision and support. I would like to also thank all the E4Water partners. Wilbert van den Broek and Niels Groot I am very thankful for sharing your ideas and accepting me on board of the E4Water team.

David De Ridder, thank you for your assistance and for being available for discussions and for sharing your ideas. Ran Shang, thank you for your patience and for making time and showing how to operate my experimental installation. I would like to acknowledge also the staff from the laboratory at TU Delft, Armand Middeldorp, Tonny Schuit and Patrick Andeweg. Without your assistance it would have been impossible to finish the experiments. Jorg Trampe, thank you for showing me around and giving me the first insight of the E4Water pilot, in Terneuzen.

Moreover I would like to show me appreciation to Mariana, Ioana and Adrian Popescu for their support and help throughout my study. Thank you for accepting me in your family and for pushing me.

Big thanks go also to all of my friends who listened, backed me up and encouraged me: Marij, Lefki, Sadie, Marisa. We started together and managed to survive the entire process. The coffees, teas, drinks, parties and dinners were a great way to disconnect. I would like to thank the crew in room 4.54 for their support and I would like to apologies if I was at times too loud or annoying. I'll make it up with cake.

I am grateful also to my professors in Romania. Without them I would have never been able to come here in the Netherlands for my study. None of this would have been possible without you.

Finally, I would like to thank my family for believing in me and for their unconditional love. You always backed me up and tried to cheer me up when I was about to give up. Thank you for all you advices and sacrifices you made for me so that I am able to finish my study. I will be forever grateful.

I apologies if I forgot to thank anybody. There were so many kind and good people passing my path in the last years. I would like to thank all of you for this amazing experience!

Raluca Olariu

Delft, August 2015

## III. Table of contents

1. 1	Intro	pduction1
1.1	L.	E4Water1
1.2	2.	Research objective
2.	Theo	pretical background
2.1	L.	Cooling towers: Classification, operation
2.2	2.	Make-up water
2.3	3.	Blowdown7
2.4	1.	Water quality
2.5	5.	Treatment of the blowdown water
2.6	5.	Evides pilot12
3. I	Biod	ispersant
3.1	L.	Theoretical background regarding biodispersant
3.2	2.	Surface tension measurements
3.3	3.	TOC of the biodispersant in demiwater solutions26
3.4	<b>1</b> .	Conclusion
4. I	Mate	erials & methods
5. (	Coag	gulation/flocculation
5.1	L.	Theoretical background
5.2	2.	Experimental procedure
5.3	3.	Experimental results43
5.4	<b>1</b> .	Conclusions
6. /	ADS	ORPTION of Biodispersant
6.1	L.	Theoretical background
6.2	2.	Experimental procedure
6.3	3.	Experimental results60
6.4	<b>1</b> .	Conclusion64
7. I	Ultra	afiltration65
7.1	L.	Theoretical background
7.2	2.	Experimental procedure74
7.3	3.	Experimental results
7.4	1.	Conclusions
8. (	Cond	clusions & recommendations
9. I	Refe	erences
10.	Ap	ppendices95

## IV. List of figures

Figure 0-1 The behavior of the biodispersant molecules based on the CMC concentrationI
Figure 2-1 Cooling tower operating in crossflow
Figure 2-2 Cooling tower operating in counter flow
Figure 2-3 Schematized representation of the operation of cooling tower
Figure 2-4 Origins of the waters used as make-up water in cooling towers10
Figure 2-5 Schematic view of ED cell
Figure 2-6 Schematic representation of the treatment processes applied in the pilot plant of Evides14
Figure 2-7 Graphic representation of the static mixer installed in the pilot
Figure 2-8 Schematic representation of the flocculator
Figure 2-9 Schematic representation of lamella separator installed in the pilot plant
Figure 3-1 The two regions of the amphiphilic molecule
Figure 3-2 Graphical representation of the biocide breaking down the slime deposits from the surfaces,
dispersing them into the bulk water, which makes them more accessible to biocides20
Figure 3-3 Representative transversal section of a spherical amphiphilic molecule (polar heads blue,
hydrocarbon chains green)21
Figure 3-4 The relation between surface tension and surfactant concentration and the 3 zones21
Figure 3-5 Different CMC curves
Figure 3-6 Surface tension measurements on Nalsperse solution prepared and measured the same day
23
Figure 3-7 Surface tension measurements obtained on Nalsperse solutions which were let to stabilize
for 7 days23
Figure 3-8 Typical shape of the conductivity-concentration relation for an ionic surfactant25
Figure 3-9 Relation between biodispersant concentration and onductivity25
Figure 3-10 TOC values measured in demiwater-Nalsperse solution relation with the biodispersant
concentrations
Figure 3-11 Schematic representation of the biodispersant molecules dispersion below and above the
CMC
Figure 4-1 Du Nouy ring
Figure 4-2 Steps for measuring the surface tension
Figure 4-3 The principle behind the turbidity measurement
Figure 4-4 The principle behind absorbance – light passes a quartz cell, part of the light gets adsorbed
by the solution and the final intensity of the light is being measured
Figure 4-5 The principle of UV-Vis spectroscopy95
Figure 4-6 Schematic representation of the steps taken for the TOC measurement
Figure 4-7 NPOC measurement steps
Figure 5-1 Ferric chloride coagulation diagram35
Figure 5-2 Graphical representation of the jar-test set-up40
Figure 5-3 Relation between G-value and rotation speed of the stirrer41
Figure 5-4 Jar-test set-up43
Figure 5-5 The flocs observed in jars at different coagulant concentrations
Figure 5-6 Biodispersant floating on the surface of the water at the end of the coagulation experiment
Figure 6-1 Simplified representation of the adsorption mechanism55
Figure 6-2 Simplified representation of pillaring mechanism
Figure 6-3 Schematic representation of alignment of non-ionic surfactant molecules at charge
solid/liquid interface

Figure 6-4 Adsorption isotherms resulting from batch experiments in demiwater with 4 mg/l
biodispersant dosed and PAC as adsorbent60
Figure 6-5 TOC measured during the 8h equilibrium experiment, using PAC as adsorbent61
Figure 6-6 TOC variation in demiwater during 8h batch experiment with PAC62
Figure 6-7 Adsorption isotherms resulting from batch experiments in demiwater with 4 mg/l
biodispersant dosed and clay as adsorbent63
Figure 6-8 TOC variation in demiwater during 8h batch experiment with clay63
Figure 7-1 Types of membranes67
Figure 7-2 Representation of inside-out and out-side in filtration67
Figure 7-3 Schematic representation of cross-flow filtration and dead-end filtration
Figure 7-4 Effect of backwashes on the flux during dead-end ultrafiltration at constant flux
Figure 7-5 UF experimental set-up75
Figure 7-6 Membrane resistance increase during CTBD filtration77
Figure 7-7 Resistance of the membrane during the simple demiwater experiment
Figure 7-8 Membrane resistance increase during the experiment performed with demiwater-
biodispersant solution
Figure 7-9 Membrane resistance recorded during the simple Schie water filtration
Figure 7-10 Membrane resistance increase recorded during Schie water with 4 mg/l biodispersant
filtration
Figure 7-11 Membrane resistance increase during Schie water +4 mg/l biodispersant filtration, after
coagulation/flocculation with 20 mg/l Fe <sup>3+</sup>
Figure 7-12 Membrane resistance increase during filtration of CTBD, after coagulation/flocculation with
20 mg/l Fe <sup>3+</sup>
Figure 7-13 Membrane resistance trend recorded during the filtration of Schie water + 4mg/l
biodispersant after adsorption with PAC 82
Figure 7-14 Membrane resistance trend recorded during the CTBD filtration after PAC adsorption 83
Figure 7-15 Membrane resistance trend observed during filtration of Schie water $+ 0.1 \text{ mg/l}$
hindispersant solution
Figure 7-16 Slope of the membrane resistance increase recorded during the different filtration
avariants
Figure 10-1 Adsorption of different biodispersant solutions
Figure 10-2 Comparison between different biodispersant solutions absorbance
Figure 10-2 comparison between unreferic biodispersant solutions absorbance
Figure 10-3 Advorption isotherms resulting from batch experiments in tan with 4 mg/l biodispersant
Figure 10-3 Adsorption isotherms resulting from batch experiments in tap with 4 mg/l biodispersant
Figure 10-3 Adsorption isotherms resulting from batch experiments in tap with 4 mg/l biodispersant dosed and clay as adsorbent
Figure 10-3 Adsorption isotherms resulting from batch experiments in tap with 4 mg/l biodispersant dosed and clay as adsorbent
Figure 10-3 Adsorption isotherms resulting from batch experiments in tap with 4 mg/l biodispersant dosed and clay as adsorbent
Figure 10-3 Adsorption isotherms resulting from batch experiments in tap with 4 mg/l biodispersant dosed and clay as adsorbent
Figure 10-3 Adsorption isotherms resulting from batch experiments in tap with 4 mg/l biodispersant dosed and clay as adsorbent
Figure 10-3 Adsorption isotherms resulting from batch experiments in tap with 4 mg/l biodispersant dosed and clay as adsorbent
Figure 10-3 Adsorption isotherms resulting from batch experiments in tap with 4 mg/l biodispersant dosed and clay as adsorbent
Figure 10-3 Adsorption isotherms resulting from batch experiments in tap with 4 mg/l biodispersant dosed and clay as adsorbent

## V. List of tables

Table 2-1 Statistical properties of the make-up water used in different industries       10
Table 2-2 Statistical characteristic of the blowdown water    10
Table 2-3 Maximum concentrations of the recirculating water in the cooling tower before blowdown.11
Table 2-4 Qualitative characteristics of the three streams used for treatment in the pilot plant
Table 2-5 Characteristics of the UF membrane used in the pilot    16
Table 2-6 Characteristics of the NF membrane used in the pilot    17
Table 3-1 Surface tension values measured in CTBD water
Table 4-1 Iron measuring ranges and their corresponding measuring cell sizes
Table 5-1 Comparison between mechanical and static mixer    38
Table 5-2 Ferric chloride hexahydrate masses required to prepare the coagulant solutions43
Table 5-3 Initial quality of the blowdown water44
Table 5-4 Quality of the blowdown water after coagulation/flocculation without biodispersant dosing 45
Table 5-5 Blowdown quality before the start of the experiment
Table 5-6 Quality of the blowdown after coagulation/flocculation and with biodispersant dosing46
Table 5-7 Initial quality of the blowdown water46
Table 5-8 Blowdown quality after coagulation/flocculation, without biodispersant dosing and with pH
adjustment46
Table 5-9 Initial quality of the blowdown water47
Table 5-10 Final quality of the blowdown after coagulation/flocculation, without biodispersant dosing
and pH adjustment47
Table 5-11 Initial blowdown quality47
Table 5-12 Blowdown quality after coagulation/flocculation, with biodispersant dosing and pH
adjustment
Table 5-13 Initial quality of the blowdown
Table 5-14 Blowdown quality after coagulation/flocculation, with biodispersant dosing and pH
adjustment49
Table 5-15 Initial quality of the Spuikom water97
Table 5-16 Spuikom water quality after coagulation/flocculation in jars with baffle and without baffles
Table 6-1 TOC measured at the end of the batch experiment, based on the PAC dosed in each jar61
Table 6-2 TOC measured at the end of the batch experiment, based on the clay dosed in each jar63
Table 7-1 Chemicalssolutions used for cleaning, compatible with polymeric membranes
Table 7-2 UF membrane characteristics
Table 7-3 FeCl <sub>3</sub> and NaOH dosed for coagulation of the Schie water, before filtration
with UF 80
Table 7-4 Initial guality of the Schie water       80
Table 7-5 Schie water guality after coagulation/flocculation with different Fe <sup>3+</sup> concentrations80
Table 10-1 TOC measured at the end of the batch experiment, based on the PAC dosed in each jar .98
Table 10-2 TOC concentration recorded during the batch experiment in tap water using clay
Table 10-3 TOC concentration recorded during the batch experiment in CTBD water using PAC100
Table 10-4 TOC concentration recorded during the batch experiment in CTBD water using clay 102
Table 10-5 Surface tension values measured in demiwater-Nalsperse solution, without stabilization
time
Table 10-6Surface tension values measured in demiwater-Nalsperse solution, meausred after 7 days
stabilization time
Table 10-7 TOC measured in simple demiwater with PAC, during 8h experiment

## VI. List of abbreviations

CTBD	Cooling tower blowdown
CMC	Critical micelle concentration
E4Water	Economically and ecologically efficient water management in the European chemical industry
ED	Electrodialysis
EDR	Electrodialysis reverse
GAC	Granular activated carbon
NF	Nanofiltration
PAC	Powdered activated carbon
тс	Total carbon
ТОС	Total organic carbon
UF	Ultrafiltration

## 1. Introduction

Industrial wastewater is one of the main pollution sources of the water environment. The water resulting from industrial processes varies greatly in the amount of flow and also the pollution strength.

Since water scarcity represents a big threat for the future generation, water reuse should be applied. Water reuse can be characterized by decreasing the fresh water intake or by reducing the total discharge of wastewater (Heidekamp, 2013). Chemical industry comprises up to 20% of the global fresh water consumption and also has a high potential for increasing the eco-efficiency in industrial water management (Jungfer, et al., 2012).

#### 1.1. E4Water

E4Water stands for "Economically and Ecologically Efficient Water Management in the European Chemical Industry" and is a research project subsidized by the Seventh Framework Program of the European Union and is aiming to introduce essential processes the (chemical) industry needs in order to avoid bottlenecks and barriers for an integrated and energy efficient water management. The main project objective is to develop, test and validate new technologies, methods and processes which will result in a more energy efficient and sustainable management of water in chemical industry, with the possibility of involving in other industries. E4Water main goals are (Dechema, n.d.):

- achieving a water use reduction of 20-40%
- reduction of the wastewater production between 30-70%
- 15-40 % energy use and up to 60% increase in the economic benefits

For the accomplishment of these goals large chemical industries, leading water companies, R&D centers and universities active in the water management sector are working together. The project consists of 6 case studies, performed in different industries, each researching a different area (Dechema, n.d.).

The technologies which are being tested and trying to be validated by E4Water comprise 6 different on-site pilot plants and demonstrations. Case study 1 is represented by DOW Chemical Company.

DOW Chemical is a world leading company which operates in the chemical production industry. The main production site of the company is located in Terneuzen, Zeeuws-Vlaanderen, where millions of tons of chemicals and other synthetic products are manufactured. For production, DOW requires world-wide, around 500 million m<sup>3</sup> per year (Jensen, 2004). Because the price of fresh water for industries is increasing, the company is trying to find new techniques and processes in which brackish water can be reused as an alternative to salty water. The company is now focusing on desalinating surface water and effluents of the industrial and urban wastewater treatment. These objectives are part of the Case study 1 (Dechema, n.d.).

Case study 1 has several goals that need to be achieved (Dechema, n.d.):

- Developing a new approach which will enable the reuse of water in industry or agriculture, approach which is based on existing innovative concepts and technologies;
- Developing an understanding of the processes and their impact on the efficiency of each treatment step, which will result in an applicable technology;
- Production of industrial grade water (with a conductivity of 1mS/cm) from industrial wastewater and urban water, for 0.40  $\in$ /m<sup>3</sup>.

#### 1.2. Research objective

Cooling tower blowdown (CTBD) water is a quite difficult stream to treat because of the high salt concentrations and all chemicals which are added in the cooling tower. In the pilot plant at the DOW site, the operation of the pre-treatment has not been very efficient. The ultrafiltration (UF) membrane experienced rapid fouling during the treatment of CTBD water. For the Spuikom (rain water) and Biox effluent (wastewater effluent), rapid fouling was not an issue.

In the pilot plant installed by Evides in Terneuzen, is assumed that the fouling of the UF membrane is caused by the biodispersant dosed in the cooling tower. Biodispersant, Nalsperse-7348 is restricting the micro-organisms to attach to surfaces while keeping them in suspension. Evides reached an agreement with the owners of the cooling tower and stopped the biodispersant dosage for a couple of weeks in order to check if the biodispersant-free blowdown has the same effect on the membrane as the normal CTBD water. The operation of the pilot was stable, with 25 minutes filtration time and a flux between 60 up to 80 lmh. After some time, because the microbial populations in the cooling tower increased significantly, the biodipersant dosage was restarted, but this time, the operation of the UF was stable. Treatment of the blowdown water was not operated for long, and the blowdown that was treated might have been with a low biodispersant concentration, since the biodispersant will form a micelle layer on the membrane surface, as it forms in the cooling tower, resulting in decreasing the efficiency of the UF.

From the fact that there was not much known about the biodispersant and there were significant operation differences of the UF membrane treating the blowdown water with and without biodispersant, the main research question originated:

#### "What is the effect of biodispersant on the operation of the ultrafiltration membrane?"

To answer this question, a systematic approach has been followed and sub-questions were formed to help answer the main research question. The sub-questions that lead to the answer of the main question are:

- What is the biodispersant, Nalsperse-7348?
- Is the UF operation affected by the biodispersant?
- Can the coagulation/flocculation step be improved?
- Can biodispersant be removed from the blowdown water?
- How does the UF membrane operation behave under the operation of different effluents containing biodispersant?
- How could the UF operation be improved?

The answers to all these questions the research has been divided into several chapters. In Chapter 1 are presented the project background and the research questions. Chapter 2 shows a small overview about cooling towers utility and their operation, together with the quality of the water that goes into the cooling tower and also the quality of the water that gets out. Chapter 3 provides information about biodispersants. In Chapter 4 are describes the measurements and materials used during the experiment.

Chapter 5 gives theoretical background about coagulation and the experimental approach and results can be found. In Chapter 6 and Chapter 7 the theory and results of the experiments for adsorption and ultrafiltration respectively are presented. In the last chapter, Chapter 8 are given the conclusions and recommendations for future research.

### 2. Theoretical background

Understanding how a cooling tower works and what are they used for is helpful understanding the process and the water quality requirements. Hence, in this chapter an insight of how cooling towers work and the characteristics of the water that gets in the system and the water that gets out of the system is given. Blowdown water is a difficult wastewater that has been treated before; therefore the different treatment steps used and the challenges encountered are discussed.

#### 2.1. Cooling towers: Classification, operation

Cooling towers are constructions which have the purpose of extracting heat. They are used to prevent the release of excess heat into the atmosphere. Due to evaporation the processed heat is removed and the water temperature is dropped down to a value close to the value of the wet-bulb air temperature. Their application is common in various industries like: petrochemical, oil refineries, chemical plants, steel mills, electronics works, power plants, food industries, textile plants etc. The most common cooling towers are the re-circulating cooling towers because of their ability to conserve fresh waters by not discharging the hot water into the natural water bodies.

Cooling towers operate based on evaporative condensation and exchange of sensible heat. While mixing two types of fluids which have different temperature, the latent heat of vaporization is released, resulting in reduction in temperature of the warmer fluid. In the case of cooling towers the hot stream is represented by the hot water, while the cool stream is the air (Cheremisinoff & Cheremisinoff, 1981). Temperature reduction is achieved by converting a part of the water into vapors which are discharged into the atmosphere (Cheremisinoff & Cheremisinoff, 1981).

During cooling with the re-circulating towers, process water is continuously recirculating and recollecting heat from a compressor or a heat exchanger. Hot water is pumped at the top of the tower and released over the packing material where it is being cooled when in contact with the chill air. Resulted hot moist air is being released into the atmosphere, while the cooled water is being collected into a reservoir at the bottom of the cooling tower from where is being returned into the system.

The operation of cooling towers is ground on the assumption that energy can be removed from hot water when it is in direct contact with cold dry air. There are many types of cooling towers and they can be classified by (Wikipedia, 2014):

- Use:
  - HVAC (heating, ventilating, air conditioning): used for the rejection of the hot water from cooling systems
- Build:
  - Package: compact, pre-assembled cooling towers which can be easily transported. They are installed in industries where the heat rejection requirement is low (food processing, textile plant, hospitals, hotels etc.)
  - Field erected: large big structures located at big refineries, power plants or petrochemical plants, which cannot be relocated and can deal with high capacities of heat.
- Heat transfer method:
  - Dry cooling towers: the heat transfer is operated over a surface which separates the fluid from the ambient air. Not based on the principle of evaporation.
  - Wet cooling towers: operate based on the principle of evaporation

- Fluid coolers: mixed coolers. The fluid is passing a tube, on which clean water is sprayed and a fan activated by a draft is applied.
- Air flow generation methods:
  - Natural draft: dependent on the buoyancy from the tall chimney
  - Mechanical draft: uses motorized air in order to eliminate the air from the tower
    - Induced draft: the fan is located at the top of the chimney
    - Forced draft: the fan is located at the intake point of the chimney
  - Fan assisted natural draft: hybrid type, it looks like a natural draft, but the air is drawn out with a fan
- Air-to-water flow
  - Crossflow: the dry cool air is directed perpendicular on the water flow
  - $\circ$   $\;$  Counter-current flow: the air flow is directed opposite to the water flow
- Water distribution
  - Deck filled towers: contain a deck which is used to increase the water distribution over the packing material
  - Spray filled nozzles: make use only on spray nozzle for the water distribution
- Configuration:
  - $\circ$   $\,$  Coil shed towers: hyperbolic configuration, large capacity  $\,$
  - Hyperbolic towers: hyperbolic shape

The heat rejection specific for cooling towers is called "evaporative" because part of the hot water is being evaporated during the cooling. The heat of the water in contact with the cool air rises the temperature of the air and also the relative humidity of the air to 100% which causes the heat to discharge in the atmosphere. Of all the types of cooling towers the evaporative is the most efficient one, because the temperature of the water is reduced significantly, it is cost effective and has an energy efficient operation (CTI, n.d.).

Process hot water is pumped at the top of the cooling tower and sprayed over the wet-deck. Cool, dry air is being introduced into the system through the filling material resulting in a small quantity of water to evaporate. Due to evaporation the heat is reduced, while the hot moist air is eliminated at the top of the tower. The cool water which resulted from the cooling process is either discharged into the public sewage system, in a natural water body or recirculated in the system (Tower components Inc., n.d.).

In the crossflow towers air is directed perpendicular to the water flow. The air flow enters the system through the vertical walls of the tower into the packing material, while the hot water is sprayed over the filling material. Because of the packing material the air is flowing turbulently. Turbulent flow is increasing the contact with the hot water and furthermore, reducing the temperature of the water (EERE , 2011). In Figure 2-1 is presented the working principle of a cross-flow cooling tower (Morvay & Gvozdenac, 2008).



Figure 2-1 Cooling tower operating in crossflow

For the counterflow system, the cool air is flowing from the opposite direction of the hot water. The hot water is collected from the system and delivered to the top if the cooling tower and sprayed over the packing material. From the bottom of the tower the cool air flows upwards, reducing the heat of the water while it is progressing. Under the tower there is a basin which collects the cold water and recirculates or discharges it. In Figure 2-2 is presented the operation principle of a counter flow cooling tower (Morvay & Gvozdenac, 2008).



## 2.2. Make-up water

flow

Water is the most common medium used in cooling processes because it is easily available and it represents a great cooling medium because of its high heat capacity. All natural waters contain certain concentrations of nutrients, gasses or suspended matter which can lead to various operating issues.

All heat transfer equipments have a pre-treatment step to prevent scale formation. Scale depositions on the metal parts of the cooling installation, the efficiency of the process will be decreased and also the life expectancy of the part will be reduced. Besides the control of the corrosion, the treatment steps must also anticipate and prevent some other scale related problems that might come up.

Pretreatment is represented as the initial conditioning step, in which a corrosion inhibitor is applied to the metallic surface of the cooling installation. Pretreatment step includes cleaning and preparation of the metallic surfaces and also addition of corrosion inhibitors. The preparation and cleaning of the metallic surfaces consists in hydroblasting, treatment of the metal surfaces with mild acid/alkaline cleaners or use of special surfactants during the cleaning process. After the cleaning step the system needs to be properly flushed in order to prevent the metal attack (Cheremisinoff & Cheremisinoff, 1981).

The chemical, physical and bacteriological characteristics of the water need to be monitored in order to determine if the water quality is adequate for the cooling process and if the treatment is adequate. If the water quality is not the desired one, the pre-treatment steps need to be changed.

One of the processes that needs to be controlled is the scale formation. Scale deposition will inhibit the efficiency of the heat transfer elements and also have a positive impact on the bacteriological growth. At the beginning of the industrial revolution many boilers exploded because of the precipitated scale on the heating elements (Bott, 1995). Scale control is normally done with the pH control and addition of chemicals. Scale formation is inhibited or advanced based on the system conditions: pH, temperature or supersaturating conditions. Lime (soda) is normally added in a clarifier for scale control, together with coagulants and flocculants which reduce the turbidity. Since crystallization is dependent of the pH, acid addition is one of the most common ways of changing the pH and controlling the scale deposits. One of the most and cheap acids used for pH control is sulfuric acid. The quantity of acid added in the system is normally sufficient to reduce the alkalinity of the water, but it will not completely remove it (Bott, 1995).

If there is no clarifier and the chemicals are added in the piping systems, the flocks will be removed with the help of a filter. The filter can be sand filter or bag filter. Suspended and dissolved solids can be removed also in the filtration step or with an ion exchanger. Waters that have high concentrations of calcium, magnesium and silica (main compounds that form scale) can be treated using electrocoagulation in order to remove these compounds.

With electrocoagulation, no addition of coagulant is required because the coagulant is made on site by electrolytic oxidation of the anode. During the process ions are removed from water by reacting with the opposite charged ions, or by forming flocks of metallic hydroxides created in the effluent. Electrocoagulation can remove metals, colloids, particles, inorganic pollutants with the use of highly charged polymeric metal hydroxide species. During the process, precipitation of metals and salts is happening. The final effluent, after filtration is clear, colorless and odorless. The formed flocks settle easily and can be removed by filtration, while the sludge is easy to dewater (Mollah, et al., 2001).

Corrosion cannot be completely removed, but it can be significantly reduced. Corrosion can be control using several methods (Nalco, n.d.), (GE , 2012), (GE, n.d.):

- Choosing corrosion-resistant materials: copper base alloys, admiralty brass, aluminium brass, cupro-nickel, aluminium bronze, stainless steel, monel etc.
- Applying organic compounds that form a protective film on the metal surface: octodecylamine, octodecylamine acetate.
- Cathode protection (reduce corrosion by making a protective layer on the cathode): zinc salts, polyphosphates, calcium calmate.
- Anode protection (prevents the electron flow to the cathode): chromates, nitrites, silicates, tannins, benzoate, orthophosphate
- Chemical addition used for pH or oxygen control: hydrazine, volatile oxygen scavengers

The most common method used is chemical addition. Chemicals which are normally used are: molybdate, phosphate, silicate, zinc etc.

Microbial growth can increase the effect of scale and corrosion in the cooling systems. The biofilm that forms on the surface of the metal components of the system together with silt and calcium carbonate will reduce in time the efficiency of the heat transfer surface (Cheremisinoff & Cheremisinoff, 1981). Microorganism enter the system through the make-up water or via airborne microorganisms which are entering the tower. The cooling tower environment represents the perfect medium for the bacteria to multiply because the temperature is ideal for biological activity and because the water contains nutrients. Metal working fluids (emulsions) made with organic compounds can grant nutrients for sustaining the micro-organisms, are the elements related with the organic chemistry: carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus etc. For the control of the bacteriological growth several methods can be used:

- Oxidizing biocides
- Non-oxidizing biocides
- Biodispersants

There are several oxidizing biocides used for disinfection in cooling towers. Most common used are gaseous chlorine or liquid sodium hypochlorite and more recently ozone. When oxidizing agents are not very effective, non-oxidizing agents are normally used. The most common are acreolin, amines, chlorinated phenoles etc. (Meltz, 1999).

Biodispersants, on the other hand do not kill or inactivate microorganisms like oxidizing and nonoxidizing biocides. Biodispersants loosen the bacteria deposits from the metal parts and further are washed out from the system with the water. In addition they also prevent the new biofilm formation.

#### 2.3. Blowdown

Water is a viable resource and many parts of the world are facing water shortages while on other parts water is being used uncontrolled and reuse is not being taken into account. Most of the cooling tower blowdown, at the moment, is not being reused in any way.



Figure 2-3 Schematized representation of the operation of cooling tower

The make-up water in the cooling systems is being reused in several cycles and due to evaporation the salt concentration increases. In order to protect the efficiency and the life expectancy of components, when the concentration of the water increases above a certain limit, the blowdown is discharged. The blowdown depends of the degree of concentration in the system, or the cycles of concentration. Cycles of concentration represent the ratio between the dissolved solids in the cooling tower water and the dissolved solids in the make-up water supply. The number of cycles of concentrations depend on the water characteristics, tower design, operating conditions and the treatment (Cheremisinoff & Cheremisinoff, 1981). The purpose of blowdown is to maintain a certain maximum concentration in the system, with respect to scaling and corrosion. When the concentration exceeds the maximum set limit blowdown has to be discharged in order to protect the system (GE , 2012).

The formula for cycles of concentrations is comparing the concentration of the dissolved salts in the recirculating water with the salt concentration in the make-up water. Salt concentration from the recirculating water is limited normally to 3-7 times the concentration of salt in the make-up water (this means that the maximum number of cycles of concentration is 3-7) (Cheremisinoff & Cheremisinoff, 1981).

Equation 2-1

## $Cycles \ of \ concentration = rac{Concentration \ in \ blowdown}{Concentration \ in \ makeup}$

Sometimes the cycles of concentrations can also be defined as the ratio between the chloride concentration in the recirculating water and chloride concentration in the make-up water. The composition of the make-up water determined the cycles of concentration . Calcium, magnesium, silica, carbonate, bicarbonate and sulfate ions are the parameters which have to be kept in mind. The chemical choice for the pH control should also be influenced by the make-up water characteristics. Sulfuric acid dosing for the adjustment of the pH should be done so that the calcium sulfate concentration will not exceed the imposed limit (Cheremisinoff & Cheremisinoff, 1981).

Blowdown is also used for the removal of the suspended solids caused by internal precipitation, external contaminants or soluble salts. If proper chemical and physical treatment is applied to control scale formation, corrosion and microbial growth, the rate of blowdown can be reduced.

