

AquaSPICE report



Case study at BASF Antwerpen

Exploratory lab-scale research

Adapted from the MSc thesis of Merel Van Ginderachter

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Main contributors

Merel Van Ginderachter, MSc, UGent – Lab work, preparation of the report and data analysis

Ivaylo Hitsov, PhD, *UGent* – Tutoring, corrections and adaptations

Prof. Arne Verliefde, UGent – Supervision

Kristof De Neve, PhD, BASF – Guidance and corrections

Pieter Plehiers, PhD, BASF – Guidance and corrections

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SUMMARY

The emerging scarcity of freshwater sources and the salination of groundwater endangers the freshwater intake of industrial companies. The reuse of industrial wastewater streams could provide an answer to these emerging problems. The AquaSPICE project aims to tackle these water quality problems and digitalize the water use in industrial settings. BASF Antwerp is the industrial partner in Case Study 3 of this project. In subcase 2 of Case Study 3, pilot-scale water treatment technologies will be deployed on site to investigate the reuse of wastewater streams. In this master's dissertation, industrial wastewater streams of the cracker site and the demineralisation plant at BASF Antwerp were investigated to determine their reuse potential on site. Different treatment technologies were tested on lab-scale in preparation for the operation of pilot-scale experiments on site in 2023.

BASF Antwerp is currently commissioning a new demineralisation plant, existing of a softener resin stage, reverse osmosis and mixed bed resins for polishing. The focus of the project is the reuse of the RO concentrate (185 m³/h, 85% recovery). Since the demineralisation plant is not yet in operation, the treatment train was simulated on lab-scale. This study investigated how to improve the recovery, increase demineralised water production and minimise the waste streams for the demineralisation plant. One of the options to increase recovery and produce more demineralised water is to apply a second stage reverse osmosis in a configuration that is less prone to scaling and fouling, such as PFRO or CCRO. To simulate this step on a lab scale, the RO concentrate was concentrated 3 times more. The quality of the permeate was not suitable for direct treatment with MB resins, but could be sent back to the main RO step. The other option is to take the RO concentrates and attempt to regenerate the softener before the main stage RO in order to reduce the chemical input and to reuse this waste stream. On lab-scale, the regeneration with the concentrates did not work. Further investigation is needed to investigate if a higher recovery for the second stage RO would result in an efficient regeneration or if NaCl could be added, since this would mitigate one waste stream and would decrease the need for chemicals.

For the cracker site streams, treatment options were also investigated. The TBA-tank (with spent caustic) was treated with nanofiltration, resulting in a good removal of organic acids. However, the stream from the TBA-tank is interesting for BASF to use in their WWTP (given the high pH) and will thus not be investigated with the pilot-scale technologies.

The NBTA-tank can be split up in two different streams. This tank is emptied periodically and before every discharge, the NPOC is measured. If the NPOC is higher than 30 mg/L, the NTBA-tank will be fed to the WWTP (Q8860), which does not happen frequently. Q8860 was concluded not to be of interest in these first lab-trials. If the NPOC of the NTBA-tank is lower than 30 mg/L, the water will be discharged into the Scheldt-Rhine Canal (Q8870). This stream has a high potential for reuse as boiler feed water or water for the air-sprayed condensers. Q8870 was prefiltered and then subsequently treated with RO. The RO permeate obtained a conductivity of 43.1 μ S/cm and a TOC concentration below 1 mg/L, which is still higher than the required quality for boiler feed water. To obtain more information on achievable recoveries on full-scale, simulations of RO performance were performed using the Membrane Master 5 software from Genesys. With the addition of antiscalant and/or acid a recovery up to 90% could be reached. The quality of the permeate stream will be investigated on site during the pilot tests.

The process steam blowdown (Q1811) is interesting for reuse as boiler feed water. First of all, a prefiltration was performed with an 8 μ m filter, which removed some of the turbidity, but was not removing the color. A nanofiltration was performed at 5 bar, which was effective in removing the organic acids and most part of the conductivity. Secondly, different treatment trains were performed, combining ion exchange (SAC-SBA), reverse osmosis and granular activated carbon. The best results were achieved with IEX-RO and IEX-GAC-RO configuration. However, since the conductivity of the stream is 1.153 mS/cm, this conductivity exceeds the feasibility limit of 1 mS/cm for ion exchange (SAC-SBA), which means that the ion exchange resins will require a significant chemical input. Thirdly, different adsorbents were investigated during jar tests. From these tests, it seemed that the scavenger resin and MPPE1 resin performed the best for TOC removal. The suggestion for testing

in the containers would be a treatment train of scavenger resins, followed by RO and GAC. The scavenger resins will protect the RO from fouling, since it removes TOC. GAC will be polishing the stream after the RO.

The steam blowdown (Q7503) and furnace blowdown (Q0106) are the cleanest streams on site. These streams only need a polishing step to be reused as boiler feed water. The technology of interest is electrodeionization, since it does not need any chemicals, is efficient in energy use, does not produce any waste streams and is thus easy to decentralize. EDI systems do have feed limitations, to avoid any fouling or scaling in the module. The steam and furnace blowdown were analysed for the different inlet parameters and pass the requirements for the EDI. Since no EDI could be performed in the lab, the quality of the polished streams was tested using mixed bed resins. These tests performed quite well on conductivity but not on TOC, which could be because of TOC release of the new resins even though they were rinsed thoroughly. EDI will be tested in the containers on site.

This thesis provided clear guidelines on technologies of interest for testing in the containers. Testing of technologies on lab-scale is always limited to a certain TOC and conductivity level, due to contamination and release of pollutants from new resins and membranes. The findings from this thesis need to be confirmed and checked on pilot-scale in the containers on site at BASF.

LIST OF ABBREVIATIONS

AEM	Anion Exchange Membrane
BTEX	Benzene, Toluene, Ethylene and Xylene
BV	Bed Volumes
CC	Closed-Circuit
CCRO	Closed-Circuit Reverse Osmosis
CEM	Cation Exchange Membrane
DOC	Dissolved Organic Carbon
ED	Electrodialysis
EDI	Electrodeionization
FM	Flushing Mode
GAC	Granular Activated Carbon
IC	Inorganic Carbon
IC (analysis)	Ion Chromatography
ICP-OES	Inductively Coupled Plasma- Optical Emission Spectrometry
ICR	Inorganic Carbon Removal
IEX	Ion Exchange
IMPROVED	Integrale Mobiele PROCeswatervoorziening Voor een Economische Delta
KPI	Key Performance Indicator
LC-OCD	Liquid Chromatography - Organic Carbon Detection
LMH	liter/m ² /h
LOD	Limit of Detection
MB	Mixed Bed Resins
MPPE	Macro Porous Polymer Extraction
MWCO	Molecular weight cut-off
ND	Not Detected
NF	Nanofiltration
NPOC	Non-Purgeable Organic Carbon
NTBA	Niet Te Behandelen Afvalwater
PFRO	Pulse-Flow Reverse Osmosis
RO	Reverse Osmosis
SAC	Strong Acid Cation Resins
SBA	Strong Basic Anion Resins
TBA	Te Behandelen Afvalwater
TC	Total Carbon
TOC	Total Organic Carbon
UF	Ultrafiltration
WAC	Weak Acid Cation Resin
WBA	Weak Basic Anion Resin
WWTP	Wastewater Treatment Plant

Introduction

1.1 Scope

This thesis is part of the AquaSPICE project, which aims to materialise circular water use in European Process Industries. In this way, awareness around resources and resource efficiency is created and compact solutions for industrial applications are being developed. The project started the first of December in 2020 and will be running until May 31 in 2024 (3.5 years). In 12 different countries, 29 partners are involved in the project, such as industrial partners, universities and research institutions etc. The project is subdivided in six different industrial case studies, each situated in another country (AquaSPICE, n.d.-a):

- Case Study 1: Technology focus for freshwater intake (DOW Boehlen, Germany and DOW Terneuzen, the Netherlands)
- Case Study 2: Water treatment and re-use within peroxide production units (Rosignano Solvay, Italy)
- Case Study 3: Sustainable and robust water system for the industrial zone of Antwerp (BASF, Belgium)
- Case Study 4: Waste to fuel transformation setup (JEMS, Slovenia)
- Case Study 5: Sustainable water use in meat production in the circular economy (Agricola, Romania)
- Case Study 6: Water treatment and re-use within refinery (Tüpras,, Turkey)

This thesis is situated in Case Study 3, which mostly focusses on the Port of Antwerp. The Port of Antwerp is a growing hub for industrial companies in the field of chemicals and oil. The water that these companies use in their processes is fresh water and is coming from the Albert Canal (which connects to the river Meuse). A rising salinity of the freshwater from the Albert Canal due to climate change, is endangering this freshwater intake. Moreover, circular water use is starting to become crucial to minimise the risk of structural water shortages. That is why companies in the Port of Antwerp need to investigate the potential to use other water sources or (even better) to reuse process water (AquaSPICE, n.d.-b).

BASF Antwerp is the biggest integrated chemical production centre in Belgium and the second largest production centre of BASF worldwide (BASF, n.d.). They are the industrial partner in Case Study 3 since they consume the largest amount of water in the Port of Antwerp. BASF Antwerp uses water mainly for cooling purposes and the rising salinity will cause a change in the way their cooling system behaves and needs to be managed. They built a new demineralisation plant, using softener resins and reverse osmosis, to treat surface water. To improve on water circularity on site, other streams that can be potentially reused as boiler feed water, will be investigated (AquaSPICE, n.d.-b).

Case Study 3 is divided in two subcases. The first subcase focuses more on the Albert Canal and the harbour by monitoring water quality and operational modelling. The second subcase is investigating the water reuse and alternative water sources for cooling. Within the second subcase, this thesis aims to investigate potential reuse of streams at two sites of BASF Antwerp (AquaSPICE, n.d.-b).

1.2 Goal

1.2.1 General

BASF Antwerp is the industrial partner in Case Study 3 of the AquaSPICE project. The main objective is to investigate which (waste)water streams have the potential to be reused on site and how they can minimise wastewater streams. Two sites at the BASF Antwerp plant are being investigated.

1.2.2 Cracker site

The first site where reuse of water will be investigated, is the steam cracker site. Different wastewater streams are being collected in two tanks to be further treated or disposed. A schematic overview is shown in Figure 1. The first one is the TBA-tank ('Te Behandelen Afvalwater') and collects the wastewater that needs treatment before it can be discharged. Streams that are collected in this tank are mostly blowdowns: furnace blowdown, steam blowdown and process steam blowdown. The wastewater from the TBA-tank will be fed continuously to the wastewater treatment plant on site.

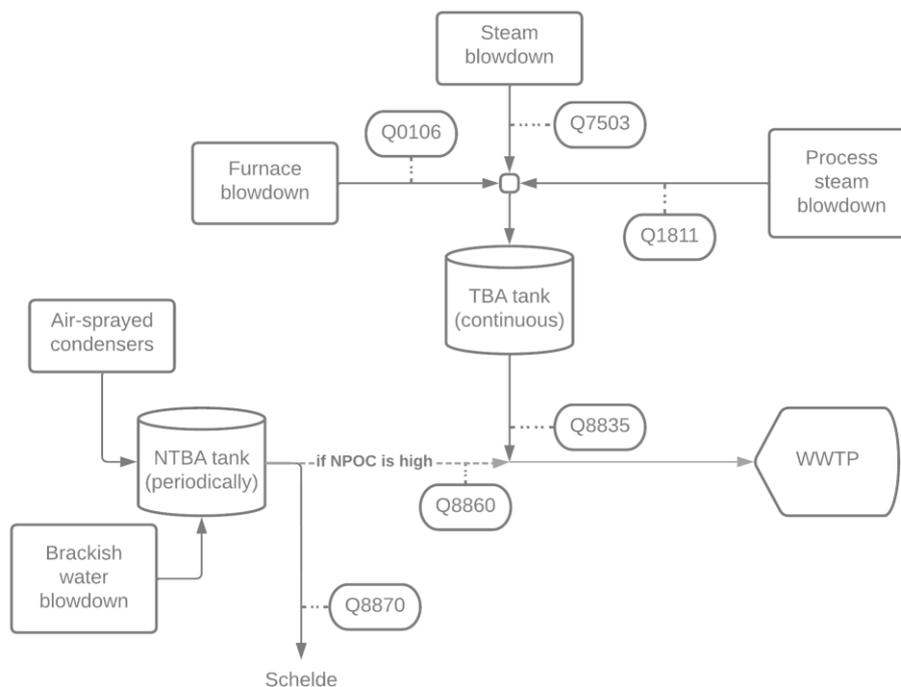


Figure 1 Schematic overview of the wastewater streams at the cracker site at BASF Antwerp

The second one is the NTBA-tank ('Niet Te Behandelen Afvalwater') and collects the water that does not require treatment and is discharged in the Scheldt-Rhine Canal. It collects the water coming from the air-sprayed condensers and the brackish water blowdowns. The air-sprayed condensers are part of the steam system. To allow the steam to condense, the steam is brought into small pipes that are in contact with the ambient air. To improve the air circulation around the pipes, fans are also part of the installation. In hot periods, extra water is sprayed over the condensers using nozzles, to ameliorate the heat exchange. Demineralised water is used for this application, but causes damage to the concrete, since it dissolves the cementing agent (Tchner, 2015). But if the water is not demineralised, corrosion of the installation could occur and the nozzles that are used to nebulise the water could get clogged due to salt.

The NTBA-tank is periodically being emptied in either the Scheldt-Rhine Canal or the wastewater treatment plant. Before the wastewater is discharged, the non-purgeable organic carbon (NPOC) content is measured and is the deciding parameter, since it is a collective measurement that represents all organic pollutants in the water. If the NPOC is lower than 30 mg/L, the water will be discharged in the Scheldt-Rhine Canal. However, if the NPOC turns out to be higher than 30 mg/L, the NTBA will be fed to the wastewater treatment plant.

At the cracker site, the main objective is to upgrade wastewater streams to boiler feed water or spray water for the air-sprayed condensers.

1.2.3 Demineralisation plant

BASF Antwerp is installing a new plant to provide the site with demineralised water. Biesbosch water will be used as feed stream, after pretreatment with sand filtration. The water will first pass through a salt-regenerated softener, then through a reverse osmosis unit and will ultimately be polished using mixed bed resins. A brine solution (NaCl) is used to regenerate the softener. Two wastewater streams are thus created in the demineralisation plant: reverse osmosis concentrate and regenerant waste stream. An overview is given in Figure 2.

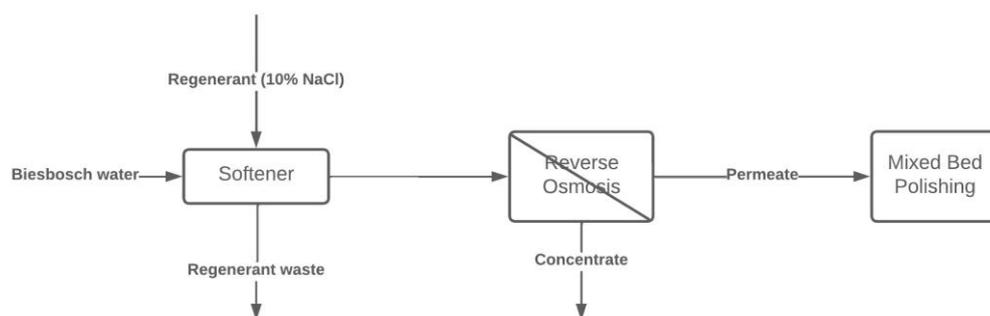


Figure 2 Schematic overview of the demineralisation plant at BASF Antwerp

The goal of the research at the demineralisation plant is to minimise the RO concentrate and to improve the recovery of the demineralisation plant.

1.3 Realisation

To investigate the reuse of these water streams, pilot-scale technologies will be used on site to determine which treatment steps are needed and feasible. The pilot-scale technologies originate from the IMPROVED project (Integrale Mobile PROceswatervoorziening Voor een Economische Delta). The IMPROVED project was funded by

Interreg Vlaanderen-Nederland and was successfully completed in 2019. The goal of this project was to explore alternative ways of producing water fit-for-use and increasing industrial water reuse. Different water sources (such as wastewater and brackish water) were tested as potential substitutes for making process water, instead of surface or ground water. For these tests, two sea shipping containers were fitted with seven water treatment technologies on pilot-scale dimensions. The containers were tested and used on three different sites: Yara Sluiskil, Dow Terneuzen and BASF Antwerp. The IMPROVED containers are deployed in the AquaSpice project and will be used on site to research the reuse potential of wastewater streams.

First, characterisation of the streams and lab tests will be performed to prepare for the operation of the pilot-scale containers. This thesis will focus on which technologies are worthwhile to test in the containers. Based on these outcome, pilot-scale experiments will be performed on site at BASF Antwerp, providing better insight on what technologies could be installed on full-scale.

CHAPTER 2

DESCRIPTION OF THE WASTEWATER

STREAMS OF INTEREST

In this chapter, the different streams of interest will be explained. Samples were provided by BASF to analyse and perform lab testing of the treatment technologies. The overview of the sites and different streams of interest can be seen Figure 1 and Figure 2.

2.1 Cracker site

- **NTBA (Q8860 and Q8870)**

The NTBA-tank is an open, buffered tank and collects the brackish water blowdowns and the water from the air-sprayed condensers. Since it is an open tank, the stream is at ambient temperature. The NTBA-tank is emptied out periodically (not continuously) and at this point, the NPOC is measured and decides whether the water is discharged (Q8870) or transferred to the WWTP (Q8860).

The air-sprayed condensers need extra cooling capacity during hot periods. Demineralized water is then sprayed on the condensers through nozzles, which creates peak loads on the demin plant. The brackish water blowdown stream is small – at least two orders of magnitude less than the spraying rate – and is used to cool certain water channels.

- **TBA (Q8835)**

The Q8835 sample is a mix of the TBA-tank and spent caustic from the caustic scrubber. The TBA is fed continuously to the wastewater treatment plant.

- **Furnace Blowdown (Q0106)**

The furnace blowdown comes from a direct steam system. This stream is at 120 bar and at saturation temperature.

This stream is already used as make-upwater for the steam system and contributes to the heat balance, which makes it less prioritised for research during this project.

- **Steam Blowdown (Q7503)**

The steam blowdown comes from an indirect steam system. This stream is at 120 °C and can be investigated for reuse.

Even though the streams are quite clean, the steam and furnace blowdown end up in the TBA-tank, because of heat integration purposes.

- **Process steam blowdown (Q1811)**

The process steam blowdown contains lots of organics since it comes from a direct

steam system. The stream is at 150 °C and is the most interesting stream to reuse, since the reuse would close the loop from process condensates to boiler feed water.

All blow-downs together generate a flow-rate that could provide up to 30% of the spray rate when recovered.

2.2 Demineralisation plant

In 2011, BASF transferred from drinking water to surface water to produce demineralised water. The surface water comes from the Biesbosch, which is a storage reservoir in the Netherlands that collects water from the Maas. This water is first treated by Evides Industriewater by adding flocculants in order to remove suspended solids by creating flocs retained by sand filtration. A biocide (i.e. MCA) is added to avoid any microbial growth in the transport pipes. After this pretreatment, a lot of organics that need to be removed for demineralised water production still remain (Vandepopuliere, 2019).

To investigate the best way to upgrade this surface water to demineralised water, the IMPROVED project performed tests on site. This project gave insight in which treatment trains could be used to upgrade their existing demineralisation plant. The conclusions from the IMPROVED project are now being implemented by BASF and Evides Industriewater by building a new demineralisation plant. The new demineralisation plant exists of seven parallel operating lines and is designed to deliver 1050 m³ of demineralised water per hour (Evides Industriewater, n.d.). Since the new demineralisation plant is currently being commissioned, no samples of the wastewater streams could be provided. So the treatment train was simulated using Biesbosch water, provided by BASF Antwerp.

Literature Review

CHAPTER 3

SEPARATION TECHNIQUES

This chapter will discuss the operation of the various technologies that could be applied for treating this streams. Also, some newly developed techniques that might give interesting results will be mentioned. The first section elaborates on membrane technology where nanofiltration, reverse osmosis and electrodialysis (and their newly developed variants) will be discussed. The second part discusses adsorption, more specific activated carbon and ion exchange.

3.1 Membrane technology

Membrane technology is a collective noun to group all kind of processes which separate molecules using a selective barrier, called a membrane. The membrane acts as a barrier that lets certain molecules pass, creating a feed side and a permeate side, displayed in Figure 3. The feed stream is split up into two resulting streams: the permeate, which is the stream that passed the membrane, and the concentrate, which is the enriched stream that remains on the feed side of the membrane. Which molecules, ions or particles can pass the membrane, is determined by the selectivity and the pore size of the membrane. Membranes are classified based on pore size, ranging from microfiltration to reverse osmosis. Membrane processes can be driven by pressure, temperature, concentration difference or an electrical field.

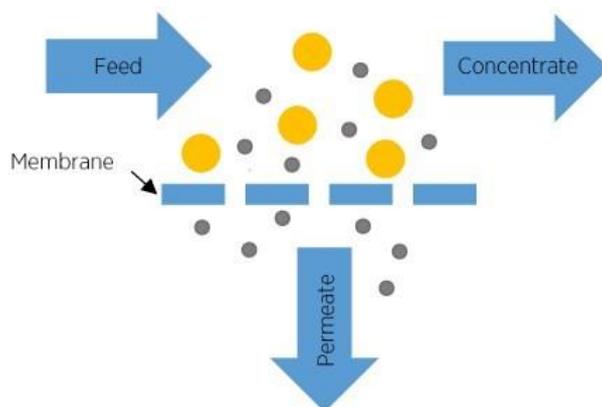


Figure 3 Schematic overview of the principle of membrane technology. Retrieved from Mann+Hummel (2019)

Different size classes of water membranes are selective for different kinds of molecules. Microfiltration (MF) is filtration with the loosest membrane (0.1-5 μm) and is rejecting bacteria and suspended solids. A microfiltration membrane is mostly operated with a pressure

difference of less than 0.5 bar over the membrane. Ultrafiltration (UF) (20 nm - 0.1 μm) retains viruses, next to suspended solids and bacteria. Since this membrane is tighter, the pressure drop will increase. Ultrafiltration membranes mostly need a pressure difference of up to 1 bar. Nanofiltration (NF) membranes reject all molecules and ions bigger than 1 nm, which means that bigger multivalent ions are retained by the membrane. Common used pressures for NF are between 3 and 20 bar. The tightest membrane is the reverse osmosis (RO) membrane (0.1 - 1 nm pore size) and will reject all molecules, except for water molecules. The pressure difference is mostly between 15 and 60 bar. MF and UF membranes are called porous membranes, NF and RO membranes are dense or non-porous membranes (Emis Vito, 2010). An overview can be seen in Figure 4.

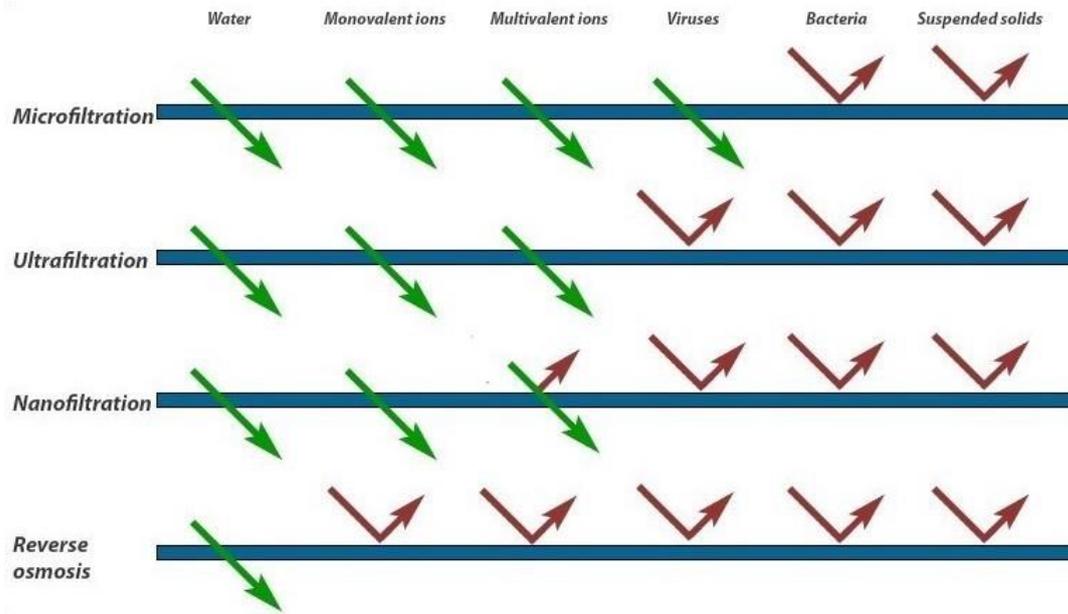


Figure 4 Overview of the rejection of different membrane classes. Retrieved from ZENA Membranes (n.d.)

Porous membranes have discrete pores that are visible using microscopy. Dense membranes are mostly composite membranes and are built out of a supportive (porous) layer and an active (non-porous) layer. The active layer is mostly a polyamide layer (around 100 nm thick), while the support material is generally polymeric (e.g. polysulfone or polyethersulfone). Most RO membranes are thin film composite (TFC) membranes, where the active and supportive layers get support from a non-woven polyesterweb (Warsinger et al., 2018). MF and UF membranes mostly retain the molecules by size exclusion, acting like a screen or a sieve. Dense membranes are described to be working with diffusion-solution, where molecules dissolve into the membrane, diffuse through the membrane and go back into solution on the permeate side (Whang et al., 2017).

The performance of membranes is defined using the parameters selectivity and recovery. The selectivity is determined by the rejection rate, which indicates how much of a certain molecule is retained by the membrane, calculated with Formula 3.1. The closer to 1, the better the molecule is rejected. Membrane selectivity is also frequently denoted by the molecular weight cut-off (MWCO, unit: Dalton), which is the molecular weight of the smallest component that is retained with an efficiency of 90% or higher (Singh, 2015).

$$\text{Rejection} = \frac{(C_f - C_p)}{C_f} \quad (3.1)$$

Where:

C_f is the concentration of a component in the feed stream

C_p is the concentration of a component in the permeate stream

The recovery of a membrane indicates how much permeate is produced, calculated using Formula 3.2. It indicates how much product flow can be produced/recovered given the feed flow. The flux of a membrane process is indicated as flow rate (L/h) per square meter of membrane in the module, resulting in a unit $L/m^2/h$, also abbreviated to lmh for simplicity.

$$\text{Recovery} = \frac{\text{Permeate flow}}{\text{Feed flow}} * 100 \quad (3.2)$$

Membranes are distributed in four main forms: tubular modules, hollow fiber modules, flat sheet modules and spiral-wound modules. Tubular membranes mostly exist of a porous supporting material (5-25 mm diameter) with on the inside a membrane and are installed in a hard housing. Hollow fiber modules are actually thinner tubular membranes (0.5-3 mm diameter). These membranes are sealed together in a housing. Flat sheet membranes can be used in plate and frame modules or be spiral-wound. In a plate and frame module, the membrane is attached with the active layer upwards to a hollow module, where the permeate can be collected (UF and MF). Different modules then are mounted parallel to a stack. A spiral wound module consists of membrane envelopes, which are two flat sheet membranes glued together, active sides facing outwards, with a spacer in between. The spacer guides the permeate to the central permeate tube in the middle of the module, at which the membrane envelopes are attached. Between the envelopes, feed spacers are inserted to guarantee a proper feed flow. The assembly of a spiral wound module is shown in Figure 5. The spiral wound module is installed in a pressure vessel to allow the system to operate at high pressures (Cui, Jiang, & Field, 2010; Panglisch, 2016).

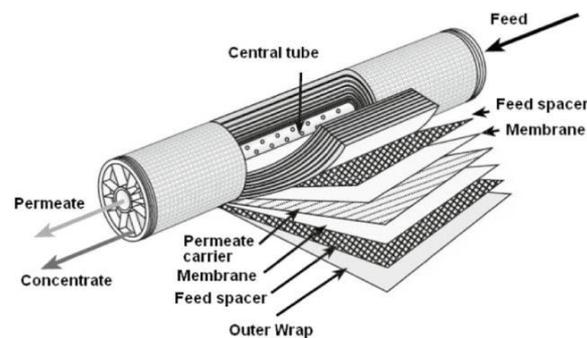


Figure 5 Schematic overview of the composition of a spiral wound module. Retrieved from Hasani et al. (2019)

Membrane technologies have two ways to operate: cross-flow or dead-end. When using dead-end operation, all feed is pushed perpendicular through the membrane and the concentrate is collected on top of the membrane (shown in Figure 6). Particles will attach to the membrane and the applied pressure needs to be increased during operation to maintain an equal membrane flux. After some time, the membrane needs to be cleaned (because the pressure drop gets too high), using a backwash with air or water. Dead-end operation is thus a discontinuous operation mode. Cross-flow filtration is a continuous process, where the feed is moving parallel to the membrane surface and two streams are created: the permeate flow (which goes through the membrane) and the concentrate or retentate (which stays at the feed side and is enriched in compounds that can not pass the membrane) (shown in Figure 3) (Panglisch, 2016).

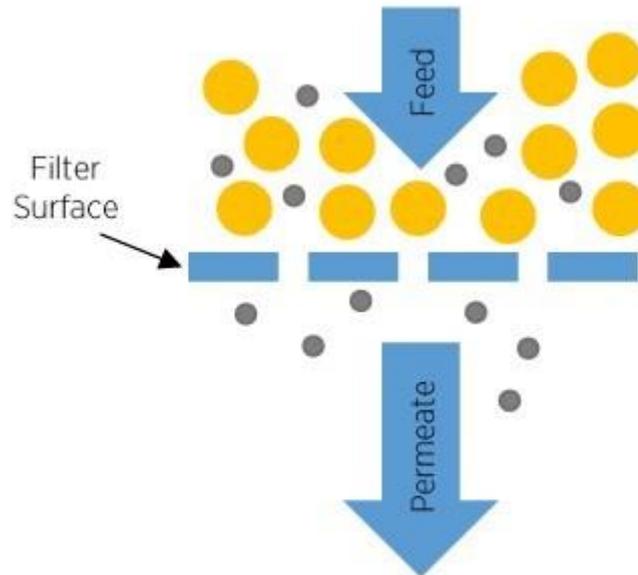


Figure 6 Schematic overview of the working principle of dead-end operation of membrane technology. Retrieved from Mann+Hummel (2019)

To increase the recovery of the treatment, the concentrate stream can be recycled to the feed tank or multiple modules can be put in series to treat the concentrate of the previous step. External concentration polarisation is a directly occurring and reversible phenomenon at the membrane surface. Molecules are retained by the membrane, which causes a concentration build-up of solutes near or at the membrane surface. This creates a boundary layer, containing a higher concentration of solutes. This increased concentration allows the solutes to migrate easier across the membrane, causing a decrease in rejection. This boundary layer also decreases the flux of water across the membrane, due to either a higher osmotic pressure (and thus lower driving force) or increased mechanical resistance. When the filtration is stopped, this boundary layer disappears completely (Mann+Hummel, 2021). Concentration polarisation can also cause irreversible and long-term effects, called fouling and scaling.

If particulates accumulate at the membrane surface, fouling can occur, causing the performance of a membrane installation to decline. Fouling is the phenomenon where the membrane gets blocked due to particles or other elements that are present in the feed stream. Fouling causes an increase in pressure drop over the membrane and a decline in the flow rate of the permeate. Compounds that can cause fouling are for example: particulate matter, organics and microorganisms. A commonly used parameter to test if feed water is susceptible to fouling, is the Silt Density Index (SDI), indicating the potential of a stream to foul a $0.45\ \mu\text{m}$ filter. A common way to reduce fouling is by using a pretreatment such as micro- or ultrafiltration, rapid sand filtration, activated carbon filters etc. (Suez, n.d.-b).

Scaling could be another reason for a declining performance. As molecules are rejected by the membrane, the concentration of rejected molecules will become higher close to the membrane surface. If this concentration exceeds the solubility of the molecule, insoluble precipitates will be formed on the membrane, blocking the membrane surface and causing a higher pressure drop. Saturation indexes are used to predict possible scaling, e.g. Langelier and Stiff-Davis (Suez, n.d.-b). Scaling can be divided into metal ion-based scales (formed via crystallisation) and silica-based scales (formed via silica polymerisation) (Yu et al., 2020).

To mitigate scaling, antiscalants (chemicals who increase the solubility limits) can be used. These chemicals use different mechanisms to inhibit scale formation, such as chelation, dispersion, crystal distortion or threshold effect. Using chelation, the antiscalants will use their ability to chelate with cations, increasing the solubility of the salts. Dispersion is the mechanism that creates a surface charge on the crystals to keep them dispersed (i.e.

electrostatic repulsion). The crystal distortion mechanism influences the crystallisation process, by interrupting the crystal growth. The threshold effect will inhibit scaling by disorganising the process of clustering and ordering of components. The most common antiscalants are polymeric antiscalants and phosphorous containing antiscalants. The polymeric antiscalants could use each of the above mechanisms, the phosphorous antiscalants can not use dispersion, but could use the other three (Yu et al., 2020).

3.1.1 Nanofiltration

A nanofiltration membrane is, based on pore size, the membrane between RO and UF.

Usually, the molecular weight cut-off (MWCO) of NF membranes is between 100 and 1000 Dalton, which indicates that it retains multivalent ions, but monovalent ions can pass the membrane to some extent, depending on the pore size of the membrane. Since the membrane has properties of both an UF and RO membrane, the mechanisms of a NF membranes are challenging to describe. The major advantage is the reduced pressure (in comparison to RO), combined with a very good removal of micro-organisms, organic matter and metals. A pretreatment is needed sometimes to avoid fouling or scaling of the membranes (Pal, 2017b).

The research of Choi et al. (2008) investigated the rejection of organic acids through NF membranes. For the membranes tested in their research, rejection of the organic acids was improving with increasing operating pressure and increasing pH. For the membrane with a MWCO of 100 Da, all organic acids were rejected more than 80% at a pH of 7 or higher. All rejection percentages were above 70% for an operating pressure of 200 kPa or higher. For the membrane with a MWCO of 200-300 Da, rejection above 70% was reached for a pH of 8 or higher. The operating pressure needed to be 275 kPa for 70% rejection of the organic acids (except for formic acid which is then at 50% rejection) (Choi et al., 2008). Even though the composition of these wastewaters is different than the streams investigated in this study, the research of Choi et al. (2008) indicates that NF performs well in regards to removing organic acids from wastewater streams.

3.1.2 Reverse Osmosis

Reverse osmosis (RO) is the tightest membrane in comparison to MF, UF and NF. To force the water molecules through the membrane, a hydrostatic pressure difference is applied. To perform reverse osmosis, the applied pressure should be high enough to overcome the osmotic pressure. Osmosis is the process where water molecules go through a semipermeable membrane from the diluted side to the concentrated side, creating an osmotic pressure. For reverse osmosis, the reverse phenomenon is required, hence a pressure higher than the osmotic pressure should be applied to overcome this effect. A schematic representation is shown in Figure 7. The higher the concentration of ions in the feed water, the higher the osmotic pressure and the higher the pressure needed to overcome the osmotic pressure (Puretec Industrial Water, n.d.; Suez, n.d.-b).

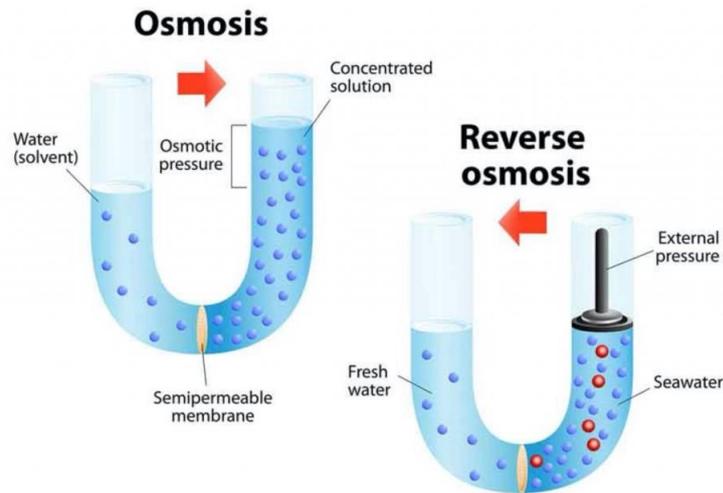


Figure 7 Schematic overview of the working principle of osmosis (left) and reverse osmosis (right). Retrieved from Brother Filtration (2020)

Typical recovery rates for RO systems are 50-85%, dependent on what feed stream is used and the design characteristics of the installation. Reverse osmosis applications can also be implemented in stages, where the permeate is extracted and the concentrate is being sent to another RO unit. By staging the units, a higher recovery is achieved. Since only the concentrate is going through multiple units, the flow will decrease after each unit. Therefore, a “Christmas tree” configuration can be used, where less units will be used after each step, as shown in Figure 8. To improve the recovery, (part of) the concentrate can also be recirculated to the feed stream. To increase the permeate quality, the permeate could be send through multiple RO units. This increases the quality of the permeate and creates a higher rejection, since the permeate is purified two (or more) times (Puretec Industrial Water, n.d.).

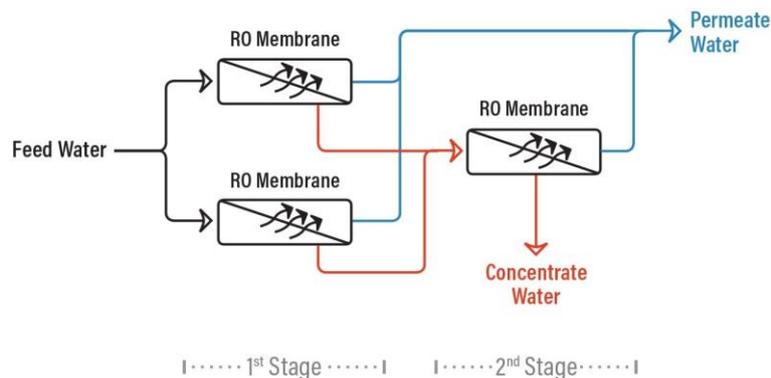


Figure 8 Schematic overview of the staging of RO units. Retrieved from Puretec Industrial Water

The bigger the molecular weight of a molecule and the greater its charge, the better it will be rejected by the membrane. Small monovalent ions could still go through to some extent. RO membranes can not remove gasses (such as CO_2 or Cl_2), due to the molecular porosity of the membrane. In the end, reverse osmosis is capable of removing 95-99% of all dissolved salts (Puretec Industrial Water, n.d.; Suez, n.d.-b).

A downside to reverse osmosis membranes is the sensitivity to chlorine or chloramines. These oxidisers can damage the membrane, resulting in poor permeate quality. Chlorines are added in different water systems to prevent microbiological growth. To prevent membrane damage due to chlorine, sodium bisulfite could be added to the feed stream to remove residual chlorine (Puretec Industrial Water, n.d.).

If membranes became scaled or fouled, cleaning mechanisms should be put to work. Typically cleaning cycles are started when the permeate flow drops 10%, salt passage increases with 5-10% or the pressure drop increases with 10-15%. Many different chemicals are used for chemical cleaning of the membranes. The most common ones are acid cleaners (to remove inorganics and iron) and base cleaners (to remove organic fouling). Enzymes could be used to hydrolyze proteins and chelators could remove multivalent cations. Commercial cleaning products are mostly mixtures of different components (DuPont, 2022).

Besides the chemical cleaners, there are also mechanical ways of cleaning a membrane. Especially for the loose membranes (MF and UF), backwash is a commonly used cleaning method, where the membrane is purged with air or water in the opposite direction of the direction in operation. Backwashing can not be applied for the dense membranes (NF and RO), since the active layer would dislocate from the supportive layer. For the dense membranes, a high cross flow without water flux can be applied to induce shear forces on the membrane surface (DuPont, 2022).

Even though reverse osmosis is a widespread used system, many developments were investigated over the years, each focused to mitigate one (or more) downsides of a conventional RO system.

3.1.2.1 Pulse Flow Reverse Osmosis

In 1974, the first experiments using a pulsed feed stream were performed by Kennedy, Merson, and McCoy (1974). They were able to improve the permeation rate of the RO membrane by more than 70% by pulsing a sucrose solution as feed stream.

Many years later, Liberman, Eshed, and Greenberg (2020) have taken this concept a step further and developed the Pulse Flow Reverse Osmosis (PFRO) technique. PFRO uses a reverse osmosis unit that is slightly adapted at the concentrate valve. The operation is split up into two parts. During the first part, the unit is operated in dead-end mode for a certain amount of time. Permeate is produced and no brine is discharged, which causes the concentration of ions to increase at the membrane surface. In the second part, a brine valve opens for a short period of time and flushes the concentrate from the unit, causing a discontinuous discharge of brine. Due to the short opening of the brine valve, the flush happens in a forceful way, which provides several advantages with regard to fouling and scaling. The PFRO system is operated for 20 - 30 seconds in dead-end mode (part 1), after which the valve to discharge the brine will open for 2 seconds (part 2). The comparison of the flows of a PFRO system to a conventional RO is shown in Figure 9.

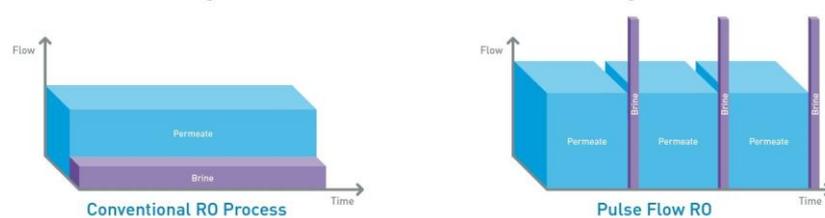


Figure 9 Comparison of conventional RO (left) to PFRO (right), with time on the x-axis and flow on the y-axis. The concentrate is shown in purple, the permeate is shown in blue. Retrieved from IDE Technologies (n.d.)

The osmotic and hydraulic conditions at the membrane are constantly changing, due to the dead-end operation and the short opening of the concentrate valve. The changing osmotic conditions provide a high variation in salinity at the membrane surface, which complicates the growth of micro-organisms and hence limits biofouling. This phenomenon makes the use of disinfection products unnecessary, eliminating the byproducts (chlorine) and the measures against the consequent membrane oxidation (e.g. sodium bisulfite) (Liberman et al., 2020).

Furthermore the changing hydraulic conditions have an effect on the membrane cleaning. Due to the quick opening and closing of the concentrate valve, a high shear velocity is created at the membrane surface and a water hammer effect is induced. In the installation, micro drum heads are integrated and will accumulate all

energy generated by the water hammer effect, which is returned when the brine valve is opened. The high shear stress and the shaking of the membrane due to the release of energy, contribute to the cleaning of the membrane. Additionally, the forward osmosis permeate back flush that takes place on the last membranes of the pressure vessel, adds to the membrane cleaning (Lieberman, 2018; Lieberman et al., 2020).

Scaling will be reduced since the operation time in the cycle is shorter than the induction time for scaling, which makes the use of antiscalants unnecessary. The operation time during PFRO is 10 to 50 times shorter than these for batch or semi-batch RO processes, where scaling could be present (Lieberman et al., 2020).

This technique was first developed and applied by IDE Technologies in a demonstration facility in the Pismo Beach wastewater treatment plant. Lieberman et al. (2020) introduce PFRO as a promising technique with a higher recovery and a higher flux, compared to conventional RO installations.

Lieberman et al. (2020) operated a pilot-scale PFRO at 86% recovery for 200 days at stable working parameters. The results from the demonstration plant are stable and no membrane damage was detected. Less fouling and scaling was detected on the membranes than for a conventional RO operation. The pilot plant also indicated power savings and operated at a 50% higher flux (around 28 lmh) than conventional systems. The conclusion of the pilot study was a decrease in overall water cost of 14-28% compared to a similar standard Fully Advanced Treatment water reuse process and that, even over a longer time period, the operation remained stable.

3.1.2.2 Closed Circuit Reverse Osmosis

Closed-circuit reverse osmosis (CCRO) is a technology that has been developed starting from conventional reverse osmosis. In the latter system, the pressure is controlled with a pressure control valve, which leads to a significant pressure drop and thus energy loss (Sutariya & Raval, 2021). Drak and Adato (2014) eliminated this pressure loss by adding an extra pump. This pump is dosing fresh feed water in the pipes to keep the desired pressure in the system, which creates much more energy efficiency.

The technology consists of a RO skid, a circulation pump, a high pressure pump and a brine valve. A schematic representation is shown in Figure 10. Two modes of operation are used during a cycle: closed-circuit mode (CC, 100% recovery) and flushing mode (FM, 15-50% recovery). The cycle starts with closed circuit mode where the brine is recirculated without any pressure loss. The operation mode is changed to flushing mode when a certain recovery is reached. Then the concentrate is purged via the brine valve and the high pressure pump adds new feed water to the system. The system is still operational during the flushing mode and permeate is still being produced. When the concentrate is purged, the system goes back to the closed circuit mode of operation. Dependent on what overall recovery is desired, the system has different operating times (e.g. 90% recovery: 20 minutes in CC, 1.5 minutes in FM). In theory, the system can reach high recovery with just one membrane element, but in practice multiple elements in parallel are used (Boyd, 2019).