The blowdown can be managed several ways:

- Discharge in the sea using tankers
- Discharge in the sea through a brine pipe from the plant to the sea
- Discharging it into a river
- Discharging it into the public sewerage
- Irrigation
- Treatment and reuse

#### 2.4. Water quality

Water is a medium highly used in the processes of cooling because of its high heat capacity and also because of the relatively low price. The price for processed water has increased for industries in the last years so the reuse of treated blowdown water became very common. Due to the dissolved solids, gases or suspended matter present in the water, treatment has been introduced on site, in order to avoid operation issues. The most common ions present in the water are iron, sodium, calcium magnesium, bicarbonate or sulfates with their concentrations depending of the abundance of which they can be found in the soil (Cheremisinoff & Cheremisinoff, 1981).

Suspended and dissolved solids can cause precipitation in time, which can lead to scaling or fouling issues. Erosion can also be caused by the suspended matter present in the make-up water. Because of the organic compounds and the conditions microorganisms have the perfect environment to grow and cause health and operation problems.

Besides the components already present in the process water, some other contaminants can be introduced in the system because of faulty equipment: oils, fats, acids, alkalies or hydrocarbons.

Contaminants which come from the atmosphere like hydrogen sulfide, acid vapors, fly ash, dust or even birds may also end up in the process water and without scaling treatment, corrosion and loss in the thermal performance can be caused (Cheremisinoff & Cheremisinoff, 1981).

The 5 most common causes for cooling towers operation issues are: scale formation, corrosion, organic growth, suspended solids and oil leakage. With proper treatment techniques these challenges can be controlled. Treatments that have been applied and ended up being successful are represented by the recirculation systems with a small quantity of makeup water, which also can or cannot make use of chemicals (Cheremisinoff & Cheremisinoff, 1981). These treatment methods are not a solution for the oil leakage.

In order to prevent scale formation, chemicals which prevent precipitation are added . The chemicals which can prevent scaling are the acids used for pH adjustment, which besides scaling inhibition can cause corrosion. For corrosion some other inhibitors can be used: chromates, polyphosphates, silicates or alkalies (SDCWA, 2009).

All waters used in the cooling tower system have a certain concentration of ions and organic compounds. Some of the compounds, present in the make-up water, can have a positive effect on the process, while others can be monitored and or treated chemically in order to prevent deterioration of the operating system. The most common parameters that affect the operation of the cooling towers are (SDCWA, 2009):

- **Hardnes**s causes scaling. High concentrations of calcium cause inverse solubility, which leads to precipitation. Magnesium in the presence of high silica concentrations also causes precipitation of magnesium silicate in the heat exchanger.
- **Alkalinity** gives information about the calcium carbonate scaling potential.
- Silica causes scale formation which is difficult to remove.
- **Total suspended solids** can either enter the system with the makeup water or can be produced in the system because of corrosion and scale formation. Solids present in the water can bind to the biofilm and cause corrosion under the biofilm layer.
- **Ammonia** stimulates microbial growth in the heat exchanger and on the packing material. For copper alloys, can be corrosive at concentrations as low as 2 ppm. Also, in combination with chloride can form chloramine, which can hinder disinfection.
- **Phosphate** at a concentration of 4 mg/l and pH between 7 and 7.5 can be a corrosion inhibitor. On the negative side, it represents a nutrient for microorganisms and at concentrations higher than 20 mg/l in combination with calcium concentrations higher than 1000 mg/l will cause calcium phosphate scaling.
- **Chloride** is corrosive for most metals.
- **Iron** in combination with phosphates can form foulants. Some polymers used to inhibit scaling may be inhibited by iron.
- **COD** gives information about the organic content present in the water.
- **Nitrates and nitrites** at concentrations higher than 300 mg/l can corrode mild steel. For copper though, nitrates do not protect it from corrosion nor does attack it.
- **Zinc** together with phosphates and nitrates can prevent corrosion at concentrations below 3 mg/l.
- **Organics** act as nutrients for the microorganisms, increasing their growth rate.
- Fluoride can combine with calcium and cause scale formation.
- Heavy metals like copper and nickel can cause galvanic corrosion.

The water used in the cooling tower is mainly surface or groundwater. In Figure 2-4 are presented the percentages of different water types used as cooling water supply in Taiwan (You, et al., 1999).



Figure 2-4 Origins of the waters used as make-up water in cooling towers

In Table 2-1 are presented the statistical values calculated for the makeup water. The average values were calculated based on data from different types of makeup water used in different industries at different locations in Taiwan (You, et al., 1999).

In Table 2-2 are presented the average values of the blowdown water produced at several cooling tower sites from different industries (You, et al., 1999).

Parameter		Range	Arithmetic average
рН		6,5-8,6	6,34
Electrical conductivity	µS/cm	0,4-1950	399,9
Alkalinity as CaCO3	mg/l	4-290	58,8
Total Hardness as CaCO3	mg/l	1-550	114,2
SO42	mg/l	5-200	17,6
Silica	mg/l	0,86-62	8,95
Cl	mg/l	1,9-450	32,2
Fe	mg/l	0-1,5	0,107

Table 2-1 Statistical properties of the make-up water used in different industries

Parameter Arithmetic average Range pН 6-9,15 7,93 Electrical conductivity µS/cm 0,4-7940 1977,12 Alkalinity as CaCO<sub>3</sub> 19,2-800 208,42 mg/l Total Hardness as CaCO<sub>3</sub> 14,4-1000 426 mg/l 200-1400 SO₄<sup>-</sup> mg/l 763,5 25-800 132,5 Silica mg/l Cl 0,5-2102 381,13 mg/l Fe mg/l 0,03-3 1,14

In Table 2-3 are presented the maximum limits for water qualities of the blowdown presented in literature. The three values in the table represent values taken from different industries (food processing, electronics manufacturing, petrochemical plants, textile plants, steel mills). In case the make-up water exceeds this values and it is desired to reuse the blowdown, it is recommended to pretreat it (You, et al., 1999).

Compound		Suggested standard		
Compound		Ι	II	III
SiO <sub>2</sub>	mg/l	50	50	19
Al	mg/l		0,1	0,06
Fe	mg/l	0,5	0,5	0,06
Mn	mg/l		0,5	0,06
Са	mg/l	-	50	40
Mg	mg/l	-	0,5	30
SO <sub>4</sub> <sup>2-</sup>	mg/l	200	200	1150
HCO <sub>3</sub> <sup>-</sup>	mg/l	-	24	-
Cl	mg/l	-	500	90
PO <sub>4</sub> <sup>3-</sup>	mg/l	1	4	0,6
Dissolved solids	mg/l	500	500	-
Suspended solids	mg/l	3	100	13
Hardness as CaCO <sub>3</sub>	mg/l	50-250	650	-
Alkalinity as CaCO <sub>3</sub>	mg/l	50-200	350	-
рН		6,5-7,8	6,9-9,0	6,8-7,2
Organics react with methyl blue	mg/l	-	1	-
Organics extracted from CCl <sub>4</sub>	mg/l	-	-	-
COD	mg/l	10	75	50
Bacteria	organisms/ml	100	-	-
Turbidity	NTU	10	50	-
BOD	mg/l	-	25	10
NH4 <sup>+</sup> N		-	1	1,3
Total Coliform	MPN/100 ml	-	-	18

Table 2-3 Maximum concentrations of the recirculating water in the cooling tower before blowdown

#### 2.5. Treatment of the blowdown water

For the treatment of cooling tower blowdown, one of the most efficient used techniques is reverse osmosis. Membrane filtration is often used in desalination because it does not require an extensive pre-treatment (only filtering is sufficient to protect the membrane from bigger particles), they have a very high removal capacity and a recovery between 50-90% for brackish water and 35-60% for sea water (Altman, et al., 2012).

In the experiment conducted by Kaliappan et al., 2005 cartridge filters with different pore sizes ranging from 1  $\mu$ m to 5  $\mu$ m and carbon filter were used as pretreatment before the RO step. DOW chemicals, for the cooling tower from Gaojing Powe Plant in China used a multimedia filter as a first step to remove suspended solids and turbidity. After the multimedia filtration step, an ultrafiltration unit was installed in order to decrease further the turbidity and protect the first pass of the RO system. The permeate of the first RO pass was further degasified and an increase in pH was performed before the second RO step. The permeate of the second RO stage was planned to be used as boiler makeup water, so in order to meet the desired characteristics, a final step was installed for demineralization, electrodionization (DOW, n.d.).

Another technique used for cooling tower blowdown treatment is electrodialysis. Eelectrodialysis (ED) is a technique used for desalination for more than 50 years. Normally they are used for desalination of natural waters but they have also been applied for wastewaters. During the process the colloids interact with water and create a negative charge on the surface of the bound water layer. A direct electrical current is applied to the ED stacks, which represents the force which directs the negatively charged colloids to the anion exchange membrane. Because of the electric field and the electrostatic

forces, the colloids remain on the membrane surface (Allison, 1995). For better understanding, a graphic representation of the EDR is shown in Figure 2-5.



Figure 2-5 Schematic view of ED cell

#### 2.6. Evides pilot

At the DOW location there are several types of water sources which can be treated and reused for production. Water sources which will be subject to treatment are: Dow sweet WWTP effluent (BIOX), Spuikomwater (rain water), cooling tower blowdown (CTBD).

Spuikom water is, in fact the rain water collected in a ditch, from the company's area and also part of the neighboring areas. Rainwater is collected in ditches and redirected to the pilot plant. The quantity and quality of the collected storm water is dependent on the season, so the amount collected and the quality vary. Because the DOW is located next to the river Scheldt, in a polder, the salinity of the water is quite high (approx. 1500  $\mu$ S/cm). Normally rain water is salt-free. The high salinity of the Spuikom water can be explained by the fact that that the Scheldt estuary became brackish due to sea water intrusion, causing the groundwater to also become brackish and because of groundwater infiltration, the Spuikom water presents a higher salinity.

Dow has a wastewater treatment plant which is biologically treating the wastewater produced on site. The effluent of the WWTP is also sent to the pilot plant, for further treatment. The quantity and quality of this effluent are more or less constant during the year.

At the location of DOW Chemical, there is also a power plant. The blowdown which comes from the cooling towers of ELSTA is the third water source of the pilot plant. Resulting blowdown has a quality which is representative for the blowdown produced by the cooling towers of DOW. Because Elsta is in the vicinity of DECO this blowdown water is tested in the pilot. The stream has a constant quality throughout the year, but has a high salinity (approx. 4000  $\mu$ S/cm).Table 2-4 presents the characteristics of the 3 types of water selected for treatment.

Several treatment techniques were tested on a lab scale for the investigation of the quality of the delivered effluent. Based on the observed results, a pilot plant has been designed and installed at the DECO, location owned and operated by Evides, in Terneuzen. Treatment of the wastewaters is done in several steps:

- Pre-treatment of the incoming wastewater using coagulation/flocculation and lamella separation
- Filtration of the pre-treated water using ultrafiltration (UF)
- Mild desalination by nano-filtration (NF)
- Mild desalination through electro-dialysis reverse (EDR)

Raw water source		Rainwater collected in Spuikom	DOW WWTP sweet effluent	Cooling tower blowdown
Origin		Rain at parts of DOW premises and forests at surroundings	Biologically treated water from chemical processes	Blowdown of cooling tower LHC-3
Volume	m3/y	500000	1500000	1000000
Seasonal impact		depends on rainfall quality impacted by season	temperature between 20-35	volume is proportional with ambient temperature
Quality				•
Chloride	mq/l	318	157	500
Conductivity	μS/cm	1500	918	3900
TSS	mg/l	20	3	12
тос	mg/l	14	14	51
Nitrate	mg/l	1.2	30.1	87
Phosphate	mg/l	0.5	11	5.9
HCO3	mg/l	295	168	51
Са	mg/l	102	62	482
Mg	mg/l	35	11	63
Sulfate	mg/l	119	104	1142
Silicate	mg/l	1.1	0.48	0.92
Iron (dissolved)	mg/l	0-1	0,1-0,3	1-1,5
Mn (dissolved)	mg/l	0.16	0.03	0.00
Ba	mg/l	0.01	0.02	0.15
Sr	mg/l	0.62	0.24	1.50
chlorofyl A	ug/l	77	<2	<2
рН		8.1	7.5	7.9
Temperature	°C	5-25 (ambient)	20-35	25-30
N total	mg/l	1.3	7.1	19.6
Turbidity	NTU	9	1.7	7.3
Free chlorine	mg/l Cl₂			<0.2
Fe dissolved	mg/l	0.02	0.14	0.05
NH4	mg/l	1.3	0.4	0
К	mg/l	20	15	99
Na	mg/l	173	115	280
F	mg/l	0.86	0.15	0.84
CI	mg/l	318	157	500
<u>SO4</u>	mg/l	119	104	1142
BOD	mg/l O₂	1	2	1.4
COD	$mg/l O_2$	57	65	203
Colony count (3d, 22°C)	N/ml	17000	80000	660
ATP	ng/l P	300	408	72
Anions	meq/l	16.3	9.9	40.3
Cations	meq/l	16.1	9.4	44
SI		0.61	0.39	0.16

#### Table 2-4 Qualitative characteristics of the three streams used for treatment in the pilot plant

The pilot plant was opened officially on November 29<sup>th</sup>, 2013 and on January 2<sup>nd</sup> first cooling tower blowdown was treated. In Figure 2-6 is presented a schematic representation of the pilot plant.

EDR and nanofiltration were chosen as desalination techniques because they proved to be the most feasible, the energy requirement is not so high and the implementation/operation/maintenance costs were proved to be the lowest (Dechema, n.d.). The pre-treatment is focused on the removal of TOC, ortho-phosphate, total phosphate and suspended solids so that biofouling of the EDR and NF nit will be reduced.

Figure 2-6 Schematic representation of the treatment processes applied in the pilot plant of Evides



#### 2.6.1. Coagulation

Coagulation represents the first step of pre-treatment. Colloidal particles are destabilized by a coagulant, which in this case is ferric chloride (FeCl3) (Dechema, n.d.). Before the coagulant is added water temperature, conductivity, pH and turbidity are measured. Iron dose depends on the type of water that is being used: 20 mg/l FeCl3 for Elsta cooling tower blowdown, 10 ppm for Spuikom water and Biox. The Coagulant dose is not yet fixed though. Dosing is varied, in order to discover the best conditions for operation.

The coagulant is mixed in the inline static mixer. There are two types of mixing mechanisms in the static mixer: laminar and turbulent. Laminar mixing in based on flow division. The mixer is equipped with helical or pseudo-helical elements, which are organized in sequence of alternating left and right hand twists of 180°. Elements divide the effluent into 2 water streams and rotate them at 180°. For the turbulent mixing, the main mechanism is radial mixing. The effluent is constantly moving from the center of the pipe to the pipe's walls, while changing direction with each succeeding element (Lenntech, n.d.).

Static elements are plain ended pipe sections, flanged with several injectors and sampling points, fitted in sections for ducts and open channel (Lenntech, n.d.). The mixing energy is applied by the pressure drop across. In the pilot, the mixer consists out of 6 spiral PMS mixing elements. In Figure 2-8 is presented the graphical representation of the static mixer installed in the pilot plant at DOW site in Terneuzen (Dion, 2014).



Figure 2-7 Graphic representation of the static mixer installed in the pilot

#### 2.6.2. Flocculation

Coagulation and rapid mixing are followed by slow mixing, step in which the coagulant is able to form stable flocs. Slow mixing is required so that particles can collide and form bigger flocs which are able to settle. The flocculator installed has a cylindrical shape and it is placed on the inside of the baffles.

Stirring is done with 3 stirrers, each consisting of a 4 blade agitator impeller, of different sizes. In Figure 2-8 can be seen the schematic representation of the flocculator with the dimensions specifications.

The diameter of the flocculator is 0.9 m and the height 2.5 m, with the volume of 1.6  $m^3$ . The residence time of the effluent in the flocculator is 21 minutes, while the rotation velocity is 15 rpm.



Figure 2-8 Schematic representation of the flocculator

#### 2.6.3. Lamella separator

In the lamella separator, the stable flocs formed in the flocculator can settle. Lamellas provide a bigger settling surface, resulting in an increased efficiency of the settling process. Flocs, under the gravitational force, sink to the bottom of the tank. Lamella separator consists of a tank with a cylindrical shape which has rectangular plates, inclined at an angle of 50° to the horizontal. Plates have the purpose of increasing the available settling area, while the sediments slide down the surface of the plates and are collected in a sludge hopper. Another advantage of lamella separator is the fact that it is more compact than a regular settling tank (Wakeman & Tarleton, 1999). In Figure 2 is shown a schematic representation of a lamella separator (USQ, n.d.)

The installed lamella separation has a total plate surface of 12 m<sup>2</sup>. The flocs formed in the flocculator have a settling velocity of 0.38 m<sup>3</sup>/h. At the bottom of the lamella separator the sludge is connected. The sludge is also sent to the collection tank which resends the backwash water to the BIOX treatment.



Figure 2-9 Schematic representation of lamella separator installed in the pilot plant

#### 2.6.4. Ultrafiltration

The effluent collected after lamella separation is sent to the UF unit for further removal of suspended solids. UF is applied for advance filtration and also as a pre-treatment step for the NF unit. In this process, hallow membranes are used and the operation is configured as "dead-end", which means that all feed water is filtrated in the UF step. The unit is operated for a certain time, after which it is stopped and flushed with the produced permeate. For a better cleaning of the membrane, chemicals can also be added in the flushing effluent (chemical enhanced backwash) (Davis, 2011).

In order to protect the UF membrane a bag filter was installed before so that bigger particles which can pass in the system will not affect the membranes. Because the Spuikom water is collected through ditches, fishes were collected in the bag filter. There are two UF modules installed, but currently only one is being operated, since the operation flow is quite low, 4.5 m3/h. From the UF filterability, flux and pressure drop is being measured. Backwash is performed every 12 minutes for 1 min, while chemical cleaning is done every 24 backwashes. Chemicals used for chemical cleaning are citric acid and caustic soda. The chemical doses are 4000 ppm citric acid and 400 ppm caustic soda.

Outside of the building there are 2 tanks. In one of the tanks is collected the filtrate and the backwash water from the UF module, while in the other tank (neutralization tank) is collected the water from chemical cleaning, water in which high chemical concentrations are present. From here, these 2 types of waters are connected with the DECO site and resent for treatment at BIOX.

Permeate of the UF is collected in a buffer tank in which again, pH, temperature, turbidity and conductivity are being measured. The tank is connected with a sensor which is measuring the level in the tank and if the level is too low the following step, NF will be stopped.

The membrane used is Inge Dizzer 60 MB 0.9 produced by Lenntech. The characteristics of this membrane are presented in Table 2-5.

Type of membrane	Applied pressure	Permeate flow rate	Temperature range
Inge dizzer 60 MB 0.9	5.6 bar	0.1-1,5 bar	1-40°C

Table 2-5 Characteristics	of the UF	membrane	used in	the pilot

#### 2.6.5. Nanofiltration

NF is mainly used in industrial water treatment for softening, partial desalination and organic matter removal. NF membranes are capable of removing divalent ions, large monovalent ions and large organics. The pore sizes of the membranes are between 1-10 nm. NF is a pressure driven mechanism, water being pushed through a semipermeable membrane. Divalent ions larger ions and organics are retained in the membrane while the clean effluent (permeate) is collected at the other end of the membrane (Hilal, et al., 2004).

There are 2 stages in the NF. In the first stage there are 2 modules, while in the second stage there is only one. In the influent NF antiscalant and NaHSO3 are being dozed for the protection of the membrane from scale formation. The antiscalant dose is 4 ppm/cm3, while the NaHSO3 depends on the chloride concentration in the effluent (for 1 mg/l Cl 3.3 ppm NaHSO3 are being dosed.

The membrane used is DOW Filmtec NF 90-4040. The properties of the membrane are presented in Table 2-6. The membrane is made of polyamide thin film composite (DOW, n.d.).

#### Table 2-6 Characteristics of the NF membrane used in the pilot

Type of membrane	Applied pressure	Permeate flow rate	Stabilized salt rejection
NF 90-4040	4.8 bar	7.6 m3/h	97%

The extreme operating conditions of the membrane are (DOW, n.d.):

•	Maximum temperature	45°C
•	Maximum operating pressure	41 bars

- Maximum operating pressure 41 bars
- Maximum flow rate 3.6 m3/h
  Maximum pressure drop 1 bar
- Maximum pressure drop 1 bar
  Operating pH range 2-11
- Short term cleaning pH range 1-12
- Maximum feed SDI 5
- Free chlorine <0.1 ppm

#### 2.6.6. Electrodialysis reverse

Eelectrodialysis (ED) is a desalination technique in which ions are passed through a membrane due to direct electric current applied in the solution. Ions are transferred by the current, through the membrane, from the less concentrated solution to more concentrated solution. For electrodialysis reversal (EDR) the polarity of the current is periodically reversed. Changing the polarity results in reverse flow of ions between demineralizing compartments, which creates automatic flushing of the formed scale on the membrane's surface (AWWA, 2003).

Automatically the pH, temperature, turbidity and electro-conductivity are measured before the ferric chloride dosing point, in the buffer tank after the UF unit and after the NF step. Weekly are made extensive laboratory analyses on all the influent types, UF feed, UF permeate, NF permeate and NF concentrate.

#### 3. Biodispersant

In this chapter are given more detailed information about what biodispersants, their action in cooling system and how they can be characterized. A small insight about surface tension is also presented together with ways to measure it. Since there is no information available about the biodispersant used in the cooling tower, some measurements were performed to determine some of its characteristics. The surface tension of the biodispersant was measured. The results obtained and the conclusions which were drawnare presented in this chapter also.

#### 3.1. Theoretical background regarding biodispersant

Microbiological growth control is a big concern in the majority of industries where water is used as a media. Depositions of biofilm on the surfaces are a natural occurring phenomenon and it also represents self-protection to the external toxic factors. Most of the industries often use cleaning and disinfection methods together with chemicals which have antimicrobial properties. For quite some time now, in some industries and medicine production more biodegradable and less toxic products have been used: surfactants (Pereira , et al., 2007).

In cooling towers, biocides, biostats and biodispersants are used for the biological control. Biocides are used to kill microorganisms, biostats control the microbiological activity, while biodispersants put an electric charge to the substrate or to the individual cells or clusters for the attachment reduction. Generally biostats and biodispersants are not used independently. The proper treatment implies the use of a biocide together with the biodispersant (Bott, 1998).

Biodispersant used together with an oxidizing biocide will reduce the residues and time required for achieving the end objective. Biodispersant breaks down the biofilm, enabling the biocides to have access to the organisms, resulting in more effective results (EnviroAqua, 2008).

Operation with biodispersants is a very effective microbiological control. Biodispersant is a term which is normally used to describe a dispersant produced by microorganisms. The biodispersant term is used in an erroneous way since they are synthetic surfactants and they are not produced by microorganisms (Cloete, et al., 1998).

The most effective products for biofilm control are biopenetrants or biodispersants. They are substances which penetrate and loosen up the matrix of the biopolymer. Their action is not only diffusing the biofilm, but will also assure a better exposure of the microorganisms to the biocides (Buckman, 2010).

Effective biodispersants should also aid in the penetration of biocides into inorganic deposits, helping in the destruction of sulfate reducing bacteria (SRB) growing in anaerobic areas. These deposits are soft, which makes the removal possible by turbulence. Poultan showed that biodispersants are removing the already formed biofilms and also induce the increase of planktonic bacteria. With its addition new biofilm formations on the clean surfaces was restricted, the minimum inhibitory concentration was reduced and the biocide efficiency was not influenced (Cloete, et al., 1998).

Surfactants and emulsifiers are components of various industries, agricultural and productive processes. The compounds are mostly chemical synthesized, while their characteristics result from the presence of the hydrophilic and hydrophobic regions on the same molecule (Cloete, et al., 1998). Surfactants are surface active agents, which mean that they are active and are capable of absorbing at surface and interface and are able to reduce the surface and interfacial tension of aqueous fluids

(Pereira , et al., 2007). A molecule with both hydrophilic and hydrophobic properties is called amphiphilic molecule. In Figure 3-1 is presented the schematic representation of this type of molecule.



Figure 3-1 The two regions of the amphiphilic molecule

Because of the presence of hydrophilic and hydrophobic group within the same molecule, surfactant partition happens at the interface between the fluid phase of different degrees of polarity and hydrogen bonding. The hydrophilic part of the surfactant can be anionic, cationic or neutral, while the hydrophobic group has a hydrocarbon chain (Ghazali & Ahmad, 1997). They are components of the biocides also, but it is very unlikely that the microorganisms will develop resistance to the action of the biodispersant or will have mutagenic reactions (Cloete, et al., 1998).

Surfactants have the properties of a detergent and also have bacteriostatic and biocidal properties. They have toxic effects since they cause membrane disruption, cellular lysis, increase membrane permeability, metabolite leakage and are capable to alter the physical structure of the membrane (Pereira , et al., 2007).

Characteristics of the surfactants are given by (Cloete, et al., 1998):

- CMC (critical micelle concentration)
- HLB (hydrophilic-lipophile balance)
- Chemical structure
- Charge (anionic, cationic, nonionic, amphoteric or zwitterionic)
- Origin (biological or chemical)

Dispersants action consists of breaking the foulants into smaller particles and keeping them suspended in the cooling water. This way deposits formation is avoided and foulants can be removed from the system together with the blowdown water (Cloete, et al., 1998).

The most common used surfactants at the moment are the synthetic water soluble polymers. Synthetic dispersants have an improved formula compared with the natural dispersants since they can be made at a specific molecular weight, they are not easily degradable by biological organisms, don't react with chlorine or iron salts, they are more cost effective (Cloete, et al., 1998).

Biodispersants are normally non-ionic surfactants. The most effective one consists of ethylene and propylene copolymers. They are nonionics which are able to gain a charge depending of the pH value (tertiary amines oxides). Polyethers (polyethylene oxides) are protonated under acidic conditions and exist in cationic form. Long-chain carboxylic acids are non-ionic under neutral and acidic conditions and anionic under basic conditions. From here it can be concluded that nonionics are surfactants that have no charge in the predominant working range of pH (Feinerman, et al., 2001).

The action consists of lowering the water surface tension, allowing the slime to disperse into the bulk water. In Figure 3-2 is a schematically representation of the action of surfactants (Choudhary, 1998).



After biodispersant added

Figure 3-2 Graphical representation of the biocide breaking down the slime deposits from the surfaces, dispersing them into the bulk water, which makes them more accessible to biocides

Nonionic surfactants are low foaming and the recommended dosage is between 10 and 20 ppm. Surfactants are also used to mobilize oily and gelatinous foulants. Their action consists in damaging the cell by lowering its permeability. The normal flow of nutrients is broken resulting in the death of the organism. Nonionic surfactants have no electrical charge and their advantage over ionic surfactants is that they are compatible with all the other surfactants and they don't depend of the pH (Cloete, et al., 1998). Nonionic surfactants are not as sensitive to the electrolytes in the system, compared with the ionic surfactants and the synthetic solubility of the ability to design the required degree of solubility into the molecule by the careful control of the size of the hydrophilic group (Myers, 2006).

Nonionic surfactants account for about 40% of the worldwide surfactant use (Schmitt, 2001). They are more tolerant than anionic surfactants to water hardness, they are more effective in the removal of oily soil from synthetic fabrics, they have a good cold water solubility, low critical micelle concentration which makes them more effective at low concentrations (Schmitt, 2001).

The feeding of the biodispersant is recommended to be done before the addition of the biocide on a slug basis. Normally biodispersant is added in the system between 1 and 4 hours before the addition of the biocide. If the system has high loading, than the addition should be continuous (EnviroAqua, 2008).

By removing the slime mass one will observe (Choudhary, 1998):

- Improved heat transfer of the metal surface by removing the biofilm
- Reduced potential for scale or fouling because less of the matrix is available for buildup
- Reduced possibility for the existence for anaerobic corrosive bacteria.

#### 3.1.1. Critical micelle concentration

In the amphiphilic molecule the hydrophobic and the hydrophilic parts present different behaviors towards the water. Polar part of the molecule is constantly trying to interact with the water, while the non-polar part rejects interaction with water.

For the achievement of both states, the molecule is able to arrange itself at the surface of the water such as: the polar part is in contact with water and the non-polar part is in contact with air or a non-polar liquid. Presence of these molecules on the surface disrupts the cohesive energy and results in lowering of the surface tension (Biolin Scientific, n.d.).

Molecules can rearrange themselves in a different way such that each part interacts with their favorite media. The amphiphiles will get together naturally in solution creating micelles in form of bilayers, spheres, ellipsoids, cylinders or other shapes. Hydrophobic carbon chains combine themselves to protect the inner core of the micelle from solution (Positron Research Group, 2006). Figure 3-3 shows a simple graphic representation of the transversal section through an amphiphilic molecule.



Figure 3-3 Representative transversal section of a spherical amphiphilic molecule (polar heads blue, hydrocarbon chains green)

Concentration of the amphiphilic molecules is given by the proportion of molecules present at the surface or, as micelles in the bulk liquid. For low concentrations, the surfactant will arrange at the surface. As the concentration increases, the surface of the liquid gets saturated with surfactant and for further increases molecules have to form micelles. When the surface gets loaded and the molecules start to form micelles, that is when the critical micelle concentration (CMC) is achieved. The CMC value can be determined from the surface tension measurements (Positron Research Group, 2006).



Figure 3-4 The relation between surface tension and surfactant concentration and the 3 zones

In Figure 3-4, where is presented the relation between the surface tension and surfactant concentration, 3 zones can be distinguished (Biolin Scientific, n.d.):

- 1. At low surfactant concentration only small changes in the surface tension are observed;
- 2. An increase in surfactant concentration decreases the surface tension;
- 3. When the water surface becomes fully saturated, there are no more changes in the surface tension.

The CMC is a very useful characteristic, since it shows the surface and interfacial activity of the surfactant molecules in solution. The ability of surfactants to reduce surface or interfacial tension is expected to be directly related to the CMC. A low CMC value shows that is thermodynamically favorable for the hydrophobic domain of the surfactant molecule to leave the aqueous solution, which results in an excess concentration at the interface and the formation of micelles. The ability to absorb at the interface and lower the interfacial tension is very important for many processes of technological interest (emulsification, foaming, wetting, solubilization, detergency, particle separation, surface coatings) (Huibers, et al., 1996).