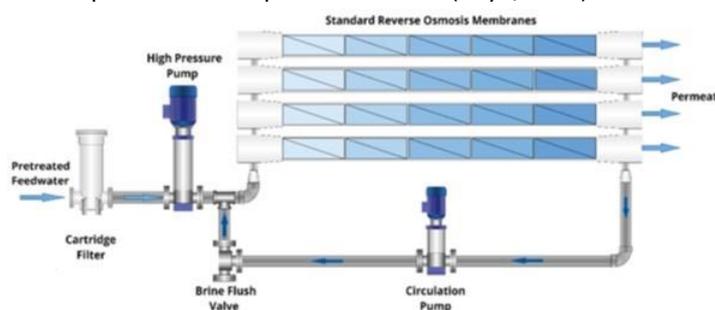


Figure 10 Schematic overview of the working principle of Closed Circuit Reverse Osmosis. Retrieved from Boyd (2019)

Boyd (2019) points to the importance of mitigation of fouling and scaling in water reuse technologies. Similar to the PFRO mentioned above, Closed Circuit Reverse Osmosis has a high variation in salinity at the membrane

surface (fresh feed water to most concentrated brine before purging), mitigating the growth of biofouling on the level due to the salinity change. The operation time in the cycle is shorter than the induction time for scaling for most salts, avoiding scaling on the membrane. The crossflow velocity can be increased, without having an impact on the recovery, to provide a better mixing, which decreases the concentration polarisation and consequently fouling. Another advantage for this technology is that the recovery can be easily adapted, dependent on the conditions of the feed water (Sutariya & Raval, 2021).

3.1.3 Electrodialysis

Electrodialysis (ED) is a desalination technique that makes use of ion exchange membranes. These are a special kind of membranes that consist of highly swollen gels that carry charged groups. There are both anion exchange membranes (charged positive) and cation exchange membranes (charged negative). Due to the charge on the membranes, they exclude all ions that have the same electrical charge and are only permeable to the ions with an opposite charge (Strathmann, 2011).

Electrodialysis is not only a membrane technology, since it also uses electrochemical properties. An electric field is applied to move the ions through the membranes (instead of a pressure difference). An electrodialysis stack consists of different flow compartments separated by ion exchange membranes. There is always a feed compartment, followed by a diluate compartment. The anion exchange membranes (AEM) and cation exchange membranes (CEM) alternate between these compartments. On the most outwards side of the stack, the cathode (-) and anode (+) electrodes are placed (Al-Amshawee et al., 2020; Gurreri et al., 2020). A schematic representation of the system is given in Figure 11. Charged molecules in the feed solution will be attracted or repulsed by the electrodes, based on the signs of their charge. Positive ions will be attracted by the cathode and will move towards this electrode. However, during their movement they will be able to pass the CEM but they cannot cross the AEM, which means that they will be retained within this compartment. This results in several separate compartments with a high salt concentration and others with diluate or product flow.

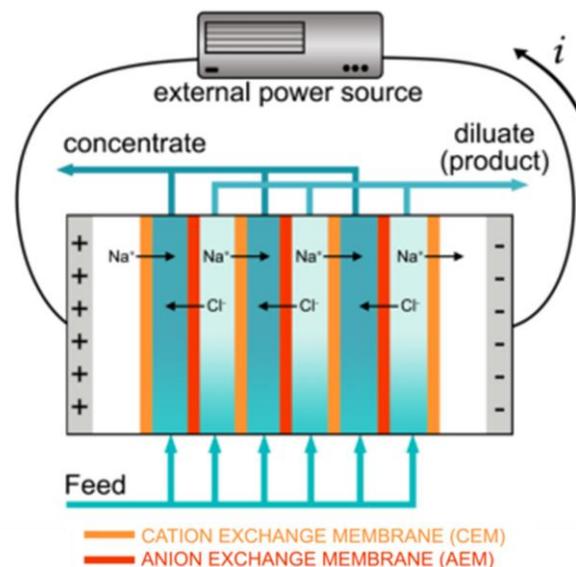


Figure 11 Schematic overview of the working principle of electrodialysis. Retrieved from Tedesco et al. (2016)

ED has numerous applications in waste water treatment, process water demineralisation and desalination of brackish water. The key points to choose ED over RO for these applications are the little pretreatment needed, since electrodialysis reversal can be applied to limit fouling. High recoveries can be reached and the ion-exchange membranes also have a long lifespan, due to the mechanical and chemical stability of the membranes. On the

other hand, ED does not remove any uncharged particles or micro-organisms and has a high investment cost (Strathmann, 2010).

3.1.3.1 Electrodialysis with bipolar membranes

Electrodialysis with bipolar membranes (EDBM) is equivalent to electrodialysis, but uses special membranes. Bipolar membranes are implemented in addition to the cation and anion exchange membranes. These bipolar membranes are polymeric membranes with both a cation and anion exchange layer with in between an interfacial layer. Technically, bipolar membranes are not membranes, since the ions are not supposed to move across. The main function of these membranes is to electro-dissociate water molecules in the interfacial layer (without gas formation). Subsequently the ions move through the corresponding (anion or cation) layer to the compartments. The membrane should be positioned so that the anion exchange layer faces the positive electrode or anode (Ghyselbrecht et al., 2013; Pärnamäe et al., 2021).

The stack is composed of alternating cation exchange membranes, anion exchange membranes and bipolar membranes. This creates different compartments. In Figure 12, one unit of a stack is depicted, in practice multiple of these units are combined into one stack. The blue zones are the feed inlets of the saline stream. By moving of the ions through the ion exchange membranes, an acid (orange) and a base (green) compartment is created next to the bipolar membrane. The salts in the feed stream can thus be separated in their corresponding acids and bases, which can be reused for another purpose. The only disadvantage of these streams is that they are mixtures of acids (e.g. HCl, H₂SO₄) and bases (e.g. NaOH, KOH, MgOH), which is not desired for certain purposes. EDBM also has a lower electrical efficiency compared to conventional ED (Ghyselbrecht et al., 2013; Pärnamäe et al., 2021).

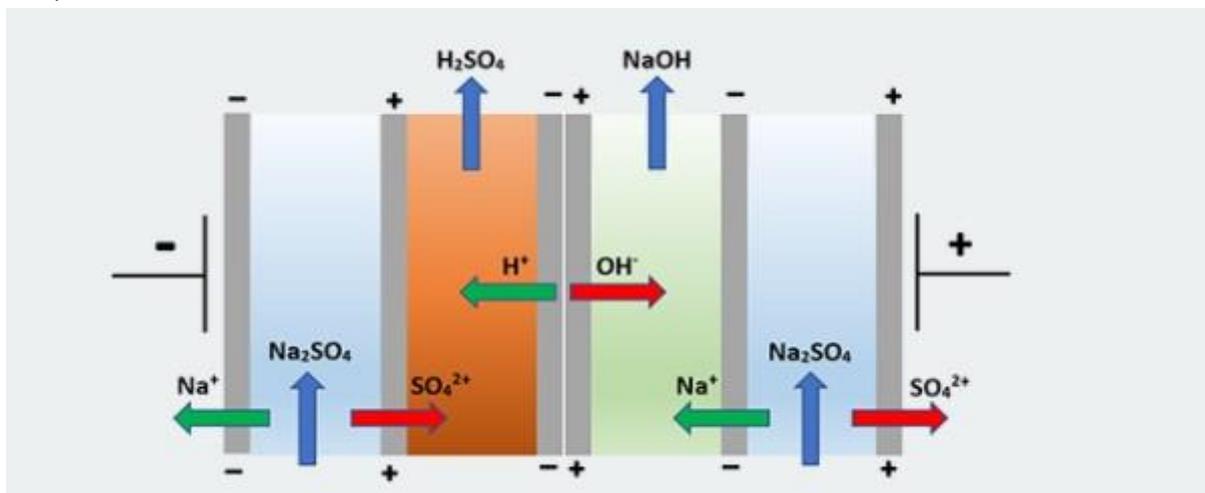


Figure 12 Schematic overview of the working principle of electrodialysis with bipolar membranes. Retrieved from Lenntech (n.d.-a)

3.1.3.2 Electrodeionization

Electrodeionization (EDI) is a technology introduced in the late 1950's to minimise the effect of concentration polarisation in ED modules. Electrodeionization is a combination of an ion exchange resin process with electrodialysis (as shown in Figure 13) and is mostly used as a polishing step for ultra-pure water production. The unit consists of alternating ion selective membranes and channels, with the diluate compartments being filled with mixed ion exchange resins (mostly strong ion exchange resins). These resins account for a lower internal resistance and are facilitating ion transport. An electrical potential is applied, which causes ions in the feed streams to move through the membranes and the resins, using the same mechanism as electrodialysis. This adaptation lead to an increase in the maximum ion separation efficiency of 50 to 90% (Alvarado & Chen, 2014).

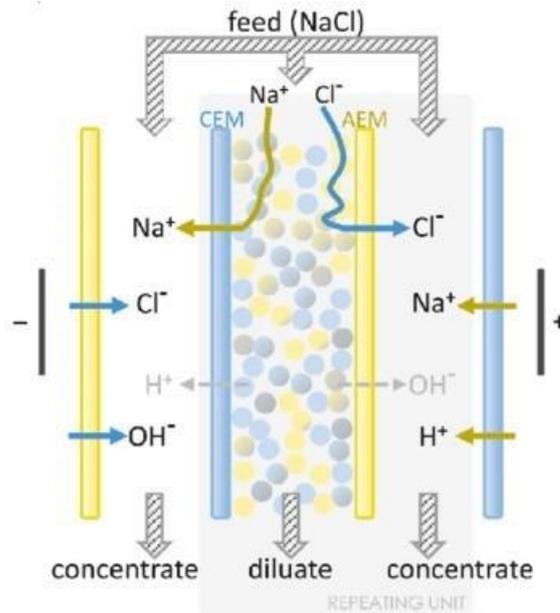


Figure 13 Schematic overview of the working principle of electrodeionization. Retrieved from Pärnamäe et al. (2021)

Due to the applied potential, electrolysis happens simultaneously and water is split into H^+ and OH^- molecules (where the ion exchange materials are in contact with each other). Due to the presence of these ions, the ion exchange resins are continuously regenerated, meaning that no chemicals for regeneration are needed (Alvarado & Chen, 2014).

EDI is used as a polishing technique (replacing mixed bed polishing) and has been proven to perform well, provided that no high concentrations of hardness ions are present. Different research papers confirm the ability of EDI to produce ultra-pure water (Arar et al., 2014; DiMascio et al., 1998; Turek et al., 2013).

Grabowski et al. (2006) investigated the effect of bipolar membranes in EDI modules. The use of bipolar membranes in an EDI module eliminates production of protons and hydroxide-ions in the ion exchange materials, as these ions can now be produced in the interfacial layer (see section 3.1.3.1). The main disadvantage is the possible leakage of co-ions through the ion exchange membrane into the permeate compartment but could be avoided by adding a protective compartment (Grabowski et al., 2008).

The main advantage of this technology is the small footprint. It only needs three reservoirs (concentrate, diluate and electrodic rinse), an EDI stack, pumps and power supply. Furthermore, no chemicals are needed, since the resin is regenerated in situ. This absence of chemicals also contributes to the small footprint, since no infrastructure is needed for the regeneration chemicals. This does not only save costs on the purchase of chemicals, but also avoids the costs for disposing of the regeneration waste streams. The system can be operated continuously, since no breaks are needed for regeneration and has a low power consumption. The recovery of EDI (95%) is lower than for a MB polishing, but in EDI, the concentrate is mainly fed back to the main desalination step, so the loss of water is minimised (Pure Water Group, n.d.).

Nevertheless, the system also has some limitations regarding the feed water. To protect the module, hardness ions and iron should be avoided or limited, to avoid scaling and fouling. Dependent on the feed stream, pretreatment could be needed, as there are stringent inlet conditions for these modules.

3.2 Adsorption

Adsorption is described as a surface phenomenon which fixes ions or molecules on the surface of a material. Molecules of a gas or liquid are transferred to the surface or interface of a solid material. Temperature and conditions (pH, contact time, particle size) affect the process of adsorption (Ali & Gupta, 2006). The solid molecule on which the gas or liquid molecule is adsorbed, is called an adsorbent. An adsorbent is usually a high porous, large specific surface area solid (Pourhakkak et al., 2021).

Physical adsorption is the phenomenon where adsorption is only driven by van der Waal's forces of attraction. If there are any chemical interactions, it's called a chemical adsorption. The process can go on as long as there is any free surface of adsorbent available. When no free surface is available, the adsorbent is saturated or exhausted (Pourhakkak et al., 2021).

The adsorption process is described by adsorption isotherms. They give the relation between the amount of solutes adsorbed per mass adsorbent, as a function of the concentration of the solutes at equilibrium. The amount of solute, adsorbed by the adsorbent, per amount of adsorbent is called the loading capacity. These isotherms are constructed using laboratory experiments under isothermic conditions. Different types of isotherms exist, the most known ones are Langmuir and Freundlich (Pal, 2017a).

3.2.1 Activated carbon

The most widely used adsorbent is activated carbon. It is created by activating carbon by chemical (metal chlorides) or thermal (CO₂ and steam) processes. These processes create a material with an extensional developed internal pore structure, creating a high specific surface area of around 300-4000 m²/g (Bart and von Gemmingen, 2005; Bhatnagar et al., 2013). This specific surface area (SSA) is the most important feature, since it determines the adsorption capacity of the material. Other properties of activated carbon are the stability over a wide pH range and its inert nature. Activated carbon is not polar. Yet, polarity can be induced due to surface oxidation. It is a hydrophilic and organophilic adsorbent (Pal, 2017a).

Activated carbon is used in two main forms: granular activated carbon and powdered activated carbon.

Powdered activated carbon contains particles between 10 and 50 nm. The PAC is mostly injected directly into the streams that need to be treated and is separated by the forming of flocs or by filtration. PAC is cheaper than GAC and the amount used can be adapted to the streams properties (DESOTEC Activated Carbon, n.d.).

Granular activated carbon contains granules. It is mostly used in a filter bed, where the stream flows over the carbon. Important properties for operating a GAC filter are the bed depth and the contact time. The granules can also act as a kind of filter and are a substrate for microbial growth (which can add to the removal of organic carbon) (Suez Group, n.d.-a).

When the activated carbon is saturated, regeneration is needed. The three possibilities for regeneration are: vapor regeneration, thermal regeneration and biological regeneration (Suez Group, n.d.-a).

3.2.2 Ion Exchange

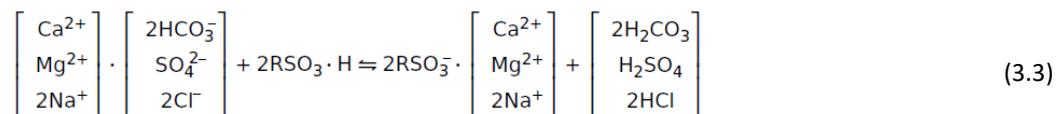
Ion exchange is described as a reversible process during which ions in an aqueous solutions are exchanged with other ions on an ion exchange material, without permanent change in the structure of this material. The driving force for this exchange is the affinity of the ions.

Types of ion exchangers Resins are usually available in the form of beads or granules. They consist of a backbone with active sites or functional groups. The backbone is mostly a type of polystyrene, acrylic or formophenol. The first two are made using polymerisation and have cross-links using divinylbenzene, to make them more durable (Suez Group, n.d.-c).

Ion exchange resins are being classified dependent on their functional groups, which can be positively or negatively charged. The four categories used are:

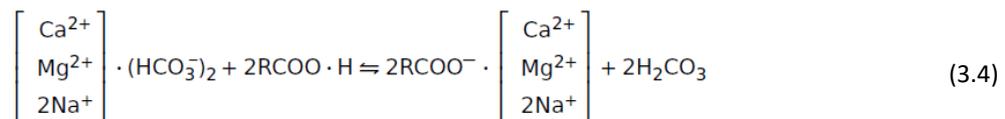
- **Strong Acid Cation (SAC)**

Strong Acid Cation resins mostly have a sulfonic acid group ($-\text{HSO}_3^-$), which is a strong acid. The cations in the liquid phase are replaced by H^+ . This type of resin can thus neutralise strong bases and convert neutral salts in their corresponding acids. SAC resins can remove nearly all raw water cations, as shown in Equation 3.3 (Suez Group, n.d.-c).



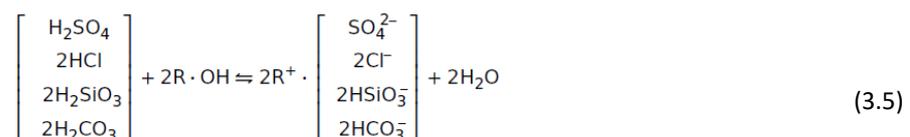
- **Weak Acid Cation (WAC)**

Weak Acid Cation resins functionality originates in carboxylic groups ($-\text{COOH}$) as functional groups. They exchange hydroxyl ions (H^+) for alkalinity associated cations (mainly Ca^{2+} and Mg^{2+}), as shown in Equation 3.4 (Suez Group, n.d.-c).



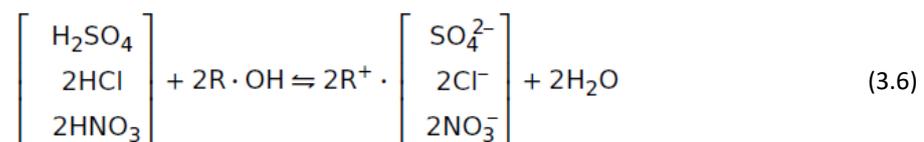
- **Strong Base Anion (SBA)**

Strong Base Anion resins derive their functionality from quaternary ammonium groups ($-\text{NR}_3$), which can be split up into two different types of ammonium groups. The first type (Type I sites) have three methyl groups. Type II sites have an ethanol group instead of one methyl group. SBA resins are mostly operated in hydroxide-form and can remove all anions, as shown in Equation 3.5 (Suez Group, n.d.-c).



- **Weak Base Anion (WBA)**

Weak Base Anion resins contain amine groups (either primary (R-NH_2), secondary (RNHR') or tertiary ($\text{R-NR}'_2$)). WBA resins can remove sulfuric acid, nitric acid and hydrochloric acid, as shown in Equation 3.6 (Suez Group, n.d.-c).



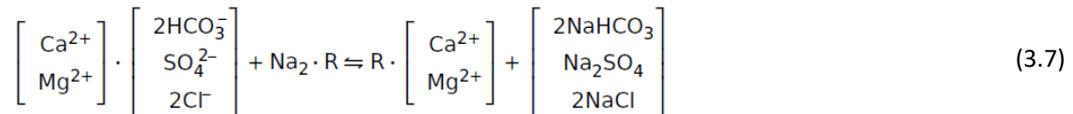
The performance of ion exchange resins is described using capacity (eq/L). It indicates how much ions (mol-equivalents) can be exchanged per liter of resin used. If the resin is exhausted, breakthrough will happen and the resin needs to be regenerated. Regeneration can be done co-current (same direction as saturation) or counter-current. Performing co-current regeneration, the lower layers will not be completely regenerated during regeneration, but will be regenerated during the following cycle, when the regenerant elutes from the top layers.

Counter-current regeneration has the advantage that the less exhausted resin will be regenerated with the fresh regenerant, which leads to an improved performance and improved water quality (Suez Group, n.d.-c).

Weak resins have a much higher regeneration efficiency than strong resins. So if weak resins are placed in front of strong resins, typically less regenerant will be needed. For SAC resins, typically HCl (or H₂SO₄) is used. For SBA resins, NaOH is used as regenerant. For weak resins, only 1 equivalent of regenerant ions is needed for removal of 1 equivalent of ions, for strong resins 3 or 4 equivalents are needed (Suez, n.d.-a).

3.2.2.1 Softener resin

Softener resins are actually strong acid cations (SAC) resins in Na⁺-form. Hardness ions (Ca²⁺ and Mg²⁺) are exchanged for sodium ions, as is described in Equation 3.7.



When the softener is exhausted, a sharp increase in calcium and magnesium is detected.

After exhaustion, the softener needs to be regenerated using a brine solution (NaCl) of 10%. Commonly, four steps are used for regeneration. First of all, a backwash to remove suspended material that is collected on the bed. Secondly, the brine is introduced in the system. Thirdly, there should be a slow rinse to displace the regenerant. The goal is to get a plug flow, so all the brine is removed while providing extra contact time for regeneration.

Lastly, there is a fast rinse to remove any residual brine or hardness from the resin bed. The time between regeneration and exhaustion, depends on the capacity of the resin, the hardness concentration in the feed water and the used flow rate (Suez, n.d.-a).

3.2.2.2 Mixed bed resins

Mixed bed resins are actually a mix of strong acid cation resin and strong basic anion resin in the same unit. This configuration is commonly used for polishing clean streams, since it produces extremely pure water and has a resulting pH close to 7. The two resins can be regenerated separately, since they can be segregated by a density difference using water (anion resins are lighter and will rise) (Suez Group, n.d.-b).

3.2.2.3 MPPE resins

MPPE resins are special resins to remove aromatics and BTEX components. MPPE stands for Macro Porous Polymer Extraction which means that the resins contain an extraction liquid. The resin can be regenerated with steam and the hydrocarbons can be recovered in an external condenser (Veolia, 2017).

3.2.2.4 Scavenger resin

Scavenger resins are macroporous SBA resins who have a strong affinity for organic matter. The resins are in chloride-form (Cl^-) and can be regenerated using alkaline brine (NaOH and NaCl). Scavenger resins exchange all anions in the water with chloride-ions and will thus increase the chloride levels in the stream, which makes this resin not suitable for every purpose (i.e. drinking water production) (Suez Group, n.d.-d).

CHAPTER 4

THE USE OF BOILER FEED WATER

On the cracker site, the goal is to upgrade some of the wastewater streams to boiler feed water. Boiler feed water is used as a medium to produce steam in a steam-water cycle. These cycles are mainly found in electricity generation and the (petro)chemical industry. The steam system and the use of boiler feed water will be discussed in this chapter.

4.1 Water-steam cycle

A schematic representation of a steam cycle is shown in Figure 14. Feed water is pumped through a pump into a steam boiler. Steam is generated by heating up the water, but restraining it physically and thermally. The steam is then leaving the boiler and being distributed over the system. In a direct steam system, the steam itself is used, so no water returns to the boiler. In an indirect system, only the heat content of the steam is used (for example in a heat exchanger), the steam will condense back to a liquid in a condenser and is normally returned to the boiler for reuse (Roberts et al., 2017).