#### 3.1.2. Surface tension of solutions

The surface tension of a solution refers to the equilibrium excess surface energy at the boundary between the liquid and its own vapor (a mixture of the vapor and other gases). When the liquid phase is not a pure liquid but a mixture of two or more components, than the surface tension of the solution should be the average of the two pure components (Myers, 2006).

If an organic material is one component of the aqueous solution, then the surface tension of the system will decrease. The surface tension decrease depends of several factors like the solubility of the system or the tendency of the organic material to preferentially adsorb at the water-air interface. Fully miscible liquids, such as ethanol and acetic acid, result in a gradual decrease in the surface tension of their aqueous solution, while longer chain organics such as 1-butanol will result in a dramatic decrease (Myers, 2006).

There are various relative easy experimental methods for the determination of the CMC of a surfactant. Chosen method depends of the availability of various techniques, relationship between the technique and the ultimate application, and the personal preference of the investigator (Myers, 2006).

#### 3.2. Surface tension measurements

Surface tension is induced by the strong interactions between water molecules (hydrogen bonds). It represents the contractive tendency of the surface of a liquid that allows it to resist to an external force (Wikipedia, 2014).

By performing surface tension measurements the CMC concentration can be detected. Different surfactant solution were measured using the Sigma KSV 701 apparatus. The concentrations varied between 0 and 100.000 mg/l. The determination of CMC should be quite easy but, due various situations the determination of the value can be quite problematic. In Figure 3-5 are presented several types of curves (Biolin Scientific, n.d.).



Figure 3-5 Different CMC curves

In graph A the CMC corresponds with the point where the graph suffers a sudden change or there is a visible slope. In graph B can be noticed a clear drop of the surface tension due to impurities found in
the solution. In graph C there is no clear point or minimum value of the surface tension. This situation can occur due to procedural errors or other strange phenomenon which resulted in unclear results. It is recommended in this situation to repeat the measurements. In case the curve has the same shape after repetition, than the CMC cannot be detected (Biolin Scientific, n.d.).

#### 3.2.1. Surface tension measurements – Results

The surface tension of various solutions of demineralized water and biodispersant was measured. Biodisperant concentration in the demineralized water varied from 0.01 mg/l to 10 mg/l. Surface tension of simple demineralized water has a value of 72 mN/m. So the measurement should start from that value.

2 set of measurements have been made. First measurements were made on solutions which were prepared and measured immediately, while the second measurements were done on solutions which were left to stabilize for 7 days (because of the poor dissolution of the biodispersant). The measurement was done in triplicates. For the samples prepared and measured immediately, there were some bigger differences compared with the measurements done after 7 day stabilization. In Figure 3-6 are presented the obtained results for the surface measurements of the samples measured immediately, while in Figure 3-7 are presented the results obtained after 7 day stabilization. The starting solution was demiwater with 4 mg/l biodispersant, which was diluted further.



Figure 3-6 Surface tension measurements on Nalsperse solution prepared and measured the same day



# Surface tension with 7 days stabilization

Figure 3-7 Surface tension measurements obtained on Nalsperse solutions which were let to stabilize for 7 days

The stabilization between water-air boundaries of surfactants occurs with the decrease in surface tension. The decrease in surface tension is dependent on the surfactant concentration. At very low concentrations the surface tension of the surfactant will have a value close to the surface tension of pure water. With an increase in concentration, surfactant is able to stabilize the surface while the surface tension is being decreased. When the surface tension is not able to decrease anymore a plateau is reached. The surfactant that is added above the CMC will result in formation of more micelles, not to the water phase and will not result in an increase of stabilization (Gentry, 2013). In conclusion, from the shape of the surface tension graph it can be deducted that the biodispersant is a surfactant with the estimated CMC reached at a concentration of 0.03 mg/l.

The obtained results for both measurements are presented in detail in Appendix C. Even though there is quite a big discrepancy between the measurements obtained with the 2 methods, the shape of the curve changes significantly at a solution concentration between 0.03 and 0.04 mg/l. The point where the shape of the surface tension curve changes is the point where the CMC is located.

#### **3.2.2.** Surface tension of the cooling tower blowdown

The surface tension measurements of demiwater and biodispersant solutions gave an indication about the CMC of the biodispersant. The biodispersant concentration in the CTBD water cannot be measured, but it is assumed by the producers based on the biodispersant concentration dosed in the makeup water and the cycles of concentrations in the cooling tower.

The surface tension of the CTBD water was also measured. Surface tension might give an estimation of the biodispersant concentration in the CTBD. One has to take into considerations that there are also many other substances in the blowdown that have been concentrated which will influence the surface tension of the blowdown water.

There were two measurements done. One measurement was done in fresher blow down water and the other measurement was done with blowdown water which was collected some months before and stored in the refrigerator.

Samula	Surface tension
Sample	mN/m
Demiwater	72,7
New sample	70,9
Old sample	72,3

Table 3-1 Surface	e tension values	measured in	<b>CTBD</b> water
-------------------	------------------	-------------	-------------------

In Table 3-1 are presented the surface tension values obtained for the 2 samples of CTBD and as a comparison the CMC of demiwater free of biodispersant. As it can be observed the surface tension value obtained in the CTBD which was stored for longer period is very close to the surface tension obtained in demiwater. These two types of waters are very different, and as presented in Chapter 1 blowdown water contains large concentrations of various inorganic compounds. Moreover, since the biodispersant concentration should be 4 mg/l, concentrations which is 100 times higher than the CMC, the surface tension should be, due to the biodispersant only, around 50 mN/m. For the new sample the surface tension was slightly lower than the surface tension of the demiwater.

The surface tension measurement in the cooling tower blowdown is not giving any relevant information about the concentration of the biodispersant present. It seems that the chemicals dosed in the cooling tower which concentrate after the 5 cycles of recirculation are also not affecting very much the surface tension. The difference between the surface tension values for the new and old samples can be explained by the fact that in the fresh blowdown there were more particles/compounds which

decreased the surface tension value. By storing the CTBD for a long time it might be that some of the particles/compounds have settled and some of the chemicals might have stabilized in time and are not affecting the surface tension.

## 3.2.3. Surfactant charge

For ionic surfactants, easier and less time consuming method to determine the CMC concentration is to measure the electro-chemical measurements function of concentration. This method is based on finding a breaking point on the curve which describes the conductivity as a function of concentration. The conductivity of any solution is dependent on its concentration, but the point where micelle formation starts, that is where the shape of the slope changes and does not have a liner trend anymore. In Figure 3-8 is presented an example of the relation between conductivity and solution concentration of an ionic surfactant (Oremusova & Lengyel, n.d.).



Figure 3-8 Typical shape of the conductivity-concentration relation for an ionic surfactant

In order to confirm the CMC value of the biodispersant, measurements of the conductivity function of concentration have been made. In Figure 3-9 are presented the obtained results.



Figure 3-9 Relation between biodispersant concentration and onductivity

As it can be seen from Figure 3-9 the relation between the biodispersant concentration and conductivity is linear. There is no point in the graph were the shape changes sudden, so the surfactant is not ionic.

#### **3.3. TOC of the biodispersant in demiwater solutions**

In order to find more information about the biodispersant, the total organic carbon (TOC) from different biodispersant solutions, were also measured. The concentrations prepared were from 1 mg/l to 10 mg/l biodispersant. Based on the initial assumption was that the biodispersant is an organic surfactant, the relation between TOC and solutions was also assumed to be linear, since the biodispersant is organic. In Figure 3-10 can be seen the obtained results measured in relation with the biodispersant solutions. Again, no concludent results were obtained. The variation in TOC is again based on the fact that Nalsperse is a very difficult solution to handle. The varying values can be because the solution was not properly mixed and the biodispersant molecules were not properly dispersed, in some cases the solution stuck to the walls of the pipette etc.



Figure 3-10 TOC values measured in demiwater-Nalsperse solution relation with the biodispersant concentrations

## 3.4. Conclusion

In this chapter more insight about what the biodispersants are, their action, composition and how they are characterized was gained. After surface tension measurements were done, together with conductivity measurements it was concluded that Nalpserse-7348 is a non-ionic surfactant.

The UV-Vis absorbance was also measured and compared with the absorbance of known non-ionic surfactants, but none matched. Since the producer does not give any information about the composition of the biodispersant and because the absorbance did not match most of the known non-ionic surfactants used as biodispersants commercially, can be assumed that Nalsperse-7348 has a new recipe or is a mixture of two or more non-ionic surfactants.

The critical micelle concentration or CMC of any surfactant represents the concentration at which aggregates become soluble in aqueous solution. CMC is then surely a concentration range above which any added surfactants appear in micelle form. Then again, below the CMC there is not a high enough density of surfactant that can precipitate spontaneously into a different phase. This means that the biodispersant molecules are flowing freely and float or attach (Myers, 2006). Figure 3-12 shows a simple explanation of the molecule dispersion at concentrations below and above the CMC.



Figure 3-11 Schematic representation of the biodispersant molecules dispersion below and above the CMC

Biodispersant molecules reach saturation when the CMC is reached and micelles start forming. That is when the solubility of the surfactant in aqueous solution was exceeded. The energy required to keep the surfactant in solution is no longer the energy state and for this energy to be lowered the surfactant is precipitated out (Wikipedia, 2015). Therefore, the more surfactant is added the more saturated the water becomes with micelles. Maximum dosed concentration should be equal or around the CMC. Lowering the concentration should not influence the microbiological growth. Though, to confirm this statement, a lower concentration should be dosed in the cooling tower to see what the effect is on the microbial populations.

## 4. Materials & methods

Three separate experiments were performed: coagulation-flocculation, adsorption and UF. All experiments were done in the Water Lab in the Faculty of Civil Engineering. Several types of water have been used: demineralized water, Schie canal water and cooling tower blowdown (CTBD). The CTBD water was collected from Elsta, while Schie water was collected from the pipe which delivers canal water into the laboratory.

For most of the experiment pH, EC, turbidity and TOC were measured. Coagulation experiment required an extra iron measurement. A description of the materials used and the principles behind the measurement are presented in this chapter.

## **4.1.1.** Force tensiometer

Force tensiometer is used for the measurement of the surface tension. The apparatus used was Sigma 700. This instrument can measure surface and interfacial tension with a platinum Du Nouy, Wilhelmy plate or rod ring. It is well suited for dynamic contact angle and wettability measurements of heavy solids powder samples (Biolin Scientific, n.d.).

The surface tension was measured with the Du Nouy ring method. In Figure 4-1 is shown the Du Nouy ring (Imeter, n.d.).



Figure 4-1 Du Nouy ring

With the Du Nouy ring the maximum weight of the liquid which is lifted by the ring while being pulled out of the liquid surface is measured. The force necessary to lift the ring is proportional with the surface tension and defined by Equation 4-1:

Equation 4-1

$$\gamma = \frac{F}{4\pi R}$$

Where:

Y	=	surface tension
Ŕ	=	radius of the ring
F	=	force required to lift the ring

The force F depends on the dimensions of the ring and on the contact angle between the surface of the ring and the liquid. Accurate measurements can be obtained only if the ring is completely wetted by the liquid. Correct determinations of the force can be done by rising and lowering the ring close to the rupture of liquid lamella hanging from the ring. Before the rupture the lamella force applied on the ring decreases seriously. The balance feels the force and lowers the ring in order to prevent the lamella rupture (KSV, n.d.).

Measuring steps (Biolin Scientific, n.d.) are presented in Figure 4-2:

- 1. Ring is placed just above the surface and the balance is zeroed.
- 2. The ring is lowered and touched the surface and gets wet resulting in positive force.
- 3. The ring is pushed through the surface into the liquid by a negative force.
- 4. When the support of the ring is wetted some positive force is kept.
- 5. The ring is being pulled out of the liquid (the sample cup is being lowered) until the ring touches the surface of the liquid and the force is increasing once again (the surface tension of the liquid prevents the ring penetrating the surface).
- 6. The ring is being pulled out and liquid is attached to it, while pulling until the maximum force is reached. When the force is maximum, the volume of the liquid being pulled up is maximum as well, resulting in the detachment of the ring from the liquid.
- 7. The force necessary to pull the ring out of the liquid is proportional to the surface tension of the liquid. The higher the force is the higher the surface tension is.



Figure 4-2 Steps for measuring the surface tension

## 4.1.2. pH and electro-conductivity (EC)

pH and EC were measured with specific sensors which were connected to inoLab<sup>®</sup> Multi 720. This device is used for the measurement of pH, ORP (oxygen, conductivity and salinity) and temperature. inoLab<sup>®</sup> Multi 720 is suitable for standard measurements due to the multifunction display. The pH electrode used (SenTix<sup>®</sup> 41) is compatible with the multimeter. SenTix<sup>®</sup> 41 is a portable electrode which has a built-in temperature probe. Conductivity electrode was also portable, TetraCon<sup>®</sup> 325. For both parameters, pH and EC, for the measurement, the electrodes had to be submerged in the liquid and wait for the value to be stabilized. pH and EC were recorded when the value displayed was constant for about 20-30 seconds.

## 4.1.3. Turbidity

Turbidity was measured with 2100N Laboratory Turbidimeter. Samples were added in the measuring vials and inserted in the turbidimeter. 2100N turbidimeter is equipped with stable halogen-filled, tungsten lamp and 860 nm LED light source to meet the standards for reporting a turbidity measurement. The optical system of the machine has a tungsten-filament lamp, lenses and apertures which focus the light, a 90-degree detector, forward scatter light detector, a backscatter detector and a transmitted-light detector. The device can measure turbidity values lower than 40 NTU to be done with to 90 degree scatter light detector or 4000 NTU using the complete set of detectors (Hach Lange GmbH, 2013). In Figure 4-3 is a simplified explanation of the measuring principle of the turbidimeter.



Figure 4-3 The principle behind the turbidity measurement

#### 4.1.4. Iron

Iron concentration in water can be determined using iron kits, Merk Millipore Spectroquant® 100796 Iron test, photometric method with a range between 0.010 and 5.00 mg/l Fe. This method gives the total iron concentration by measuring in two steps the Fe<sup>2+</sup> and Fe<sup>3+</sup> concentrations. Iron ions are reduced to Fe<sup>2+</sup> ions by ascorbic acid. Within a buffered media ions react with 1,10-phenanthroline which forms a red complex that can be determined photometrically (Merk KGaA, n.d.).

For the determination of the iron concentration the sample has to have a pH between 2 and 8. If the pH is not within this range it needs to be adjusted by sodium hydroxide solution or nitric acid. 8 ml of solutions are necessary for the measurement. The 8 ml were pipetted in a test tube and 1 drop of Fe-1 (reagent 1) was added to the mix together with 0.5 ml of Fe-2 (reagent 2), which were well mixed and left for 5 minutes to react. After the reaction was complete solution was transferred to a measuring cell. The size of the cell depends by the iron concentration range expected (Merk KGaA, n.d.). In Table 4-1 are shown the available concentration ranges of the measuring cells.

Concentration range	Cell size
mg/l Fe	тт
0.10-5.00	10
0.05-2.50	20
0.010-1.00	50

Table 4-1 Iron measuring ranges and their corresponding measuring cell sizes

The proper cell with sample was inserted in the photometer NOVA 60 A Spectroquant® together with the appropriate measuring cell which determines the parameter to be measured by scanning the bar code. This first measurement is the  $Fe^{2+}$ .  $Fe^{3+}$  can be measured after the  $Fe^{2+}$  sample was used. A dose of Fe-3 (reagent 3) needs to be dosed in the sample and properly mixed until all reagent is dissolved. After 10 minutes, reaction time, the  $Fe^{3+}$  concentration can be read. The final iron concentration is given by the sum of  $Fe^{2+}$  and  $Fe^{3+}$ .

Photometers work based on the absorption principle (Figure 4-4). When a ray of light passes through a colored solution, its intensity is decreased, or adsorbed by the solution. Absorption takes place at different wavelengths, based on the solution. Monochromators (narrow-band interference filters, lattices) are used to choose the wavelength from the spectrum (Merk KGaA, 2014):

- Wolfram-halogen lamp for VIS spectrum
- Deuterium lamp for UV spectrum
- Xenon lamp





Absorption intensity is characterized by transmittance. 100% transmittance means that the light was not adsorbed at all by the solution. If the light was completely adsorbed in the solution this means 0% transmittance. Transmittance is characterized by Equation 4-2:

$$T = \frac{I}{I_0}$$
 Equation 4-2

Where:

Absorption of light is characterized generally by absorbance, which is also directly related with the concentration of the adsorbing substance. Absorbance and transmittance are defined through Equation 4-3:

$$A = -logT$$
 Equation 4-3

With:

A = absorbance

Furthermore, the relation between absorbance and concentration is given by the Lambert-Beer law, and is dependent on the thickness of the absorbing layer of the measuring cell. Equation 4-4 describes the Lambert-Beer law:

$$A = \varepsilon_{\lambda} \cdot c \cdot d \qquad \qquad \text{Equation 4-4}$$

In which:

ε <sub>λ</sub>	=	molar absorptivity	[l/mol/cm]
d	=	path length of the cell	[cm]
С	=	concentration of the analyte	[mol/l]

## 4.1.5. TOC

Total organic carbon (TOC) represents the amount of carbon bound in an organic compound. TOC value is measured using Schimadzu TOC-L Analyzer. The machine measures the amount of total

carbon, inorganic carbon and total organic carbon in water. Oxidative combustion-infrared analysis is a TOC measurement often used.

For the TOC measurement 30 ml of sample needs to be added in carbon free vials. Sample is then acidified by adding 1.6 ml of analytical grade hydrochloric acid (2 M). The vial will be sealed with aluminum foil and cap and stored in the fridge until measuring.

TOC-L analyzer operates on the principle of  $680^{\circ}$  combustion catalytic oxidation method. This method makes it possible to efficiently oxidize easily-decomposed, low-molecular-weight organic compounds and also hard-to-decompose insoluble and macromolecular organic compounds (Schimadzu, 2014).  $680^{\circ}$ C combustion catalytic oxidation is attaining total combustion of samples by heating them up to  $680^{\circ}$ C in an oxygen-rich medium inside the total carbon (TC) combustion tubes, which are filled with platinum catalysts. In order to boost operation, pretreatment and post-treatment of the samples using oxidizing agents is required. The carbon dioxide produced due to oxidation is detected by an infrared gas analyzer (NDIR). The apparatus has a detection limit of 4 µg/l, the highest for the combustion catalytic oxidation method. Figure 4-6 present a schematic representation of the TOC measurement using the 680° combustion catalytic oxidation method and the NDIR method (Schimadzu, 2014).



Figure 4-5 Schematic representation of the steps taken for the TOC measurement

The sample is sent to the combustion furnace, which is equipped with purified air. The sample is further heated to 680°C with a platinum catalyst, it decomposes and is transformed into carbon dioxide. Formed carbon dioxide is after cooled and dehumidified and detected by the NDIR.

First TC concentration is determined by comparison with the calibration curve formula. During the second step the oxidized sample is being sparged, so that the inorganic carbon (IC) is converted to carbon dioxide. Thirdly the concentration of inorganic carbon is determined with the NDIR. Secondly, the concentration of organic carbon is calculated by subtracting the inorganic carbon concentration from the TC concentration (Schimadzu, 2014).

Organic carbon in all samples is measured via non-purgeable organic carbon. Non-purgeable organic carbon (NPOC) is the total organic carbon left in the acidified sample after purging the sample (Wikipedia, 2009). Measuring NPOC is the same as TOC measurement using acidification and sparging. Figure 4-7 shows a schematic representation of the method (Schimadzu, 2014).



Schematic Diagram of NPOC Measurement

Figure 4-6 NPOC measurement steps

Sparging acidified samples the IC is converted to carbon dioxide and removed, and TOC is determined by measuring the TC in the sample. After the carbon dioxide from the IC is removed, purgeable organic carbon (POC) is also removed. The TOC resulting using this method is called NPOC and offers more detailed TOC measurement (Schimadzu, 2014).

# 5. Coagulation/flocculation

In this chapter is presented the theoretical background regarding coagulation/flocculation processes in order to understand how this basic particle and colloidal removal mechanism works. As it was presented before, the floc formation in the pilot is not performing very well, so to improve it, some factors which can affect the binding and growth of flocs are presented.

Secondly the experimental planning is presented and thirdly, the results obtained in the coagulation/flocculation experiments are explained. There were several experiments done. It was assume that the biodispersant would decrease the efficiency of the coagulant by preventing particles to stick to each other. So a comparison of the coagulant was made in water with and without biodispersant.

## 5.1. Theoretical background

In any water or wastewater materials like suspended/dissolved, organic/inorganic matter, bacteria, algae or viruses are present. The origins of these matters are from land erosion, dissolution of minerals, vegetation decay, waste damage etc. (Bratby, 1980).

The solids present before can be present in 3 forms: suspended particles, colloids and molecules. Coarse or fine suspended particles can be easily removed by filtration or settling, while molecules are generally removed by reverse osmosis. Colloidal removal can be more difficult in water treatment (Binnie, et al., 2002).

Colloids can be mineral substances, small aggregates of precipitated and flocculated matter, silt, bacteria, plankton, viruses, biopolymers and macromolecules. Smaller particles are able to keep a dispersed or dissolved state due to their characteristics which stimulate their stability (Bratby, 1980). Colloidal particle can be characterized by their size (0.001 micron to 1 micron) or by their affinity for the water (hydrophobic or hydrophilic) (Qasim, et al., 2000). Hydrophobic colloids are unstable and do not reform easily as colloids after the particles aggregate (clay particles, non-hydrated metal oxides), while hydrophilic colloids when are being mixed with water form colloidal solutions which cannot be destabilized (soap, wallpaper paste) (Binnie, et al., 2002).

Removal of colloids can be done by changing the surface properties of the particulate matter (increasing the adsorptivity of the particles to a given filter medium) or by precipitating dissolved materials (creating particulate material for which separation by sedimentation or filtration is suitable) (Bratby, 1980). For hydrophobic colloids, the forces keeping the particles apart need to be overcome. When these forces have been overcome, the particles collide forming larger particles which do not split into colloids again (Binnie, et al., 2002). The transformation from a stable state of a given dispersion or solution to an unstable state is called destabilization (Bratby, 1980). Particle destabilization and formation of larger particles is called coagulation, while flocculation is the mixing mechanism which increase the collisions between the particles formed during coagulation, and results in the formation of larger particles that are easily removed (Binnie, et al., 2002).

For coagulation chemicals are added to the water, which are able to break down the stabilizing forces and boost the destabilizing forces. The chemicals which are traditionally added are metal salts like aluminum sulfate (alum), ferric sulfate, ferric chloride and ferrous sulfate. More recently polymers (long-molecular-chain organic compounds) have been used together with metal salts for improving the coagulation process (Qasim, et al., 2000).

When iron or aluminum coagulant is added to the water, several reactions are triggered. First trivalent iron or aluminum ions are formed, which hydrate and form complexes of the metal with the water molecules. The water molecules are later replaced by hydroxide ions, creating more complexes. Depending of the pH value and coagulant concentration, iron or aluminum will start precipitating hydroxide flocs. Intermediate complexes which are formed have a high efficiency in the double layer compression and in charge neutralization, but have a very short life. This is the reason why proper mixing is required when using iron or aluminum as coagulant. If the mixing is not efficient higher coagulant doses have to be added in order to have proper coagulation (Binnie, et al., 2002).

pH monitoring and control is very important for coagulation with iron or aluminum. Ferric hydroxide and aluminum hydroxide have very low solubility at certain pH values, for given waters. Consequently, by controlling the pH the precipitation of metal hydroxides is controlled and the charges of the intermediate products formed by dosing metal salts. Generally, the goal is to coagulate at pH values where the solubility of iron or aluminum hydroxide is minimum. This certain pH value can be determined from solubility diagrams for particular water at a given temperature. These diagrams are impractical and cannot be applied for all types of water, so for the best pH value for the precipitation of hydroxides jar tests should be performed. In Figure 5-1 is presented the solubility diagram for ferric chloride, indicating how solubility is varying with the pH. The minimum solubility of iron is as seen in the diagram, is between 7 and 10. At lower pH values the solubility increases fast, while at higher pH values the solubility increases less rapid. When iron is used as coagulant, if the pH value is kept around 7, than dissolved iron will not pass to the next treatment steps (Binnie, et al., 2002).



Figure 5-1 Ferric chloride coagulation diagram

Ferric chloride is corrosive and it is known as a substance difficult to handle, store or dose. It can be found in a liquid or solid form, but the liquid solution is more difficult to store and dose. It is more pH tolerant than alum and is more efficient in certain processes, such as decolorization of waters with low pH, manganese removal at high pH or clarification of waters of low temporary but high permanent hardness (Binnie, et al., 2002).

## 5.1.1. Coagulation of dissolved solids and chemical precipitation

Dissolved solids in natural waters, most of the times consists of ions of dissolved minerals like calcium, magnesium, sodium, iron and manganese or in combination, such as bicarbonates, carbonates, chlorides, sulfates, nitrates, phosphates, fluorides etc. Most of the ionic compounds found in waters (such as iron, manganese, calcium, and magnesium) can be removed from water mostly by chemical

precipitation; on the contrary, molecular compounds cannot be removed by precipitation (Qasim, et al., 2000).

When ionic compounds dissolve in water, the ions which form the compound dissociate. In other words, when  $Ca(HCO_3)_2$  is dissociated,  $Ca^{2+}$  and two  $HCO^{3-}$  ions are formed. These ions are both free to react with other ions in the solution. The compound will dissolve until it will reach a limiting value when the solution is saturated. Solubility product is the term used for the calculation of solubility of an anionic compound. Equation 5-1 and 5-2 are used for the calculation of solubility (Qasim, et al., 2000):

Equation 5-1

 $K_{Sp} = [M^+] \times [X^-]$ 

Equation 5-2

With:

VVICI II		
K <sub>Sp</sub>	=	solubility product constant of compound MX
[M <sup>+</sup> ]	=	molar concentration of the cation
[X <sup>-</sup> ]	=	molar concentration of the anion

In the case the product of the molar concentration of ions of a compound is lower than the solubility product, the solution is undersaturated. Then again, if the product of the molar concentration of the ions is higher than the solubility product, then the solution is supersaturated and precipitation of the compound will take place until the product of the molar concentration equals the solubility product (Qasim, et al., 2000).

## 5.1.2. Aqueous chemistry of iron chloride salt

Coagulation processes are taking place when a coagulant (metal salt, most often) is added to water. Most common used coagulants are ferric sulfate, iron chloride, alum (Qasim, et al., 2000).

Ferric chloride can be purchased in a liquid, crystal or anhydrous form. The reaction of iron chloride with the alkalinity of water is characterized by the following reaction (Bratby, 1980):

$2\text{FeCl}_3 + 3\text{Ca}(\text{HCO}_3)_2$	$\leftrightarrow$	$2Fe(OH)_3 + 3CaCl_2 + 6CO_2$
$2\text{FeCl}_3 + 3\text{Ca(OH)}_2$	$\leftrightarrow$	$2Fe(OH)_3 + 3CaCl_2$

It is important to mention that iron chloride will produce about 0.66 mg of  $Fe(OH)_3$ , which precipitates and consumes about 0.92 mg of alkalinity (CaCO<sub>3</sub>). Due to the alkalinity consumption CO<sub>2</sub> is produced and the pH will drop after coagulation, function of the coagulant dose and initial alkalinity of the raw water. Stoichiometric equations can be used to calculate the coagulant dose, but the actual amount of coagulant required for colloid destabilization depends on the stoichiometric reaction, pH, temperature, ions present in the water, types and properties of particles, mixing energy input and the effective content of metal ions in the coagulant (Qasim, et al., 2000).

At low pH values ( $\leq$ 4.5) carbon dioxide is in equilibrium and alkalinity is not present. At pH values between 4.5 and 8.3 the first reaction shifts to the right. The carbon dioxide concentration starts to drop and bicarbonate ions start to form. When the pH value is higher than 8.3, bicarbonates convert to carbonate ions, with a maximum concentration taking place at pH 10.5 (Qasim, et al., 2000).

pH can be raised by adding ionic compounds which contain hydroxide ions. The chemicals mostly used are lime (CaO), hydrated lime (Ca(OH)<sub>2</sub>), soda ash (Na<sub>2</sub>CO<sub>3</sub>) or caustic soda (NaOH). The chemical reaction of lime softening using caustic soda is presented below:

CO <sub>2</sub> + NaOH	$\leftrightarrow$	$Na_2CO_3 + H_2O$
$Ca(HCO_3)_2 + 2NaOH$	$\leftrightarrow$	$CaCO_3 + Na_2CO_3 + 2H_2O$
$Mg(HCO_3)_2 + 4NaOH$	$\leftrightarrow$	$2Na_2CO_3 + 2H_2O$

For the calculation of the sodium hydroxide dosage (for the softening reaction), the following reactions are used:

 $\begin{array}{rcl} \mbox{FeCl}_3 + 3NaOH & \leftrightarrow & 3NaCl + \mbox{FeOH}_3 \\ \mbox{Fe}^{3+} + 3Cl^{-1} + 3Na^{+1} + 3OH^{-1} & \leftrightarrow & 3Na^{+1} + 3Cl^{-1} + \mbox{FeOH}_3 \\ \mbox{Fe}^{3+} + 3OH^{-1} & \leftrightarrow & \mbox{FeOH}_3 \end{array}$ 

Taking out the common ions (Na<sup>+1</sup> and Cl<sup>-1</sup>) from the reaction results the net ionic reaction. This means that for every  $Fe^{3+}$  ions, there are 3 ions of  $OH^{-1}$  needed to neutralize the acidity created by the  $Fe^{3+}$  ions.

For the design of the best coagulation process, first a selection of the right coagulant and the dosage has to be made, followed by the design of rapid-mixing and flocculation basin. Selection of coagulant and doses are best made experimentally by jar tests (Qasim, et al., 2000).

## 5.1.3. Rapid mixing

The main objective of coagulation and flocculation is to produce particles big enough to be removed by sedimentation, flotation or filtration. Rapid mixing is the stage in the coagulation/flocculation process when the chemicals are added into the effluent. Rapid mixing is one of the most important steps in the process, because besides dispersing the coagulant efficiently, during this step the destabilization reactions take place and the primary flocs are created. The time required for the mononuclear complexes to form is about  $10^{-10}$  s, so a retention time longer than 5 s will not increase the flocculation efficiency (Bratby, 1980).