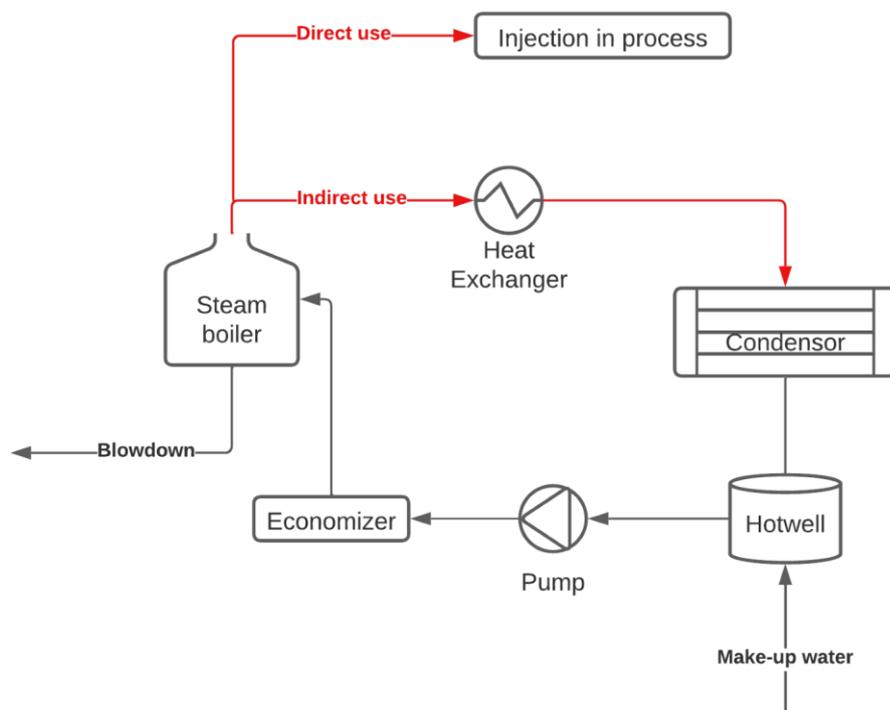


Figure 14 Schematic representation of a steam cycle. Adapted from Roberts et al. (2017)

Condensates will be formed due to heat or energy losses during distribution. These condensates are returned to the boiler. As the feed water turns into steam, impurities (such as dissolved or suspended solids) will increase in concentration in the boiler. To get rid of this, some of the liquid is discharged, called 'bottom blowdown'. Impurities (such as hardness) can also scale or cause corrosion in the boiler and must be avoided (Roberts et al., 2017).

These blowdowns and direct use of steam create a decrease in feed water in the system. Make-up water is dosed gradually into the system as the amount of water is decreasing. It is of utmost importance to have a good feed water quality to compensate for the lost water in the system. Components to avoid are salts of calcium and magnesium, chlorides, ammonium salts, traces of heavy metals and dissolved gasses (e.g. O₂ or CO₂) (Roberts et al., 2017). The water fed into the boiler is thus a mixture of recovered water and additional water.

4.2 Problematic components

Many industries in Flanders are now shifting to alternative water resources, instead of surface, ground or tap water, due to groundwater salinisation, decrease in groundwater levels or the decreasing reserves of freshwater resources (De Meyer, 2020). The streams that are used in steam-water cycles need to be of excellent quality. These alternative water sources are often of a lower quality than for example tap water and have a higher variation in quality (e.g. TOC, inorganic components etc.). An additional polishing unit is sometimes installed for the recovered water, to further remove any impurities (De Meyer, 2020).

TOC is one of the main components that can be problematic in the system. The organics can cause damage in the steam system, since organic matter is mostly a precursor for organic acids (especially at high temperatures and pressures). Organic matter is degraded during the hydrothermolysis process into organic acids (mainly acetic and formic acid) and CO₂. This causes a lower pH in the first condensate area and corrosivity of the steam, which is problematic for the equipment and parts of the steam system (Moed et al., 2014). De Meyer (2020) also indicated in her research that not only the concentration of TOC, but also the composition is important to assess the corrosive properties.

4.3 Conditioning of the water

Polished make-up water is often conditioned before it is introduced into the steam-water cycle. The pH is increased to an alkaline pH to avoid corrosion. The most common method is the all volatile treatment method, which uses ammonia. The limitation of this treatment is that the protection is limited due to the high volatility of ammonia. BASF uses ammonia in their steam system. New treatments have been developed to overcome the limitations, such as all volatile organic treatment, which uses alkalizing amines and/or film forming amines, but will not be further discussed (De Meyer, 2020; The International Association for the Properties of Water and Steam, 2015).

Materials and methods

CHAPTER 5

ANALYSIS TECHNIQUES

5.1 Conductivity and pH

Conductivity was measured to know the solution's capability to conduct an electric current and is an indication of the ionic content in the solution. The conductivity was analysed using a C3020 multi-parameter benchtop analyser (Consort, Belgium), with a SK10T conductivity electrode (Consort, Belgium).

On the same benchtop analyser, a SP10T pH electrode (Consort, Belgium) was fitted to measure the pH.

5.2 Turbidity

Turbidity was measured with HI-98703 meter (Hanna, Belgium), which determines the turbidity through the ratio of scattered and transmitted light (adaptation of the USEPA Method 180.1 and Standard Method 2130 B). The meter has a range from 0 - 1000 NTU (Nephelometric Turbidity Units) and multiple measurements are collected into one final average value.

5.3 Ion chromatography

Ion chromatography was used to determine the concentration of anions and cations in the samples. Ion chromatography was performed with the 930 Compact IC Flex (Metrohm, CH) using an 858 Professional Sample Processor (Metrohm, CH).

For anion analysis (F^- , Formate, Acetate, NO_2^- , Cl^- , Propionate, Br^- , NO_3^- , SO_4^{2-} , PO_4^{3-}), a Metrosep A Supp 16-250/4.0 column (Metrohm, Switzerland) was used, with an eluent solution of 7.5 mmol/L Na_2CO_3 and 0.75 mmol/L NaOH. Calibration curves from 0.02 mg/L to 10 mg/L were available. Samples were diluted using milli-Q water to obtain a concentration within this range.

For cation analysis (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}), a Metrosep C 6-150/4.0 column (Metrohm, Switzerland) was used, with an eluent solution of 1.7 mmol/L HNO_3 and 1.7 mmol/L dipicolinic acid. Calibration curves from 0.05 mg/L to 5 mg/L were available. Samples were diluted using milli-Q water to obtain a concentration within this range.

CHAPTER 5. ANALYSIS TECHNIQUES

5.4 ICP-OES

To analyse metals, Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES Thermo ScientificTM iCAP 7400DUO) was performed. This device is able to determine simultaneously the concentration of multiple trace elements from $\mu g/L$ levels up to mg/L levels. To keep the metals in solution, samples were acidified using 2% HNO_3 , prior to analysis.

Any particles needed to be removed before analysis. Most samples were filtered using a 0.45 μm syringe filter (Chromafil). For some samples, a sample digestion was performed before analysis to also take the particulate matter into account. This digestion was performed in an open vessel on a hotblock. Samples were acidified, heated to 100 °C (covered) and kept at 100 °C for one hour. After the digestion, samples were diluted to 50 mL and analysed using ICP-OES.

5.5 TOC analysis

Total Organic Carbon is a measurement that represents all organics in the system and is used as an indicator for water quality.

5.5.1 Shimadzu

The first TOC analyser used, was the TOC-V_{CPN} total organic carbon analyser (Shimadzu Corp., Japan). The analyser was operated according to Standard Method 5310 (American Public Health Association et al., 2017). Samples were prepared by storing them in glass vials at 4 °C and some samples were diluted with milli-Q water. Both total organic carbon (TOC) and non-purgeable organic carbon (NPOC) were determined with this equipment.

5.5.2 Sievers

For TOC analysis with inorganic carbon removal, a Sievers 900 Portable TOC Analyser (GE Power & Water, USA) was used. This analyser can be used in online mode or in grab sample mode and can measure TOC between 0.3 $\mu\text{g/L}$ and 50 mg/L TOC. The analyser was used in grab sample mode. For the inorganic carbon removal (ICR), an additional automatic Inorganic Carbon Removal unit was added to the setup and connected to the main analyser.

During inorganic carbon removal, inorganic carbon (IC) is removed by vacuum degasification. The unit consists of a teflon degassing module, a vacuum pump and a carbon and soda lime trap, which prevents contamination from organics or CO₂ in the atmosphere. First, acid is added to the sample, then the sample is directed through the teflon degasser. Bicarbonate and carbonate will react with the acid to carbon dioxide and will be removed by the vacuum. The ICR unit can remove up to (approximately) 98% of the inorganic carbon (up to 25 mg/L). ICR is required if TOC is less than 10% of IC for accurate TOC measurements (GE Power & Water, 2011).

5.6 LC-OCD

Liquid Chromatography - Organic Carbon Detection (LC-OCD) analysis was performed by DOC-Labor GmbH (Germany).

5.7 Particle Size Distribution

To determine the size of Fe-particles, an analysis for particle size distribution was performed using the Zetasizer 3000HS (Malvern Panalytical, UK) which uses the technique of dynamic light scattering.

5.8 UV absorbance

UV absorbance at 254 nm is a commonly used measurement that may relate to organic carbon and is used to indicate the efficacy of treatment processes that remove organic carbon (Thermo Fisher Scientific, 2016). For these analyses, a WPA Lightwave II UV/Visible Spectrophotometer (Biochrom Ltd., United Kingdom) was used, with the samples loaded in a quartz cell.

CHAPTER 6

LAB TESTS

6.1 Characterisation of the samples

All samples were stored at 4°C and a full characterisation was performed on all initial samples obtained from BASF. Conductivity, turbidity and pH were determined. Ions were analysed with ion chromatography. Total organic carbon (and NPOC for a new round of samples) was determined with TOC-analysis. Metals were analysed using ICP-OES for all possible elements (Cu, Fe, Ca, Mg, Zn, Cr, Ni, Pb, Cd, Mn, B, Be, Co, Ba, Na, K, Al, Bi, Ga, Li, Se, Sr, Te, Tl, As, P, Ti, Si, In, Sb and V).

For the Q7503 and Q0106 streams, ICP-OES was performed a second time on a digested sample to obtain the total Fe-content.

The full characterisation of each sample is shown in Appendix B.

6.2 Filtration setups

6.2.1 Nanofiltration

Nanofiltration was performed using a fixed setup in the lab, shown in Figure 15. The membrane unit is made for flat-sheet membranes and a Synder filtration NFX membrane was used (Synder Filtration, n.d.). The membrane is a thin film composite membrane and has a MWCO between 150 and 300 Da. A feed flow rate of 1 L/min was used and the setup was operated at 5 bar. A heat exchanger was used to keep the temperature stable at 25 °C. New membranes were installed in the module (membrane area : 119.4 cm²) and were flushed with demineralised water for one hour to get rid of any unwanted contamination present after storage. Afterwards, the membrane was compressed by running the unit at 5 bar with demineralised water for one hour.

The reservoir that was collecting the permeate was put on a scale to log the behaviour of the membrane flux. The resulting permeate was sampled and analysed for TOC, pH, conductivity and turbidity. Anion IC and ICP-OES (Na, Ca, Mg, K, Li, Se, Si, P) were performed. NF filtration was performed on Q8835 and Q1811.

6.2.2 Reverse Osmosis

Reverse osmosis experiments were carried out using two different setups.

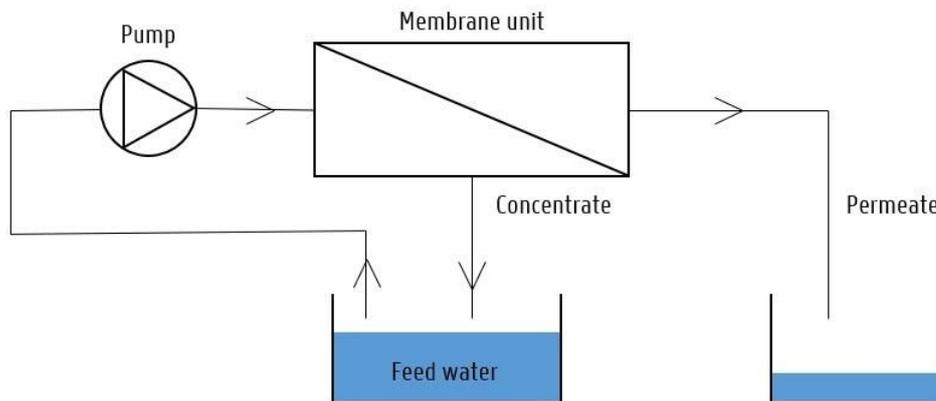


Figure 15 Schematic representation of the membrane lab setup

Dead-end RO cell

The first setup used was the lab-scale dead-end RO cell. The pressure for the RO process is obtained using high-pressure N_2 -gas. Using pressure regulators, a pressure of 20 bar was used. The membrane used was an FilmTec™ LCLE-4040 coupon with a membrane area of 12.56 cm^2 . The system was flushed and the membrane compressed with demineralised water for 30 minutes at 20 bar. The system was operated at 63.7 l/h . The setup was used for treatment of Q8870 and MQ1811 and is shown in Figure 16. Permeate samples were analysed for conductivity and NPOC. Anion IC was performed.



Figure 16 Figure of the dead-end RO cell setup

Pilot RO unit

The second RO setup was a pilot-scale setup. It is suited for spiral wound membranes and a FilmTec™ XLE 2521 membrane (DuPont, 2020; Lenntech, n.d.-b) was used. The working principle is the same as shown in Figure 15, except that a spiral-wound membrane was used, instead of a flat-sheet. Before each experiment, the system was flushed with demineralised water for 30 minutes.

For the experiments with the softened Biesbosch feed water, the setup was used at 6 bar and run at 17.5 l/h. The module is shown in Figure 17. A sample of the concentrate and permeate was collected and analysed for conductivity, turbidity, pH and TOC. Anion IC and ICP-OES (Ca, Cr, Cu, Fe, K, Mg, Na, Ni, Zn) were performed.

For the experiment with the RO concentrate as feed stream, the module was operated at 5 bar and 15 l/h. Both the permeate and concentrate were sampled and analysed for pH and conductivity. Cation IC was performed.

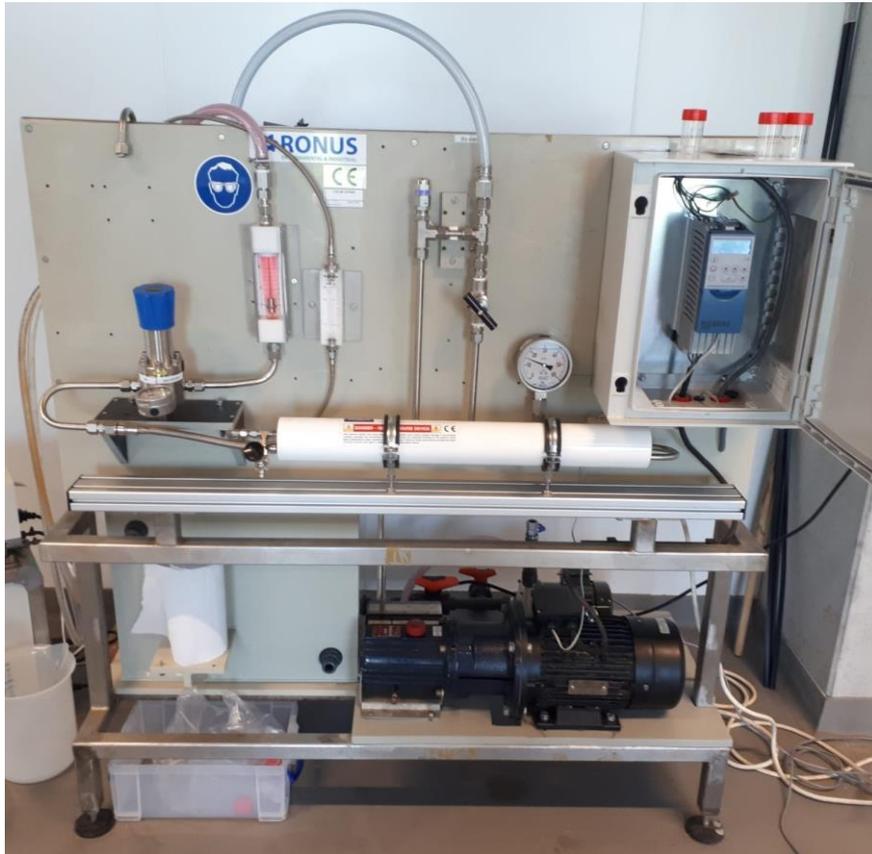


Figure 17 Figure of the pilot-scale RO unit

6.2.3 Vacuum filtration

Vacuum filtration was performed using a Büchner filter. A Büchner filter is a cylindrical, ceramic funnel with a porous plate. On top of the plate, a filter paper is placed, which determines the pore size of the filtration. The ceramic funnel is placed on top of a Büchner flask and a vacuum is created to perform the filtration, as shown in Figure 18. The filter paper is wetted initially with demineralised water to prevent any leakage. The sample is fed step by step onto the filter paper. When the filtration has slowed down due to clogging of the filter paper, a new paper was used. The filter papers used for this prefiltration, were Whatman Grade 2 Qualitative Filter Papers (Cytiva, USA) and had a pore size of 8 μm . A prefiltration was performed for NQ1811, NQ8860 and Q8870.

Samples were taken from the filtrate and analysed for conductivity and TOC.

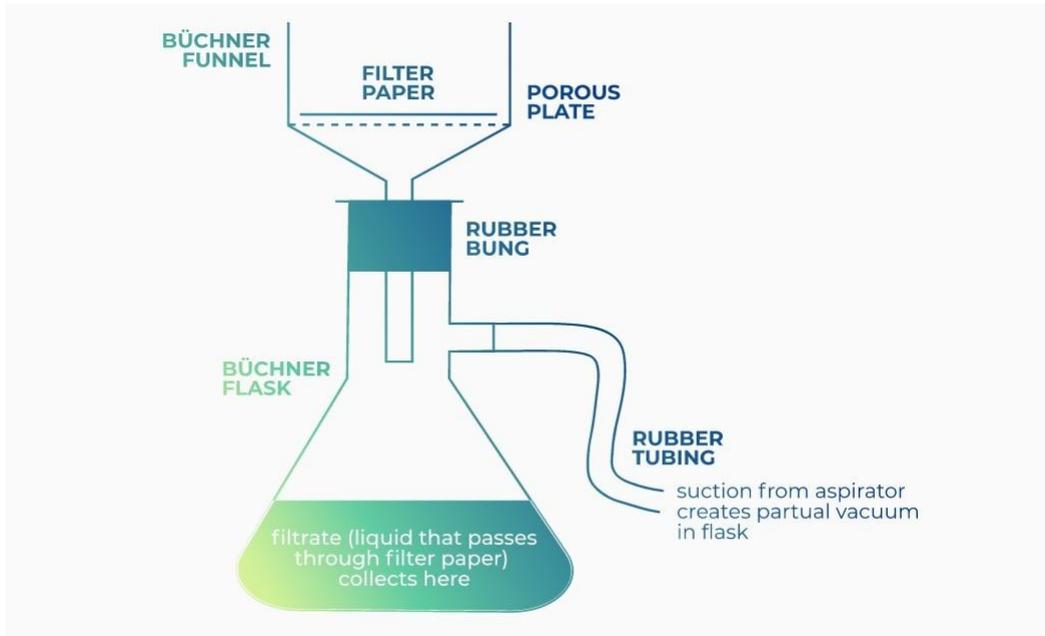


Figure 18 Schematic representation of the setup for vacuum filtration. Retrieved from Lab Society (n.d.).

6.3 Adsorption experiments

6.3.1 Column setup

Two different setups for adsorption tests were used.

6.3.1.1 Single column setup

The first setup was a single column setup using a glass column, filled with resins dependent on the application, and a 530S pump from Watson-Marlow (Cornwall, UK). The setup is shown in Figure 19.



Figure 19 Figure of the single column setup

Softening

The Biesbosch water was softened using SAC resin (LEWATIT Monoplus S 108 H (Lanxess, 2020)). The test was performed in a glass column with an internal diameter of 26 mm. The resin had a bed depth of 400 mm.

First, the resin was regenerated in upflow mode using 10 liters of a 10% brine solution (100 g NaCl per L demineralised water) at 7.8 L/h. Afterwards a co-current rinsing with 10 liters demineralised water was performed.

The softening of the Biesbosch water was performed in downflow mode at a flow rate of 15 L/h. Samples of the resulting stream were analysed for turbidity, pH, conductivity and TOC. Anion IC and cation IC were also performed.

Mixed bed For mixed bed resin experiments, LEWATIT UltraPure 1294 MD (Lanxess, 2018) was used. The resin was loaded in a glass column with an internal diameter of 26 mm to a height of 400 mm. The mixed bed resins were new, so no regeneration was needed. The mixed bed was flushed with demineralised water for one hour at a flow rate of 19.2 L/h. The experiments were also conducted at a flow rate of 19.2 L/h. MB polishing was performed using the RO permeate of the demineralisation plant, NQ7503 and Q0106.

Samples were taken after each experiment and analysed for conductivity and TOC.

Activated Carbon Column experiments with activated carbon (NORIT GAC 830W (NORIT, 2005)) were performed with a glass column with an internal diameter of 26 mm and a bed height of 400 mm. The activated carbon was first rinsed with 10 L demineralised water at a flow rate of 100 mL/min. The sample was introduced in downflow mode at a flow rate of 16 mL/min to obtain a contact time of 20 minutes. MQ1811 was treated using activated carbon. Samples were analysed for conductivity and NPOC. Anion IC was performed.

Regeneration tests

The resin from the softener tests was removed from the column after the softening of the second sample of Biesbosch water and stored in three separate parts (bottom, middle, top) in demineralised water. For the regeneration tests, the softener resin was loaded in a glass column with an internal diameter of 13 mm. To replicate the sequence of the initial column, the thin column was filled with 46.46 mL bottom resin, 19.91 mL middle resin and 26.55 mL top resin. The regeneration was performed in upflow mode to ensure a good regeneration of the best resin at the bottom.

The regeneration was performed with a flow rate of 6 bed volumes per hour. First the regenerant stream of interest was introduced as regenerant for two hours, followed by two hours of regeneration with a 10% NaCl solution.

Every 10 minutes, a sample was taken and analysed for conductivity and cations using cation IC.

6.3.1.2 Multiple column setup

To simulate a multiple column treatment train, a fixed setup in the lab was used. The resins are in glass columns with an inner diameter of 26 mm and bed depth of 700 mm, connected with rubber tubing. Pumps and valves were directed by computer software. The setup contained two columns, the first one being filled with a SAC resin (AMBERJET 1200 H (Lenntech & Rohm and Haas, n.d.-a)) and the second one with a SBA resin (AMBERJET 9000 OH (Lenntech & Rohm and Haas, n.d.-b)). Before starting the experiment, a regeneration run was executed with a 5% NaOH and a 5% HCl solution. The experiment was performed with a flow rate of 7.5 L/h. The multiple column setup was used for the treatment of MQ1811.

Samples were taken during the experiment and analysed for TOC and conductivity to obtain a breakthrough curve.

6.3.2 Jar tests

For the adsorption test in jars, the amount of adsorbent added was equal to the amount of TOC present in the sample. The specifications are given in Table 1. The jars were placed on a Promax 2020 shaker (Heidolph Instruments GmbH, Germany) for 24 hours at 120 rpm. The jar tests were performed using MQ1811 sample. Samples after 24 hours were analysed for TOC and UV absorbance at 254 nm. Anion IC was performed.