The rapid mixing devices are designed based on the velocity gradient (G-value). This parameter measures the amount of energy dissipated in the water. Higher energy input results in better mixing (HDR, 2002). The velocity gradient can be determined suing Equation 5-3:

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

Equation 5-3

Where:

G	=	velocity gradient	[s⁻¹]
Р	=	power input	[W]
μ	=	dynamic viscosity	[Pa·s]
V	=	volume of water	[m³]

For a high turbidity removal, a high G-value (with the same mixing time) or a higher GT (the product between the G-value and residence time, t) results in a denser floc (HDR, 2002). High G-values resulted in less coagulant dosage and bigger floc formation under certain conditions: chemical dosage is minimized by maximizing the effectiveness of coagulation/flocculation, effective coagulation is necessary since the retention times in the clarification step are short and feed water has to be properly conditioned (Binnie, et al., 2002). Nevertheless, that does not mean that higher G will result in denser flocs, because at high shear rates the previously formed flocs can be broken (HDR, 2002). If the residence time in the rapid mixer is higher than 1 or 2 minutes or, if the G-value is reduced suddenly, floc formation will be reduced during flocculation (Bratby, 1980).

In the relation above the power imparted to the water, is given by the power of the mixer and can be calculated from Equation5-4:

Equation 5-4

۱۸/	h-0	-	
vv	ne	ie.	

which			
Np	=	power number of the impeller	
d	=	impeller diameter	[m]
ρ	=	mass density of the fluid	[kg/m <sup>3</sup> ]
n	=	impeller speed	[rps]

Mixing equipment for metal coagulants are typically designed for high G-values (1000 s<sup>-1</sup> and higher). To minimize the coagulant dose where destabilization is induced by charge neutralization or double layer compression a G-value higher than 5000 s<sup>-1</sup> would be necessary. Retention time in the mixing zone has to be very short since sufficient mixing is provided (Binnie, et al., 2002).

Most common used rapid mixing devices are mechanical mixer with an impeller or propeller, or static mixers. Mechanically agitated mixers use an impeller or a propeller to create turbulence in the mixing chamber. The impeller or propeller used in a rapid mixer depends on the shape of the tank or the flow pattern wanted in the basin.

This type of mixers requires a lower G-value and the retention time cannot be very low. The coagulant addition has to be done in a region where it can be fast dispersed into the full flow (Binnie, et al., 2002).

Static mixers create turbulence with hydraulic jumps, baffles, turbulent flow in a pipe or channel, or due to contractions and enlargements in a pipe (Qasim, et al., 2000). The head drop in the static mixer is usually about 0.05 bars. Static mixers are installed in pressurized pipes and have a length twice or three times bigger than the diameter. They are not recommended for large flow variations since they are optimized for treating specific flows (Binnie, et al., 2002). In Table 5-1 are presented the advantages and disadvantages of the mechanical and static mixers (Qasim, et al., 2000):

Type of mixer	Advantages	Disadvantages
Mechanical mixer	Agitation independent of flow	Additional equipment necessary for maintenance
	Adjustable agitation	Reliability depends of the equipment failure
	High flexibility in operation	
Static mixer	Little or no maintenance	Agitation dependent on flow
	Reliable	High head loss
		Not very flexible in operation

Table 5-1 Comparison between mechanical and static mixer

## 5.1.4. Flocculation

Hence, after the small particles have been formed due to coagulation, it is necessary to have a following flocculation step. During flocculation the primary particles are persuaded to approach close together, make contact and slowly form large agglomerates (Bratby, 1980). Flocculation is also an

important for precipitation step. The precipitate is formed in the beginning from small particles which are not readily settleable. Gentle mixing during flocculation, promotes the floc growth to a size which makes it easier to be removed by sedimentation or filtration (floc size between 0.1 to 2mm) (Qasim, et al., 2000).

Flocculation occurs in two stages: perikinetic flocculation and the orthokinetic flocculation. Perikinetic flocculation represents the particle growth because of the inter-particle contacts due to Brownian motion. Whereas, orthokinetic is related to the particle growth as a consequence of inter-particle contacts due to fluid motion (Qasim, et al., 2000).

Flocculation during perikinetic flocculation is a natural random process. During this step flocculation starts immediately after destabilization and it is over in within seconds, considering that there is a limiting floc size above which Brownian motion has no effect (Bratby, 1980). Orthokinetic flocculation is induced by velocity gradients in the water. These velocity gradients can be created by putting the liquid in motion by passage around baffles or mechanical agitation in a flocculation basin, by tortuousing the path through interstice of a granular filter bed, when the flocs are big enough by sedimentation in a settling tank (Bratby, 1980).

The main parameter which influences the rate of orthokinetic flocculation is the velocity gradient applied and time of flocculation. These parameters determine the rate and extend of particle aggregation and the rate and extent of breakup of these aggregates (Bratby, 1980).

There are 2 major types of flocculators: hydraulic and mechanical flocculators. Hydraulic flocculator use cross-flow baffles or 180° turns to produce the required turbulence. The main purpose of the hydraulic flocculator is to achieve gentle, uniform mixing that will not break the floc. Mechanical flocculators are using mixers to create turbulence. The mixers used usually in flocculation basins are horizontal-shaft paddle-wheel flocculators. The turbine type flocculators are axial- and radial- flow vertical and horizontal (Qasim, et al., 2000).

Agitation applied in flocculators is much lower than the agitation applied in rapid mixers. Generally the velocity gradients for flocculators range between 15 to 60 s<sup>-1</sup>.Flocculation basins are designed with several compartments in series and velocity gradient successively decreasing. A high G-value in the first compartment generates a fast transformation of the primary particles into higher-density flocs. ; a lower G-value in the following compartments leads to a buildup of progressively bigger flocs, for better settling (Qasim, et al., 2000).

Retention time in the flocculator is much longer compared to the rapid mixer (between 20 and 60 minutes). The main parameter which for the flocculation tank is the G value, since the number of particles colliding in the basin is proportional with GT (Qasim, et al., 2000).

In the beginning, when particles are lower than 0.5  $\mu$ m, flocculation is influenced by the Brownian motion. As particles grow, collision must be enhanced by stirring. Stirring energy depends though, by the size and strength of the flocs (Binnie, et al., 2002).

## 5.2. Experimental procedure

## 5.2.1. Objective of the experiment

The objective of the jar-test experiment is to compare the coagulant efficiency in the cooling tower blowdown under different conditions, using ferric chloride as coagulant. Different concentrations of iron chloride were added to the blowdown in order to check which quantity of coagulant is appropriate for this type of water. It is known that coagulation with metal coagulants is sensitive to pH. Experiments with and without pH adjustment were done also to observe the difference between the results.

## 5.2.2. Experimental set-up

Jar-testing installation consists out of 6 identical 2 I beakers, equipped with stirrers. Solution of iron chloride with different concentrations was added in the jars in order to find out which is the optimal  $Fe^{3+}$  concentration for this type of water. Hydrolysis reactions occur with the addition of ferric chloride, resulting in iron ions acting as acids and reducing the pH. For this situation a base was dosed (NaOH) to increase the pH, because the ferric chloride coagulation is efficient at a pH ranging between 6.5 and 8. In Figure 5-2 is presented a graphical representation of the jar-test installation.



Figure 5-2 Graphical representation of the jar-test set-up

The jar test was trying to imitate the operating conditions from the pilot plant. In the pilot the coagulant is added first and after, a static mixer is following in the pipeline. The static mixer operates at a velocity gradient of  $3021 \text{ s}^{-1}$ , while the residence time is 0.86 s. For the jar-test the same conditions were tried to be simulated. A G-value of  $3021 \text{ s}^{-1}$  corresponds with 500 rpm in the jar test.

In the laboratory, the jar tests were performed with the flocculator JLT 6, produced by Velp Scientifica. The maximum shear rate at which the installation can operate is 300 rpm. All positions have identical speed, which can be set from an electrically controlled DC gear motor. Each position has also 2 dosing test tubes and a siphon with Erlenmeyer flask. One of the test tubes is for dosing the coagulant, while the other is for dosing acid or alkaline solution for the pH correction.

There is no clear relation between the retention time of the liquid in the mixer and the shear rate. It is assumed that there is a relation though between the retention time and the shear rate since rapid mixing for long periods of time may have a negative effect on the subsequent flocculation (Bratby, 1980). In the static mixer the retention time is 0.86 s. It can be assumed that since the shear rate in the jar-test is almost half of the shear rate in the static mixer, the retention time in the jar should be double the retention time in the static mixer.

In the report of Dion (Wirokarso, 2014) rapid mixing was performed for 2 minutes at 200 rpm. 2 minutes retention time in the rapid mixing is quite a long time. 0.86 s or 1.72 s is impossible to simulate in the jar test so it was concluded that the rapid mixing should be performed for 30 s. 30 s retention time for the rapid mixing is a time which can be easily reproduced, it is longer than the actual time in the static mixer but it is more appropriate than the 2 minutes used by DION.

The flocculator from the pilot was costume made and has 3 compartments. Because the distance between the blades differs in the 3 compartments the velocity gradient for each of the compartment differs.

Equation 5-5

## 5.2.3. Compartments

In the first compartment the distance between the stirrer and the end of the blade is 250 mm. Several calculations were made to determine the velocity gradient at different rotation speeds.

Taking into consideration the characteristics of the compartment, the G-value for different rotational velocities have been calculated. For 15 rpm the velocity gradient is 5 s<sup>-1</sup>. In order to have the same velocity gradient in the jars the rotation speed needs to be calculated. In Figure 5-3 is presented the influence between the rotational speed and the velocity gradient for the apparatus used in the experiment, at 20 °C for a volume of 1.8l.

The relation between them is given by equation 5-5:

$$\log(G) = 1.345 \log(RPM) - 0.345$$

From this relation the RPM corresponding for 5 s<sup>-1</sup> was determined to be 15 rpm.

In the second compartment the distance between the stirrer and the blade is 200 mm. In this compartment the G-value for 15 rpm is 17.4 s<sup>-1</sup>. The G-value in the jar-test was determined to be 11 rpm.



Figure 5-3 Relation between G-value and rotation speed of the stirrer

In the third compartment there is the shortest distance between the stirrer and the blade, 150mm. G-value in the flocculator at 15 rpm is 5 s<sup>-1</sup>, while in the jar-test for the same velocity gradient a stirring velocity of 5 rpm would be required.

The residence time of the effluent in the flocculator is 21 minutes. Taking into consideration the fact that the flocculator is divided into 3 compartments it was calculated that, in each compartment the water stays for 7 minutes.

## 5.2.4. Procedure

For analyzing the performance of ferric chloride as a coagulant in the cooling tower blowdown, several experiments have been performed. Cooling tower blowdown has been collected from the ELSTA site. The company has agreed to stop the biodispersant dosing for about a month so that Evides can run the pilot plant on blowdown without biodispersant in order to check if the biodispersant is indeed fouling the membrane and inhibiting coagulation. Collected water was biodispersant free. In some of the experiments biodispersant was added manually in the jars in order to observe the difference in coagulation in the blowdown with and without biodispersant. Several experiments have been performed:

- Simple ferric chloride dosing in biodispersant free blowdown
- Ferric chloride dosed together with NaOH in biodispersant free blowdown
- Ferric chloride dosed in water with biodispersant
- Ferric chloride and NaOH dosed in water with biodispersant
- Comparison between the coagulation performance in jars with and without baffles.

Before and after each experiment pH, turbidity, electrical-conductivity (EC), iron concentrations and TOC were measured. Based on these measured concentrations the best coagulant dose can be determined.

The jars used for the experiments are 2l jars with baffles. 1.8 l of CTBD was used in all experiments. The FeCl<sub>3</sub> quantities necessary to reach 5, 10, 15, 20, 25 and 30 mg/l Fe<sup>3+</sup> was measured and added in plastic eprouvettes. From each corresponding jars, CTBD was added to the eprouvettes to dissolve the FeCl<sub>3</sub>. The eprouvettes were agitated so that the FeCl<sub>3</sub> would dissolve faster. The eprouvettes are fixed on the rack, the jars placed on their position and the stirring started at 300 rpm. Stirring rates are different so a timer is required. After the coagulant was added the timer was started for 30 seconds. After the 30 seconds mixing at 300 rpm, the stirring rate was changed to 15 rpm. 15 rpm mixing was done for 7 minutes, followed by 7 minutes of stirring at 11 rpm and 7 minutes stirring at 10 rpm, since 5 rpm was not possible (minimum stirring rate of the apparatus is 10 rpm). After 21.5 minutes of stirring, the stirrers are stopped and taken out of the water to allow settling. Settling is done for 21 minutes. This procedure is done for all the experiments.

## Iron dosage variation (cooling tower blowdown without biodispersant)

The effluent used for this experiment is CTBD water.

## Iron dosage variation (cooling tower blowdown with biodispersant)

The difference was that 4 mg/l biodispersant were added to each jar in order to observe if biodispersant has any influence on the coagulation-flocculation. Biodispersant addition was done before the ferric chloride dosing and the solutions were mixed for a couple of minutes, before the coagulant dose.

## pH adjustment before the coagulant dosage

From the previous experiments it can be observed how much the pH drops with the ferric chloride addition. Taking into consideration the drop in pH, NaOH must be added in order to increase the pH. The pH must be increased with a value which is equal with the decrease in pH observed in the experiment without NaOH addition. Ferric chloride concentrations and operating conditions were the same as in the previous experiment.

## pH adjustment after coagulant dosing

1.8 l of cooling tower blowdown were used with the same variation of ferric chloride concentrations (5-30 mg/l  $Fe^{3+}$ ). After the ferric chloride dose, when the pH was stabilized, NaOH was added again in

order to increase the value of the pH until around 7. The operating conditions were kept the same as in the previous experiments.

## Chemical solution

Stock solutions of ferric chloride was prepared by dissolving ferric chloride hexahydrate salt in demi water. The concentration of the solution was chosen so that the volumes corresponding to the dosage could be easily and accurately measured. Different iron concentrations were dosed in the jars: 5, 10, 15, 20, 25 and 30 mg/l Fe<sup>3+</sup>. The ferric chloride solution was prepared using ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O). Solutions were dosed in all 6 jars in the same time. Dosing was done from plastic eprouvettes. The tubes which have been used have a volume of 14 ml, but solution of 9 ml were prepared. In Table 5-2 are presented the necessary FeCl<sub>3</sub>\*6H<sub>2</sub>O masses which have to be dissolved in 9 ml of demineralized water, in order to have the desired Fe<sup>3+</sup> concentrations.

Concentration	Dilution	Iron c	oncentration	Mass FeCl <sub>3</sub> .6H <sub>2</sub> O diluted
mg/l Fe3+		g/l	moles/l	g
30	200	6	0,11	0,26
25	200	5	0,09	0,22
20	200	4	0,07	0,17
15	200	3	0,05	0,13
10	200	2	0,04	0,09
5	200	1	0.02	0,04

Table 5-2 Ferric chloride hexahydrate masses required to prepare the coagulant solutions

Iron chloride solution needs to be prepared before the experiment has to be started. In order to dose the coagulant in all jars at the same time a special device was used. This device has a simple configuration and consists out of a bar which has clips where eprouvettes can be clipped-on. When dosing is performed, the bar is just rotated and the coagulant and caustic soda can be dosed at the same time in all jars. In one eprouvette the maximum volume which can be dosed is 9 ml.

## 5.3. Experimental results

Figure 5-4 Jar-test set-up

In the past, when the pilot plant was running on cooling tower blowdown several problems have been noticed. One of the main issues is poor coagulation. Ferric chloride is used as coagulant. The dosage of iron has been chosen after performing jar tests at different concentration of iron. From those jartests performed previously it was concluded that the best coagulation efficiency was at an iron concentration of 20 mg/l. This dose can be modified also in the pilot plant in order to observe the pilot's performance.

There are two theories which could explain bad coagulation and also the membrane fouling. One of the theories is based on the pH range of the coagulant solution. Ferric chloride gives good performance at a pH higher than 6.5. In the pilot at the moment he pH is not being increased after the iron dosage and the pH decrease is not being monitored. It is assumed that the pH after the iron dosage is decreasing until a value lower than 6, so this is the reason the formed flocs are very small and difficult to settle.

Another assumption is the effect of the biodispersant. The composition of the added biodispersant is not known because the manufacturer does not provide any information about it. Its action is known though. Biodispersant prevents the biofilm of attaching to the surfaces and also forms a layer around the microorganisms. Normally biodispersant are surfactants, so their effect has the opposite effect of coagulation and because of their opposite action, coagulation could be neutralized by the biodispersant.

Dilute dispersion is based on the mean separation of the particles compared with the range of the interaction forces between the particles. In dilute state the particles are well separated so that particle interactions are negligible at the mean separation. As a result the particles diffuse in a random fashion due to Brownian motion. Dispersion behavior can be described as Brownian motion, in which any two particles will experience many changes in direction before colliding (Goodwin, 2009). On the other hand, coagulation/flocculation processes are able to overcome or reduce the zeta potential of the particles letting the attraction forces (van der Waals) to concentrate particles together and form flocs. Light stirring of the solution create flocculation, which brings particles together and form larger, heavier flocs which can be settled and filtered (AWWA, 2003).

## 5.3.1. Coagulation flocculation in CTBD without biodispersant

The first performed experiment was with cooling tower blowdown biodispersant free and iron dosage. In the 6 jars, different iron concentrations were added and stirred at 4 different stirring rates according to the experimental operation presented before. In Table 5-3 are the characteristic of the CTBD water recorded before the start of the experiment, in the raw water.

	Turbidity	EC	TDS	Fe <sup>3+</sup>
рп	NTU	mS/cm	g/I	mg/l
6,63	8,96	3,73	3,53	1,09

Table 5-3 Initial	quality of	the blowdown	water
-------------------	------------	--------------	-------

The starting pH measured before the beginning of the experiment is not the same as the pH measured in the pilot plant in Teneuzen in the day the water was collected (the pH measured in the pilot was 7.83). A faulty measurement can be because the pH meter was not calibrated prior the start of the experiment.

In Table 5-4 the results obtained after coagulation/flocculation and settling were obtained. No visible flocs were observed in most of the jars. Only in the jar in which were dosed 30 mg/l  $Fe^{3+}$  were observed some small flocs after about 10 minutes.

It can be seen from the obtained results that the pH drops below 6. This is also the cause most of the iron stays in the effluent and no visible flocs are being formed. Because of the poor coagulation the turbidity of the water increases drastically, resulting in a water quality worse than the quality of the raw CTBD.

Fe <sup>3+</sup> dosage	рН	Turbidity	EC	TDS	Fe <sup>3+</sup>
mg/l		NTU	ms/cm	g/I	mg/l
30	5,09	28,2	3,74	3,74	12,7
25	5,71	51,5	3,7	3,69	24,2
20	6,01	44,51	3,66	3,67	19,6
15	6,09	30,5	3,69	3,69	15,6
10	6,13	24,1	3,67	3,67	11,5
5	6,06	15,1	3,66	3,65	7,2

Table 5-4 Quality of the blowdown water after coagulation/flocculation without biodispersant dosing

## 5.3.2. Coagulation/flocculation experiment in CTBD with biodispersant

For this experiment biodispersant had to be added in each jar manually before the experiment was started. Because it was desired to keep the conditions as much as possible similar with the conditions in the pilot plant or in the cooling tower, the biodispersant concentration added was 4 mg/l (final concentration assumed to be in the cooling tower blowdown).

The increased viscosity of the biodispersant made it quite difficult to dose it. When pipetting the liquid was filling the pipette very slowly and when there was no increase observed in the volume of biodispersant in the tip, the tip of the pipette was extracted slowly. In contact with the open air there was a small suction which may interfere with the actual volume present in the pipette. Injecting the liquid into the water was also quite complicated and also hindered the actual dosage because the biodispersant was sticking to the walls of the pipette. The pipette was rinsed with CTBD a couple of times but it was obvious that there was still some on the walls. After the biodispersant was dosed in the jars the liquid was dispersed in the entire volume of the liquid and a chaotic movement was also visible. The liquid was mixed for about 15 minutes at 300 rpm before the actual experiment was started, so that the biodispersant will dissolve as much as possible. After about 10 minutes there were still small particles floating in the liquid and even when the iron was dosed, but less. On the surface of the water there were flowing tiny patches of biodispersant, meaning that not all biodispersant was dissolved. In Table 5-5 presents the starting values of the water.

nH	Turbidity	EC	Fe <sup>3+</sup>
рп	NTU	mS/cm	mg/l
7,42	3,03	3,72	0,14

Table 5-5 Blowdown quality before the start of the experiment

The results obtained in this experiment were slightly more different than the results obtained in the cooling tower blowdown without biodispersant. Again, no visible flocs were observed, except for the jar in which was dose 30 mg/l Fe<sup>3+</sup>. There is a better coagulation though, for the 15 and 20 mg/l Fe<sup>3+</sup>, since iron concentration and the turbidity are lower than in the previous experiment. Table 5-6 shows the final quality of the effluent.

The pH dropped also, but again not as much as in the previous experiment. Highest pH drop was for 5 mg/l  $Fe^{3+}$  dose, lower than 5, which is a somehow unexpected since in the previous experiment the pH dropped with the increase in iron concentration

Fe <sup>3+</sup> dosage	pН	Turbidity	EC	Fe <sup>3+</sup>
mg/l		NTU	mS/cm	mg/l
30	5,73	47	3,77	20,02
25	6	55,4	3,74	23,65
20	6,27	39	3,74	8,76
15	6,37	27,2	3,72	8,82
10	6,35	20,4	3,71	9,24
5	4,97	4,2	3,77	3,41

Table 5-6 Quality of the blowdown after coagulation/flocculation and with biodispersant dosing

#### 5.3.3. Coagulation/flocculation in CTBD without biodispersant and pH adjustment

For this experiment pH was adjusted. Together with the ferric chloride was dosed the NaOH so that the pH would increase after the iron dosage. Table 5-7 shows the initial quality of the water.

Table 5-7 Initial quality of the blowdown water

mLl	Turbidity	EC	Fe <sup>3+</sup>	тос	ТР
рп	NTU	mS/cm	mg/l	mg/l	mg/l
7,74	1,84	3,65	0,098	55,49	<0,001

Two experiments were performed with the pH increase. In the first experiment the pH was increased at a higher value, while in the second experiment,t pH was tried to be kept at the initial value. The volume of NaOH was calculated beforehand. It is known that, in order to maintain a constant pH for every mol of  $Fe^{3+}$  added, 3 moles of OH<sup>-</sup> are necessary. In Table 5-8 are presented the NaOH volumes added together with the final results of the coagulation test.

Fe <sup>3+</sup> dosage	Volume NaOH	рН	Turbidity	EC	Fe <sup>3+</sup>	тос	ТР
mg/l	ml		NTU	mS/cm	mg/l	mg/l	mg/l
30	3,13	7,4	3,04	3,83	1,6		0,002
25	2,61	7,5	1,89	3,8	1,2	45,03	<0,001
20	2,09	7,43	3,62	3,78	1,7	45,58	<0,001
15	1,57	7,5	9,92	3,72	5,8	49,12	0,001
10	1,04	8	3,34	3,73	1,3	49,47	0,003
5	0,52	7,16	10,2	3,67	4,65	53,59	0,008

Table 5-8 Blowdown quality after coagulation/flocculation, without biodispersant dosing and with pH adjustment

Addition of sodium hydroxide was done at the same time with the ferric chloride solution in all jars. Flocs were visible in almost all jars from the first minutes of the flocculation. Only in the jar in which 5 mg/l Fe<sup>3+</sup> was dosed there were no visible flocs and worst results were obtained. In all the other jars turbidity decreased, being lower than the initial one, with the lowest turbidity achieved for 25 mg/l Fe<sup>3+</sup> added. For 5 mg/l iron the turbidity increased significantly and also the iron concentration.

For this experiment TOC was also measured. It can be seen that TOC concentration decreased with the increase in concentration. Highest removal (19%) was achieved with 30 mg/l Fe<sup>3+</sup>, which is not sufficient, since the final TOC concentration desired in the effluent in the EDR stream should be lower than 15 mg/l.

Total phosphate (TP) was monitored in this experiment also. It can be seen that in the raw blowdown the concentration was under the detection limit. The concentration increased though with the iron

addition. The highest increase noticed was in the jar in which 5 mg/l  $Fe^{3+}$  was dosed. In all the others the concentrations remained very low, with negligible values.

Another coagulation test was performed in which the pH was tried to be kept at the initial value. In Table 5-9 can be seen the initial quality of the blowdown.

	Turbidity	EC	Fe <sup>3+</sup>
рп	NTU	mS/cm	mg/l
7,74	1,84	3,65	0,098

Table 5-9 Initial quality of the blowdown water

For this experiment the NaOH concentration dosed was half. Similar results were obtained. Visible flocs were in all jars except the jar with the lowest iron concentration dosed. In this jar the turbidity and iron concentration was higher than in the majority of the other jars. In contradiction with the previous experiment for 15 mg/l  $Fe^{3+}$  dosed, the turbidity increased and also the final  $Fe^{3+}$  concentration. For all the other concentrations, improvement in coagulation was observed compared with the simple iron dosage. The residual  $Fe^{3+}$  concentration in the effluent is very low for this situation and it almost all  $Fe^{3+}$  was consumed for the floc formation. In Table 5-10 are presented the final results obtained after performing the coagulation/flocculation experiments.

Table 5-10 Final quality of the blowdown after coagulation/flocculation, without biodispersant dosing and pH adjustment

Fe <sup>3+</sup> dosage	Volume NaOH	рН	Turbidity	EC	Fe <sup>3+</sup>
mg/l	ml		NTU	mS/cm	mg/l
30	3,13	7,4	3,04	3,83	1,6
25	2,61	7,5	1,89	3,8	1,2
20	2,09	7,43	3,62	3,78	1,7
15	1,57	7,5	9,92	3,72	5,8
10	1,04	8	3,34	3,73	1,3
5	0,52	7,16	10,2	3,67	4,65

## 5.3.4. Coagulation/flocculation in CTBD with biodispersant and pH adjustment

For this experiment biodispersant was again dosed before the start of the experiment. Table 5-11 shows the initial concentrations measured in the cooling tower blowdown water for the experiment performed at a constant pH.

		_	-
	Turbidity	EC	Fe <sup>3+</sup>
рн	NTU	mS/cm	mg/l
7,74	1,84	3,65	0,098

Table 5-11 Initial blowdown quality

Same methods were used, with high pH and pH kept at a constant value, around 7.6. Within Table	e 5-
12 are the obtained results for the experiment performed with iron dosage and constant pH.	

Fe <sup>3+</sup> dosage	Volume NaOH	рН	Turbidity	EC	Fe <sup>3+</sup>
mg/l	ml		NTU	mS/cm	mg/l
30	3,13	7,6	2,88	3,78	1,2
25	2,61	8,2	2,45	3,73	1,4
20	2,09	7	7,6	3,74	3,5
15	1,57	7,4	4,35	3,7	1,7
10	1,04	7,3	6,36	3,67	2,4
5	0,52	7,2	11,9	3,7	3,1

 Table 5-12 Blowdown quality after coagulation/flocculation, with biodispersant dosing and pH adjustment

Better coagulation was observed in the blowdown with biodispersant and NaOH addition. No visible flocs were seen for 5 mg/l  $Fe^{3+}$  dosage. The initial turbidity was quite low. Compared with the previous experiments the final turbidity was not lower than the initial one. Best results were recorded with an iron dose of 25 and 30 mg/l. At 20 mg/l with a pH of 7, turbidity iron concentrations were higher, compared with the other iron doses.



Figure 5-5 The flocs observed in jars at different coagulant concentrations

The parameters measured in the blowdown for the next experiment (CTBD with biodispersant and pH adjustment at higher pH values) are displayed in Table 5-13. This experiment was done by adjusting the pH at higher values.

		-		
	Turbidity	EC	Fe <sup>3+</sup>	
рп	NTU	mS/cm	mg/l	
7,24	2,84	3,72	0,07	

Table 5-13 Initial quality of the blowdown	n
--	---

Results obtained for this coagulation test are presented in Table 5-14. Again good coagulation was reached at higher pH. Flocs were observed in all jars except for the jar with 5 mg/l Fe<sup>3+</sup> dosage (Figure 5-5). Turbidity in this jar increased considerably reaching the value of 11.4. Good results were seen for iron concentration of 30 and 20 mg/l when the turbidity was slightly lower than the initial turbidity but the iron dose in the effluent decreased to 1.4 and 0.8 mg/l Fe3+ respectively.

Fe <sup>3+</sup> dosage	Volume NaOH	pН	Turbidity	EC	Fe <sup>3+</sup>
mg/l	ml		NTU	mS/cm	mg/l
30	6,27	9,46	2,74	3,84	1,4
25	5,22	9,38	6,83	3,8	0,6
20	4,18	9,27	2,08	3,78	0,8
15	3,13	9,04	3,22	3,73	1,4
10	2,09	8,76	3,23	3,7	2,1
5	1,04	8,53	11,4	3,68	3,8

Table 5-14 Blowdown quality after coagulation/flocculation, with biodispersant dosing and pH adjustment

After the settling time ended and the samples of supernatant were collected for analysis (Figure 5-6) the biodispersant was still floating on the surface of the water at the end of the settling period. It can be assumed that a part of the biodispersant was dissolved while a small part remained in the water.



Figure 5-6 Biodispersant floating on the surface of the water at the end of the coagulation experiment

## 5.4. Conclusions

After performing the jar-tests with the cooling tower blowdown water with and without biodispersant one of the theories was confirmed. Poor coagulation was observed in all experiments performed. Significant results were observed only at higher iron concentrations. The TOC concentration was slightly removed but the turbidity was increased, which is not really an improvement for the following UF step.

Jar-test performed without pH adjustment showed poor results. Small flocs were observed only for the  $30 \text{ mg/l Fe}^{3+}$  concentration. In all the other jars, no visible flocs were formed and the final quality of the effluent water was worse than the initial quality of the blowdown water, independent of the biodispersant.