Table 1 Specifications of the (amount of) resins used for the jar tests on the mixed process steam blowdown (MQ1811)

Adsorbent	Specifications	Sample volume (mL)	Mass adsorbent (g)
SBA resin	AmberJet 9000 OH (Lenntech & Rohm and Haas, n.d.-b)	150	0.0666 0.0440 0.0441
		100	
		100	
WBA resin	LEWATIT MonoPlus MP 64 (Lanxess, 2017)	150	0.0667 0.0440 0.0442
		100	
		100	

CHAPTER 6. LAB TESTS

Scavenger resin	AmberLite SCAV4 Cl (DuPont, 2019a)	150 100 100	0.0665 0.0444 0.0442
MPPE01 resin	MPP-041 (Veolia, 2022)	150 100 100	0.0666 0.0444 0.0444
MPPE02 resin	MPP-042 (Veolia, 2022)	150 100 100	0.0667 0.0444 0.0442
Activated Carbon	NORIT GAC 830W (NORIT, 2005)	150 100 100	0.0666 0.0443 0.0443

Results and Discussion

CHAPTER 7

DEMINERALISATION PLANT

In this chapter, the results of the lab tests for the demineralisation plant will be discussed. The first section goes into detail on the characterisation of the Biesbosch water. The second section focusses on the results of the simulation of the demineralisation treatment train in the lab. In the third section, the option for improving the recovery by adding a second stage RO is investigated. The fourth section discusses the potential regeneration of the softener resin with the RO concentrates.

7.1 Characterisation

The first step in investigating the demineralisation plant, was characterising the Biesbosch water. Two separate samples of Biesbosch water were obtained from BASF Antwerp. The first one is labeled 'BB1' and the second one 'BB2'. Both samples were 50 liters, resulting in a total of 100 liters of Biesbosch water available for experiments.

Table 2 : Characterisation of the Biesbosch water

		Unit	BB1	BB2
Properties	pH		7.99	7.86
	Turbidity	NTU	0.58	1.17
	Conductivity	$\mu\text{S}/\text{cm}$	406	464
	TOC	mg/L	1.08	3.78
ICP-OES	Fe	mg/L	0.02	-
	Si	mg/L	1.59	-
IC	Na	mg/L	30.2	36.26
	K	mg/L	4.44	4.76
	Ca	mg/L	34.74	19.76
	Mg	mg/L	6.58	9.04
	Acetate	mg/L	ND	0.89
	Cl-	mg/L	50.76	54.45
	NO ₃ -	mg/L	9.66	11.63
	SO ₄ ²⁻	mg/L	46.99	49.79

In Table 7.1, a summary of the most interesting characteristics of the Biesbosch samples is shown. The pH (around 7.9) and conductivity (around 400-450 mg/L) do not differ much between the two samples. The turbidity of the second sample was higher than the turbidity of the first one, because of some visible particles in the sample. The TOC of the second sample was slightly higher than that of the first sample. Not all elements of the ICP-OES analysis were inserted in the table, either because they were close to the IC results (Ca, Mg, Na, K) or because they were not detected. The full characterisation is given in Table B.1 in Appendix. There is 1.59 mg/L silica in the first Biesbosch sample. No organic acids were detected in IC analysis, except for 890 $\mu\text{g/L}$ of acetate in the second Biesbosch sample. The samples contain around 4.5 mg/L K, 50-55 mg/L Cl, 30-35 mg/L Na and 45-50 mg/L sulfate. The important parameters for the softening step in the demineralisation plant are the calcium and magnesium levels, since they need to be removed to mitigate scaling of the RO. In the first sample, the calcium concentration was around 35 mg/L, whereas the concentration in the second sample was lower, around 19.76 mg/L. The magnesium concentration was higher (9.04 mg/L) in the second sample than in the first sample (6.58 mg/L).

7.2 Simulation of new demineralisation plant

BASF Antwerp is currently commissioning a new demineralisation plant in collaboration with Evides Industriewater. Biesbosch water will be softened using a softener resin and will subsequently be treated using reverse osmosis and mixed bed resins for polishing. Since the containers will be operated at the new demineralisation site, the new treatment train needed to be simulated in the lab in order to obtain samples of the RO concentrate for research. The lab simulation is done according to the scheme in Figure 20. The simulation was performed for the first and second sample, but at a different time.

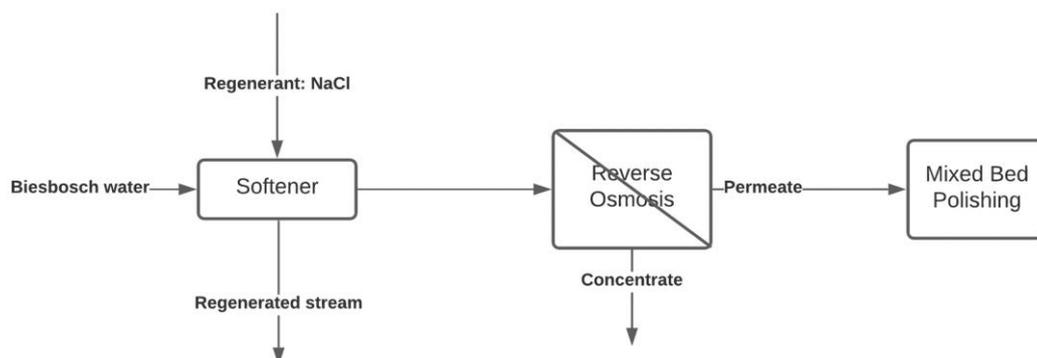


Figure 20 Schematic overview of the demineralisation plant at BASF Antwerp

Table 3 Results of the simulation of the new demineralisation plant using the first sample (BB1) and the second sample (BB2) of the Biesbosch water

	Conductivity ($\mu\text{S/cm}$)	TOC (mg/L)	Na (mg/L)	Ca (mg/L)	Mg (mg/L)
BB1					
Feed	406	1.075	30.2	34.74	6.58
Softened	406	1.077	88.32	4.56	2.66
RO concentrate	1665	7.618	463.282	1.22	0.11
RO permeate	8.86	0.9273	1.05	0.05	<LOD
Mixed Bed	1.96	0.537	-	-	-
Milli-Q water	1.99				
BB2					
Feed	464	3.78	36.26	19.76	9.04
Softened	436	3.92	77.66	11.18	4.9
RO concentrate	1435	12.6	408.65	17.08	6.3
RO permeate	10.48	0.420	1.894	0.338	0.209

The results of the simulation are given in Table 3. The first sample was softened using freshly regenerated SAC resin (in Na⁺-form). The softener was able to remove 86.89% Ca and 59.6% Mg. These removal rates are lower than expected, hence Vanoppen et al. (2015) were able to remove 98.8% of calcium using softener resins.

In order to check whether the resin was not exhausted already from softening the first sample, the used equivalents were calculated using the resin's capacity (2.1 equivalents/L). After the first softening, around 584 milli-equivalents were still available for exchange of hardness ions. The calculations are shown in Table 7.3, the remaining equivalents after each softening are indicated in bold. Enough capacity was left to soften the second sample using the same resin. The removal rates for the second sample were 43.42% for Ca and 45.8% for Mg, which is much lower compared to the first softener experiment. In Table 7.3, it is clear that only 21.41 milli-equivalents of calcium were removed, which is much lower than the 75.3 milli-equivalents calcium removed in the first sample. A possible explanation for these lower removal rates is that the resin remained idle for 73 days between the softening of the first and the second sample, so the resins could have lost part of their capacity, the efficiency could have gone down or there could be a leakage of calcium and magnesium from the resin. According to DuPont, the resins should be regenerated two or three times after storage to guarantee their performance (DuPont, 2021). The resin was not regenerated after storage because of future regeneration tests (see section 7.4).

Table 4 Residual equivalents of the softener resin after the softening of the first sample (BB1) and the second sample (BB2) of Biesbosch water.

	Concentration (mg/L)	Concentration (meq/L)	Removed (meq Ca or Mg)	Residual available (meq Na)
Initial				445.98
First softening (BB1)				
Feed (Ca)	34.74	1.73		
Softened (Ca)	4.56	0.23	75.3	370.68
Feed (Mg)	6.58	0.54		
Softened (Mg) Second	2.66	0.22	16.12	354.55
softening (BB2)				
Feed (Ca)	19.76	0.99		
Softened (Ca)	11.18	0.56	21.41	333.15
Feed (Mg)	9.04	0.74		
Softened (Mg)	4.9	0.4	17.03	316.12

Using the softened Biesbosch water, RO was performed using the pilot-scale unit in the lab at a recovery of 80%. The results of this reverse osmosis experiment can be found in Table 3. For the first sample, the conductivity of the RO concentrate is approximately four times higher in comparison to the conductivity of the feed, which is expected at a recovery of 80%. TOC and sodium concentration are approximately 7 and 5 times higher in the concentrate, respectively. For calcium and magnesium, the concentrations in the RO concentrate are lower than in the feed stream, which could indicate that scaling occurred. Yet, this does not seem likely since the concentration in the feed stream (softened Biesbosch) was not that high. The RO permeate obtained a good quality, although the remaining TOC concentration in the permeate of around 1 mg/L is high. During the IMPROVED project, RO tests were also performed on the Biesbosch water and a TOC concentration of 50 $\mu\text{g/L}$ was achieved for the RO permeate at a flux of 20 l/mh and recovery of 75% (Hitsov et al., 2019). The high TOC result in this test is probably contamination. The RO permeate will be sent through mixed bed resins as polishing step to complete the simulation the demineralisation train.

Reverse osmosis was performed separately for the second sample (BB2). The TOC and conductivity of the RO concentrate are around three times higher than the concentration in the feed water. The sodium concentration is more than 5 times higher, but for calcium and magnesium it drops back to around 1.4 times, where we also would expect a ratio around 4. Again, the RO permeate is of good quality with slightly higher calcium and magnesium concentrations than for the permeate of the first sample.

To conclude the demineralisation train, a test using mixed bed resins was performed with the RO permeate of the first sample. The mixed bed resin was used as a polishing step and a conductivity of 1.96 $\mu\text{S/cm}$ was obtained. This is not as low as expected. As a reference the conductivity of milli-Q water was measured with the same probe and showed a result of 1.99 $\mu\text{S/cm}$, which indicates that the MB effluent has around the same conductivity as milli-Q water. The TOC after the MB was reduced to 573 $\mu\text{g/L}$. The TOC concentration and conductivity after mixed bed resins are still too high for boiler feed water, since BASF has a boiler feed water limit of 250 $\mu\text{g/L}$ TOC and <0.2 $\mu\text{S/cm}$. It should be noted that on lab-scale it is very difficult to achieve conductivity below 1 $\mu\text{S/cm}$ and organics below 1 mg/L, due to contamination and residual organics that are present in new membranes and resins as preservatives.

The goal of this section was to simulate the demineralisation train to obtain the composition and samples of the wastewater streams. Subsequently, the RO concentrate is investigated to be treated even further (to improve the recovery of permeate) or to be reused as a regenerant for the softener resin (to mitigate the use of chemicals for the brine solution), discussed in the following sections.

7.3 Reverse osmosis on RO concentrate

To improve the recovery of the water in the demineralisation plant, the RO concentrate of the softened Biesbosch water could be treated again to increase the recovery and to reuse more water. One option to achieve this is implementing an additional RO system that uses the original RO concentrate as feed stream, as shown in Figure 21. In this way, the permeate, obtained from the second stage RO system, can still be sent to the mixed bed polishing and the wastewater stream will be reduced. If the quality does not meet the inlet limitations of the mixed bed resins, it could also be injected back in the feed stream of the first reverse osmosis unit.

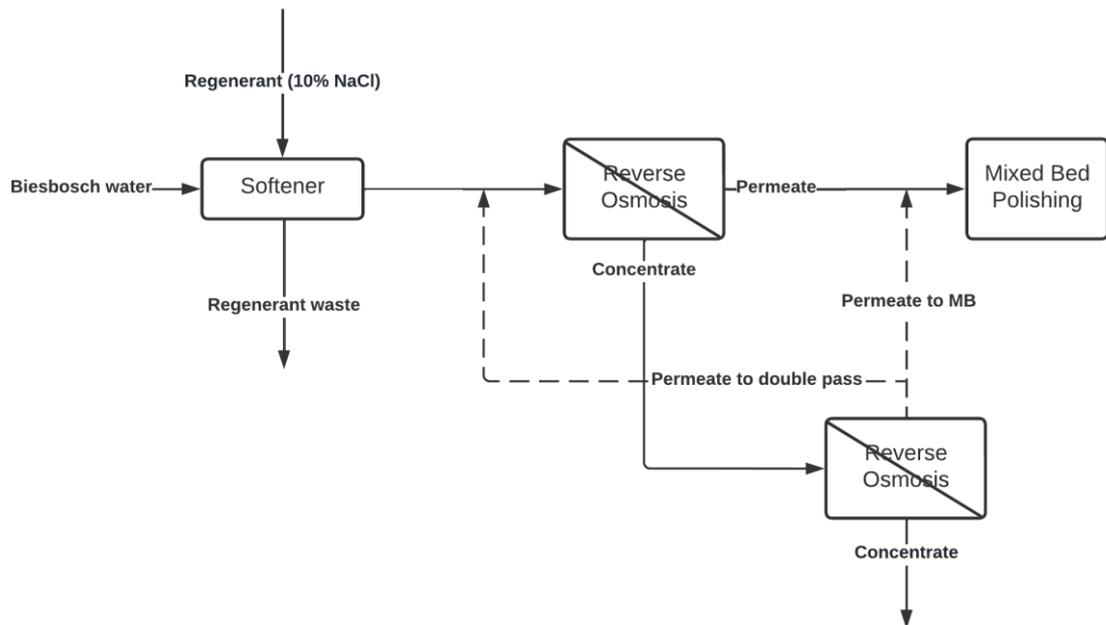


Figure 21 Schematic overview of the implementation of an additional reverse osmosis

The additional RO was performed on the pilot-scale unit in the lab using a 2521 XLE spiral wound module. To obtain enough feed sample to perform the pilot tests, both the concentrates of the first and second Biesbosch sample (BB1 and BB2) were mixed. The characterisation of this mixed stream is given in Table 5, together with the results of the additional RO experiment. The permeate still contains some calcium and magnesium, but only in the lower ranges of $\mu\text{g/L}$. Sodium was removed for 98.3%, which leaves a remaining concentration of 6.5 mg/L Na. The conductivity of the permeate was reduced to $27.8 \mu\text{S/cm}$. The concentrate stream has a conductivity of 3.62 mS/cm and contains 923 mg/L Na, 2.67 mg/L Ca and 0.45 mg/L Mg.

One of the key performance indicators (KPI) for the project is the 'amount of water reused'. Since the feed stream of this additional reverse osmosis is a higher salinity stream than for example surface water, scaling could have an impact on the efficiency of the additional RO. To limit potential scaling, a recovery of 66.6% was used in this test. As the main RO will be operated at 85% recovery, approximately 185 m^3 concentrate will be produced per hour. If the additional RO would operate at 66.6% recovery, 123 m^3 of extra water could be recovered per hour.

For this more concentrated stream, it is interesting to test some new RO configurations to improve the recovery, without increasing the scaling potential. A promising option is Pulse Flow RO, where the unit is operated in cycles of 20 - 30 seconds operation in dead-end mode and 2 seconds opening of the concentrate valve. Since the cycle times are shorter than the induction time for scaling, this could have a positive impact on the mitigation of scaling of these higher salinity streams (Lieberman et al., 2020). Another option is closed circuit reverse osmosis, which has the advantage of limiting scaling (Boyd, 2019). During the operation of the PFRO in the research of Lieberman et al. (2020), the recovery was 86% for water with similar properties to the concentrate of the additional RO. This would increase the possible additional water recovery to 159 m³/h. These configurations could not be tested in the lab during this thesis, due to a shortage of modifiable RO setups. Nevertheless, these technologies will be performed and tested in the containers on site at BASF Antwerp, since they seem to be promising techniques.

Table 5 Conductivity and ICP-OES results of the additional reverse osmosis on the RO concentrate

	Conductivity ($\mu\text{S}/\text{cm}$)	Na (mg/L)	Ca (mg/L)	Mg (mg/L)
Feed (mix of the RO concentrates)	1152	378.6613	0.857	0.16
Concentrate	3620	923.34	2.67	0.45
Permeate	27.8	6.51	0.027	0.003

The options for the permeate of the additional RO were to either send it directly to the mixed bed polishing or recirculate it back into the feed of the main reverse osmosis step. As shown in Table 5, the conductivity (and sodium concentration) is higher than the conductivity of the RO permeates of the main treatment train (shown in Table 21). Based on these results, it would thus be advised to recirculate the permeate to a second RO stage, to avoid a heavy loading on the mixed bed resins. In this case, this means that the RO permeate will be sent back to the main reverse osmosis step. The results could be different on pilot-scale than lab-scale and the consideration above can be adapted to the results on pilot-scale operation.

The second stage reverse osmosis will not mitigate the production of a waste stream, but will decrease the flow rate of the concentrate stream. The concentrate of the additional RO was, together with the concentrate of the main RO, investigated in this thesis as an alternative for the regeneration brine of the softener. This could possibly eliminate the concentrate as waste stream and reduce the chemical input needed for the regeneration of the softener. The results of these tests are discussed in the following section.

7.4 Regeneration of softener column

The reuse of the concentrate stream from the reverse osmosis, as well as from the second stage reverse osmosis was investigated. As the RO concentrates are high salinity streams, these could potentially be reused as a regenerant for the softener resin. The use of these streams as regenerant could mitigate the need for chemical regenerant (10% NaCl solution).

The reuse of RO concentrate as regenerant has been investigated before by Vanoppen et al. (2015). The authors performed a regeneration of a SAC resin with RO concentrate of tap water and RO concentrate of industrial wastewater. They state that the efficiency of regeneration depends mainly on the monovalent-to-multivalent cations ratio. During a regeneration of a softener resin, multivalent ions (e.g. Ca and Mg) need to be replaced with monovalent ions (e.g. Na and K). Hence, enough monovalent ions need to be present to ensure the driving force needed for the regeneration. In the research of Vanoppen et al. (2015), the regeneration experiment was successful with the industrial wastewater (ratio of monovalent-to-multivalent cations of 25), but did not work

out for the tap water (ratio of 0.5), unless NaCl was added to the concentrate. They were able to save 50% of the costs if the concentrate could be reused as a regenerant (Vanoppen et al., 2015).

For the tests in this study, the regeneration of the used softener resin was performed for two hours with one of the concentrates, followed by a regeneration with the standard regenerant (10% NaCl) to see how many remaining cations were released. For the regeneration with the RO concentrate from the demineralisation treatment train, the concentrate of the first sample (BB1) was used.

The results are shown in Figure 22 and Figure 23 for the concentrate of the RO in the demineralisation treatment train and the concentrate of the additional RO, respectively. The ions in the initial stream were subtracted from the regenerant waste stream, so the graphs show the released calcium and magnesium ions or retained sodium ions (negative value) during the regeneration.

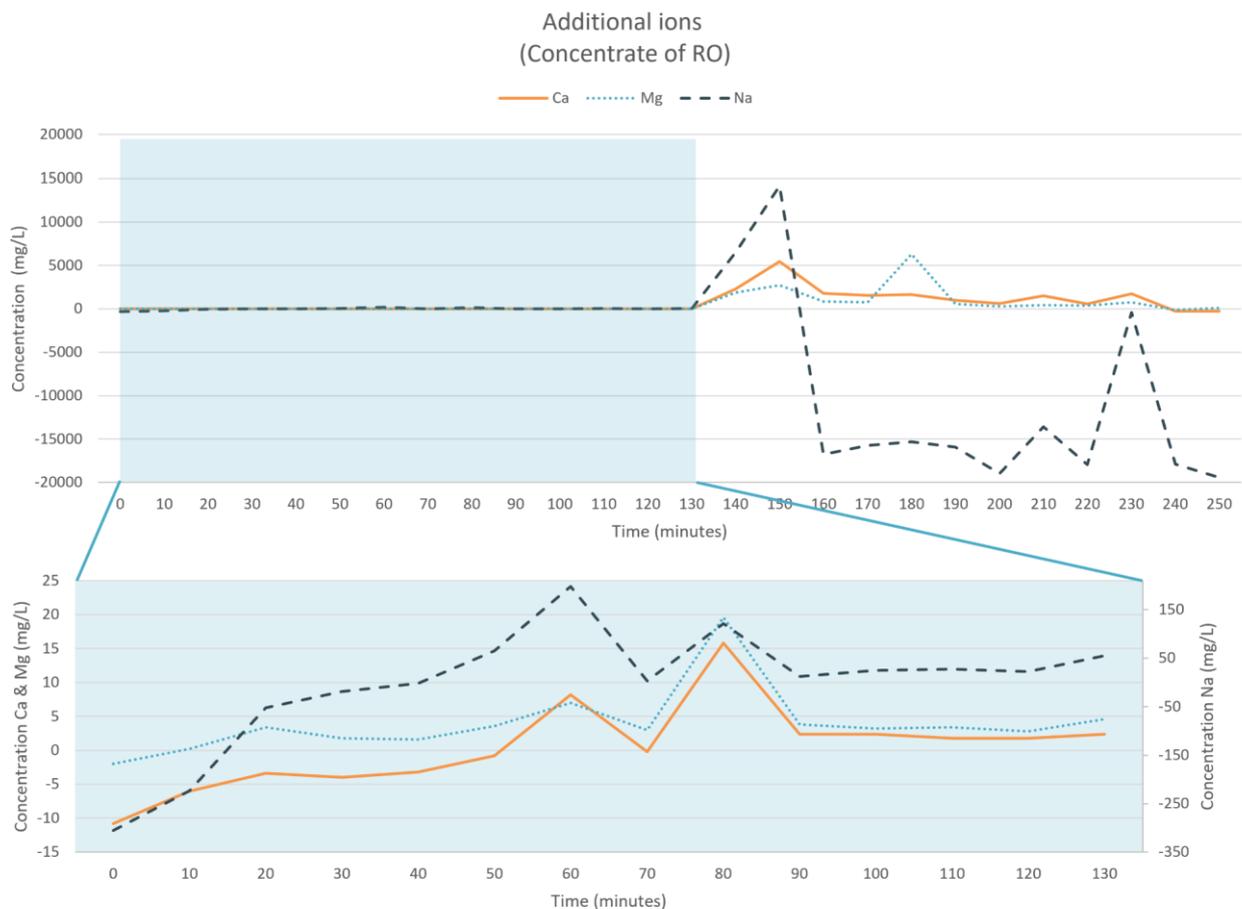


Figure 22 Graph of the additional ions released during regeneration of the softener resin using RO concentrate. The additional ions are calculated by subtracting the ions of the RO concentrate and brine from the resulting regeneration waste stream. Calcium is shown in orange, magnesium in light blue and sodium in dark blue. The graph on top shows the entire regeneration time. In the bottom graph, only the regeneration with the RO concentrate is shown