The experiments performed with NaOH addition showed better results from the first minutes. Flocs were formed in almost all jars, except for the jars in which 5 mg/l  $Fe^{3+}$  was dosed. The flocs were quite big and easy settleable, resulting in a good coagulation with lower turbidity and lower TOC concentrations than in the influent water. The residual iron measured in the effluent is very low, meaning that most of the iron was consumed for the floc formation.

Biodispersant addition in the blowdown showed a difference in the results. The TOC and turbidity decrease was not anymore dependent on the iron dose. In the experiments with biodispersant free blowdown, TOC and turbidity were linear. Better coagulation and turbidity removal was observed at higher pH (above 9). In the experiment performed to observe the difference between the jars with

and without baffles, no big differences were noticed. The pH was adjusted here also so that the pH drop will not give poorer results.

The theory of the biodispersant neutralizing coagulation was not confirmed. Biodispersant has an effect on coagulation, but relative good results were obtained with the pH adjustment. Biodispersant is still fouling the UF membrane and a removal solution should be found in order to protect the membranes.

# 6. ADSORPTION of Biodispersant

Considering that the biodispersant is an organic surfactant and that it is contributing to the fouling of the UF membrane, than a removal method should be investigated. Powdered activated carbon (PAC) has one of the highest physical adsorption capacity and the highest volume of adsorbing porosity. It is widely used in the treatment of drinking water and removal of organic contaminants from water. Clay is also known for its adsorption properties, but the surface area is not as high as in the case of PAC (Cheremisinoff, 2002).

In this chapter firstly, an introduction of the adsorption theory was made and properties of PAC and clay were presented. Adsorption experiments were also performed to investigate the adsorption capacity of the 2 selected materials, PAC and clay. The results of these experiments are also presented.

## 6.1. Theoretical background

All natural waters and wastewaters contain varying amounts of substances that contain carbon which are dissolved from soil and vegetation, in the case of natural waters and addition of carbon containing chemicals or because of organic contaminants in the case of wastewaters. Organics can be removed from waters by standard treatment techniques like oxidation by chlorine, chlorine dioxide, ozone, UV. If the organic load is not so high aeration or coagulation can be applied. When the loading is high and the standard treatment steps are not efficient, adsorption is applied (AWWA, 2003).

Adsorption is based on the principle of adhesion. Organic contaminants are attracted by the adsorbing material and they adhere to its surface due to the physical forces and chemical action. Effective adsorption is assured by a large surface area onto which the contaminants can adhere. Porous adsorbing materials are good adsorbents (AWWA, 2003). Independent of the type of forces holding a solid together, it can be seen as a field of forces around every ion, atom or molecule. The forces (van der Waals, electrostatic forces) cannot disappear and reach out in the space beyond the surface of the solid. Due to these forces, the solid has the tendency to attract and hold on its surface molecules and ions from other substances with which it interacts. When a solid compound gets in contact with a gas or a liquid, the concentration of the gas or the liquid is higher on the surface of the solid than in the bulk liquid or gas. These processes define adsorption (Bansal & Meenakshi, 2005). Adsorbate represents the substance which attaches to the surface, while adsorbent is the substance to which it is attached.

In drinking water treatment adsorption of the compounds by activated carbon occurs mostly by nonspecific physical adsorption. Physical adsorption is caused by non-specific secondary binding mechanisms, in which electrons are shared between the adsorbate and the adsorbent, rather than electrons being transferred, as occurs in chemical adsorption. Physical adsorption can be reversed in response to a change in the concentration gradient between the bulk liquid phase and the adsorbed solid phase. Activated carbon has a nonhomogeneous surface with specific function groups which make them have a limited degree of chemical adsorption for certain compounds (Chowdhury , et al., 2013).

Activated carbon is effective because it has a vast network of pores with different pore sizes which make them accept small and large molecules. 0.45 kg of activated carbon has a surface area of about 60 ha, which can trap and hold more than 0.25 kg of carbon tetrachloride (AWWA, 2003). When the pore surface is covered by the contaminant the carbon is not able to absorb anymore. Used carbon can be reactivated by the same processes used for the activation, or can be replaced with new one.

Adsorption process can be implemented quickly but it can be also quite cost-effective compared with different treatments, because of the size or the location of the plant. Activated carbons are unique and versatile adsorbents used for the removal of odour, colour, taste, organic and inorganic impurities, solvent recovery, air purification etc. (Bansal & Meenakshi, 2005).

Activated carbon is a material which consists of a wide range of amorphous carbonaceous materials that exhibit a high degree of porosity and an extended interparticulate surface area. It is obtained by combustion or thermal decomposition of carbonaceous substances and can be obtained in a powdered or granular form. Granular activated carbon (GAC) has a high internal surface area and small pores, while the powdered form has large pore diameters and small internal surface area (Bansal & Meenakshi, 2005). Pore size of the porous solids used for adsorption can be divided in micro, meso or macro, based on their width. Adsorption is triggered by the interactions between the solid molecules and the molecules from the liquid phase. The forces which generate adsorption can be classified as chemisorption (chemical bonding) or physisorption (non-chemical bonding) (Clark & Rhodes, 2000).

Activated carbon is used in two ways: as fixed bed reactors with GAC and slurry applications of the small PAC. PAC can be recovered from the water after treatment, but the recovery of the material is quite problematic. GAC represent the filter media (filter adsorber) or can be applied in a reactor after the filter. When the adsorption capacity of the media has been exhausted GAC must be removed and reactivated (Chowdhury , et al., 2013).

## 6.1.1. Powdered activated carbon (PAC)

PAC is contacted with the water as a slurry absorbs the contaminant and is removed with the particles. PAC cannot be recovered so the amount used can be high. The adsorbent properties of activated carbon are based in the large surface area between the particles, universal adsorption effect, high adsorption capacity, high degree of surface reactivity and a favorable pore size which makes the internal surface accessible and increases the adsorption rate (Bansal & Meenakshi, 2005). The highest efficiency of PAC is achieved when it is suspended in the water. Once it is not suspended anymore and not in contact with the pollutant its efficiency is decreasing significantly. Full capacity of PAC is reached when the net uptake of the adsorbate is 0. After the PAC addition, the liquid-phase concentration of the adsorbate starts decreasing with time. The time to reach equilibrium state depends on the size of PAC and the mixing rate (Chowdhury , et al., 2013).

Most common point where PAC is added is before or after the rapid mixing, when combined with coagulation/flocculation. Besides the fact that it will adsorb the organic coagulant PAC will help coagulation by providing a center or nuclei on which flocs will form (AWWA, 2003). Rapid mixing and flocculation steps keep coagulation particles in suspension so if it will be added before the rapid mixing it will remain suspended through the rapid mixer, flocculation basin and part of sedimentation tank (Chowdhury , et al., 2013).

The organic content of the effluent will decrease with more PAC addition since more adsorbate can be removed. However, the effluent decrease is not proportional with the PAC dose since it also depends on other factors. If the residence time in the reactor is not longer than the time of equilibrium, than the full removal capacity will not be achieved. For most of the PAC-adsorbate pairs the equilibrium time is in order of hours, while the residence time in the reactor is much less. The equilibrium time is decreasing with the decrease in PAC particle size (Chowdhury , et al., 2013).

The addition of PAC can be made almost at any point in the treatment plant before filtration but certain things need to be taken into consideration (AWWA, 2003):

- The contact time between PAC and the pollutants depends of the ability of PAC to remain suspended. Minimum contact time advisable is 15 minutes.
- The particles surface loses the ability to adsorb if it is coated with coagulants or other chemicals.
- PAC removes chlorine (by reducing it to a non-oxidative chloride ion) (DeSilva, 2000).

PAC dosage depends on the types of concentrations of organic compounds. Normally dosages between 2 and 20 mg/l are used, but they can go up to 100 mg/l in case of high organic loads. For example for a water with a TOC=10 mg/l a 40% decrease in geosmin was achieved with a dose of 5 mg/l PAC. With 17 mg/l PAC added 90% removal in geosmin was recorded (Chowdhury , et al., 2013).

## 6.1.2. Granular activated carbon (GAC)

GAC is normally used in systems where continuous removal of organics is needed. If the organic concentrations are not very high, GAC can be installed in place of a sand filter or anthracite filter. GAC can also be part of a multimedia layer as a capping layer, in which case it will act as adsorbent and filtering media (AWWA, 2003). This operation is not a steady-state process since the concentration of the effluent increases with time. When the target effluent concentration was reached, the absorption stops and GAC needs to be reactivated or replaced. GAC in a fixed bed reactor is in equilibrium with the contaminant in the effluent, so it can remove more contaminant per mass of activated carbon applied compared to PAC (Chowdhury , et al., 2013).

When installing a GAC as a filter, one must take into consideration how long the adsorptive capacity of the GAC will last, how much will cost to remove the inactivated material, how much will it cost to reactivate the material or to replace it. Effective life of GAC in typical installations is between a few months to 4 years, depending of the organic loading of the influent and also on the other removed substances (AWWA, 2003). The adsorbate breakthrough is complete when the effluent concentration is increasing from 0 to that of the influent. GAC adsorbers are operated until the effluent concentration approaches a target concentration and at that point GAC must be replaced in order to maintain continous adsorption treatment (Chowdhury , et al., 2013).

GAC installed as a fixed-bed filter can be best modeled as a plug flow reactor. The performance of the GAC is affected by the several design and operating parameters. One of the main parameters is the velocity, or the hydraulic loading rate (HLR) which represents the ratio between the flow rate and the cross-sectional area (Chowdhury , et al., 2013).

The time water is in contact with the GAC as it passes through the bed is called empty bed contact time (EBCT). EBCT does not represent the true fluid residence time, because it does not account for the reactor volume occupied by the GAC. GAC takes about 50% of the bed, resulting in an EBCT value twice as high as the actual fluid residence time (Chowdhury , et al., 2013).

The minimum recommend GAC bed is 610 mm thick, but the deeper it is the longer the contact time will be and the longer the effective time will be. Most of the times, the old GAC is replaced with new material. After the bed has been changed it needs to be backwashed in order to remove the trapped air and small particles of carbon (AWWA, 2003). Filters that use GAC as a medium are normally operated as regular sand filters are operated at a filtration rate of 1.4 mm/s, which results in an EBCT between 7.5 and 9 minutes, enough to remove sufficient organic compounds (AWWA, 2003).

GAC are installed most of the times after the sedimentation basin either as a media in the filter bed or after the filters as a post-filter contactor. GAC can be used in filter adsorbers in a direct filtration plant, because the activated carbon media makes it an effective filter media (Chowdhury , et al., 2013).

Pretreatment before the GAC can have a benefic effect on the removal efficiency, like the steps applied for the removal of competing compounds (Chowdhury, et al., 2013).

Pollutant removal by activated carbon consists out of 3 steps:

- External mass transfer (EMT)
- Internal mass transfer (IMT) •
- Adsorption •

During the first step the compound is extracted from the bulk liquid-phase through the hydrodynamic layer which bounds the activated carbon particle. EMT is important because it can influence the kinetics of the adsorbate uptake, when the mixing velocity in the PAC reactor is low. After EMT transfers the aggregate to the external layer of the activated powder particle, IMT sends the adsorbate to an adsorption site on the surface of the AC where adsorption takes place (Chowdhury, et al., 2013).

Adsorption reaction is quite fast and is not rate limiting and consists of 2 step mass transfer. EMT and IMT are diffusion-based processes to which thrust is the concentration gradient of the adsorbate difference between bulk concentration and internal concentration at equilibrium. IMT is a slow process and generally dominated the total uptake of an adsorbate. The transfer takes place through the pore fluid or along the pore wall in parallel processes. Diffusion, through pores and along the pore surface is led by the pore structure of the activated carbon and the properties of the adsorbate (Chowdhury, et al., 2013).

In a completely mixed batch reactor can be illustrated the kinetics of adsorption. Mixing velocity inside the reactor is important since the EMT resistance can be decreased by the thickness of the stagnant film surrounding particles (Chowdhury, et al., 2013).

After the PAC was added in the system, the liquid phase concentration of the compound will decrease as a function of time. Ultimately the net uptake will become 0, when the adsorbate-adsorbent reach equilibrium (Chowdhury, et al., 2013).

As the PAC dose increases also the equilibrium liquid-phase concentration decreases and also the time to equilibrium decreases. Kinetics is also influenced by diameter of the particles, diffusion coefficient of the adsorbate and the initial concentration in the effluent. The equilibrium mass balance is given by Equation 6-1:

 $q = (C_o - C_e) \cdot \frac{V}{m} = \frac{(C_0 - C_e)}{dose}$ 

Equation 6-1

Where:

solute concentration in the adsorbent =

initial solute concentration in the liquid phase

 $\begin{array}{c} C_0 \\ C_e \end{array}$ final solute concentration in the liquid phase =

- volume of solution =
- weighed mass of activated carbon m =

In an experiment where the adsorbent dose varies and/or initial concentration, the equilibrium solidphase can be calculated and a relation between liquid-phase can be established. The adsorption equilibrium (isotherm) allows the adsorption capacity of the adsorbent to be determined at any liquidphase concentration (Chowdhury, et al., 2013).

## 6.1.3 Clay

Adsorption is the enhancement of materials or the increase in density of the fluid close to an interface. Depending on certain conditions this results in a high enhancement of the concentration of a particular substance, which depends on the surface of the interfacial area (Clark & Rhodes, 2000). All the industrial adsorbents and most of the industrial catalysts have large surface area, higher than 100  $m^2/g$ .

Adsorption of a solute from a solution onto a solid surface occurs as the result of the characteristics of the given solvent-solute-solid system (Carberry et al., 1977):

- Lyophobic (solvent disliking) character of the solute in relation with the solvent
- The affinity of the solute for the solid

The lyophobic characteristic is determined by the degree of solubility of a dissolved substance. This can be interpreted as the more a substance likes the solvent the less likely it is that it will move towards a surface to be adsorbed. Hydrophobic substances will get adsorbed more from aqueous solutions (Carberry, et al., 1977).

Pollutants or unwanted compounds can be intercalated from vapor, liquid or solid state. When they are intercalated from solution, solvent molecules are co-adsorbed in the interlayer space. In Figure 6-1 is presented a graphical representation of the adsorption mechanism (Lagaly , et al., 2006).



Figure 6-1 Simplified representation of the adsorption mechanism

Intercalation of neutral compounds into montmorillonite or vermiculites is not followed by cation movement in the middle of the silicate layers. Cations can stay in contact with one silicate layer. Nonetheless no exact relation was found between the intercalation and bulk properties of the liquid guest molecules. Various large molecules are not intercalated directly. But can be introduced by further expansion of the interlayer space (Lagaly , et al., 2006).

Physisorption can be characterized by:

- Physisorbed molecules keep their identities and desorb back to the liquid phase
- It is an exothermic reaction and is involving energies below those typical of chemical bond formation
- At high pressures, physisorption produces multi layers.

Chemisorption can be defined by:

- Chemisorbed molecules can be expected to change as a result of adsorption and are not recovered unchanged on desorption;
- Is restricted to a monolayer;
- Involves energies of the same magnitude as the chemical bond formation.

Clay has been used for various purposes throughout the history as a raw material for pots and ceramics, for its medical and therapeutic properties or in various industries. Many application of clay are based on the ability of these minerals to absorb and hold noxious and unwanted substances. The

sorptive property of clay is linked to their small particle size, big surface area, structure and charge (Huang, et al., 2008).

Clays are normally naturally occurring (kaolin, ball clay, fuller's earth, china clay) made out of fine mineral (<4  $\mu$ m) which takes a plastic form when is wetter and a solid form when is dry. Clay minerals are hydrous layer silicates with colloidal dimensions and particle sizes ranging between 1nm and 1 $\mu$ m (Rouquerol, et al., 2014).

Smectite clays have three properties which characterize their catalytic activity intercalation, swelling and cationic exchange capacity. When introduced in water intercalation of the molecules and swelling occurs (Clark & Rhodes, 2000). Swelling and thixotropic properties of the smectic clays have made them of great importance in agriculture and civil engineering. Fuller's earth (calcium montmorillonite) has high absorbent and cationic exchanger qualities and bentonite is highly use as a constituent of drilling mud, mortar and putty. Activated bentonite acidic properties made it vastly exploited for the production of gasoline from higher molar mass oils (Rouquerol, et al., 2014).

Swelling is the result of interlayer sorption of polar molecules by smectite. When the internal area is increased to 800 m<sup>2</sup>/g, due to sorption of water vapor is associated with the development of an interlayer width of minimum 0.6 nm

Clays are used for refining mineral oils, regeneration of solvents for dry cleaning, discoloration, dye adsorption, adsorption of radio-active materials, adsorption of heavy metals (lead, chromium, cadmium), de-inking in waste paper recycling etc. As catalysts clays are used as acid-treated or cation exchange.

Non-ionic surfactants have a molecular structure which includes both hydrophobic and hydrophilic groups. The ratio between the hydrophilic to hydrophobic fraction gives information about the hydrophilic-hydrophobic balance (HLB). A HLB between 9 and 11 indicates a balanced medium, while a HLB higher than 11 implies a hydrophilic nature.

For non-ionic surfactant and activated carbon the hydrophobic part of the molecule will be active on the surface and will get adsorbed, while the hydrophilic part will be directed towards the solvent. In the case of clay adsorption the hydrophilic group of the molecule will undergo adsorption onto the polar surfaces of the clay particle and attachment is caused by overlapping of the hydrophobic part (Carberry, et al., 1977).



Figure 6-2 Schematic representation of alignment of non-ionic surfactant molecules at charge solid/liquid interface

Adsorption theory states that surface interactions involve one of the electrical attractions of the solute to the adsorbent, of the Van der Waals attraction, or by the formation of chemical bonds. Physical adsorption is prevailing at low temperatures and is characterized by a low energy of adsorption, while the regeneration of the sorbent at the end of the run can be accomplished. Chemical adsorption mechanism manifest high adsorption bonds at the active center of the adsorbent (Carberry, et al., 1977).

For the organic molecules which have a complex structure adsorption depends on the type of clay or degree of purification, interlayer cation, mean layer charge, concentration (vapor pressure) of the adsorptive, pH, temperature, fine structure of the clay, particle size, degree of dispersion, ionic strength, types of salts present. Various experiments were performed with different types of clay in order to observe the adsorption properties. Surfactants are one component which is often found in residual waters and removal was tried with different types of clays.

One of the experiments was performed by Narkis & Ben-David, (1985) using two types of surfactants, nonyl-phenol ethoxylate and dinonyl-phenol ethoxylate. The solution had a concentration of 10 mg/l nonionic surfactant, concentration which is very close to the concentrations found in the municipal wastewater.

The experiment was done in Erlenmeyer flasks with clay doses varying from 25 to 1500 mg/l and a contact time of 6 h, time deducted from preliminary studies. The flasks were shaken for 24 h at about 25°C. At the end of the experiment the suspended clay was left to settle and the supernatant was centrifuged for 30 minutes at 8000 rpm.

From the results obtained it was observed that in order to achieve a removal of 99.3% of the surfactant, 500 mg/l clay was required. The adsorption on clay was achieved via the hydrophilic part of the molecule. This mechanism can be due to the hydrogen bonds which are formed between the  $OH^-$  groups of the clay in the broken bonds and etheric oxygen atoms in the polyethoxylate in the surfactant molecule. It is possible that the cationic-exchange of Na<sup>+</sup> on the clay surface for the H<sub>3</sub>O<sup>+</sup> ions bonded to the hydrophilic ethoxylate chains takes place.

Montmorillonite is able to absorb various organic chemicals. This clay has a negative charge which is able to attract the positive charged cationic molecules. Nonionic surfactants are also adsorbed by it because of the hydrogen bonding and van der Waals attraction forces (Hower, 1970).

Hower (1970) performed several adsorption experiments using montmorillonite and different surfactants (ionic and nonionic). The specific weight of the surfactant varied from 0.5 to 2 g and dissolved in 100 ml distilled water. Various ratios of clay and surfactant were used, with the biggest ratio being 1500 mg surfactant to 1 g of clay. The mix was made in Erlenmeyer stop flasks and the flasks were shaken periodically for 24 h. After the 24 h contact time between the solution and clay the samples were centrifuged in order to remove the clay and for the analysis of the effluent. Final surfactant concentration was checked by measuring the surface tension.

It was observed that the clay dispersed well in the surfactant solutions, but started settling with time. Formed solids had a sticky texture and were difficult to re-disperse. The adsorption values plotted smooth curves, with a maximum adsorption of 550 mg surfactant per gram of dry montmorillonite.

## 6.1.3. Equilibrium adsorption isotherm

Isotherm relationships can be fitted with the model equation: Langmuir or Freundlich models. Langmuir model is fundamental, has conceptual endpoints as it gets closer to a maximum solid-phase concentration at the very high liquid-phase concentration and has a linear equilibrium relation at low concentrations. Langmuir adsorption isotherm was initially made to describe the gas-solid-phase adsorption onto activated carbon and has been used to evaluate the performance of different bio-sorbents. The derivation of the Langmuir equation is related with the homogeneous adsorption, where

each molecule has constant enthalpies and sorption activation energy (all sites possess equal affinity to their adsorbent). The equation is characterized by a plateau, an equilibrium saturation point where once a molecule occupies a site, no adsorption can take place anymore. The theory reported fast decrease of the intermolecular attractive forces to the rise of distance (Foo & Hameed, 2010).

In a solution in which activated carbon is added and is also allowed to reach equilibrium, the rate at which molecules are adsorbing to the surface is equal with the rate at which molecules are leaving the surface. Langmuir equation is based on several important assumptions (Cooney, 1999):

- Adsorption takes place at defined local sites on the surface
- Each site can only bind one molecule of the adsorbing species
- The energy of adsorption is the same for all sites
- There are no forces of interactions between adjacently adsorbed molecules.

Langmuir equation is given by Equation 6-2:

Equation 6-2

With:

b = a constant

From experience it was concluded that the empirical Freundlich model is better. Freundlich equation isotherm is describing the non-ideal and reversible adsorption, without being restricted to the formation of monolayer. The model can be applied to multilayer adsorption, with non-uniform heat adsorption distribution and preference for the heterogeneous surfaces (Foo & Hameed, 2010). The amount that is adsorbed is the total adsorption at all sites, with the stronger binding sites being taken first, until the adsorption energy is decreasing exponentially until the end of adsorption process (Foo & Hameed, 2010).

 $q = \frac{Q_0 b C_e}{1 + b C_e}$ 

Freundlich model can be derived from the Langmuir model, resulting in Equation 6-3:

Equation 6-3

With:

K<sub>F</sub> = Freundlich constant n = Freundlich exponent

From here the linearization can be derived Equation 6-4:

Equation 6-4

$$q = K_F \cdot C^n \iff \log q = \log K_F + n \log C$$

 $q = K_F \cdot C_e^n$ 

Plotting the isotherm data on a log scale the value of n can be determined since it represents the slope of the line.  $K_F$  is evaluated on the  $\gamma$  axis at a concentration of 1 mg/l.  $K_F$  value is used as an indicator for the difference in the adsorption capacity of a given activated carbon, for a range of compounds or the adsorption capacity of a given compound for a range of activated carbons as long as n is constant (Chowdhury , et al., 2013). From the equation if the curve the  $K_F$  and n values can be determined using Equation 6-5:

Equation 6-5

$$y = K_F \cdot x^n$$

With y having the  $q_{eq}$  value and x the  $C_{eq}$  value (Cooney, 1999). Freundlich is mainly used in heterogeneous systems, specifically for organic compounds or highly interactive species on activated carbon and molecular sieves. The slope's value is between 0 and 1 and it gives information about the
adsorption intensity or surface heterogeneity (as the value approaches 0, the heterogeneity increases). If the value is below 1 indicates chemisorption process where n higher than 1 is an indication of cooperative adsorption (Foo & Hameed, 2010).

The linear form of the Freundlich isotherm is given by Equation 6-6:

Equation 6-6

$$\log q_{eq} = \log K_f + n \cdot \log C_{eq}$$

With (Okeola & Odebunmi, 2010):

- $q_{eq}$  = the amount adsorbed per gram of adsorbent
- $C_{eq}$  = equilibrium concentration
- $K_{f}$  = constant which represents the relation between the energy of adsorption and temperature, giving information about the adsorptive capacity, while n is another constant which determined the intensity of adsorption

The slope n, which represents the adsorption intensity, becomes more heterogeneous as it gets closer to 0. A value above 1 for n indicates cooperative adsorption. A small slope shows that the adsorption is efficient over the entire range of concentrations analyzed, while a steep slope (small n) indicates that adsorption is only efficient at high concentrations and very poor at low concentrations (Muherei & Radzuan J., 2009). In the case of K<sub>f</sub> value, compounds with values above 10 (mg/g)/( $\mu$ g/l)<sup>n</sup> can be considered well removed by activated carbon, while K<sub>f</sub> values lower than 1will be poorly removed by activated carbon (Chowdhury , et al., 2013).

### 6.1.4. Batch experiment

A certain mass of carbon with an m weight is mixed in a certain V volume of a solution at an initial concentration  $C_0$  and stirred well. After equilibrium the final concentration of the solute in solution at equilibrium  $C_e$  is reached (after about 20 minutes). The mass of solute adsorbed in the carbon per unit mass of carbon is q. Different  $C_e$  values can be generated by using different carbon masses in different containers (jars). The carbon is removed from solution after the equilibrium was reached with the use of a membrane filter or by centrifugation. At the end of the experiment when V,  $C_0$ ,  $C_e$  and m are known, q can be determined and a plot of the determined q values vs. the concentrations values will give the isotherm of the solution (Cooney, 1999).

### **6.2. Experimental procedure**

## 6.2.1. Objective of the experiment

The biodispersant added in the cooling tower is assumed to foul the membrane. Nalsperse 7348 is a non-ionic surfactant. From previous studies, it was observed that non-ionic surfactants may be removed by being adsorbed on porous materials. The most common used adsorbent is activated carbon. Another adsorbent, less used, but also efficient for the removal of certain pollutants is clay. For the evaluation of the removal potential of the two adsorbents the adsorption isotherm of the PAC and clay was made by monitoring the TOC removal at different doses of PAC and clay. The second experiment done was observing the TOC removed in 8 hour time.

## 6.2.2. Adsorption isotherms

The same procedure was applied for PAC and clay. 3 types of water were used: demiwater, tap water and CTBD. In all these waters 4 mg/l biodispersant was added manually and stirred on a stirring plate overnight.

Varying amounts of adsorbent were dosed in 250 ml of effluent. The mass of adsorbent varied between 0 and 60 mg/l in seven Erlenmeyer flasks. PAC dose depends on the contaminants that have

to be removed and the targeted removal. PAC doses vary between 10 and 50 mg/l, with higher doses needed for the removal of unusually high TOC, odor or taste (Chowdhury , et al., 2013).

The PAC and clay were weighed (separately) and added in the Erlenmeyer flasks. 250 ml of effluent (demiwater, tap water and CTBD containing 4 mg/l biodispersant) was added in the flasks on top of the adsorbent. Magnets were also added in the beakers, while the beakers were placed on a stirring plate. One of the flasks was adsorbent free (as blank) for comparison. Rotational speed was set to 50 rpm for all jars and mixing time set to 48 h, to reach adsorption equilibrium.

At the beginning of the experiment there was a sample collected of the raw effluent for the TOC measurement. After the 48 h of constant mixing the stirring plate was stopped and samples were collected from each jar for TOC analysis. Samples were filtered through  $0.45\mu m$  filter for adsorbent removal.

### 6.2.3. Equilibrium experiments

For the equilibrium experiment the TOC concentration was measured every half an hour to determine when equilibrium is reached. Only the minimum and the maximum adsorbent concentrations were monitored, 10 and 60 mg/l PAC and clay. Demiwater, tap water and CTBD with a 4 mg/l biodispersant concentration were used as effluent.

The coagulation/flocculation setup was used and set to a 50 rpm stirring rate. Two jars were used filled with 2 I of effluent in which was added 10 and respectively 60 mg/I PAC and/or clay. Experiment was conducted for 8 hours straight and samples were collected every 30 minutes. Water samples were filtered through a 0.45  $\mu$ m filter for the adsorbent removal and TOC files were prepared for the TOC analysis.

### **6.3. Experimental results**

Several experiments have been performed in order to see what the adsorption capacity of PAC and clay is on different types of water: demiwater, tap water and CTBD. In the case of demiwater and tap water, the 4 mg/l biodispersant solutions have been prepared in advance and used for both, batch experiment and equilibrium experiment. Since the composition of the biodispersant is unknown, the concentration of only biodispersant in the tap water or CTBD is unknown. As an indication TOC measurements were done, but the exact amount of biodispersant which was adsorbed by PAC or clay cannot be determined since in tap water and CTBD there are other organics also.

The results obtained from the experiment performed with demiwater and biodispersant solution are presented in this chapter, while in Appendix B are presented the results obtained in tap water-biodispersant solution and CTBD water.



### 6.3.1. Adsorption results in demiwater



In Figure 6-4 are presented the obtained results of the adsorption experiment using PAC. The arithmetic plot shows the relation between the mass of activated carbon added in the solution and the equilibrium liquid-phase and solid-phase concentration. From the logarithmic plot the  $K_f$  and n value can be determined. Resulted  $K_f$  was 0.8077 while n is 2.1507. Because n is higher than 1, the adsorption coefficient is increasing with the increase in the solution concentration. The  $K_f$  value is close to 1 and the n indicates cooperative adsorption, and the efficiency is higher at high concentrations also.

In Table 6-1 are presented the results based on the TOC concentration obtained before the 48h batch experiment and after the 48h experiment.

PAC dose	C <sub>0</sub>	$C_{eq}$	<b>q</b> <sub>eq</sub>	Removal
mg	mg/l	mg/l	mg/mg PAC	%
0,00	2,31	2,31		0,00
10,00	2,31	1,29	0,10	44,13
20,00	2,31	0,89	0,07	61,39
30,00	2,31	0,86	0,05	62,57
40,00	2,31	0,71	0,04	69,12
50,00	2,31	0,67	0,03	71,10
60,00	2,31	0,62	0,03	72,94

Table 6-1 TOC measured at the end of the batch experiment, based on the PAC dosed in each jar

It can be seen from Table 6-1 that the removal of biodispersant using PAC in demiwater is more than 50%. All TOC measured is represented by the biodispersant. The higher removal is occurring at a PAC dose of 50 mg/l, removal which is comparable with 60 mg/l PAC dosed.

For the equilibrium experiment two PAC dozes have been chosen, 10 mg/l and 60 mg/l. Samples were taken every 30 minutes, filtered with a 0.45  $\mu$ m filter and prepared for TOC measurement. In Figure 6-5 are presented the obtained results during the 8h experiment.

The TOC values present some variations. Biodispersant is quite a difficult substance to work with and it requires some time to stabilize. Because the dosed concentration is much higher than the CMC concentration the micelles will cause some instability for the measurements. From both representations it can be seen that a more or less stable state is reached in less than 100 minutes.



Figure 6-4 TOC measured during the 8h equilibrium experiment, using PAC as adsorbent

Also what it can be observed from the kinetic experiment is that in the first hour a big drop in TOC is recorded; after this hour the TOC is not really stabilized, but increasing slightly. This increase is caused by the organic carbon present in PAC. During production of PAC there can be some residual TOC attached to the particles which dissolve in the water and cause the increase in TOC. Another reason for the TOC increase can be due to some airborne contamination which ended up in the water and also affected the final concentration. It can be seen also that this increase is happening after the first hour of experiment, after which the TOC concentration becomes more or less stable.

In order to see if the TOC increase noticed after the first hour is caused by the PAC and the residual organic carbon attached to the particles during production, an extra experiment has been performed. A kinetic experiment using demiwater and PAC (no biodispersant added) was done to monitor the TOC in demiwater during the 8h experiment. 2 PAC doses were used (10 and 60 mg/l) and samples were taken every hour for TOC measurement. In Figure 6-6 are presented the varying TOC values observed during the 8h experiment.



Figure 6-5 TOC variation in demiwater during 8h batch experiment with PAC

It can be seen that TOC concentrations are not stable during the experiment. For the 10 mg/l PAC situation, in the first 2 h is recorded a decrease in TOC followed by a decrease and an increase again. On the other hand for the 60 mg/l PAC dosed in the beginning the TOC is increasing after which it is decreasing again. The TOC values in demiwater are quite low (between 0.3 and 0.5 mg/l). Even though the calibration of the TOC analyzer was made for concentrations between 0 and 50 mg/l, it is possible that at this low concentrations errors might come up. Also for the sample preparation HCL (2M) is added for the pH drop. This solution may be not 100% pure and it may also contain some TOC which can contribute to the total TOC observed in demiwater. From this experiment it cannot really be confirmed the assumption that the PAC may contain residual organic carbon which contributed to the total TOC concentration recorded in the demiwater and tap experiments.

For clay there was a similar situation as with PAC. Figure 6-7 shows the adsorption isotherm of clay. The  $K_f$  value recorded was 1.5436 while n was 1.8529. n is again higher than 1 which means than good adsorption can be achieved at high concentrations. The  $K_f$  value is also higher than 1 but not very high to have an efficient adsorption at lower concentrations.

In Table 6-2 are shown the TOC values recorded for the batch experiment using clay as an adsorbent. A comparable biodispersant removal is observed in demiwater using clay also. The maximum TOC removal recorded at a dose of 60 mg/l clay, when the removal was 67.75%. For both solutions what was removed was only biodispersant. For this situation again it was observed that n>1. Taking into considerations the values recorded for  $q_{eq}$  and  $C_{eq}$ , this observation leads to competition. In demiwater competition is not expected since there are no substances which could adsorb besides the dissolved biodispersant. One reason the competition behavior is present is because of the micelles. At low carbon dozes PAC can remove the monomer fraction of the surfactant. At higher surfactant dozes the

monomer fraction is already removed and new monomers are formed from micelles. Another explanation would be that the surfactant is not only one substance, but a mixture of substances and compounds, out of which some can be adsorbed by PAC and some cannot.



Figure 6-6 Adsorption isotherms resulting from batch experiments in demiwater with 4 mg/l biodispersant dosed and clay as adsorbent

Clay dose	<b>C0</b>	Ceq	qeq	Removal
mg	mg/l	mg/l	mg/mg PAC	%
`0,00	2,21	2,21		0,00
10,00	2,21	2,13	0,01	3,89
20,00	2,21	1,88	0,01	15,23
30,00	2,21	1,96	0,01	11,48
40,00	2,21	1,25	0,01	43,74
50,00	2,21	1,63	0,02	26,43
60,00	2,21	1,25	0,02	43,47

Table 6-2 TOC measured at the end of the batch experiment, based on the clay dosed in each jar

In Figure 6-8 are presented the results obtained for the equilibrium experiment with clay. Also for this experiment 2 dozes have been monitored: 10mg/l and 60 mg/l. Again it can be seen that equilibrium is reached before 100 minutes and unfortunately, again there are some strange variations of the TOC concentration.





As in the previous experiment, there is a big drop in TOC concentration in the beginning of the experiment (first 100 minutes) followed by a small increase in concentration, after which the TOC concentration stabilizes. Same reason as for PAC may explain this increase after the 100 minutes. The TOC increase may be because of some residual TOC on the glassware or airborne which ends up in the beakers

### 6.4. Conclusion

In this chapter adsorption of the biodispersant using PAC and clay was tested. It is assumed that biodispersant is the main cause for UF membrane fouling, so a solution to prevent fouling would be to remove it before the filtration step. Since the biodispersant is an organic based nonionic surfactant, adsorption using PAC or clay was investigated to check the removal potential.

Biodispersant is a substance very difficult to measure and detecting the actual concentration in the effluent is very difficult. In all experiments the biodispersant concentration was based on the TOC concentration. In demiwater, TOC was represented indeed by the TOC, since no other substances are present. Because the surfactant molecules attach to surfaces, it is very difficult to assume how much surfactant was actually adsorbed by the PAC/clay and how much surfactant was lost due to handling and preparation of the solution. 4 mg/l biodispersant was dosed when the solution was prepared, but it can be observed that the starting concentration is 2.31 mg/l TOC. Same thing was observed in tap water, when the initial concentration was 4.02 mg/l, lower than it would be expected, since the tap water also contains some TOC. Biodispersant is a very complex substance which cannot be measured accurately, and TOC is not the right parameter to give information about the concentration.

From the adsorption experiments in demiwater it was concluded that using PAC it can be achieved a removal up to 72% when 60 mg/l was dosed, while with clay 43.47% surfactant was removed with 60 mg/l clay. A strange behavior was observed in the kinetic experiment. In the first 100 minutes a high TOC reduction as observed, followed by a slight increase. Most of the TOC reduction is also taking place in the first 100 minutes, after which the TOC concentration is stabilized. Fast removal can be because at the beginning of the experiment the surfactant is in colloidal form, after which micelles are formed which cannot be adsorbed by PAC or clay.

The biodispersant may be a mix of substances out of which some can be adsorbed easily by PAC or clay and some cannot be adsorbed. Biodispersabnt has been adsorbed from demiwater, but the moment tap water was used, the removal of TOC was lower, since competition was present. Tap water contains a low concentration of TOC which is removed first by the PAC and clay and after the substances from biodispersant get adsorbed. The equilibrium concentration in tap water was reduced with 65%, while in clay with only 16% (at 60 mg/l PAC/clay). The low removal in clay is because of the lower surface area available for adsorption. In tap water, as in CTBD water the removal with PAC was not very efficient since the TOC removal is not varying very much between the PAC doses. At low concentrations, there is the possibility of causing experimental errors, or some analysis measures. But even if one ignores the errors which may have appeared, the total TOC concentration at equilibrium is varying with only 5 mg/l from one PAC dose to another.

In CTBD the situation is much more complicated. The initial TOC without taking into consideration the TOC of the biodispersant is more than 40 mg/l. The TOC in CTBD is composed mainly from humic acids, which are not absorbable by PAC. Generally humic acids are removed from water by using ion exchange or granular activated carbon. From the experiment it can be concluded that very little TOC was adsorbed and, what was also noticed in tap water, no biodispersant was adsorbed.

# 7. Ultrafiltration

In order to find out the cause of the ultrafiltration membrane fouling, it is important to understand how the technology works and what has an influence on its operation. First, it is presented a theoretical background of the membrane filtration components, configuration and operation are presented. Some theoretical information about factors affecting fouling of the membranes are also described.

Since it was assumed that the fouling is caused by the biodispersant, a short literature review about membrane fouling caused by biodispersants was made. Experiments consist of comparison between waters with and without biodispersant. Lastly the results of the UF experiments made on CTBD water, Schie and demiwater are explained.

## 7.1. Theoretical background

Ultrafiltration membranes have most of the times anisotropic structure. The surface layer is finely porous and separation is done on its surface. Ultrafiltration membrane pore diameter can be determined from the molecular cut-off value and the value can vary between 0.001  $\mu$ m to about 10  $\mu$ m (Zeman & Zydney, 1996). At low pore sizes, the charge of the membrane can act as a separation mechanism also (Janssen, 2011).

In ultrafiltration processes 3 streams can be defined:

- Feed water: the water which needs to be filtered
- Permeate: the clean water stream
- Concentrate: the water containing the retained compounds

Filtration through porous membranes is performed by applying a fixed pressure to the feed solution, hydraulic transmembrane pressure (TMP) or a fixed flux. Permeate is collected at atmospheric pressure (Baker, 2012). UF membranes are very efficient in removing suspended solids, bacteria, large macro-molecules or pathogens resulting in a high quality permeate. During the entire filtration time, UF membranes produce a stable high quality effluent, independent of the feed characteristics. Operated in dead-end mode, UF membranes can operate at high flux, low TMP and low energy (Janssen, 2011).

When using ultrafiltration membranes, a good water quality can be achieved free of suspended solids, bacteria, large macro-molecules or pathogens. Ultrafiltration membranes are used generally in reuse applications for agricultural, industrial and urban water, or can be treated further using reverse osmosis for the production of ultrapure water. Besides high quality permeate, ultrafiltration has some other advantages like relatively high flux, low transmembrane pressure and low energy costs when applied in dead-end mode (Poele, 2005).

When choosing the ultrafiltration membranes, there are three different aspects which have to be taken into consideration: material of the membrane, configuration and operation.

## 7.1.1. Membrane material

Membranes are made from different organic or inorganic materials. For water treatment the most often applied are the organic membranes made out of different materials, with different pore sizes or configurations (Janssen, 2011).

Organic membranes were formerly made out of cellulose acetate, but nowadays they are mainly made out of synthetic polymers such as acrylates and polysulfones. Ultrafiltration membranes used for salt retention are manufactured from more hydrophilic materials (hydrogen-bonding properties). Hydrophobic materials are applied when thermal stability and mechanical strength are the main requirement. Hydrophobic membranes have a bigger mechanical, thermal and chemical stability (AWWA, 1996). Hydrophobic membranes have little to no impulse to adsorb water, which means that water tends to bead on the surface. On the other hand, hydrophilic membranes have an active group able to form hydrogen-bonds with water, so that membranes are easily wetted (Abdelrasoul, et al., 2013).

Polymers used for the fabrication of UF membranes are amorphous (glassy) polymers. These polymers are used because of their small pore sizes. During manufacturing, amorphous polymers can be easily generated, regulated or controlled (AWWA, 1996).

One of the most widely used membrane materials is polysulfone. The main characteristics of polysulfone materials are (AWWA, 1996):

- High pH resistance
- High temperature tolerance (up to 75°C)
- Resistant to oxidants
- Broad range of pore sizes (1 to 20 nm) with molecular weight cut-offs that differ from 1000 to 500,000.

Hydrophobic UF membranes must be stored wet, because if they are left to dry out without appropriate treatment, will result in irreversible flux loss, the membrane structure might collapse and the original wetting will not be achieved (AWWA, 1996).

In comparison with organic materials, membranes made out of inorganic materials have a higher mechanical, chemical and thermal resistance. The advantages of ceramic membranes include (AWWA, 1996):

- Low maintenance cost
- High pH resistance (range 0-14)
- High temperature resistance (up to 140°C)
- Wide pressure limitations (2MPa)
- Higher fluxes
- Fouling resistance
- Great selectivity

## 7.1.2. Configuration

Membrane configuration depends on the geometry: flat sheet or tubular. The choice of membrane depends by the type of water to be treated. The most used types of membranes are (Roorda, 2004):

- Tubular membranes: inner diameter bigger than 3 mm, bundled in a module.
- Hollow fiber and capillary membranes: inner diameter lower than 3 mm, bounded in a module with hundreds/thousands of fibers.
- Plate or frame membranes: made out of series of flat sheets and support layers with a packing density of 100-400  $m^2/m^3$ .
- Spiral wound membranes: flat membranes wound around a spacer, with a packing density of 300-1000 m<sup>2</sup>/m<sup>3</sup> used for nanofiltration and reverse osmosis.

In Figure 7-1 are presented the four types of membranes explained previously.



#### Figure 7-1 Types of membranes

In the case of tubular and hollow fiber membrane, the flow of the feed water can be inside-out or outside-in. For the inside-out filtration, permeate is collected outside the membrane, while for the outside-in, permeate is collected inside the fibers. In Figure 7-2 is presented a schematic representation of the inside-out and outside-in filtration (Poele, 2005).



Figure 7-2 Representation of inside-out and out-side in filtration

#### 7.1.3. Membrane operation

The process configuration of the membrane influences the filtration process. There are 2 main operations modes: dead-end and cross-flow operation. In dead-end mode the total volume of feed-water passes the membrane, while the larger compounds are retained in the membrane pores or membrane material, which results in a pressure increase (Roorda, 2004). During cross-flow filtration part a part of the fees is flowing along the surface of the membrane, limiting the accumulation of retained compounds.



Figure 7-3 Schematic representation of cross-flow filtration and dead-end filtration

### 7.1.4. Factors contributing to membrane fouling

A major disadvantage of membrane filtration is fouling. Fouling is confirmed by the flux reduction with time of operation. Flux decline should take place when the operating parameters are kept constant (pressure, flow rate, temperature, feed concentration).

Besides the parameters presented before, the filtration performance is also influenced by the type of feed which will be treated, TMP or temperature. Membrane characteristics have a big impact as well. In membranes with narrow pore distribution, hydrophilic and with a negative surface charge will experience less fouling (Roorda, 2004). The particles which have the tendency to foul the membranes are generally hydrophobic. They manage to bundle up or group together and form colloidal particles. A high charge density on the surface of the membrane is related with higher membrane hydrophilicity. For water and wastewater treatment, the membranes used are made out of polysulfone, cellulose acetate or ceramic, have on a certain extend a negative charge and are hydrophilic (Abdelrasoul, et al., 2013).

Membrane fouling is also highly affected by the characteristics of the feed. More fouling will be observed when the suspended solids concentration will be higher; fouling will be also determined by the particle properties, pH or ionic strength. When the concentration of the feed water is increased, usually a decline in the feed flux is observed (Abdelrasoul, et al., 2013). High feed concentration has little effect on the membrane retention, excluding the case when the size of the particles changes with concentration (Zhao, et al., 2000).

Another reason of fouling is due to the changes which may occur to the properties of the membrane. These changes could have physical or chemical origins. Due to high pressure the membrane may suffer from compaction, which can also affect the permeability of the membrane. Chemical damaging can happen when the pH, temperature or other properties of the feed are not compatible with the membrane. Often chemical cleanings or chemical enhanced backwashes (CEB) will decrease the lifespan of the membrane (AWWA, 1996).

The effect of flux-depression caused by membrane fouling is often confused with the flux reduction related with concentration polarization (Cheryan, 1998). Concentration polarization is a process in which the solute or the concentration of particles near the surface of the membrane is higher than in the bulk. This phenomenon takes place only if the membrane shows different permeability for the various particles present in solution (Song & Elimelech, 1995). By lowering the TMP, feed concentration, or by increasing cross-flow velocity or turbulence the effects of concentration polarization can be reversed. If these measures are successful the cause for flux reduction is concentration polarization and not fouling (Cheryan, 1998).

Membrane fouling will result in a flux decline. Fouling is caused by depositions and accumulations of the components present in the feed (suspended particles, impermeable dissolved solutes, normally permeable solutes) on the surface of the membrane and within the pores (Cheryan, 1998).

### 7.1.5. Membrane cleaning

A fundamental step for membrane processes is cleaning. All membranes will foul sooner or later, leading to decrease in performance. When the performance has dropped below a minimum acceptable level, then it is the time to remove the foulants from the membrane (Zeman & Zydney, 1996). One way to remove the layer of retained particles is by applying forward-flushing of the membrane. Forward-flushing can be improved by adding air bubbles (AirFlush®) ( (Roorda, 2004).

The most common applied method for partial removal of the retained particles is backwashing (backflushing). Backwashing is applied between filtrations by reversing the flow and flushing permeate through the membrane pores. Rejected materials in the pores of the membrane and on the surface of the membrane are released, lifted up and flushed out of the module. Backwashing is not effective in the case of the particles strongly adsorbed into the pores. The backwashing time is between 30 and 120 seconds at every 10 to 30 minutes of filtration. Applying regular backwashes on the membrane, a typical curve is determined. In the beginning the flux decreases, but after backwashing is performed the flux comes back to its initial value (Roorda, 2004). In Figure 7-4 is presented the curve resulting at constant flux operation of the UF.



Time (hour)

Figure 7-4 Effect of backwashes on the flux during dead-end ultrafiltration at constant flux

Besides the mechanical cleaning (forward-flushing, backwashing) chemical cleaning is also applied using specific cleaning solutions (detergents, chemicals). Chemical cleaning is applied by circulating the solution through the membrane module for 1 or 2 h; regular cleaning is necessary to keep the high performance of the UF membranes. The frequency of cleaning can vary from daily (food industry) to monthly (ultra-pure water systems) (Baker, 2012). The parameters which have to be taken into account when applying chemical cleaning is the concentration of the chemicals together with the cleaning time and the characteristics of the membrane, in order to prevent the degradation of the membrane. The chemicals applied for clearing can be classified as follows (Roorda, 2004):

- Acids: dissolve calcium salts and metal oxides;
- Alkalis: remove silica, inorganic colloids and many biological/organic foulants;
- Surfactants: displace foulants, emulsify oils, dissolve hydrophobic foulants;
- Oxidants: oxidase organic matter and bacteria;
- Sequestrates (chelating agents): remove metal cations;

• Enzymes: degrade foulants.

In Table 7-1 are presented some substances used for chemical cleaning and their compatibility with cellulose triacetate, polysulfone and polyvinylidene fluoride (PVDF) membranes. Cellulose triacetate membranes have least compatibility, which makes it more difficult to choose the appropriate chemicals (Zeman & Zydney, 1996).

Chemical	Cellulose triacetate	Polysulfone	PVDF
Hydrochloric acid	-	+	+
Sodium hydroxide	-	+	+
Methanol	0	0	+
Isopropanol	+	0	+
Dioxane	-	-	-
Glycerine	+	+	+
Ethylene glycol	0	+	+
Benzene, toluene	+	-	+
Chloroform	-	-	+
Acetone	-	-	-

Table 7-1 Chemicalssolutions used for cleaning, compatible with polymeric membranes

Note: (+) = resistant, (-) = not resistant, (0) = limited resistance

### 7.1.6. Membrane fouling caused by biodispersants

Fouling of the UF membrane can be caused by many factors as described in the previous section. Various types of biodispersants have been assumed to clog membrane pores. Several researchers have tested different types of biodispersants on UF, NF or RO membranes to see if indeed they had an influence. Some of their results are presented in this section.

Mizoguchi et al., 2002 performed filtration experiments with a new developed amine oxide type nonionic surfactant. This surfactant has a high stability and low environmental load. In the paper it was presented the phenomenon which was focusing on the pre-micelle formation in the low concentration range of the surfactant, below the CMC.

Mizoguchi used a nonionic surfactant, N-lauryl-N, N-dimethyl-aminoxide (LDAO), with a CMC of 0.028%. Surfactant solutions tested were in the range of 0 to 0.1 wt.% and monitored by TOC measurements.

Below a surfactant concentration of 0.001 wt.% it was observed that the total permeation flux was the same as the permeation flux for pure water, but started decreasing when the surfactant concentration reached 0.012 wt.%. Above 0.012 wt.% permeation flux increased gradually with the increase in concentration and recovered again to the pure water level above 0.03 wt.%.

Surfactant concentration in permeate had almost the same levels as the surfactant concentration in the feed for low concentrations. Above concentrations of 0.014 wt.% some of the surfactant was removed, since the concentration in the permeate was lower than in the feed. For concentrations between 0-0.01 wt.%, LDAO molecules in the feed are present as monomers and cannot be removed by the membrane because the size of the monomer is lower than the size of the membrane pores. Under these conditions the total permeation flux was the same as the permeation flux of the pure water.

For concentrations between 0.012-0.03 wt.% the permeation flux was decreased. It is assumed that the monomers formed small aggregates (pre-micelles) due to concentration polarization which resulted in pore blocking. At concentration higher than 0.014 wt.% (<CMC) surfactant concentration in the permeate was lower than the concentration in the feed so it is assumed that due to concentration polarization pre-micelles formed micelles on the membrane surface. Micelles are bigger in size than the membranes pores, so they will not block the pores and will not decrease the permeation flux. When the surfactant concentrations were higher than 0.03 wt.% (>CMC) micelles were formed in the entire solution and the permeation fluxes were again equal with the pure water permeation flux.

Mizogochi concluded that for the surfactant removal with UF membrane, the concentration fluxes were slightly decreased when the surfactant concentration in the feed was lower than the CMC concentration. It is assumed that due to concentration polarization on the surface of the membrane pre-micelles were formed which clogged the pores of the membrane.

Kishimoto & Kimura, 2012 performed filtration experiments with RO membranes and three types of surfactants, out of which one was nonionic surfactant. Experiments showed that permeability during filtration was dependent of the surfactant concentration in the feed and also by the charge. At higher concentrations the permeability was decreased because of the concentration polarization. From previous studies (Santra, et al., 2001) was concluded that surfactants are a major cause for membrane fouling. Here as a nonionic surfactant polyoxyethylene-pisooctylphenol (Triton X-100) was used, with concentrations ranging between 60 and 1900 mg/l (typical range dosed in industries). The membrane used was a polyamide thin-film composite produced by DOW, operating at low pressures (max. TMP 1000 kPa).

Experimental setup consisted of a membrane module with a pump, a regulator for the flow changes, pressure gauge, flow meter a reservoir equipped with a stirrer. Both permeate and concentrate were recirculated to the reservoir and the TMP was controlled between 36 and 629 kPa with the regulator.

During the experiment first pure water was filtered for about 60 minutes in order to record the TMPs. After different surfactant solutions were filtered for 6 to 10 h. During filtration permeability was monitored. After the surfactant filtration the membrane was flushed with pure water in order to remove all the residual surfactant. In the end the permeability was measured again with pure water. During filtration the surfactant solution was constantly sampled for the measurement of the TOC and surfactant concentration (calorimetric kits).

The surfactant concentration in permeate was not in the detectable range, so a rejection of 99% was assumed. With a concentration of 0.093 mM of Triton X-100 the permeability was the same as the permeability of pure water. Permeability of pure water decreased after filtration under different conditions.

If permeability decrease is caused by concentration polarization, the pure water permeability is not changed before and after filtration. When permeability was dropping because of foulant adsorption on

the membrane, the permeability of pure water dropped after filtration. So in the case of 0.093 mM Triton X-100 was caused by concentration polarization. There were also cases when the deterioration of pure water filterability was observed, but the pure water permeability after filtration was higher than the permeability during filtration. This means that the permeability decrease was caused by concentration polarization and the adsorption of the surfactant.

Kishimoto assumed that the adsorption of surfactant happens: a hydrophilic group of the surfactant is first adsorbed on the membrane surface and after the hydrophobic group is adsorbed on the membrane surface. The adsorption of the hydrophilic group depends by the membrane charge and also the charge of the hydrophilic group.

Fouling control is dependent of the electrostatic interactions between the surface of the membrane and the surfactant. In order to observe the changes the charge of the surfactant was changed by addition of sodium lauryl sulfate (SLS).The authors observed that the permeability was slightly increased than in the case of Triton X-100 dosage only. Pure water filterability was 1.06 l/(m2\*d\*kPa) before filtration and 1.04 l/(m2\*d\*kPa). For Triton X-100 solution the permeability decreased from 1.01 to 0.71 l/(m2\*d\*kPa). So SLS addition is effective for the decrease in adsorption of the nonionic surfactant on the membrane and thus permeability improvement.

Kishimoto and Kimura concluded that the higher the surfactant concentration is the lower the permeability decrease because of concentration polarization. For fouling control SLS addition changed the charge of the surfactant into anionic and permeability during filtration was increased. Pure water filterability was not decreased after, filtration did not decrease after the SLS addition, thus charge modification of the surfactant was useful for the fouling prevention.

Fernandez et al., 2005 performed ultrafiltration experiments with 2 types of surfactants, anionic, sodium dodecyl sulfate (SDS) and nonionic Tergitol NP-9 (nonylphenol polyethylene glycol ether). During the experiments the influence of cross-flow velocity, temperature, pressure and surfactant concentration on the permeate flux were monitored. Permeate flux and surfactant retention were measured for the evaluation of concentration polarization and fouling.

Surfactant solutions were prepared with deionized water. The concentrations in the experiment were 0.25, 0.5, 1 and 2 times the value of the CMC. The membrane used was UF ceramic membrane with pore diameter of 20 nm. One module was installed with an active layer of microporous zirconia.

The authors observed an initial decrease in permeate flux and steady state permeate flux  $(J_{ss})$  is reached in within seconds. The permeate flux increased with the increase in TMP and increase in surfactant concentration.

When the surfactant concentration was equal with the CMC a decrease in the permeate flux was seen, which was not restored at higher cross-flow velocities. This decrease may be because of concentration polarization, formation of a gel layer on the membrane surface, membrane fouling and surfactant/membrane interactions. The more likely explanation is the occurring of concentration polarization in the vicinity of the membrane surface, since the concentrations at which the gel layer forms on the surface of the membrane are much higher than the concentrations used in the experiments.

As TMP increases, concentration polarization increases and also surfactant concentration on the surface of the membrane increases resulting in higher permeate flux and higher surfactant concentrations in permeate. The permeate flux is slightly more increased at low cross flow velocities

which is unexpected, and could be explained by some interactions between the membrane and the surfactant.

The permeate flux of the membrane in the experiment with the nonionic surfactant was very high and higher than the permeate flux recorded with pure water. This situation is because of the interactions between the hydrophobic chain and the Tergitol molecules and the non-polar sites of the membrane surface and pores, which increased at lower turbulence of the aqueous surfactant near the membrane.

The reduction of permeate flux as the surfactant concentration increased is due to concentration polarization. Higher permeate fluxes were obtained for lower concentrations. When the surfactant concentration was higher than the CMC the permeate flux reduction was increased due to the micelles formation. At higher temperature the permeate flux increased because with the temperature increase the influences of the phase behavior of the surfactant, the viscosity decreases.

High surfactant retention was measured at low concentrations. High Tergirol-9 retention can be explained by the surfactant membrane interactions mentioned before and also by the surfactant adsorption inside the membrane support. At concentrations higher than CMC retention decreases because of the build-up of the surfactant polarization layer and because of the micelles arrangement which cannot permeate through the membrane.

Fernandez concluded that there is an interaction between the ceramic membranes and the surfactant at the surface of the membrane. Because of the interactions between the membrane and the nonionic surfactant resulting in hydrophilization of the membrane surface and pores, resulted in high permeate flux and high surfactant retentions at low concentrations. Surfactant retention was between 60 and 70 % depending on the concentration.

#### 7.1.7. Ultrafiltration parameters

TMP is the most important parameter for ultrafiltration. Permeate flux is permeate which flows through the membrane and is defined as the volume of permeate flowing through the membrane per unit of membrane area. The unit for flux is  $m^3/m^2$ 's or  $l/m^2$ 'h. Equation 7-1 gives the flux expression (Janssen, 2011):

Equation 7-1

Equation 7-2

$$J = \frac{dV}{dt} \cdot \frac{1}{A_{membrane}}$$

Or Equation 7-2:

$$J = \frac{\Delta P}{\eta \cdot R}$$

flux	[l/²·h]
filtered volume	[m <sup>3</sup> ]
time	[s]
area of the membrane	[m <sup>2</sup> ]
trans-membrane pressure	[N/m <sup>2</sup> ]
dynamic viscosity of the permeate	[N·s/m <sup>2</sup> ]
	flux filtered volume time area of the membrane trans-membrane pressure dynamic viscosity of the permeate

From here, the total resistance of the membrane can be calculated using Equation 7-3 (Shang, 2014): Equation 7-3

$$R = \frac{\Delta P}{\eta \cdot J}$$

With:

 $[m^{-1}]$ R filtration resistance

Dynamic viscosity of the water is temperature dependent and can be calculated from Equation 7-4: Equation 7-4

$$\eta = \frac{497 \cdot 10^{-3}}{(t+42.5)^{1.5}}$$

Where:

t feed water temperature [°C] =

The total surface area for capillary membranes depends of the number of fibers. The formula which gives the total membrane area is presented in Equation 7-5:

Equation 7-5

$$A_{membrane} = n \cdot (2 \cdot \pi \cdot r^2 + 2 \cdot \pi \cdot r \cdot h)$$

In which:

r

n =

number of fibers [-] [mm]

capillary internal diameter =

length of fiber h = [m]

### 7.2. Experimental procedure

The ultrafiltration set-up was designed to operate at constant flow filtration and constant flow backwashes. Three operational phases were applied for the set-up configuration: filtration (production), forward flush (from the feed vessel to the vessel of backwash) and backwash (Shang, 2014).

The experiments were performed during 8 hours of filtrations (12 minutes at a flux of 60  $l/m^2/h$ ) and backwashes with permeate water (2 minutes at a flux of 120 l/m2/h). The first 3 backwashes were done with demiwater since there was yet no enough permeate produced. After each experiment, the membrane was soaked overnight in hypochloric acid (10%). After the chemical cleaning the membrane was flushed with demiwater and the clean membrane resistance measured. The resistance was almost completely restored and the experiment restart. All filtration cycles were performed in dead-end mode. In Figure 7-5 is shown the experimental UF installation used.