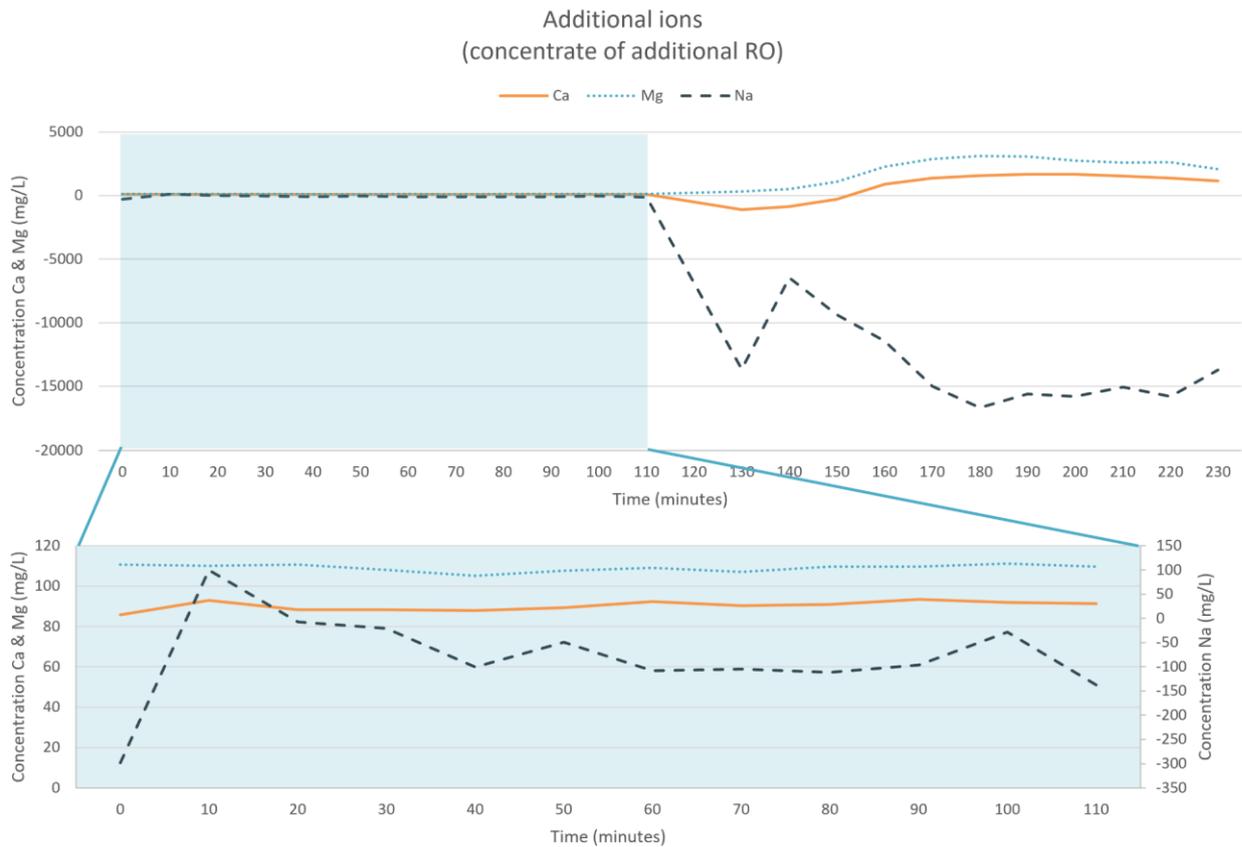


Figure 23 Graph of the additional ions released during regeneration of the softener resin using concentrate of the additional RO. The additional ions are calculated by subtracting the ions of the RO concentrate and brine from the resulting regeneration waste stream. Calcium is shown in orange, magnesium in light blue and sodium in dark blue. The graph on top shows the entire regeneration time. In the bottom graph, only the regeneration with the concentrate of the additional RO is shown

In Figure 22, it can be seen that some calcium and magnesium was released in the first two hours during the regeneration with the RO concentrate, but higher peaks were seen after the regeneration with the brine, meaning that more calcium and magnesium was released. This indicates that the regeneration with the RO concentrate was not successful. The same phenomenon can be seen in Figure 23 for the concentrate of the additional RO. It can be concluded that the regeneration with these streams is not working and is certainly not efficient.

The first difference with the research of Vanoppen et al. (2015) to be addressed, is the difference in the recovery of the reverse osmosis. The RO in the experiments for this thesis was performed with a recovery of 80% and 66.6% for the main RO and the additional RO, respectively. This means that the concentrate will be five times more concentrated than the feed water for the 80% recovery and three times more for the 66.6% recovery. The recovery used in the experiment of Vanoppen et al. (2015) was 95%, which means that the concentrate will be 20 times more concentrated than the feed water. This difference has an impact on the concentration of ions in the concentrate, which will be significantly lower for the experiments performed during this thesis.

The second difference worth mentioning, is the lower concentration of ions of the initial streams. In the article of Vanoppen et al. (2015), the levels of cations are already much higher than the feed stream used here, for the Biesbosch water as well as the RO concentrate. The concentration of monovalent ions in the experiment of Vanoppen et al. (2015) is around 2100 mg/L, where for the Biesbosch water this is around 80 mg/L and for the RO concentrate around 400-450 mg/L. Overall, there is a much larger driving force in the article, in comparison with these experiments.

Furthermore, the wastewater used in the experiments of Vanoppen et al. (2015) contained a much higher concentration for potassium (1400 mg/L) in comparison with sodium (680 mg/L). For the Biesbosch water, the concentration of potassium is around 4 mg/L and is much lower, even after concentrating it with the RO and the second stage RO. Potassium has approximately a 50% higher affinity on cation exchange resins than sodium (DuPont, 2019b). The difference in composition can also explain why the concentrates failed in the regeneration during the lab experiments.

An option to still be able to reuse these concentrates is to make them efficient in the regeneration of the softener by adding NaCl to the streams. If it would be feasible and efficient, it would decrease the need for chemicals and will avoid the concentrate as a wastewater stream. Further research should indicate whether this option is feasible, efficient and does not create any additional costs in treating the wastewater stream (in comparison to the treatment of the concentrate and brine separately).

CHAPTER 8

CRACKER SITE

In this chapter, the results of the lab tests will be discussed separately for each wastewater stream and propositions for pilot-scale experiments will be made.

The initial obtained samples are labelled starting with 'Q'. Over the course of this study, a batch of new samples (for some streams) was available. The second batch of samples is labelled starting with 'NQ'. For the process steam blowdown, the initial and new sample were mixed for some tests, this sample is labelled starting with 'MQ'.

The most important results of the analyses are discussed in the following section. The complete characterisation of each stream is shown in Appendix B.

8.1 NTBA (Q8870)

The NTBA-stream is coming from the NTBA-tank and discharged in the Scheldt-Rhine Canal. As this stream is not recovered in any way, it is of great importance for closing the water cycle on the site of BASF Antwerp. This tank contains the wastewater from the air-sprayed condensers and brackish blowdowns. Because the air-sprayed condensers can use in peaks 100-200 m³ of demineralised water per hour during hot periods, this puts pressure on the production capacity of the demineralisation plant. The stream is not heavily polluted with organics, but has a high conductivity due to the brackish water blowdowns. The ideal purpose for this stream would be reuse as spraying water for the air-sprayed condensers, as this would mitigate the need for demineralised water for this purpose. A prefiltration with a filter of 8 µm and reverse osmosis were tested for this stream.

8.1.1 Characterisation

The characteristics of the Q8870 stream are shown in Table 6. The Q8870 stream has a high conductivity of 3 mS/cm, caused by the brackish blowdowns. These brackish blowdowns are also responsible for the higher concentrations of sodium, calcium, magnesium, chloride and sulfates.

Table 6 Characterisation of the NTBA-stream (Q8870)

		Unit	Q8870
Properties	pH		
	7.25		
	Turbidity	NTU	3.48
	Conductivity	µS/cm	3000
	TOC	mg/L	5.32
ICP-OES			
	Ca	mg/L	106
	Mg	mg/L	59.3

	Na	mg/L	386
	K	mg/L	20.9
	Si	mg/L	3.75
IC	NH ₄ ⁺	mg/L	45.1
	Cl ⁻	mg/L	1038.1
	NO ₃ ²⁻	mg/L	5.3
	SO ₄ ²⁻	mg/L	199.2

8.1.2 Prefiltration with an 8 µm filter

The sample contained some orange particles, which could be iron flocs. To prevent fouling of the reverse osmosis system, a prefiltration with a pore size of 8 µm was performed. The results of the filtration step with a pore size of 8 µm, are shown in Table 7. The prefiltration step is able to remove 82.47% of the turbidity. It is strongly advised to provide some kind of prefiltration system (e.g. cartridge filters, sand filtration, UF or GAC) in the containers to prevent fouling of the system and guarantee an efficient operation, unless the flocs are not present in the actual stream and are due to sampling contamination (e.g. from an insufficiently flushed sampling point).

Table 7 Results of prefiltration and reverse osmosis on the NTBA-stream (Q8870)

Description	Q8870		
	Conductivity (µS/cm)	Turbidity (NTU)	TOC (mg/L)
Sample	3000	3.48	5.32
Filter 8 µm	3000	0.61	4.853
Reverse Osmosis Permeate	43.1		0.9869

8.1.3 Reverse osmosis

The filtered sample was then treated using the RO dead-end cell. Based on the results in Table 7, the reverse osmosis membrane had an overall rejection of 98.6% for conductivity and a TOC rejection of 79.66%. Since this RO was performed using a dead-end cell, a high membrane flux was used (63 l/mh), where in a full-scale RO unit this should be around 20 l/mh. This difference in membrane flux could result in slightly different composition of the permeate and concentrate quality.

Since one of the KPI's of the project is the amount of reused water, it is also important to consider how much water could be recovered in a reverse osmosis unit. To check what recovery would be achievable and how this stream would perform on a full-scale RO, a simulation was performed using the Membrane Master 5 scaling prediction tool of Genesys. The parameters are entered in the system in the Feed Water columns, as shown in Figure 24. It was assumed that all inorganic carbon was present as bicarbonates. The inorganic carbon concentration (32.7 mg/L) was used to calculate the concentration of bicarbonates (176.68 mg/L) using the molecular mass of carbon and bicarbonate. The pH of the feed water was reduced to 6, to mitigate scaling of calcium carbonates on the membrane surface. The calcium carbonates will be present as CO₂ at this pH and pass the membrane. The result of the simulation can be seen in Figure 25, where the green bars show the initial stream and saturation of the elements, and the blue bars show the behaviour when chemicals are added (antiscalant and/or acid (35% HCl)). The results of the different simulations are given in Table 8.

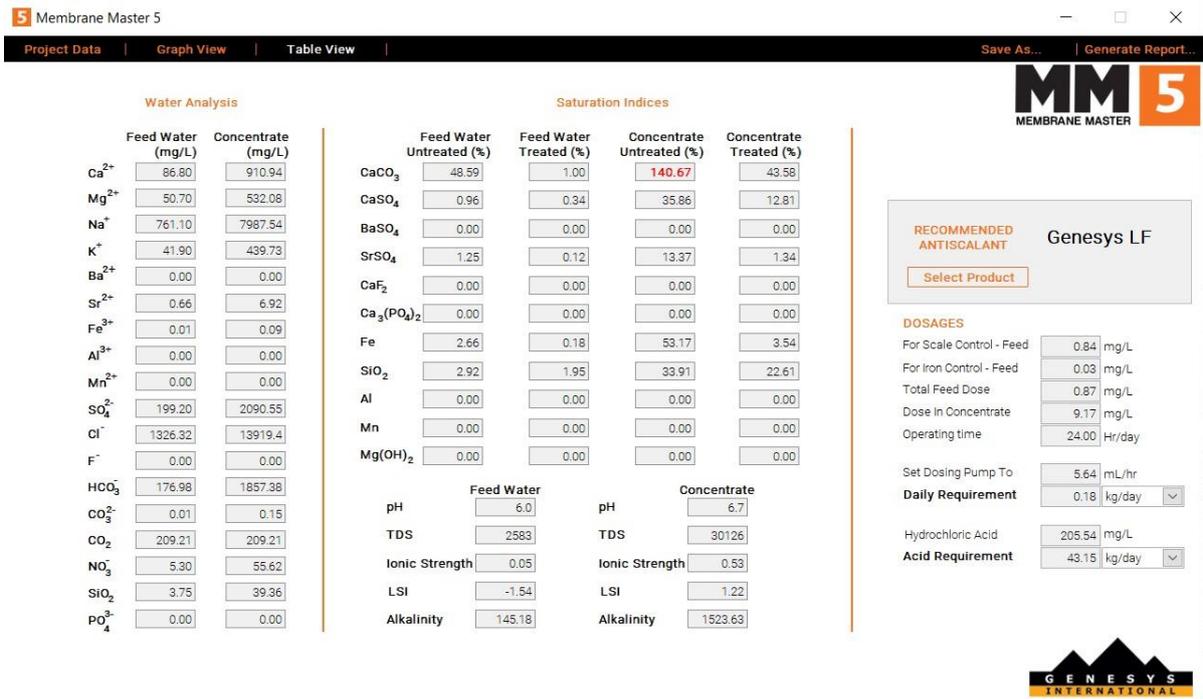


Figure 24 Membrane Master Results from simulation of the NTBA-stream (Q8870) with acid and antiscalant (part 1)

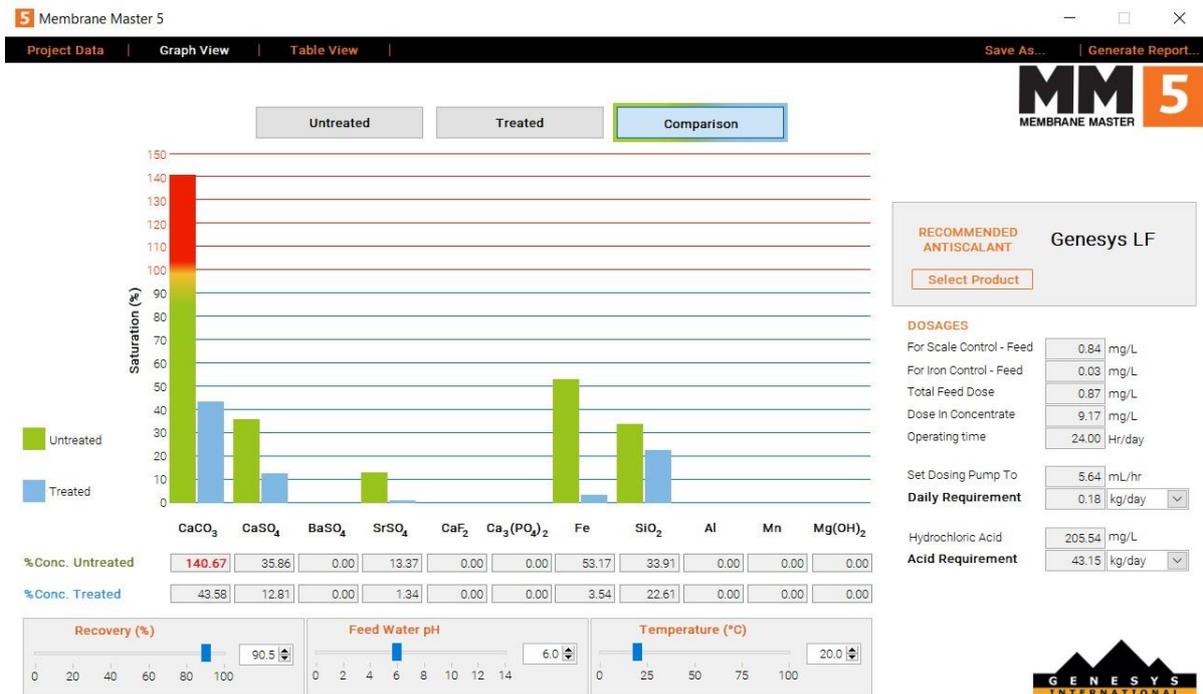


Figure 25 Membrane Master Results from simulation of the NTBA-stream (Q8870) with acid and antiscalant (part 2)

Table 8 Results of RO simulation for Q8870 with Membrane Master 5 with the addition of acid and/or antiscalant

Recovery (%)	Acid (kg/day)	Antiscalant (kg/day)	TDS Feed (mg/L)	TDS concentrate (mg/L)
90.5	205.54	43.15	2583	30126

90	0	0.29	2583	25 828
60	65.09	0	2583	7155
90	43.15	0.18	2583	30 126

The results in Table 8 indicate that a recovery of 90% can be achieved with antiscalant and acid dosing, where CaCO_3 would be the limiting factor. The acid requirement for lowering the pH to 6, would be 43.15 kg acid/day if HCl is used. HCl was chosen, instead of H_2SO_4 , since HCl is available on site as a by-product and H_2SO_4 could form persistent scaling. There should also be an antiscalant dosing of 0.18 kg/day to obtain this recovery.

A second simulation was performed using only antiscalant dosing. In this case, the CaCO_3 concentration would reach 85% saturation at a recovery of 90%. The dosing would be 0.29 kg antiscalant/day. If only acid would be added to reach a pH of 6, CaCO_3 would again be saturated to 85%. The highest recovery to achieve in this scenario, would be 60% by adding 65.09 kg of acid per day.

Achieving a high recovery (by adding antiscalant and/or acid) is beneficial for the KPI of water reuse. The downside of the adding of antiscalant is that the concentrate discharge to the Scheldt-Rhine Canal may be restricted due to permit limitations. The use of antiscalant and/or acid could possibly create a new wastewater stream that needs to be treated, even though antiscalants are non-toxic and biodegradable (American Water Chemicals, 2022). These results will be verified during the operation on pilot-scale.

8.2 NTBA if high NPOC (Q8860)

Q8860 is (together with Q8870) originating from the NTBA-tank, collecting brackish blowdowns and spray water from the air-sprayed condensers. The NTBA-tank is emptied periodically and the NPOC is measured. In normal circumstances, the water is discharged into the Scheldt-Rhine Canal, but if the organic loading of the tank is too high (e.g. due to leakages or soiled due to heavy rain) the water is sent to the wastewater treatment plant. The threshold is set on 30 mg/L NPOC or 5 mg/L BTEX. Q8860 is representing the stream that would be sent to the WWTP due to high organics.

This stream is normally not present in the system, except for when the NPOC or BTEX limits are exceeded. For this reason, the stream is not of high interest for reuse and will therefore not be taken into account during the lab tests. Before this consideration was made, a prefiltration was already carried out. The results are given in section 8.2.2.

8.2.1 Characterisation

The characterisation of the Q8860 stream is shown in Table 9. Q8860 has a pH around 7.8 and a high conductivity. Since this is a discontinuous discharge, the composition of the water can change between samples, as can be seen in the second sample (labelled with NQ8860) that was received. The conductivity stayed around 2800 $\mu\text{S}/\text{cm}$, where the turbidity differed from 1 to 26.3 NTU and the color was way darker for the second sample. In the TOC content there was also a high variation (3.5 mg/L - 2292 mg/L).

Table 9 Characterisation of the initial sample of the NTBA-stream with high NPOC concentration (Q8860) and a second sample (NQ8860)

		Unit	Q8860	NQ8860
Properties	pH		7.76	7.83
	Turbidity	NTU	1.02	26.3
	Conductivity	$\mu\text{S/cm}$	2860	2800
	TOC	mg/L	3.554	2292
ICP-OES	Ca	mg/L	71.5822	24.4
	Mg	mg/L	60.02	14.2
	Na	mg/L	454.5	663
	K	mg/L	21.06	8.69
	Si	mg/L	3.0992	1.69
	Fe	mg/L	<LOD	17.5
IC	Formate	mg/L	ND	56
	Acetate	mg/L	ND	329.6
	Cl ⁻	mg/L	825	235.7
	NO ₃ ⁻	mg/L	7.5	ND
	SO ₄ ²⁻	mg/L	137.7	0.432
	Propionate	mg/L	ND	1889.3

The second sample (labelled NQ8860) seemed to deviate from the first sample. For this reason it was discussed with BASF Antwerp that the second sample was not representative and will not be taken into account.

8.2.2 Prefiltration with an 8 μm filter

Before the results of characterisation of the NQ8860, a prefiltration was already performed. The results will be shown in this thesis, but will not be taken into account for further testing in the containers.

The results of the filtering with a pore size of 8 μm is given in Table 10. The NQ8860 sample was colored dark brown. The filter papers needed to be changed multiple times during the vacuum filtration of two liters of sample. The conductivity before and after the filter stayed approximately the same. The turbidity was reduced by 58.6% and some of the TOC was also retained by the filter paper (15.6%). Keeping the variability of this stream in mind, it would be recommended to use a prefiltration system if this stream is considered to be treated, to protect the systems against the variations in, for example, turbidity.

Table 10 Results of prefiltration with an 8 μm filter on the NTBA-stream with high NPOC concentration (Q8860)

Description	Q8860		
	Conductivity ($\mu\text{S/cm}$)	Turbidity (NTU)	TOC (mg/L)
Sample	2800	26.3	2292
Filter 8 μm	2810	10.9	1935.4

8.3 TBA (Q8835)

The TBA-sample includes the blowdowns (Q0106 and Q7503), the process condensate (Q1811) and also contains the spent caustic from the caustic scrubber. This stream was treated using nanofiltration on lab-scale. After consultation with BASF, it became clear that this stream is not a prioritised stream for reuse as boiler feed water, since the high pH is beneficial for the wastewater treatment plant on site. So, besides the nanofiltration, no other technologies were tested.

8.3.1 Characterisation

The characterisation of the Q8835 stream is given in Table 11. The spent caustic from the caustic scrubber is causing this stream to have a really high pH, around 12.95. The conductivity is around 16 mS/cm and the stream contains 173 mg/L of TOC. It was clear that this sample contained a lot of sodium ions (around 1950 mg/L) and also contained a lot of organic acids, probably originating from the process condensates (Q1811).

Table 11 Results of characterisation and nanofiltration experiment of the TBA-stream (Q8835)

		Unit	Q8835	Nanofiltration Permeate	Removal Rate
Properties	pH		12.95	12.19	
	Turbidity	NTU	25.3	0.79	96.3%
	Conductivity	$\mu\text{S}/\text{cm}$	16222	3030	81.3%
	TOC	mg/L	173.46	33.09	80.9%
IC	Formate	mg/L	90.4	1.844	98.0%
	Acetate	mg/L	237.6	8.86	96.3%
	Cl ⁻	mg/L	32.4	0.192	99.4%
	Propionate	mg/L	69.2	2.876	95.8%
	NO ₃ ⁻	mg/L	27.2	0.144	99.5%
	SO ₄ ²⁻	mg/L	186.4	ND	<100%
ICP-OES	Ca	mg/L	1.296	0.226	82.6%
	Mg	mg/L	0.37	<LOD	<100%
	Na	mg/L	1956.8	488.218	75.1%
	K	mg/L	2.36	1.309	44.5%
	Sr	mg/L	0.746	0.365	51.1%

8.3.2 Nanofiltration

First, nanofiltration was performed with demineralised water to investigate the clean water membrane flux. In Figure 26, the membrane flux (lmh) is shown in blue. In orange, a moving average with a window of 10 is displayed. The membrane flux starts quite high and then takes a dip, which is due to the compression of the membrane. The membrane flux then continues to oscillate between 20 and 25 lmh. The average clean water flux is around 23 lmh.

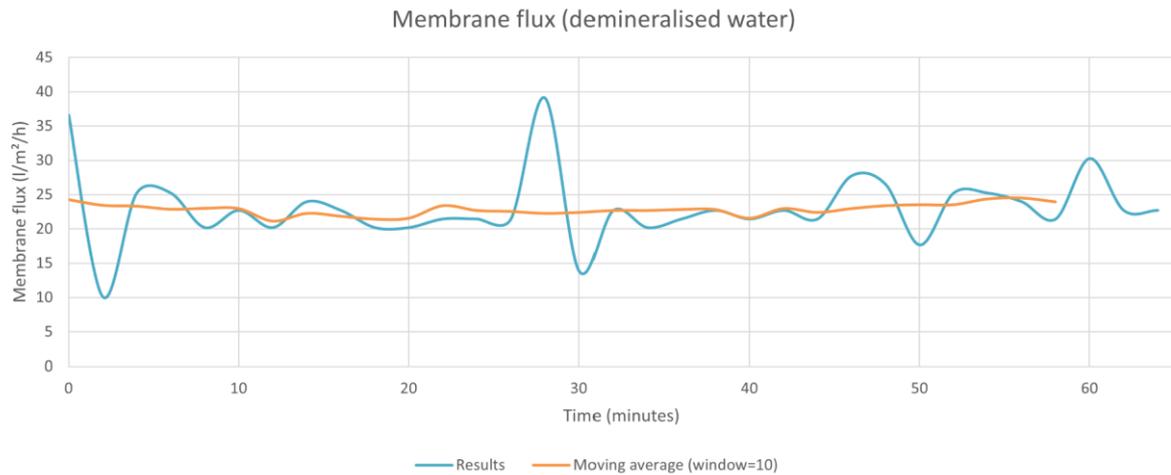


Figure 26 Graph of the NF membrane flux of demineralised water. The results are shown in blue, the moving average with a window of 5 is shown in orange

After determining the clean water flux, the experiment with Q8835 was performed. The results are shown in Figure 28, with results shown in blue and a moving window average with a window of 10 shown in orange. The membrane flux oscillates a lot, but the moving average does not show a decline in flux over the membrane during the experiment, which indicates that the membrane permeability did not decrease significantly during the experiment. The membrane flux is much lower than the clean water flux, with an average membrane flux around 10.3 l/mh, which can be explained by the higher osmotic pressure of the stream.

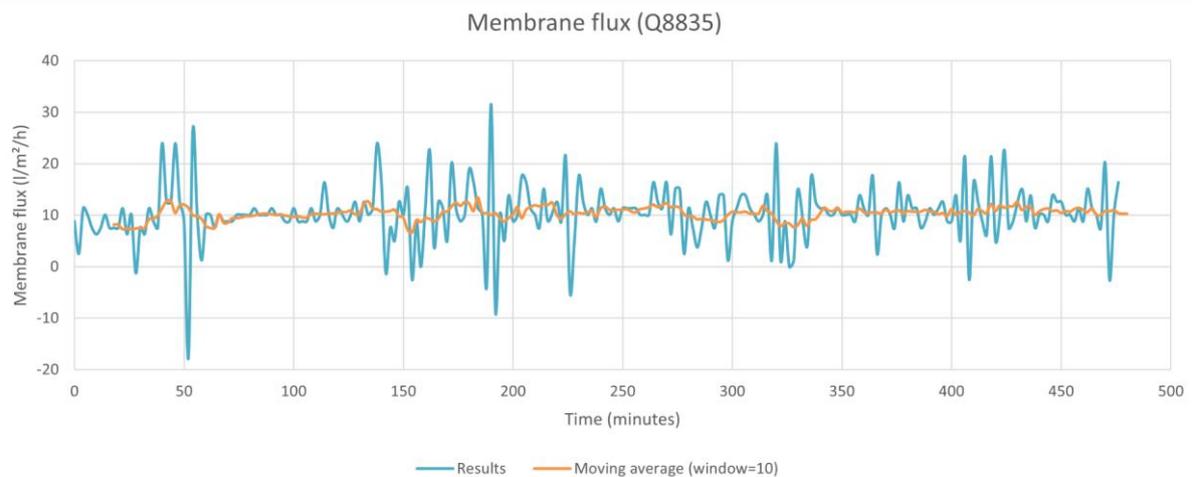


Figure 27 : Graph of the NF membrane flux of the TBA-stream (Q8835). The results are shown in blue, the moving average with a window of 5 is shown in orange

To indicate the removal efficiency of the nanofiltration membrane, removal rates were calculated, given Table 11. 96.6% of the turbidity was removed and TOC was reduced by 80.9%, resulting in a TOC of 33 mg/L. For the organic acids, removal rates between 95.8 and 98% were obtained. Chlorides were removed up to 0.192 mg/L (99.4% removal rate). For the cations (analysed with ICP-OES), especially calcium and magnesium were removed well, since these are multivalent ions. Sodium was removed as well up to a concentration of 488.218 mg/L. The removal rate of sodium is lower, since this is a monovalent ion and can pass the membrane easier than the multivalent ions. The nanofiltration proved to perform well in removing organic acids and multivalent ions.

8.4 Process steam blowdown (Q1811)

The Q1811 stream is the process condensate coming from the steam crackers. This stream is of high interest to reuse, since it would contribute largely to closing the loop from the process steam condensates to boiler feed water. Many technologies were tested on this stream, such as nanofiltration, ion exchange, adsorption and reverse osmosis. A prefiltration with a filter of 8 μm was also performed.

8.4.1 Characterisation

The results of the characterisation of Q1811 are shown in Table 12. Since this is a process condensate, the stream contains a lot of organics and has a TOC of 647.4 mg/L. The sample has a yellow color and a turbidity of 2.84 NTU. The conductivity is 1467 $\mu\text{S}/\text{cm}$ and is caused mostly by a high sodium content and a lot of organic acids. There is 814 mg/L acetate present and 154.8 mg/L of propionate.

Table 12 Results of characterisation and nanofiltration of the process steam blowdown (Q1811)

		Unit	Q1811	Nanofiltration	Removal rate
Properties					
	pH		10.14	9.71	
	Turbidity	NTU	2.84	2	29.5%
	Conductivity	$\mu\text{S}/\text{cm}$	1467	101	93.1%
	TOC	mg/L	647.4	60.78	90.6%
ICP-OES					
	Ca	mg/L	0.1585	0.30346	82.6%
	Mg	mg/L	<LOD	<LOD	<100%
	Na	mg/L	423.8	18.768	75.1%
	K	mg/L	0.63	0.411	44.5%
	P	mg/L	3.4	<LOD	
IC					
	Formate	mg/L	23.45	3.3	85.9%
	Acetate	mg/L	814	30.42	96.3%
	Cl-	mg/L	17.7	ND	<100%
	Propionate	mg/L	154.8	2.25	98.5%
	SO ₄ ²⁻	mg/L	6	ND	<100%
	PO ₄ ³⁻	mg/L	24.8	4.17	83.2%

The interest in reusing this stream is quite high, since it would close the loop from process condensate to boiler feed water, minimising the need of additional external feed water.

That is why many different technologies were performed in the lab.

On this stream, nanofiltration, reverse osmosis, ion exchange and adsorption to activated carbon were tested. A prefiltration with a pore size of 8 μm was performed, to evaluate the impact on the quality of the sample.

8.4.2 Prefiltration with an 8 μm filter

A new sample of Q1811 (NQ1811) was obtained from BASF Antwerp and characterised, shown in Table 15. The NQ1811 sample was filtered using a pore size of 8 μm , the results are shown in Table 13. The sample does not contain a lot of visible particles, but has a dark yellowish color. The filter permeate has approximately the same conductivity and TOC values. The TOC is higher than the initial concentration. This could be due to the analysis on a different day or due to contamination. After the filtering, 40% of the turbidity is removed, but the water still remains colored. We can conclude that particles smaller than 8 μm are mostly responsible for the color of the sample. If a membrane technology would be the first step in the treatment train, a prefiltration would be advised to mitigate the effects of fouling.

Table 13 Results of prefiltration with an 8 μm filter on the process steam blowdown (NQ1811)

Description	NQ1811		
	Conductivity ($\mu\text{S}/\text{cm}$)	Turbidity (NTU)	TOC (mg/L)
Sample	915	2.75	356
Filter 8 μm	912	1.61	370.4

8.4.3 Nanofiltration

A nanofiltration was performed in the same way as for the Q8835. In Figure 28, the demineralised water membrane flux is shown. In Figure 26, the results of the nanofiltration on Q1811 are shown in blue and the moving window average (with a window of 10) in orange. We can see that over the time of the experiment, the average membrane flux did not decline and remained in the same range. The average membrane flux of demineralised water was around 23 l/mh. In the experiment with Q1811, an average membrane flux of around 19 l/mh was calculated, which is as expected lower than the clean water flux due to the higher osmotic pressure of the stream.

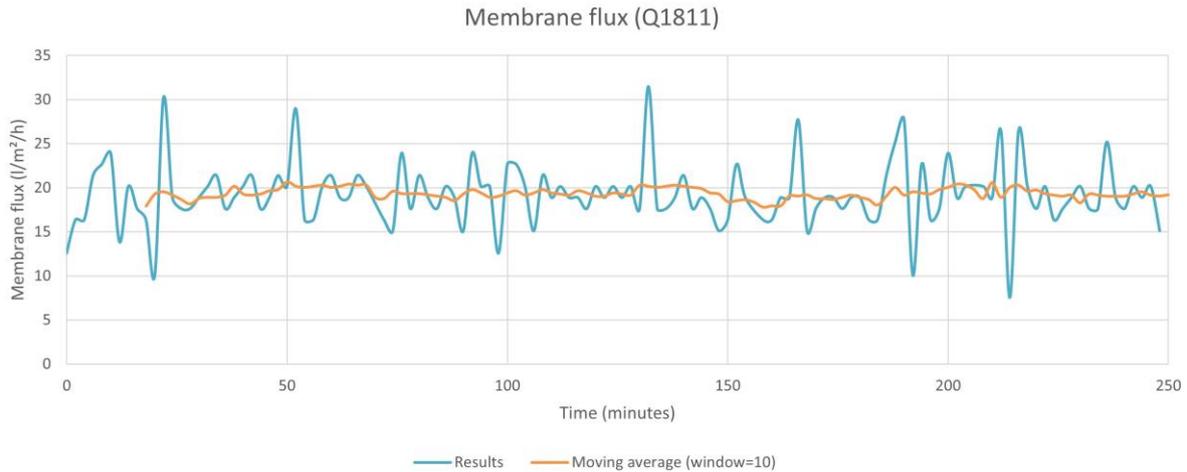


Figure 28 Graph of the NF membrane flux of the process steam blowdown (Q1811). The results are shown in blue, the moving average with a window of 10 is shown in orange

In Table 12, the results of the nanofiltration are depicted. 93% of the conductivity was removed, together with 90.6% of the TOC levels. The organic acids were the targeted components to remove with nanofiltration. Acetate was removed with 96.3%, propionate with 98.5% and formate with 85.9%, which are high removal rates.

All in all, this technology seems really promising for the removal of the organic acids and thus the TOC.

8.4.4 Jar adsorption tests

To investigate the behaviour of different adsorbents on the adsorption of TOC for the MQ1811 stream, jar tests were performed. A limited amount of adsorbent was added to an amount of sample, as described in Table 1. Since a limited amount of adsorbent was added, it can be assumed that the adsorbents would be completely saturated and at equilibrium, so the adsorption capacity can be calculated. A measurement of UV adsorption at 254 nm was performed and the TOC content of each sample was analysed. The UV results are given in Figure 29, the TOC results in Figure 30. The feed was analysed for TOC in triplicate, and showed a big difference between the first and second/third sample, which is indicated in Figure 30. For TOC as well as UV, it became clear that all adsorbents were capable of removing some TOC. In the UV graph, it is clear that the sample of the scavenger resin has a lower absorbance than the other adsorbents, meaning that more TOC was adsorbed than for the other adsorbents. Using the same reasoning, it is clear that the MPPE2 performed the worst, according to the UV adsorbance measurements. The other adsorbents (AC, SBA, WBA and MPPE1) show around the same value. Since the TOC analysis will be more accurate, conclusions on these adsorbents will be made based on Figure 30.

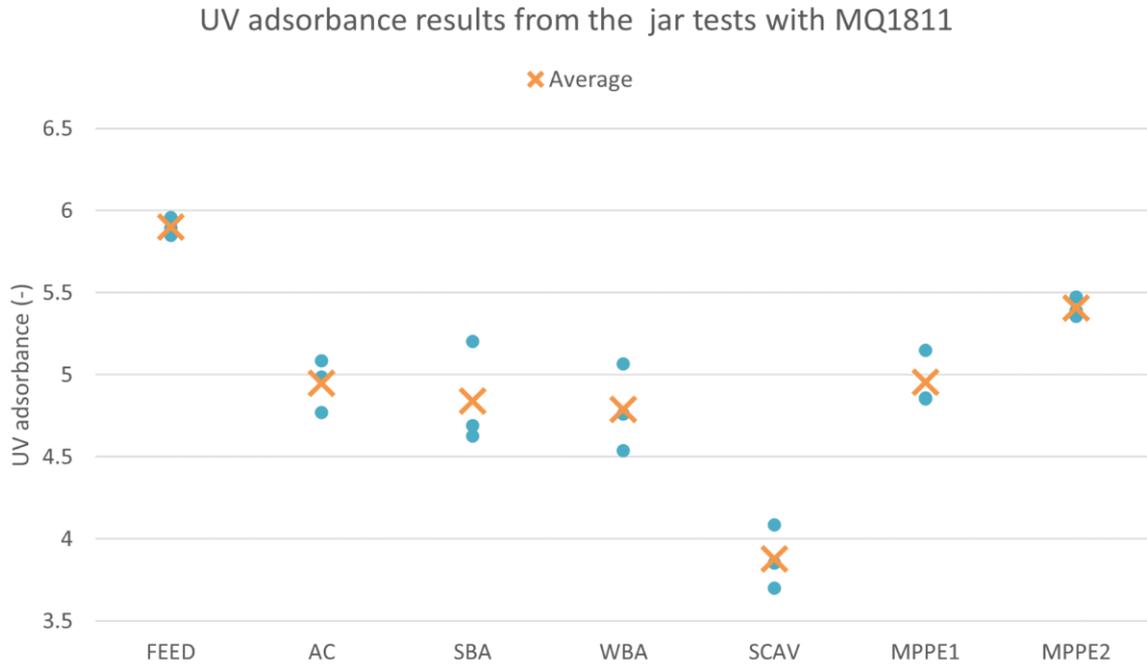


Figure 29 Results of UV absorbance at 254 nm for the jar adsorption tests of the mixed sample of the process steam blowdown (MQ1811). The results are shown in blue, the average is shown in orange

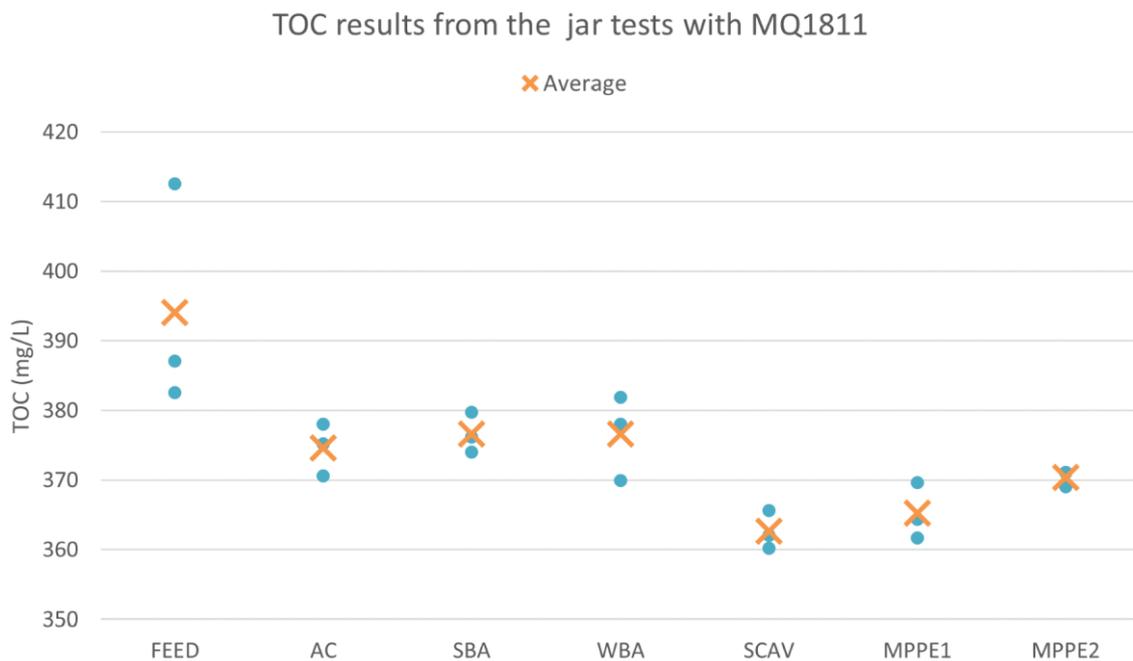


Figure 30 Results of TOC analysis for the jar adsorption tests of the mixed sample of the process steam blowdown (MQ1811). The results are shown in blue, the average is shown in orange

In Figure 30, we can see that again the scavenger resin performed the best and shows the lowest remaining TOC content. In second comes the MPPE1 resin, also showing a significant removal. MPPE2 has a lower removal than MPPE1, but is performing better than the SBA, WBA and activated carbon. Activated carbon performs best out of these three, but the differences are small.

To check the adsorption capacity of each adsorbent, some calculations were made, shown in Table 14. We can see the same trends as in the TOC graph, which is expected since the same values were used. The scavenger resin

and MPPE1 resin are the best performing resins, with an adsorption capacity of 0.071 and 0.065 g TOC per g adsorbent, respectively.

The scavenger and MPPE1 adsorbents are thus recommended to try during the pilot-scale operations. It is especially interesting to use the scavenger as a pretreatment for reverse osmosis. The scavenger is in Cl^- -form, so the chemical usage will be low. The scavenger will remove the organics, reducing the fouling potential on the RO membrane.

Table 14 Results of the adsorption capacity calculation based on the jar adsorption tests with the mixed sample of process steam blowdown (MQ1811)

Adsorbent	Mass adsorbent (g)	TOC removed (mg)	Adsorption capacity (g TOC per g adsorbent)	Average adsorption capacity (g TOC per g adsorbent)
GAC	0.0666 0.0443	3.525 1.6 1.888	0.053 0.036 0.023	0.04405
SBA	0.0666 0.0441	2.148 1.786 2.008	0.0323 0.0406 0.0455	0.0395
WBA	0.0667 0.0442	2.409 1.216 2.416	0.036117 0.0276 0.0547	0.03947
SCAV	0.0665 0.0442	4.803 3.388 2.842	0.07223 0.0763 0.0643	0.07094
MPPE1	0.0667 0.0444	3.66 2.974 3.323	0.05496 0.06698 0.07293	0.064955
MPPE2	0.0666 0.0443	3.75 2.302 2.296	0.05622 0.05185 0.05195	0.05334

8.4.5 Extensive testing with ion exchange, activated carbon and reverse osmosis

Different treatment trains were investigated to research the reuse possibility of this stream. To obtain enough sample volume to perform these tests, Q1811 and NQ1811 were mixed, resulting in the sample MQ1811. This sample was again characterised and the results are shown in Table 15. The results of the different technologies are shown in Figure 31.

Table 15 Characterisation of the second sample of the process steam blowdown (NQ1811) and the mixed sample of the process steam blowdown (MQ1811)

		Unit	NQ1811	MQ1811
Properties	pH		10.97	9.71
	Turbidity	NTU	2.75	2
	Conductivity	$\mu\text{S}/\text{cm}$	915	1153
	TOC	mg/L	356.4	443.9
ICP-OES	Ca	mg/L	0.197	
	Mg	mg/L	0.023	
	Na	mg/L	207	
	K	mg/L	4.12	
	P	mg/L	16.4	
IC	Acetate	mg/L	427.6	558.8
	Cl ⁻	mg/L	9	11.9
	Propionate	mg/L	64.7	94
	SO ₄ ²⁻	mg/L	10.1	8.2
	PO ₄ ³⁻	mg/L	31.9	27.7

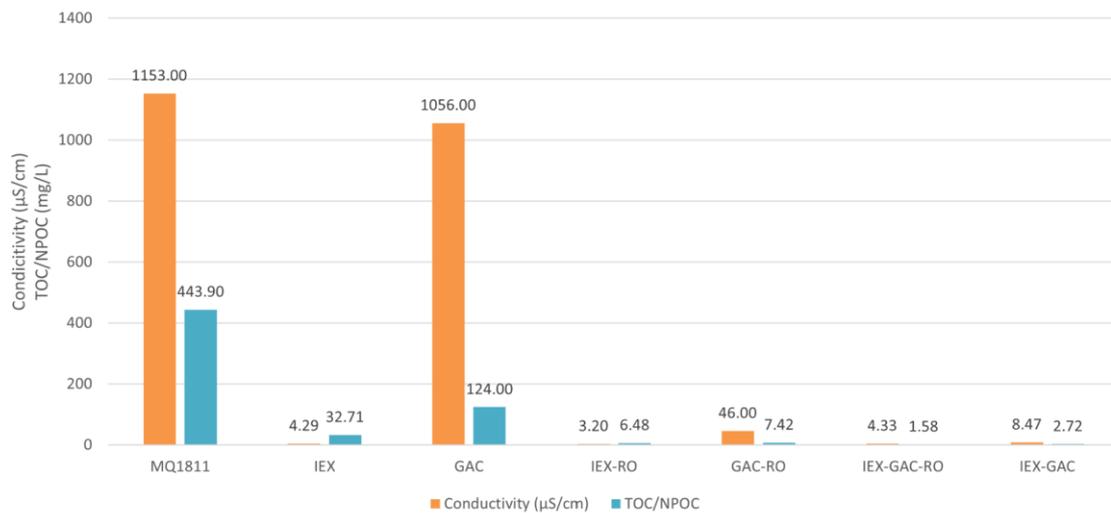


Figure 31 Conductivity (orange) and organic carbon (blue) results from experiments with IEX, GAC and RO on the mixed sample of the process steam blowdown (MQ1811). MQ1811 was measured using TOC-analysis, the other technologies using NPOC-analysis

The first technology tested was ion exchange with SBA and SAC. During this treatment, around 410 mg/L of TOC was removed, which means that the removed TOC were charged organics. Since a treatment train of SBA and SAC was used, the conductivity also reduced to 4.29 $\mu\text{S}/\text{cm}$.