The feed and backwash flow were pumped using two pairs of programmable DUAL syringe pumps (New Era Pump Systems, Inc.). The DUAL syringes work in parallel, having a continuous infusion mode: while one syringe is withdrawing the feed the other is pumping it. Before the membrane a digital pressure meter was installed to measure the pressure during filtration. The pressure of the permeate was the same as the atmospheric pressure, so no pressure meter was installed after the membrane module. The pressure was recorded using a data-logger (EL-USB-3 Voltage Data Logger), every 10 seconds. Two manual valves were applied to control the direction of the flow. These valves were changed after each filtration and backwash cycle.

Samples of the feed and permeate were collected for the TOC analysis. The feed temperature was also measured for the determination of the dynamic viscosity of the feed. Before each experiment the membrane was flushed with demiwater and the clean membrane resistance was measured. After, the system was flushed with air and filled with the filtration effluent.



Figure 7-5 UF experimental set-up

The membrane module was manually constructed. It was made out of 5 capillary ultrafiltration membranes (Norrit X-Flow) with an internal diameter of 0.8 mm, made out of PES coated with PVP, which gives it the negative charge. In Table 7-2 are presented some of the UF membrane characteristics (Poele, 2005), (Roorda, 2004).

ם עם
5/FVP
) k Da
ide-out
nm
mm
37 cm
045 m <sup>2</sup>
9999%
99%
) ic n ic 37 0 9 9

Table 7-2 UF	membrane	characteristics
--------------	----------	-----------------

## 7.2.1. Experimental procedure

Before a new membrane was used, the membrane was swollen by soaking in demiwater overnight. Before each experiment the membrane was flushed with demiwater and the clean membrane resistance was measured. For the clean membrane resistance, demiwater was filtered for about 5 minutes. The pressure was constant during the 5 minutes and the temperature was also recorded for the calculation of the viscosity. After the 5 minutes the system was flushed out using air and refilled with the actual feed.

As feed there were several types of water used:

- CTBD
- Demiwater
- Schie canal water

All these water types were used in order to see what the effect of the biodispersant is on the resistance of the membrane. The effect of the biodispersant can only be determined by comparing the membrane resistance during operation of the feed with and without biodispersant. Since there is no CTBD without biodispersant, in demiwater and Schie canal water there were added 4 mg/l of biodispersant which were continuous mixing on a stirring plate for at least 12 hours.

Schie water was filtered with a 0.45  $\mu$ m filter before preceding the UF experiment. This step was added in order to remove the bigger particles present in the water.

UF experiments were always performed with the feed being at room temperature. Before starting the experiment the data recorded on the data-logger was saved and the data logger reset in order to make sure that will be enough space for the new recordings and the data-logger connected to the system. After the system has been filled with the feed the permeate valve was open, the feed pump and a stop watch were turned on for 12 minutes, the filtration time. After the 12 minutes the feed pump is stopped and the permeate valve closed. The permeate tank is the same as the backwash feed. For the backwash the backwash pump and the backwash valve are opened and the stopwatch is set for 2 minutes. These 2 cycles are repeated for 4 hours, with all types of feed.

At the end of the experiments the system is flushed out and hypochloric acid solution (10%) is added for the chemical cleaning of the membrane. The data logger is disconnected and the data saved for interpretation.

### 7.2.2. Coagulation/flocculation combined with UF

Coagulation/flocculation and adsorption experiment were combined with UF also. Only Schie water was used for these experiments. For coagulation/flocculation, a jar test was done in order to decide which iron chloride concentration should be added for the most optimal coagulation/flocculation results. For the jar test the same procedure as in the "Coagulation /Flocculation" chapter was used. At the beginning of the experiment pH, EC, turbidity and iron concentration were measured. The iron chloride solutions added were between 10 mg/l and 30 mg/l (10, 15, 20, 25 and 30 mg/l iron chloride) in 1.8 l Schie water. Sodium hydroxide was added as well in order to keep the pH in the "sweep coagulation" zone. The NaOH solutions were calculated as in the previous chapter also.

After the 21.5 minutes (30 seconds 300 at rpm, 7 minutes at 15 rpm, 7 minutes at 11 rpm and 7 minutes at 10 rpm) of stirring, the stirrers have been stopped and withdrawn from the jars so that flocs could settle on the bottom. After about 20-30 minutes of settling the supernatant was removed and again pH, EC, turbidity and iron concentration have been measured. The iron dosage used for the combined coagulation/flocculation – UF experiment was chosen based on the results obtained in the jar test. The best dose was the one which gave the lower iron concentration, turbidity and EC.

For the coagulation/flocculation – UF experiment 2 l of Schie water in which 4 mg/l biodispersant were added was left to stir for 12 h on a stirring plate. In 1.8 l of Schie solution were added 20 mg/l iron chloride and stirred for 21.5 minutes (30 seconds at 300 rpm, 7 minutes at 15 rpm, 7 minutes at 11 rpm and 7 minutes at 10 rpm). After that time the feed was left untouched for 30 minutes so that the formed flocs would settle on the bottom of the jar. In order to remove all the formed flocs the

supernatant was also filtered with 0.45  $\mu m$  filter. The filtrate was then used as feed for the UF experiment.

### 7.2.3. Adsorption combined with UF

Before doing the adsorption experiment, 2I of Schie water solution with 4 mg/l biodispersant was prepared and mixed for 12 h. The applied PAC dose was chosen based on the results of the adsorption experiments obtained before. The higher the dosage the better the removal, but PAC is an expensive material so it was chosen to dose only 30 mg/l PAC.

Schie solution was at room temperature and after the PAC was added it was left to stir for 2h at 50 rpm. After the 2h stirring the water was filtrated through a 0.45  $\mu$ m filter in order to remove the PAC before UF.

### 7.2.4. Lower biodispersant concentration

Last UF experiment done was with Schie water and lower biodispersant concentration, 0.1 mg/l. Dosing 0.1 mg/l biodispersant is very difficult since it is such a small amount. In this situation, the water which already had 4 mg/l biodispersant dosed was diluted.

2 l of Schie water with a concentration of 0.1 mg/l bodispersant were made by mixing 50 ml of Schie water with a 4 mg/l biodispersant concentration with 1950 ml of raw Schie water. Raw Schie water was before mixing, filtered through a 0.45  $\mu$ m filter in order to remove bigger suspended solids. Filtration procedure was the same as for all the other experiments.

## 7.3. Experimental results



### 7.3.1. Filtration of cooling tower blowdown water

Figure 7-6 Membrane resistance increase during CTBD filtration

The hydraulic backwashes performed on the membrane were able to recover partially the resistance of the membrane during the CTBD filtration. After each backwash the resistance was slightly increased. The clean membrane resistance was measured before the experiment and it was  $0.06 \cdot 10^{11}$  m<sup>-1</sup>. At the end of the 8 hour filtration time, resistance increased up to  $0.05 \cdot 10^{11}$  m<sup>-1</sup>. The TOC of the feed 44.06 mg/l, while in permeate the TOC left was 42.69 mg/l. Figure 7-6 is a graphical representation of the resistance of the membrane during ultrafiltration with CTBD.

The increase in resistance is assumed to be because of the biodispersant left in the CTBD has formed micelles which are being rejected by the membrane. Part of the micelles are flushed out during backwash, but the one that was adsorbed in the membrane pores is causing the resistance increase.

Besides the micelles being rejected by the membrane, the biodispersant molecules before saturation attach to the surfaces so, in this case, molecules will also attach to the membrane forming a layer which is also contributing to fouling.

#### 7.3.2. Filtration of demiwater

In demiwater there are no particles or components which could be adsorbed in the membrane pores. There is expected to see no increase what so ever in the resistance of the membrane. In Figure 7-7 are presented the obtained resistances for the filtration experiment performed with demiwater.



Figure 7-7 Resistance of the membrane during the simple demiwater experiment

As expected the membrane resistance was constant during the entire experiment. The starting pressure for the first 2 filtration cycles was 0.25 bar, but stabilized to 0.30 bar starting with the third cycle. The high pressure recorded during the experiment performed with simple demiwater can be explained by the fact that the membrane used was not new, but it was used in other experiments before, and the cleaning did not remove all the retained particles.

### 7.3.3. Filtration of demiwater with 4 mg/l biodispersant

As it can be seen from Figure 7-7, during the experiment in which demiwater with 4 mg/l biodispersant was used as feed, the resistance was increased slightly. The experiment started with a TMP of 0.24 bar. After each subsequent backwash the membrane resistance did not come back to its initial value. The increase is very small, but one has to keep in mind that the increase in TMP is caused by the biodispersant alone, since there are no other compounds present in the feed. At the end of the 4 h experiment the TMP was 0.27 bar.



Figure 7-8 Membrane resistance increase during the experiment performed with demiwater-biodispersant solution

#### 7.3.4. Filtration of Schie water

In Figure 7-9 is presented the membrane resistance trend recorded during the filtration experiment in which Schie canal water was used as feed. As it can be seen from the graph, the resistance of the membrane was completely recovered after each backwash. The starting pressure at the beginning of the filtration cycle was 0.12 bar which increased to 0.13 bar after the 12 minutes time. The TOC value of the Schie water was 22.52 mg/l. UF membranes cannot remove dissolved organic carbon, so the TOC measured in the permeate is very low, 18.74 mg/l.



Figure 7-9 Membrane resistance recorded during the simple Schie water filtration

#### 7.3.5. Filtration of Schie water with 4 mg/l biodispersant

Same batch of Schie water was used for this experiment also. The effluent was filtered with a 0.45  $\mu$ m filter, 4 mg/l Nalsperse 7348 was added and stirred for 12 hours in order to obtain an even distribution of the biodispersant. In Figure 7-10 is presented the trend observed during the 4 hours filtration time. The initial TMP is around 0.1 bar and increasing every minute. After the backwash the resistance cannot be completely recovered. After the 8 hours of filtration, the TMP was increased significantly reaching 0.22 bar. The slope of the increase in resistance is very high compared with the slope of the resistance increase recorded in the experiment done with simple Schie water.

TOC present in the feed was 25.55 mg/l, while in the permeate there was still left 20.12 mg/l TOC. The extra TOC found in the Schie water is because of the added biodispersant. TOC removal can be comparable in the 2 cases, Schie without biodispersant and Schie with 4 mg/l biodispersant filtration experiments.





with UF		
Fe <sup>3+</sup> FeCl <sub>3</sub> NaOH		
mg/l	g	ml
10	9.67	1.04
15	14.5	1.57
20	19.33	2.09
25	24.17	2.61
30	29	3.13

#### 7.3.6. Coagulation of Schie canal water combined with UF

Table 7-3 FeCl<sub>3</sub> and NaOH dosed for coagulation of the Schie water, before filtration

For the jar test,  $Fe^{3+}$  concentrations between 10 and 30 mg/l have been tested.  $FeCl_3$  solutions have to be prepared in order to achieve the  $Fe^{3+}$  concentrations desired. In Table 7-3 are presented the required quantities.  $FeCl_3$  is known to drop the pH of the solution, so in order to stay in the "sweep coagulation" area (pH between 6.5 and 9), NaOH has to be added. The added volumes of NaOH are also presented in Table 7-3 In Table 7-4 are shown the starting values of the Schie water.

After the 5 jars have been filled and the FeCl3 solutions were prepared, the experiment was started. After the 21.5 minutes of stirring and 30 minutes of settling, samples of the supernatant were collected and analyzed in order to see what was the effect of coagulation. In Table 7-5 are presented the results obtained after coagulation/flocculation.

Fe <sup>3+</sup>	рН	EC	Turbidity	Fe	тос
mg/l		µS/cm	NTU	mg/l	mg/l
10	7.13	904	1.36	1.493	7.004
15	7.1	913	1.1	2.656	6.138
20	7.02	928	1.14	1.611	5.373
25	6.92	937	3.81	1.549	5.401
30	6.79	952	0.903	1.662	4.874

Table 7-5 Schie water quality after coagulation/flocculation with different Fe<sup>3+</sup> concentrations

Analyzing the quality of the feed after coagulation-flocculation, it was decided that the most optimum  $Fe^{3+}$  dosage would be 20 mg/l. Using this amount of  $Fe^{3+}$  the turbidity is significantly lowered from 4.55 NTU to 1.14 NTU and the residual iron is not very high, 1.611 mg/l Fe.

The coagulation/flocculation effluent was filtrated so that no flocs would be present and used as the feed for the UF experiment. In Figure 7-11 is presented the membrane resistance experiment.

It can be seen that the resistance of the membrane is not very much affected. After the backwashes the resistance is not completely recovered but the increase is not very high. The initial TMP is quite low 0.07 bar, reaching 0.11 bar at the end of the 8 hour experiment. The increase in resistance is very much reduced in this case, compared with the Schie water with 4 mg/l biodispersant without the coagulation step.

Comparing the slope of the membrane resistance increase for the combined experiment UFcoagulation/flocculation and simple filtration of Schie with biodispersant, it can be seen that the increase is less in the case of combined experiment. For simple coagulation the value of the slope was 0.0003 while for the combined experiment is 1e-04, which means that coagulation is improving the filtration trend.



Figure 7-11 Membrane resistance increase during Schie water +4 mg/l biodispersant filtration, after coagulation/flocculation with 20 mg/l Fe<sup>3+</sup>

#### 7.3.7. Cooling tower blowdown water

For CTBD water, coagulation was also combined with UF. The Fe<sup>3+</sup> dosage was chosen based on the previous jar tests done. 20 mg/l Fe<sup>3+</sup> was dosed together with 2.09 ml NaOH (0.2 M) which kept the pH in the "sweep coagulation" area (pH=7.48). In Figure 7-12 is presented the membrane resistance trend for ultrafiltration of CTBD after coagulation.



Figure 7-12 Membrane resistance increase during filtration of CTBD, after coagulation/flocculation with 20 mg/l Fe<sup>3+</sup>

The slope of the resistance increase of CTBD is comparable with the slope of the Schie water, but steeper. The water quality for Schie was better (see TOC=5.373 mg/l) compared with CTBD's TOC=44.89 mg/l. If one compares the slopes of the simple filtration of CTBD and CTBD combined with coagulation/flocculation will see no difference. The increase is basically the same (m=0.0001).

The starting pressure for this experiment is 0.08 bar, higher than in the case of simple CTBD filtration ( $\Delta P=0.06$  bar). This pressure increase can be explained by the higher iron concentration left in the feed due to coagulation/flocculation.

### 7.3.8. Adsorption combined with UF

#### Schie water

First filtration experiment performed in combination with PAC was with Schie water. 30 mg/l PAC were added in 2 l Schie water and stirred for 2 hours at 50 rpm. After equilibrium was reached, the effluent was filtered through 0.45  $\mu$ m filter in order to remove the PAC. In Figure 7-13 is presented the membrane resistance trend recorded during the 4 hour experiment.

When PAC was added to the Schie water+4 mg/l biodispersant, not much TOC removal was observed. Initial TOC measured in the Schie was 10.62 mg/l, while after 2 h of adsorption there was still left 7.069 mg/l. Membrane increase slope for the adsorption experiment combined with UF was lower than in the case of simple Schie filtration, but the difference is not that much. The slope for membrane increase in the case of Schie+4 mg/l biodispersant was 0.0003, while for adsorption+UF the slope was 0.0002. Filtration process was slightly increased but in these conditions PAC is not really making a big difference.



Figure 7-13 Membrane resistance trend recorded during the filtration of Schie water + 4mg/l biodispersant, after adsorption with PAC

### Cooling tower blowdown water

30 mg/l PAC were also added in CTBD to see what the TOC removal would be and also what the effect on the membrane resistance would be. The total TOC measured in cooling tower blowdown was 44.89 mg/l, while after the 2 hours of adsorption there were still left 40.11 mg/l TOC.

Even though the TOC removal was quite low, as it can be seen from Figure 7-14, the membrane resistance increase observed during this experiment was very low compared with the simple CTBD experiment. The pressure increase was from 0.03 to 0.06 bar at the end of the 8 hour filtration time.

From all experiments performed this seems to be the most efficient method. The lowest membrane resistance increased was observed during the adsorption and UF combination for the CTBD.



Figure 7-14 Membrane resistance trend recorded during the CTBD filtration, after PAC adsorption

#### 7.3.9. Schie water + 0.1 mg/l biodispersant

Last experiment done was with Schie water with a biodispersant concentration of 0.1 mg/l. It is assumed that a lower dose of biodispersant , but higher than the CMC would have a lower impact on the membrane resistance, since the number of formed micelles is lower, and the micelles are actually fouling the pores of the membrane.

Figure 7-15 shows the membrane resistance increase noticed during the 4 hours filtration. The resistance of the membrane is increasing during filtration but is almost completely recovered after the backwashes. From the initial TMP of 0.08 bar, at the end of the experiment the increase was only until 10 bar. The slope of the resistance increase can be compared with the resistance increase slope obtained for the experiment in which Schie water (without biodispersant) was used as feed.



Figure 7-15 Membrane resistance trend observed during filtration of Schie water + 0.1 mg/l biodispersant solution

### 7.4. Conclusions

Different experiments were performed using the UF system. CTBD water, Schie water and demiwater with or without 4 mg/l biodispersant were used as feed. CTBD without biodispersant was not available so a comparison between the operation with or without biodispersant could not be done.

In Figure 7-16 are presented the slopes of the increase in membrane resistance for all experiments. It can be noticed from the graph that various trends were recorded.

One important thing which needs to be outlined is regarding the varying initial resistance recorded for all experiment. It can be observed for the previous presented graphs that the starting membrane resistance is not the same. This is because for some experiments there were new membranes used, while for other experiments the membrane were soaked overnight with hydrochloric acid. It is possible that the solution was not strong enough so that all retained particles were removed, or that soaking time was not sufficient, and with longer soaking time, better cleaning would have been obtained so that the clean membrane resistance would have been more or less the same for all runs.



Figure 7-16 Slope of the membrane resistance increase recorded during the different filtration experiments

That is why the membrane fouling graphs were made also. The resistance of the membrane is given by the initial resistance of the membrane and the fouling resistance created during the filtration experiment.

$$R_m = R_c + R_f$$
 so  $R_f = R_c - R_f$ 

With:

The fouling resistance membrane represents the actual membrane fouling caused by filtrating the feed, without taking into consideration the foulants which could not have been removed during chemical cleaning. This representation is more realistic for the situation compared with the total membrane resistance. It can be noticed that the slope of the membrane increase is the same as the slope of the membrane fouling.

Demiwater is pure water with no particles or components which could contribute to the membrane fouling. The slope of the membrane resistance was not steep. When biodispesant was mixed in the demiwater an increase in membrane resistance was observed quickly. Fouling resistance difference between the two demiwater experiments is given by the biodispersant addition. This fouling can be explained by the micelle formation due to the higher CMC concentration, which cannot pass the membrane and contribute to the membrane resistance increase.

For the simple Schie filtration the membrane resistance increase is very low during the 4 hours experiment. On the contrary, when 4 mg/l biodispersant are added in the water, the membrane suffers a big resistance increase. Unlike demiwater, Schie canal water contains particles which have a big influence on the resistance increase. The backwashes are not very efficient either, since the membrane resistance after backwashes is not being well recovered. The particles in the water may be interacting with the surfactant molecules and form clusters which get adsorbed into the membrane's pores.

Adding iron chloride as a coagulant and letting it flocculate for 21 minutes had a big impact on the membrane resistance. In this situation coagulation was successful because together with the iron addition, sodium hydroxide was also added to keep the pH in the sweep coagulation area. The particles in the canal water were very well flocculated with the help of iron and the obtained effluent did not foul the membrane as much as the Schie canal water and biodispersant mixture.

On the other hand, when PAC was added to the Schie-biodispersant mixture, fouling resistance was decreased, but not as good results were obtained. As it can be seen the membrane fouling resistance is lower, meaning that some of the biodispersant has been removed, but the adsorbed part is very low. It is assumed that the organics present in the canal water are being removed by the PAC, while the biodispersant still remains in the water, contributing to the fouling of the membrane.

When less biodispersant is being dosed into the water a considerable difference can be observed. The membrane is still affected by fouling but the resistance increase is much lower. No other treatment is applied before filtration and it can be seen that the fouling resistance can be compared with the fouling increase of the simple Schie water.

For the CTBD water the situation is somehow different. It can be seen that the fouling resistance is not as high as the fouling caused by Schie. In CTBD there are not as many particles as there are present in the Schie which cause the rapid increase in resistance. Coagulation does not really have an impact on the resistance of the membrane. The fouling trend of the membrane is similar for the case of simple CTBD filtration and the case where coagulation/flocculation is applied as pre-treatment. Coagulation/flocculation is not removing any organics; there are no particles either, so that is why the fouling of the membrane is the same. Another assumption would be that biodispersant can be removed by coagulation, but the actual biodispersant concentration in the CTBD is not 4 mg/l anymore. Since the biodispersant molecules attach to surfaces and only form micelles when saturation is reached, it is assumes that the actual concentration of biodispersant in the CTBD is lost due to transport in pipes or by changing containers. If indeed the concentration has been lost, than coagulation/flocculation does not have any biodispersant to remove and that is why there is no difference seen between the 2 experiments.

When PAC is added to the CTBD less fouling is observed in the membrane. PAC is adsorbing part of the organics present in the blowdown resulting in less increase in the membrane resistance. As it was mentioned before, from the adsorption experiments, it is possible that the biodispersant is a mixture of substances and some of them can be adsorbed by the PAC and some cannot.

PAC gave better results in CTBD water compared with Schie canal water. On the contrary, since the concentration of the biodispersant in the CTBD cannot be controlled it is not known if the membrane resistance would be less with lower biodispersant dose, like in the case of Schie water.

# 8. Conclusions & recommendations

This last chapter is structured in two main parts. The first part will outline the conclusions drawn from the research done, while the second part contains the recommendations for future research.

### 8.1. Conclusions

The research of this thesis was focusing in determining if the biodispersant added in the cooling tower if contributing to the rapid increase of the UF membrane resistance. Cooling tower blowdown water is a very difficult water to treat because of the high salt concentrations and all the chemicals added for scaling, corrosion and microbial growth. Since the UF stands as pretreatment for the desalination steps, the operation needs to be improved for an efficient system. The research made helped determine little information about the biodispersant, but the experiments showed that biodispersant is indeed causing the rapid fouling of the UF membrane.

From the measurements performed in biodispersant solution it was determined that, the unknown solution, Nalsperse-7348 is a non-ionic surfactant. From the surface tension measurements it was also established that the critical micelle concentration of the solution is between 0.03-0.04 mg/l. From the adsorption experiments was not concluded anything since there were no other substances that have a similar adsorption trend. The biodispersant can be composed out of one solution, or may be a combination of solution which end up as one, but in order to determine it, more research needs to be done.

Surface tension measurement is not the appropriate method to measure the surfactant concentration. Knowing that the CTBD water has a final biodispersant concentration of about 4 mg/l, and knowing that surface tension in the demiwater solution at concentrations higher than the CMC was around 50 mN/m, it was expected that the surface tension of the blowdown to be around that value also. In reality the CTBD water had a surface tension closer to the surface tension of pure demiwater, even though the composition of the blowdown water is completely different.

Before UF, there is also the coagulation/flocculation step which could be improved. At the moment there is not a set dosage of iron chloride and the amount added varies. As seen from literature and from the experiments performed with cooling tower blowdown, as well as with Spuikom water, at iron concentrations higher than 10 mg/l the pH drops under 7, resulting in inefficient coagulation because flocs are not growing. The more iron is dosed the more the pH drops. To coagulate with sweep flocs the pH needs to be in the 6-9.5 range. To form bigger flocs, easy settleable, the pH should be kept stable and in the range by adding a base to compensate for the iron added. It was observed that more turbidity was removed and less residual iron was in the effluent after settling in the experiment in which NaOH was dosed together with the iron chloride, compared with the experiment where only iron chloride was added. No TOC was removed, and there was not a big difference between the experiments in which there was biodispersant dosed, but it was known from before that coagulation does not remove a lot of TOC. Controlling the pH during coagulation would produce a better effluent for the UF and will increase the life of the membrane since the residual iron in the effluent will be reduced.

The experiments performed with the UF system showed that in the moment the effluent contains biodispersant the fouling pattern of the membrane changes. Since there was no more CTBD water which did not have biodispersant in it, experiment without biodispersant could not be performed.

When Schie canal water was used as an effluent for the UF, the resistance of the membrane was increasing, but came back to the initial resistance after each backwash. The moment, when biodispersant was mixed in the canal water, the operation changed. The initial resistance of the membrane was increasing after each filtration cycle, but the in-between backwashes did not restore the resistance to the clean membrane resistance. It was observed that when the effluent was subject to coagulation/flocculation (with pH control) the resistance the fouling was less. Less fouling and more stable operation was observed when 30 mg/l of PAC were added in the effluent and let it adsorb for 2 hours. PAC adsorb a part of the organics present in the water or organics from the biodispersant. Also if Nalsperse is a mixture of solutions, it is possible that PAC adsorb some of it, while some other cannot be adsorbed.

A promising finding was observed during filtration with effluent which contained less biodispersant. All the experiments were done with Schie water containing 4 mg/l biodispersant, except for one. One experiment was a solution of canal water with only 0.1 mg/l biodispersant, a concentration which is closer to the CMC of the biodispersant. The UF membrane resistance was still increased, but the overall increase in 8 hours of experiment was not even half the increase observed with the 4 mg/l biodispersant solution. At a concentration so high compared with the CMC it is assumed that the micelles formed cannot pass the membrane pores and buildup a layer on the surface of the membrane. Lower concentration, less micelles, filtration operation is significantly increased.

By dosing less biodispersant in the cooling tower it is not known if the efficiency of Nalsperse is the same. It is assumed that any concentration around the CMC would keep the microbial growth under control and there should not be an increase in the populations. There will still be micelles in the solution since a 0.1 mg/l Nalsperse the concentration would be 2.5 times higher than the CMC, but less, which means less buildup in the pores of the membrane. This assumption cannot be confirmed, so more research needs to be done.

Biodispersant removal requires more research. Since the composition it is unknown, removal using adsorption was experimented. As a reference, the biodispersant concentration was linked to the TOC concentration.

As adsorbents, PAC and clay were used. PAC showed a higher efficiency for removal than clay, but in CTBD the TOC removal was only about 20% (with 60 mg/l PAC dosed), while with clay the TOC removal was lower than 5%. In demiwater the removal was significantly higher, but because of all the salts and chemicals present in the blowdown water, competitive adsorption occurred and PAC did not adsorb a lot of TOC. As it was concluded from the experiments, even a higher dose of PAC will not be able to adsorb more TOC.

### 8.2. Recommendations

The recommendations for further research were made based on the experimental results obtained, the challenges encountered during the research and discussions had with the people involved in the project. After completing the experiments, the assumption made about the biodispersant was confirmed. There are still many questions left unanswered so the recommendations will help answer them.

#### In the laboratory

For more information about the biodispersant more tests need to be done in the laboratory to determine the composition of the biodispersant. By determining the composition, methods to remove it from the blowdown water would be easier to find.

More research should be done using PAC and GAC for the removal of the biodispersant. Since the fouling is caused by the biodispersant and coagulation cannot remove it, other technologies could be tested and PAC and GAC are excellent absorbers of organic compounds. Moreover, from the UF results it was concluded that PAC addition had a better influence on the membrane resistance during the 8 h filtration time.

### In the pilot

The iron dosing for the coagulation flocculation should be higher than 5 mg/l, since in the jar tests it was shown, both in Spuikom and CTBD, no flocs were formed and the iron added ads up and will be removed by the UF. Also the coagulant dose should be done together with a base to compensate for the pH drop caused by the iron chloride. Better quality effluent will be used as effluent for the UF.

Coagulation step could also be taken out during the operation with CTBD since from the experiments performed in the laboratory, iron chloride addition was not really beneficial, but added more iron in the effluent. The pilot operation should be monitored when coagulation/flocculation would be stepped during the treatment of CTBD water.

Mixing the wastewater sources that end up in the pilot would also be something that needs to be observed. By mixing CTBD water with Spuikom the quality of the blowdown water will be improved because of dilution and a lower biodispersant concentration is expected to be in the UF effluent. Less fouling should be expected by mixing the two or three types of water.

### In the cooling tower

The biodispersant dosage in the cooling tower should be decreased, so that from a 4 mg/l biodispersant concentration in the cooling tower will reach to 0.1 mg/l. This change should be monitored in order to make sure that no changes in the number of microbial population occur. If the lower dosage turns out to be successful there will be a decrease also in the amount of money spend on Nalsperse-7348 and the UF will have a stable operation.

Some other biodispersants could be tested also. From literature it was observed that different biodispersant at different concentrations have a different effect on the UF/NF membranes. Other biodispersants should be tested before in the lab, before deciding to switch.

### 9. References

Abdelrasoul, A., Doan, H. & Lohi, A., 2013. Fouling in membrane filtration and remediation methods. In: Mass transfer - Advances in sustainable energy and environment oriented numerical modeling. s.l.:InTech, pp. 196-218.

Allison, R., 1995. Electrodialysis reversal in water reuse application. *Elsevier Desalination*, Volume 103, pp. 11-18.

Altman, S. et al., 2012. Membrane treatment of side stream cooling tower water for reduction of water usage. *Elsevier Desalination,* Volume 285, pp. 177-183.

Anon., 2011. *Kibaran Ternama Sdn. Bhd.* [Online] Available at: <u>http://www.kibaran.com/2011/05/types-of-mbr-membrane-configurations.html [</u>Accessed 16 10 2014].

Anon., n.d. *Biolin Scientific.* [Online] Available at: <u>http://www.biolinscientific.com/attension/applications/?card=AA8</u> [Accessed 2014].

AWWA, A. W. W. A., 2003. *Water treatment.* Third edition ed. s.l.:s.n.

AWWA, L. d. E. W. R. C. o. S. A., 1996. Water treatment membrane processes. s.l.:McGraw-Hill.

Baker, R., 2012. Membrane technology and applications. s.l.: John Wiley & Sons Ltd..

Bansal, R. C. & Meenakshi, G., 2005. Activated carbon adsorption. s.l.:CRC Press.

Bhatia, A., n.d. Cooling water problems and solutions. s.l.:s.n.

Binnie, C., Kimber, M. & Smethurst, G., 2002. *Basic water treatment. Third edition.* s.l.:Thomas Telford Publishing.

Biolin Scientific, n.d. *Biolin Scientific.* [Online] Available at: <u>http://www.biolinscientific.com/attension/?applications/measurements/critical-micelle-concentration [Accessed 10 2014].</u>

Blauch, D., n.d. *Virtual Chemistry experiments.* [Online] Available at: <u>http://www.chm.davidson.edu/vce/spectrophotometry/Spectrophotometry.html</u> [Accessed 2015].

Bott, T., 1995. Fouling of heat exchangers. Amsterdam: Elsevier.

Bott, T., 1998. Techniques for reducing the amount of biocides necessary to counteract the effects of biofilm growth in cooling systems. *Pergamon Applied Thermal Engineering*, pp. 1059-1066.

Bratby, J., 1980. Coagulation and flocculation. s.l.: Uplands Press Ltd..

Buckman, L. I. I., 2010. Biofilms, s.l.: s.n.

Carberry, J., Twardowski, C. & Eberhart D.K., 1977. Clay adsorption treatment of non-ionic surfactants in wastewater. *Water Pollution Control Federation*, Volume 49, pp. 452-459.

Cheremisinoff, N. P. & Cheremisinoff, P. N., 1981. *Cooling towers: selection, design, and practice.* Michigan: Ann Arbor Science Publishers.

Cheremisinoff, N., 2002. *Handbook of water and wastewater treatment technologies.* s.l.:Butterworth-Heinemann.

Cheryan, M., 1998. Ultrafiltration and microfiltration Handbook. Basel: Technomic Publishing Company Inc..

Choudhary, S., 1998. Emerging microbial control issues in cooling tower systems, s.l.: Tata chemical Ltd..

Chowdhury , Z. et al., 2013. Activated carbon: Solutions for improving water quality. s.l.:Royal Society of Chemistry.

Clark, J. & Rhodes, C., 2000. *Clean synthesis using porous inorganic solid catalysts and supported reagents.* s.l.:Royal Society of Chemistry.

Cloete, T., Jacobs, L. & Brozel, V., 1998. The chemical control of biofouling in industrial water systems. *Biodegradation*, pp. 23-37.

Cooney, D., 1999. Adsorption design for wastewater treatment. s.l.:CRC Press LLC.

CTI, n.d. *Cooling Technology Institute.* [Online] Available at: <u>http://www.cti.org/whatis/coolingtowerdetail.shtml</u> [Accessed 12 03 2014].

Davis, L., 2011. Water and wastewater engineering. s.l.:s.n.

Dechema, n.d. *E4Water.* [Online] Available at: <u>http://www.e4water.eu/</u> [Accessed 2014].

DeSilva, F., 2000. *Water Treatment Guide: Activated carbon filtration.* [Online] Available at: <u>http://www.watertreatmentguide.com/activated\_carbon\_filtration.htm[</u>Accessed 24 11 2014].

Dion, W., 2014. Stage verslag. Opstart en optimalisatie van de voorzuivering van E4Water pilot, s.l.: s.n.

DOW, C., n.d. *DOW FILMTEC Membranes BW30-365FR, BW30-400 and DOW Ultrafiltration SFP2660 Coolong tower blowdown reuse in Gaojing power plant.* [Online] Available at:

http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh\_0314/0901b80380314edf.pdf?filepath=liquidseps/p dfs/noreg/609-02176.pdf&fromPage=GetDoc [Accessed 214].

DOW, C., n.d. *Lenntech.* [Online] Available at: <u>http://www.lenntech.com/Data-sheets/Dow-Filmtec-NF90-4040.pdf</u> [Accessed 2014].

DuPont, S. & Cates, R., 2010. *Lesson: Surfactants: Helping Molecules Get Along.* [Online] Available at: <u>https://www.teachengineering.org/view\_lesson.php?url=collection/usf\_/lessons/usf\_surfactants\_les1/usf\_surfactant</u>

EERE , I. C., 2011. *Energy.gov Office of Energy Efficiency & Renewable Energy.* [Online] Available at: <u>https://www1.eere.energy.gov/femp/pdfs/waterfs\_coolingtowers.pdf</u> [Accessed 2014].

EnviroAqua, C. I., 2008. *Biofilms in cooling systems,* s.l.: s.n.

Feinerman, V., Mobius, D. & Miller, R., 2001. Surfactants:chemistry, interfacial properties, applications. *Elseview*.

Foo, K. & Hameed, B., 2010. Review: Insights into the modelling os adsorption isotherm systems. *Chemical Engineering Journal,* Volume 156, pp. 2-10.

GE, P. &. W., 2012. *GE Power & Water Water & Process Technologies.* [Online] Available at: <u>http://www.gewater.com/handbook/cooling water systems/ch 24 corrosion.jsp</u> [Accessed 2014].

GE, P. &. W., n.d. *GE Power & Water Water & Process Technologies.* [Online] Available at: <u>http://www.gewater.com/handbook/boiler\_water\_systems/ch\_19\_Condensate.jsp</u> [Accessed 2014].

Ghazali, R. & Ahmad, S., 1997. Biosurfactants- A review. *Elaeis*, pp. 34-53.

Hach Lange GmbH, 2013. 2100 Series Laboratory Turbidimeters Data Sheet. s.l.:s.n.

HDR, E. I., 2002. Handnook of public water systems. Second edition ed. s.l.: John Wiley & Sons, Inc..

Heidekamp, M., 2013. *Mild desalination of cooling tower blowdown water with electrodialysis and membrane capacitative deionization: a comparative study,* Delft: s.n.

Hilal, N. et al., 2004. A comprehesive review of nanofiltration membranes: Treatment, pretreatment, modelling, and atomic force microscopy. *Elsevier Desalination*, Volume 170, pp. 281-308.

Hower, W., 1970. Adsorption os surfactants on montmorillonite. *Clay and Clay Minerals,* Volume 18, pp. 97-105.

Huang, Q., Huamg, P. & Violante, A., 2008. *Soil microbe organic interactions.* s.l.:Springer.

Huibers, P. et al., 1996. Prediction of critical micelle concentration using a quantitative structure - Property relationshoip approach. 1. Nonionic surfactans. *L:angmuir,* pp. 1462-1470.

Imeter, n.d. *Imeter.de.* [Online] Available at: <u>http://www.unimeter.net/interim/4 oberflspannung a.htm</u> [Accessed 2014].

Janssen, A., 2011. *The applicability of the SUR measurement for ultrafiltration of WWTP effluent,* Delft: Arie Janssen.

Jensen, R., 2004. Water solutions and strategies in the chemical industry. In: P. Norling , F. Wood-Black & T. Masciangioli, eds. *Water and sustainable development. Opportunities for the chemical science*. s.l.:s.n., pp. 75-80.

Jungfer, C., Korfer, R., Wendler, K. & Track, T., 2012. *Economically and Ecologically Efficient Water Management in the European Chemical Industry*. s.l., E4Water.

Lagaly , G., Ogawa , M. & Dekany, I., 2006. Clay mineral organic interactions. In: F. Bergaya , B. Theng & G. Lagaly , eds. *Handbook of clay science*. s.l.:s.n., pp. 309-377.

Lenntech, n.d. Lenntech. [Online] Available at: http://www.lenntech.com/static-mixers.htm [Accessed 2014].

Li, S., 2011. A new concept of ultrafiltration fouling control: backwashing with low ionic strength water, Delft: s.n.

Meltz, A., 1999. Water Treatment for Cooling Towers (1 of 2). HPAC, pp. 23-27.

Merk KGaA, 2014. Spectroquant® NOVA 60 General information. s.l.:s.n.

Merk KGaA, n.d. Spectroquant® Iron Test. s.l.:s.n.

Midwest Cooling Towers, n.d. *Midwest Cooling Towers.* [Online] Available at: <u>http://www.midwesttowers.com/crossflow-cooling-towers/</u> [Accessed 2014].

Midwest Cooling Towers, n.d. *Midwest Cooling Towers*. [Online] Available at: <u>http://www.midwesttowers.com/counterflow-cooling-towers/</u> [Accessed 2014].

Mollah, M., Schennach, R., Parga J.R. & Cocke, D., 2001. Electrocoagulation (EC) - science and applications. *Elsevier Journal of Hazardous Materials*, Volume B84, pp. 29-41.

Morvay, Z. & Gvozdenac, D., 2008. Part III: Fundamentals for analysis and calculation of energy and environmental performance. In: *Applied industrial energy and environmental management.* s.l.:Wiley -IEEE Press, pp. 1-34.

Muherei, M. & Radzuan J., 2009. Equilibrium adsorption isotherms of anionic, nonionic surfactants and their mixture to shale and sandstone. *Modern Applied Science*, 3(2).

Myers, D., 2006. *Surfactants science and technology.* s.l.:Wiley-Interscience.

Nalco, A. E. C., n.d. *Nalco An Ecolab Company.* [Online] Available at: <u>http://www.nalco.com/documents/Brochures/B-34.pdf</u> [Accessed 2014].

Okeola, F. & Odebunmi, E., 2010. Freundlich isotherm and Langmuir isothermparameters for adsorption of methylene blue by carbon derived from agrowastes. *Advances in natural and applied sciences*, 4(3), pp. 281-288.

Oremusova, J. & Lengyel, A., n.d. *Univerzita Komenskehov v Bratislave Farmaceuticka Fakulta.* [Online] Available at: <u>http://www.fpharm.uniba.sk/fileadmin/user\_upload/english/Physical\_Chemistry/9-</u> <u>Critical micelar concentration.pdf</u> [Accessed 2014].

Pereira , M., Machado , I., Simoes, M. & Vieira, M., 2007. *Preventing biofilm formation using surfactants,* Braga: Biofilm Club.

Poele, S. t., 2005. Foulants in ultrafiltration of wwtp effluent, Delft: s.n.

Positron Research Group, 2006. *Micelle Theory*. [Online] Available at: <u>http://www.stolaf.edu/academics/positron/micelle\_theory.htm</u> [Accessed 2014].

Qasim, S., Motley, E. & Zhu, G., 2000. *Water works engineering: Planning, design and operation.* s.l.:Prentice Hall PTR.

Roorda, J. H., 2004. Fikltration characteristics in dead-end ultrafiltration of wwtp-effluent, Delft: s.n.

Rouquerol, F., Rouquerol, J., Sing, K. & LLewellyn, P., 2014. *Adsorption by powders and porous solids. Principle, methodology and applications. Second edition.* s.l.:Elsevier.

Sadrzadeh , M. & Mohammadi, T., 2008. Sea water desalination using electrodialysis. *Elsevier Desalination,* Volume 221, pp. 440-447.

Schimadzu, 2014. *Schimadzu*. [Online] Available at: <u>http://www.shimadzu.com/an/toc/lab/toc-l.html</u> [Accessed 11 11 2014].

Schmitt, T., 2001. Analysis of surfactants. s.l.:s.n.

SDCWA, S. D. C. W. A., 2009. *San Diego County Water Authority.* [Online] Available at: <a href="http://www.sdcwa.org/sites/default/files/files/water-management/recycled/techinfo-cooling-towers.pdf">http://www.sdcwa.org/sites/default/files/files/water-management/recycled/techinfo-cooling-towers.pdf</a> [Accessed 2014].

SDMC, S. D. M. C., n.d. *UV Visible Absorption Spectroscopy.* [Online] Available at: <u>http://faculty.sdmiramar.edu/fgarces/LabMatters/Instruments/UV Vis/Cary50.htm#Operation</u> [Accessed 2015].

Shang, R., 2014. Ceramic Ultra- and Nanfiltration for Municipal Wastewater Reuse, Delft: s.n.

Song, L. & Elimelech, M., 1995. Theory of concentration polarization in crossflow filtration. *J. Chem. SOc. Faraday Trans.*, pp. 3389-3398.

TechnoKontrol-CAT, n.d., *TK-ANFHCTS AntiFire/Heat/Thermal Cooling Tower Systems*. [Online] Available at: <u>http://www.technokontrol.com/en/research-development/towers.php</u> [Accessed 2015]

Thermo Scientific , F. I., 2013. *UV-Visible analysis of bitterness and total carbohydrates in beer,* s.l.: Thermo Fisher Scientific Inc..

Tower components Inc., n.d. *Tower Components Inc.*. [Online] Available at: <u>http://www.towercomponentsinc.com/operation-cooling-tower.php</u> [Accessed 2014].

USQ, n.d. *University of Southern Quenslaand.* [Online] Available at: <u>http://www.usq.edu.au/course/material/env4203/summary5-70861.htm</u> [Accessed 2014].

Wakeman, R. & Tarleton, E., 1999. Filtration: Equipment selection. Modelling and process simulation. *Elsevier Science.* 

Wikipedia, 2009. *Total organic carbon.* [Online] Available at: <u>http://en.wikipedia.org/wiki/Total organic carbon</u> [Accessed 11 11 2014].

Wikipedia, 2014. *Cooling tower.* [Online] Available at: <u>http://en.wikipedia.org/wiki/Cooling\_tower</u> [Accessed 2014].

Wikipedia, 2014. *Ultraviolet-visible spectroscopy*. [Online] Available at: <u>http://en.wikipedia.org/wiki/Ultraviolet%E2%80%93visible\_spectroscopy</u> [Accessed 01 2015].

Wikipedia, 2014. Wikipedia. [Online] Available at: http://en.wikipedia.org/wiki/Surface tension [Accessed 2014].

Wirokarso, D., 2014. *Stage verslag Opstart en optimalisatie van de voorzuivering van E4Water pilot,* Groningen: s.n.

You, S., Tseng, D., Guo, G. & Yang J.J., 1999. The potential for recovery and reuse of cooling water in Taiwan. *Elsevier Resources, Conservation and Recycling,* Volume 26, pp. 53-70.

Zeman, L. & Zydney, A., 1996. Microfiltration and Ultrafiltration. s.l.:Marcel Dekker, Inc..

Zhao, Y. et al., 2000. Fouling and cleaning of membrane - a literature review. *Journal of Environmental Sciences,* pp. 241-251.
# **10.** Appendices

# **Appendix A**

### Spectrophotometer

UV-Visible spectroscopy is the most common technique used for testing various materials. Spectrophotometry is a routine method applied for quantitative and qualitative determination of different compounds (Thermo Scientific , 2013). UV-Visible spectroscopy is referring to the absorption spectroscopy or the reflectance spectroscopy in the ultraviolet-visible region. Absorption of reflectance in the visible range influences the perceived color of the chemicals. Molecules that contain  $\pi$ -electrons or non-bonding electrons can absorb the energy in the form of UV or visible light to excite the electrons to higher anti-bonding molecular orbitals (Wikipedia, 2014).

The principle of spectrophotometers is to measure the amount of light that the sample absorbs. A beam of light passes through a sample and measures the intensity of light reaching a detector. The beam of light consists of a stream of photons. When a photon meets a molecule of the analyte, the molecule might be absorbed by the light. Absorption decreases the photons in the beam of light and reduces the intensity of the beam (Blauch, n.d.). In Figure 4-5 is presented the basic principle of how UV-Vis spectroscopy works (SDMC, n.d.).



Figure 10-1 The principle of UV-Vis spectroscopy

For the absorbance measurement, Thermo Scientific Evolution 60S UV-Visible Spectrophotometer was used. The sample and blank were measured in a quartz cuvette of 10 mm.

First the intensity of light that passes through the blank is measured. The blank is the same as the sample solution, but does not contain the solute that absorbs light. Light intensity represents the number of photons per second. Second the intensity of light that passes through the solution is measured (SDMC, n.d.).

For absorbance measurements, the spectrophotometer measures the absorbance at different wave lengths. UV spectrum is at a wavelength between 10 and 400 nm, visible spectrum responds to wavelength between 390 and 700 nm, while infrared spectrum responds to wavelength between 700 nm and 1 mm.

#### UV visible adsorption

For many years spectrophotometry was one of the standard methods for determining surfactants. Nonionic surfactants do not adsorb radiation in the visible spectrum so the easiest form to analyze nonionic surfactants is by direct measurement of the UV absorbance of the sample (Schmitt, 2001).

When measuring the UV adsorption of a solution the maximum wavelength is dependent by the presence of some chromophores in the molecule. In order to find which compounds are in the solution the resulting peak needs to be compared with already known peaks.

Several solutions have been measured at wavelength between 190 and 400 nm. The first solution to be measured was the pure water, after a solution of 5 mg/l biodispersant was measured and in the end the pure biodispersant solution was measured. In the graph below (Figure 3-10) can be seen the obtained peaks.



Figure 10-2 Adsorption of different biodispersant solutions



Figure 10-3 Comparison between different biodispersant solutions absorbance

It can be seen from the graphs that the adsorption for the pure water is the same as the adsorption for the 5 mg/l biodispersant solution (Figure 3-11). There is no visible difference between the two solutions, so no conclusion can be drawn from these measurements.

For the pure biodispersant the maximum peak is at 207.5 nm and the maximum adsorption is 3.581 UA. Many known adsorption peaks and maximum wavelengths were compared in order to find the components of the biodispersant solution but unfortunately no relevant information was found.

# Appendix B

# Coagulation-flocculation efficiency comparison between jars with baffles and without baffles

For this experiment Spuikom water was used. It was observed from the previous executed experiments that cooling tower blowdown is quite unstable and the coagulation-flocculation treatment step is encountering many variations.

From the experiments performed previously with Spuikom water it was concluded that this type of water is not as troublesome for coagulation as the blowdown is. In order to observe the influence of the baffles in the jars, experiments an extra experiment was done with Spuikom water.

The flocculation apparatus has 6 stirrers, which indicates that 6 jars can be used in the experiment. 3 of the jars were with baffles, while the other 3 jars were baffle free. The stirring rate operation was the same as in the previous experiments, while the ferric chloride concentrations was varied. 3 iron concentrations were observed: 5 mg/l, 15 mg/l and 25 mg/l and the pH was not adjusted.

#### Comparison between the results obtained in jars with baffles and jars without baffles

The final experiment was performed as a comparison between the results of the jars with baffles and the jars without baffles. Coagulation tests were done with Spuikom water because it is the easiest to coagulate and quite stabile compared to the other 2 water sources. Quality of the Spuikom water is presented in Table 5-14.

nH	Turbidity	EC	Fe <sup>3+</sup>	
рп	NTU	mS/cm	mg/l	
7,5	9,53	1,508	0,5	

Table 10-1 Initial quality of the Spuikom water

Same operation characteristics were maintained as in the previous experiments. NaOH was also added in order to have a better coagulation at pHs which characterizes sweep coagulation. In Table 5-15 are presented the obtained results.

Fe <sup>3+</sup> dosage	Volume NaOH	pН	Turbidity	EC	Fe <sup>3+</sup>	
mg/l	ml		NTU	mS/cm	mg/l	
10	1,05	7,4	1,9	1,54	0,8	No baffle
20	2,09	7,41	1,42	1,6	1	No baffle
10	1,05	7,37	1,45	1,6	1	Baffle
20	2,09	7,27	1,3	1,7	1,4	Baffle

Table 10-2 Spuikom water quality after coagulation/flocculation in jars with baffle and without baffles

No big differences was observed between the results obtained in this experiment. Only 4 jars were used because the volume of Spuikom available was only 10 I, so it was decided to check only 2 concentrations. The concentrations chosen were the ones which showed the best coagulation results in the experiments performed before. Good results were observed, turbidity was decreased considerably from 9.53 NTU to lower than 2 while the final iron concentration was low. Results should be compared with the results obtained in the pilot when it was ran on Spuikom water.

# Appendix C

#### Adsorption experiment in tap water

Same procedure as with demiwater was followed. First batch experiments were ran for 48h at concentrations between 0 and 60 mg/l PAC and clay. Biodispersant solution was dosed in the tap water collected in the same day. Results for PAC are presented in Figure 10-3.



Figure 10-4 Adsorption isotherms resulting from batch experiments in tap with 4 mg/l biodispersant dosed and clay as adsorbent

Good values for the  $K_f$  and n constants were observed in the batch experiment performed with tap water. For PAC adsorption  $K_f$  value obtained was 1.414, while n 1.7309. As in the previous case the n and  $K_f$  values indicates that the organic removal can be achieved at higher PAC doses.

The adsorption isotherm in tap water is much smoother than in demiwater. The better result is due to the fact that in tap water with biodispersant competition is present. TOC of tap water in the Netherlands is around 2 mg/l. It is very possible that the organic carbon present in tap water is adsorbed more easily than the carbon from biodispersant.

In Table 10-1 can be seen the actual TOC values recorded before and after the 48h batch experiment. In the case of tap water the TOC reduction was not as high as it was in demiwater. This is because in tap water there are some other compounds present and competitive adsorption takes place. Some compounds present in tap water are more easily adsorbed than the biodispersant that is why lower removal was recorded. Nonetheless, the TOC was removed with 69% in when 50 and 60 mg/l PAC was added, which also gave high expectations for the reduction in CTBD water.

PAC dose	<b>C0</b>	Ceq	qeq	Removal
mg	mg/l	mg/l	mg/mg PAC	%
0	3,63	3,63		0,00
10	3,63	1,53	0,21	57,80
20	3,63	1,96	0,08	45,92
30	3,63	1,34	0,08	63,20
40	3,63	1,42	0,06	60,83
50	3,63	1,24	0,05	65,82
60	3,63	1,24	0,04	65,88

As mentioned before, at low PAC doses the probability of making an experimental or analytical measurement error is high. The first 2 batches with the lowest dozes have varying values which vary

significantly. It is assumed that the error is in the batch in which 20 mg/l PAC was dosed since it has a higher removal than in the case where more PAC was added.

In Figure 10-4 can be seen the graphical representation of the equilibrium experiment using PAC. Samples were collected every hour and filtered with 0.45  $\mu$ m filters for the preparation of the TOC samples. Most of the TOC removal was again done in the first hour of experiment.



Figure 10-5 TOC variation in tap water during 8h batch experiment with PAC

Figure 10-5 gives the Freundlich isotherm for the adsorption experiment in tap water, where clay was used as adsorbent. Here the obtained  $K_f$  value is higher than 1 ( $K_f$ =3.4255). Since the value of n is also higher than 1 (n=3.7936), cooperative adsorption is again present and because  $K_f$  is higher than 1 good adsorption can only be achieved at very high concentrations of adsorbent. In Table 10-2 are shown the TOC results obtained. It can be seen that for the batch where 10 mg/l PAC was added the  $C_{eq}$  was higher than the initial concentration. At low PAC doses the adsorption is not very high and also the probability of an experimental error is higher. This equilibrium concentration cannot be higher than the initial concentration of the effluent so the  $C_{eq}$  for 10 mg/l is not correct. This error can be an experimental error.



Figure 10-6 Adsorption isotherms resulting from batch experiments in tap with 4 mg/l biodispersant dosed and clay as adsorbent

Adsorption with clay was much less than with PAC. If in demiwater the TOC removal between PAC and clay was comparable, in tap water the removal is very low. This can be because the surface area available for adsorption of clay (270 m<sup>2</sup>/g) is lower than surface area of PAC (925 m<sup>2</sup>/g) so the organics present in tap water were removed first by clay, followed by some biodispersant.

Clay dose	<b>C0</b>	Ceq	qeq	Removal
mg	mg/l	mg/l	mg/mg clay	%
0,00	3,83	3,83		0,00
10,00	3,83	3,94	0,01	-2,66
20,00	3,83	3,57	0,02	6,83
30,00	3,83	3,53	0,02	7,82
40,00	3,83	2,84	0,03	25,87
50,00	3,83	2,45	0,03	36,18
60,00	3,83	3,19	0,01	16,85

Table 10-4 TOC concentration recorded during the batch experiment in tap water using clay



Figure 10-7 TOC variation in tap water during 8h batch experiment with PAC

With 10 mg/l clay it can be seen from Figure 10-6 that there is no reduction of TOC during the 8 hours. In the case in which 60 mg/l clay was dosed there was recorded a reduction of about 23% TOC. Much more clay would be necessary to dose in order to have a significant biodispersant and organic removal from the effluent. Adsorption on clay is a fast process, most of the removal being recorded in the first hour.

#### 10.1.1. Adsorption experiment in CTBD water

Last adsorption experiment was done in CTBD. CTBD is the most difficult water to treat and the water with high organic concentration. In Table 10-3 are presented the obtained results after the 48h batch experiment.

PAC dose	C <sub>0</sub>	C <sub>eq</sub>	<b>q</b> <sub>eq</sub>	Removal
mg	mg/l	mg/l	mg/mg PAC	%
0,00	47,68	47,68		0,00
10,00	47,68	44,53	0,32	6,61
20,00	47,68	42,17	0,28	11,56
30,00	47,68	40,95	0,22	14,11
40,00	47,68	40,27	0,19	15,54
50,00	47,68	41,05	0,13	13,91
60,00	47,68	38,20	0,16	19,88

Table 10-I		concentration	recorded	during the	hatch	ovnoriment		wator	ucina	DAC
Table 10-3	5100	concentration	recorded	uuring the	Datch	experiment	пстьр	water	using	FAC

In CTBD water PAC was able to adsorb very little organic carbon. There are many compounds present in the water and again competitive adsorption takes place. Only a 20% removal was obtained with 60

mg/I PAC. In tap water there was more reduction than in CTBD which gave good expectations for the adsorption in CTBD, but unfortunately much more PAC would have to be dosed in order to have a significant TOC removal.

In Figure 10-7 is presented the Freundlich isothermobtained for CTBD adsorption. The shape of the graph is more or less linear, with an outlier point. If the isotherm is being extrapolates, it can be observed that the lowest Ceq which could be obtained is still higher than 30 mg/l. This means that, even if more PAC would be dosed in the water, a TOC concentration lower than 30 g/l is not possible. For this type of water PAC is not the most efficient method which could be used for reducing the organic carbon.



Figure 10-8 Adsorption isotherm resulting from batch experiments in CTBD with 4 mg/l biodispersant dosed and PAc as adsorbent

In Figure 10-8 are presented the results obtained during the equilibrium experiment in CTBD water with 10 and 60 mg/l PAC. It can be seen that with 10 mg/l PAC dosed there is no TOC reduction. At higher PAC concentration, 60 mg/l, there is a 15% reduction in TOC after 8 hours of experiment.



Figure 10-9 TOC variation in CTBD water during 8h batch experiment with PAC

Last experiment performed was using CTBD and clay as an adsorbent. Table 10-4 shows the TOC results obtained during the batch experiment. The reduction using clay was very low.

The adsorption results obtained in CTBD using clay are less promising than the results obtained with PAC. Highest TOC removal was obtained with 60 mg/l clay dosed, resulting in almost 5% TOC reduction.

Clay dose	C <sub>0</sub>	$C_{eq}$	<b>q</b> <sub>eq</sub>	Removal
mg	mg/l	mg/l	mg/mg clay	%
0,00	47,68	47,68		0,00
10,00	47,68	45,03	0,27	5,56
20,00	47,68	44,64	0,15	6,38
30,00	47,68	44,71	0,10	6,23
40,00	47,68	44,73	0,07	6,19
50,00	47,68	44,56	0,06	6,54
60,00	47,68	45,50	0,04	4,57

Table 10-6 TOC concentration recorded during the batch experiment in CTBD water using clay

Equilibrium experiment in CTBD using clay was also done. Because of the high loading of the CTBD water and the small surface area for adsorption for clay, no reduction was noticed for either of the concentrations. During the 8 hours concentrations did not change at all. In Figure 10-9 are presented the trends recorded for the equilibrium experiment in CTBD with 10 mg/l and 60 mg/l clay added.



Figure 10-10 TOC variation in CTBD water during 8h batch experiment with clay

Appendix D Table 10-7 Surface tension values measured in demiwater-Nalsperse solution, without stabilization time

Concentration	Surface tension				
ma/l	Value 1	Value 2	Value 3	Average	
	mN/m	mN/m	mN/m	mN/m	
0.01	62.1	63.0	63.0	61.7	
0.02	59.6	60.5	60.7	59.8	
0.03	58.1	59.2		58.6	
0.04	51.4	52.8	53.5	52.7	
0.05	52.9	52.2		52.5	
0.06	51.2	52.0		51.8	
0.07	51.4	51.6		51.5	
0.08	51.0	50.8		50.9	
0.1	51.2	51.0		50.8	
0.5	50.75	50.25	50.13	50.38	
1	50.5	49.8	49.8	50.1	
2	50.5	50.5		50.5	
4	48.52	48.66		48.59	
6	48.55	48.51		48.53	
8	46.97	47.45	47.45	47.29	
10	47.08	47.33	47.36	47.26	
12	46.93	46.82	46.62	46.79	
14	45.99	46.60	46.48	46.35	
16	45.55	46.14	46.06	45.92	
18	46.21	46.18	46.06	46.15	
20	45.76	45.99	45.87	45.88	
22	45.67	45.72	45.53	45.64	
24	45.27	45.69	45.48	45.48	
26	45.85	45.62	45.55	45.67	
28	44.95	45.46	45.47	45.29	
30	45.18	45.40	45.38	45.32	
32	45.03	45.28		45.15	
34	45.27			45.27	
36	51.66	52.16		51.91	
38	45.01			45.01	
40	44.82			44.82	
45	44.31	44.93	44.88	44.71	
80	44.04	44.19		44.11	
120	41.49	44.07	44.00	44.03	
160	43.57	43.61		43.59	
200	43.15	43.26		43.20	
500	40.28	40.81		40.55	
1000	39.52	39.49		39.51	

Table 10-8Surface tension values measured in demiwater-Nalsperse solution, meausred after 7 days stabilization time

Concentration	Surface tension
mg/l	mN/m
0.01	72.1
0.03	70.7
0.05	70.4
0.08	68.8
0.08	66.1
0.10	67.0
0.22	60.6
0.43	58.4
1.06	52.5
1.17	55.5
1.58	52.6
4.90	48.9

#### **Appendix E**

Table 10-9 TOC measured in simple demiwater with PAC, during 8h experiment

TOC							
mg/l							
Time	10 mg/l PAC	60 mg/l PAC					
h	mg/l	mg/l					
0	0.5282	0.5282					
1	0.4694	0.6335					
2	0.3831	0.5256					
3	0.4857	0.3949					
4	0.4204	0.4252					
5	0.5051	0.545					
6	0.4961	0.4528					
7	0.3776	0.4398					
8	0.4576	0.5369					