The second technology was the granular activated carbon adsorption in the single column setup. With GAC, 320 mg/L of TOC was removed and the conductivity decreased to around 1056 $\mu\text{S}/\text{cm}$. When ion exchange was followed by reverse osmosis, the conductivity decreased to 3.2 $\mu\text{S}/\text{cm}$ and the TOC to 6.48 mg/L. Which means that in total 98.7% of the TOC was removed by this combination of technologies.

If granular activated carbon was combined with reverse osmosis, the TOC removal is almost to the TOC removal for IEX-RO, but the conductivity is higher (around 46 $\mu\text{S}/\text{cm}$).

It can be noted that after the IEX-RO and GAC-RO still a lot of TOC can pass through the RO membrane. This could be caused by small molecules (such as benzene, xylene, toluene), which can pass the RO membrane. If the water is sent through activated carbon in the containers as pretreatment, it is expected that micro-organisms develop

on this activated carbon during the operation time. The micro-organisms degrade these small organic molecules, so they will not pass the membrane anymore and result in a lower TOC level. This is something that is hard to test on lab-scale level, since a longer operation time is needed to develop the microbial community in the activated carbon and investigate the effects.

Ion exchange and granular activated carbon combined, also give quite good results. The TOC is reduced to 2.72 mg/L and the conductivity to 8.47 $\mu\text{S}/\text{cm}$. These results for TOC are lower than with the IEX-RO setup, but higher in conductivity.

If we combine all three technologies together, we get a final result of 4.33 $\mu\text{S}/\text{cm}$ conductivity and a TOC level of 1.58 mg/L. This combination generates the stream with the lowest TOC concentration, but also involves the most technologies.

The conductivity did not reach boiler feed water levels ($<0.2 \mu\text{S}/\text{cm}$) for any of the combined technologies. As a reference, the conductivity of milli-Q water was measured with the same probe and showed a result of 2.7 $\mu\text{S}/\text{cm}$. This reference value taken into account, the IEX-RO and IEX-GAC-RO were able to reach similar values.

During the ion exchange tests a combination of SAC and SBA resins was tested. Samples were taken to track the quality of the effluent and to compose a breakthrough curve. The NPOC and conductivity were measured, the results are shown in Figure 32. After 108 minutes, the conductivity was increasing rapidly and the breakthrough point was reached. On the figure, it can be seen that the conductivity reached 15.2 $\mu\text{S}/\text{cm}$. On the setup, an online conductivity meter was attached and showed 30 $\mu\text{S}/\text{cm}$ at the breakthrough point. But due to dead volume (tubing), this result was not showing yet in the taken sample. The NPOC did not change significantly, which means that conductivity breaks through earlier than the organics.

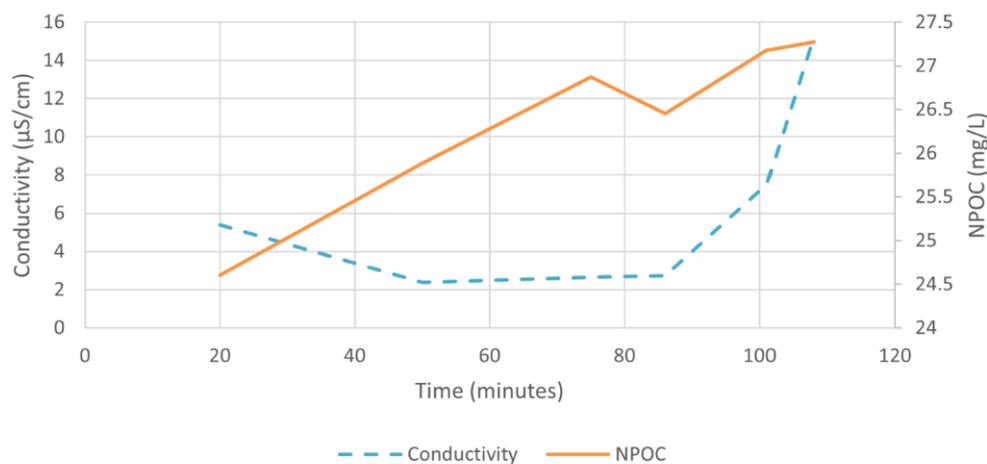


Figure 32 Breakthrough curve for the treatment of the mixed sample of process steam blowdown (MQ1811) with the ion exchange setup with SAC-SBA. The conductivity is shown in blue, NPOC is shown in orange

The breakthrough happened quite quickly and is due to the high conductivity of this stream. The common cut-off for IEX as a feasible technology is 1 mS/cm for feed water, before the chemical input becomes significant. Since the conductivity of the feed (MQ1811) was 1153 $\mu\text{S}/\text{cm}$, this threshold value is exceeded. The time between regenerations can be influenced by the volume and the amount of reactors/columns, up to certain limitations. To conclude, IEX might not be the best provided technology for the treatment of the process condensate.

A consideration must thus be made between the technologies based on their performance on pilot-scale and their capital and operational costs. Since the scavenger resins performed well for the jar adsorption tests, these resins could be positioned in front of the RO. They would remove TOC and reduce the fouling potential of the stream. Reverse osmosis could be the second step in the treatment train, to remove the majority of TOC and

conductivity. Afterwards, a polishing step might be needed, which could be GAC. Different treatment trains and combinations could be tested in the containers to find the best treatment train for this stream.

8.5 Steam blowdown (Q7503) and furnace blowdown (Q0106)

The steam blowdown (Q7503) and furnace blowdown (Q0106) are both clean streams. For these streams, only a polishing step is needed. Since the steam blowdown and furnace blowdown are investigated to be treated with the same installation, these streams are considered together in this part. The technology of interest is electrodeionization, which is a new promising polishing technique, instead of mixed bed resins. EDI avoids the need for regeneration chemicals and has a low energy consumption. The streams are characterised to investigate if they meet the inlet limitations of the EDI technology. Since no EDI technology was available on lab-scale, the quality after a polishing step was tested using mixed bed resins on lab-scale.

8.5.1 Characterisation

During the characterisation, both streams turned out to be relative clean streams. For the Q7503 stream, two different samples were delivered to Ghent University for testing. ICP-OES results in Table 16 are results from filtered samples (0.45 μm) to prevent any problems in the system. Since this does not represent the total amount of iron in the water, new ICP-OES samples were analysed using a digestion method. The results are given in Table 17. In consultation with BASF, it became clear that the ammonium in the streams comes from the ammonium treatment used in the steam system.

Table 16 Characterisation of the steam blowdown (Q7503) and furnace blowdown (Q0106)

	Unit	Specifications	Q7503	NQ7503	Q0106
Properties					
pH			9.45	9.42	9.27
Turbidity	NTU		0.61	0.34	0.78
Conductivity	$\mu\text{S}/\text{cm}$		11.7	15.42	7.55
TOC	mg/L	<0.5	0.26	0.142	0.45
IC					
Ca	mg/L	<1	0.467	0.244	0.429
Mg	mg/L	<1	0.182	0.164	0.183
ICP-OES					
Fe	mg/L		<LOD	0.291 (with digestion)	<LOD
Si	mg/L		<LOD	<LOQ	<LOD
Ca	mg/L		0.01985	0.104	0.031
Mg	mg/L		not measurable	0.00844	not measurable

Table 17 ICP-OES results for the iron analysis with digestion of the second sample of steam blowdown (NQ7503) and furnace blowdown (Q0106)

	Unit	NQ7503	NQ7503 filtered	Q0106	Q0106 filtered
ICP-OES					
Fe	mg/L	0.291	<LOQ	0.014	<LOQ
Ca	mg/L	0.104		0.0452	
Mg	mg/L	0.045		<LOQ	

8.5.2 EDI suitability

The technology of interest for these streams is electrodeionization (EDI). From the manufacturer of the EDI system, it was stated that the following criteria should be met for the operation of the EDI unit:

- TOC < 0.5 mg/L
- Ca and Mg < 1 mg/L
- Metals < 10 µg/L
- Silica < 0.05 mg/L

In the characterisation, calcium and magnesium were detected in the range of 100 -500 µg/L with IC analysis. In the ICP-OES analysis, the concentrations were way lower. Since these streams are blowdowns from the boiler, normally there should not be any hardness present, since this would scale immediately in the system. Moreover, calcium and magnesium are not detected in the boiler feed water by the measurements of BASF Antwerp. After discussion with BASF Antwerp, it was concluded that these µg/L concentrations of hardness are coming from sampling contamination or the inability of the IC analysis to measure these low concentrations. No hardness should be expected during the operation of the EDI in the pilot containers. TOC concentrations were below the limit. For the NQ7503 sample, the iron content was above the limit.

To check the calcium, magnesium and iron content of the samples again, a digestion was performed and the samples were re-analysed using ICP-OES. The results are shown in Table 17. The filtered samples were filtered using a 0.45 µm filter. After filtering, no iron could be detected, which indicates that if a prefiltration system is installed, iron would not be a problematic component. Calcium and magnesium concentrations remained approximately in the same range.

Particle Size Distribution

In front of the EDI, a filter will be installed to avoid any particulate fouling issues. The use of a filter will be beneficial to retain possible organics (forming biofouling inside buffer tanks) as well as corrosion products inside piping and tanks. To determine what pore size would be sufficient, a particle size distribution measurement was performed. No particles could be detected using the Zetasizer 3000 hs (Malvern Panalytical, UK). From these results, it was decided to use a 1 µm filter as prefiltration.

LC-OCD

For the further exploration of what organics are in these streams, a liquid chromatography - organic carbon detection was performed by an external lab (DOC Labor, Germany). The analysis showed lower results for dissolved organic carbon compared to the total organic carbon values measured with the Sievers TOC analyser, which is expected as not all TOC is dissolved.

For Q0106, the DOC was 134 µg/L, of which 72 µg/L was hydrophilic. 50 µg/L of the hydrophilic DOC was coming from building blocks and 21 µg/L from low molecular weight neutrals. For Q7503, the DOC was 49 µg/L, of which 11 µg/L was hydrophilic. 8 µg/L of the hydrophilic DOC were also low molecular weight neutrals. In the low molecular weight neutrals, SOM is also included. Here X115 (or isopropylalcohol) was detected in concentrations of 7 µg/L and 9 µg/L for Q0106 and Q7503, respectively. In both samples there is also ammonium present, which is added as a corrosion inhibitor in the boiler feed water loop of BASF Antwerp, 623 µg/L and

>1080 $\mu\text{g/L}$ for Q0106 and Q7503 respectively. The hydrophobic organic carbon is thus the most present fraction and according to DOC Labor, should reflect lubricants and grease. This was discussed with BASF Antwerp and is most likely due to sampling contamination. The results of this analysis are added in Appendix A.

To conclude, these streams are suitable for treatment with EDI.

8.5.3 Mixed bed polishing

Since no EDI unit is available at the lab of Ghent University, these tests could not be performed in the lab. To get an indication of the quality after EDI treatment, adsorption tests with mixed bed resins were performed on lab-scale. The results are shown in Table 18. Both streams obtained a low conductivity (around the value for milli-Q water as reference value), which indicates that the streams were polished properly. For Q0106, 64.8% of the TOC is removed, up to a level of 157 $\mu\text{g/L}$. For NQ7503, there is an unexpected increase in TOC level. The TOC levels of both streams are below the boiler feed water limit of 250 $\mu\text{g/L}$. The value for the conductivity is above the limit of 0.2 $\mu\text{S/cm}$, but this could be due to the conductivity probe.

Table 18 Results of the mixed bed tests on the second sample of steam blowdown (NQ7503) and furnace blowdown (Q0106)

	Conductivity ($\mu\text{S/cm}$)	TOC (mg/L)
Q0106		
Sample	7.55	0.446
Mixed Bed	1.99	0.157
Milli-Q	1.99	
NQ7503		
Sample	15.42	0.142
Mixed Bed	2.09	0.163
Milli-Q	1.99	

The low TOC removal rates could be explained by the release of TOC by the new MB resins. The RO permeate of the demineralisation plant, NQ7503 and Q0106 were treated using the same resin in this listed order. In Table 3, it is shown that the TOC after mixed bed resins for the RO permeate could only be reduced to 537 $\mu\text{g/L}$. For the NQ7503, the TOC increased and for the Q0106, TOC was removed for 64.8%. It could be that some TOC could not be captured by the resins. A more plausible explanation seems that the new resins still contained some TOC, possibly leaking out, even though the resins were flushed and rinsed for one hour at a flow rate of 90 BV/h with demineralised water. It should be noted that on lab-scale it is very difficult to achieve conductivity below 1 $\mu\text{S/cm}$ and organics below 1 mg/L due to contamination and residual organics that are present in new membranes and resins as preservatives.

Part VI

Conclusion and further research

CHAPTER 9

CONCLUSION

The goal of this thesis was to investigate which technologies perform well on lab-scale for the treatment of wastewater streams at BASF Antwerp to upgrade to boiler feed water. This thesis focused on preliminary research and testing of the treatment technologies on lab-scale. These tests will be upscaled to pilot-scale tests on site with the IMPROVED containers. The wastewater streams that are investigated are situated on two different sites on the BASF plant, the demineralisation plant and the cracker site. Different treatment technologies were tested on lab-scale. The results of pilot-scale experiments could deviate in terms of removal rates and resulting quality, due to contamination and limitations of lab-scale experiments.

Demineralisation plant

The demineralisation plant of BASF Antwerp exists of a softener resin, followed by reverse osmosis and a polishing step using mixed bed resins. The wastewater stream to be investigated is the RO concentrate, generated in the demineralisation train. To be able to investigate this stream, the demineralisation train needed to be simulated in the lab, since the demineralisation plant is currently in commissioning.

The RO concentrate was treated using a second stage RO unit to improve the recovery of the demineralisation plant. The additional RO was performed using a recovery of 66%, resulting in a permeate stream that needs to be fed again to the RO in the demineralisation treatment train, since the conductivity was too high for directly feeding it to the mixed bed polishing. The additional RO could be operated at higher recovery if some new RO technologies were to be used, such as PFRO or CCRO. A higher recovery indicates a larger permeate stream and a higher percentage of water reuse.

To mitigate waste streams, regeneration tests of the softener resin were performed using the RO concentrate and the concentrate of the additional RO. This way, the RO concentrate would no longer be a waste stream and could replace the NaCl regenerant solution. The regeneration of the softener was not successful with both the RO concentrate and the RO concentrate of the additional RO, since most of the calcium and magnesium was released with a brine regeneration, after the concentrate regeneration. Probably, the concentration of monovalent ions in the concentrate was not high enough to have a sufficient driving force to perform the regeneration. It might be worthwhile to try the regeneration with additional NaCl added to the concentrate, since this would also mitigate the treatment of one waste stream.

Cracker site

The most prioritised stream for reuse on the cracker site is the **Q8870** or NTBA. This tank collects water from the air-sprayed condensers and brackish blowdowns and is currently discharged in surface water. It would be of high impact if the loop between the air-sprayed condensers and the NTBA-tank could be closed, since it would mitigate the use of demineralised water as spraying water. Due to the brackish blowdowns, the Q8870 stream has a high conductivity and a high concentration in chloride and sodium for example. The sam

ple contained some visible flocs. These flocs were removed using a prefiltration with a pore size of 8 micron. This prefiltration is strongly advised (if the actual stream also contains flocs), to avoid fouling of the membrane modules. In the lab, this stream was treated using RO, resulting in a TOC removal of 80% and a decrease in conductivity with 98.6%. The required quality for reuse on the air-sprayed condensers is not defined. Demineralised water causes damage to the concrete, as it tends to dissolve the cementing agent (Tcherner, 2015). Too much ions cause corrosion and clog the nozzles. Further investigation on the required quality needs to be conducted.

If the NPOC in the Q8870 stream is above 30 mg/L, the water is not discharged but sent to the WWTP. This stream is labeled with **Q8860** and is thus not a permanent available flow in the system. Therefore, this stream will not be tested in the containers separately.

The **Q8835** stream is coming from the TBA-tank (containing steam blowdown, furnace blowdown, process condensate and spend caustic) and was treated using nanofiltration, obtaining 96 - 98% removal rate of organic acids and 80% removal of TOC. Despite these promising results, this stream is not of high interest to reuse since the caustic is beneficial to use in the WWTP on site.

Besides the Q8870 stream, the **Q1811** stream also has a high importance for reuse and closing the loop from process condensate to boiler feed water. Prefiltration with 8 micron filter is an option to remove particles, but does not seem necessary. Nanofiltration is able to remove 86 - 98.5% of the organic acids, reducing the TOC with 90.6%. Treatment trains using ion exchange (SAC-SBA), granular activated carbon and reverse osmosis gave good results. Ion exchange (SAC-SBA) performed well on lab-scale in terms of conductivity, but was exhausted quickly. The conductivity of the feed stream was 1156 $\mu\text{S}/\text{cm}$, which is higher than what is considered feasible for IEX (1 mS/cm). By exceeding this limit, the required input of chemicals will be too high to make this technology feasible. To test different kind of adsorbents, jar tests were performed, indicating scavenger resins and MPPE1 resins as the most effective in removing TOC. These adsorbents are highly recommended to try on lab-scale and even on pilot-scale. Different variations in treatment trains of activated carbon, reverse osmosis and resins could be tested, certainly incorporating the scavenger resins. The (scavenger) resins are best positioned in front, to remove organics. Activated carbon could be positioned before the RO (to protect the RO from fouling) or after the RO (for polishing purposes). When the pilot-tests are finalised, a trade-off will be made between costs and permeate quality to conclude which treatment trains are feasible.

The steam blowdown (**Q7503**) and furnace blowdown (**Q0106**) are relatively clean streams. The main technology of interest for these streams is electrodeionization, to upgrade these streams back to boiler feed water. In the lab, different analyses were performed to confirm that these streams meet the limitations of the EDI unit. Since EDI on lab-scale was not possible, mixed bed resins were used to check the quality of the streams after a polishing step, where the conductivity reached adequate levels but TOC content remained for the most part (probably due to the leakage of TOC from the new resins). The streams will be tested in the containers using EDI on pilot-scale, probably improving the quality that the mixed bed resins showed in the lab.

The lab experiments brought forward promising results and established guidelines for testing these technologies in the IMPROVED containers on site. Since the streams at the cracker site are mostly blowdowns and condensates, they are at high temperatures, as described in section 2.1. The technologies in the containers can not handle these high temperatures, hence a chiller need to be installed on site to cool the streams down to the adequate temperatures. The findings of these lab-scale experiments will be further investigated during the pilot-scale trials on site at BASF Antwerp.

CHAPTER 10

FURTHER RESEARCH

This research was only the beginning of the AquaSPICE project at BASF Antwerp. In 2023, the IMPROVED containers will be installed, first on the demineralisation plant and subsequently at the cracker site. Pilot-scale tests will be conducted based on this research (and future research) in the lab. The pilot-scale operation on the different streams will allow to decide which treatment train performs best and to optimise parameters of the different technologies (i.e. dosing of chemicals, operating pressure etc.). Afterwards, the optimal treatment train for both sites can be suggested, taking CAPEX, OPEX and ecological footprint into account, and possibly installed on full-scale.

There will also be further research on other technologies of interest. Advanced oxidation processes (AOP) will be investigated for the process condensate stream (Q1811). The ozonation will be conducted in the lab at campus Kortrijk of Ghent University to investigate the potential of this technology. The aromatics in this stream, mostly BTEX, can be oxidated to CO₂, H₂O and O₂ using ozonation and can thus have a significant impact on the removal of organics from this stream.

Further research is also possible for the additional RO system to treat the concentrate of the demineralisation plant. The recovery on lab-scale was 66% , but since the goal of these trials is the reuse of water, increasing the recovery of this additional RO would be the ultimate goal. Pulse-Flow RO and closed-circuit RO are novel technologies that are interesting to test. Their abilities to perform at higher recoveries without scaling, makes them highly suitable for this purpose. It is advised to test these technologies on lab-scale (if possible) and on pilot-scale in the containers on site.

It is important to know what water quality should be obtained, since it determines what technologies are feasible or capable. BASF Antwerp brought the question forward of what water quality is needed for the spray water in the air-sprayed condensers. At this moment highest quality demineralised water is used, which damages the concrete in the installation. If the water is not demineralised, corrosion and clogging of the nozzles can cause trouble. Further research to investigate the optimal water quality is needed, especially on the corrosion aspect.

Over the course of this thesis, another wastewater stream also came up as interesting and worthwhile to investigate during the pilot-scale trials. The F200 stream is a stream that will be introduced into the new demineralisation plant. It contains some small organics (i.e. methanol, acetone, butanol). In the current train, a sand filter (with microbial activity) is present, acting as a bioreactor and biodegrading these small organics. If this stream will also be included in the new demineralisation plant, the small organics could cause problems, since no sand filter is integrated in the new setup and the small organics could pass the RO step. Therefore, the installation of a sand filter (or alternatives) for the F200 will need to be investigated.

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Appendices

APPENDIX A

LC-OCD ANALYSIS

The results of the Liquid Chromatography - Organic Carbon Detection (LC-OCD) analysis by DOC-Labor Gbmh are given in Figure A.1 and Figure A.2

www.doc-labor.de



Results

DOC-Labor GmbH

DOC = Dissolved Organic Carbon
 HOC* = Hydrophobic Organic Carbon
 CDOC = Colloidal Dissolved Organic Carbon
 NOM = Natural Organic Matter
 SOM = Specific Organic Matter
 LMW = low molecular weight
 cTEP = colloidal Transparent Exopolymer Particles: membrane fouling potential: 1-5 ppb C: low 5-20 ppb-C: moderate > 20 ppb-C: high

Legend:
 *: Gray colour in HOC: significance unclear
 **: under the presumption that all org. N in the Biopolymer fraction originates from proteins
 ***: pale green: false positive signal by inorg. colloids inferred

Table 1

Project: ugent_14	DOC		HOC*		CDOC		NOM										SOM		NO ₃ ⁻	NH ₄ ⁺	Inorg. Colloid. SAC (SAC/DOC)	SUVA L/(mg*m)	
	% DOC	ppb-C	% DOC	ppb-C	% DOC	ppb-C	BIO-polymers	DON (Norg)	NIC	% Proteins in BiOpol.**	Building Blocks	LMW Acids	LMW Neutrals incl. SOM	X115	115*	ppb-N	ppb-N	m ⁻¹					L/(mg*m)
Q0106	134	72	72	53,9%	1	1,1%					50	<1	21	15,6%	7	<1	623	0,01	5,09				
Q7503	49	37	11	23,4%						3	<1	8	16,2%	9	<1	>1080	0,04	8,22					

Matches with library:
 Library matches are suggestions only and do not infer identification!
 IPA

Figure A.1: Result of the LC-OCD analysis of Q7503 and Q0106.

APPENDIX A. LC-OCD ANALYSIS

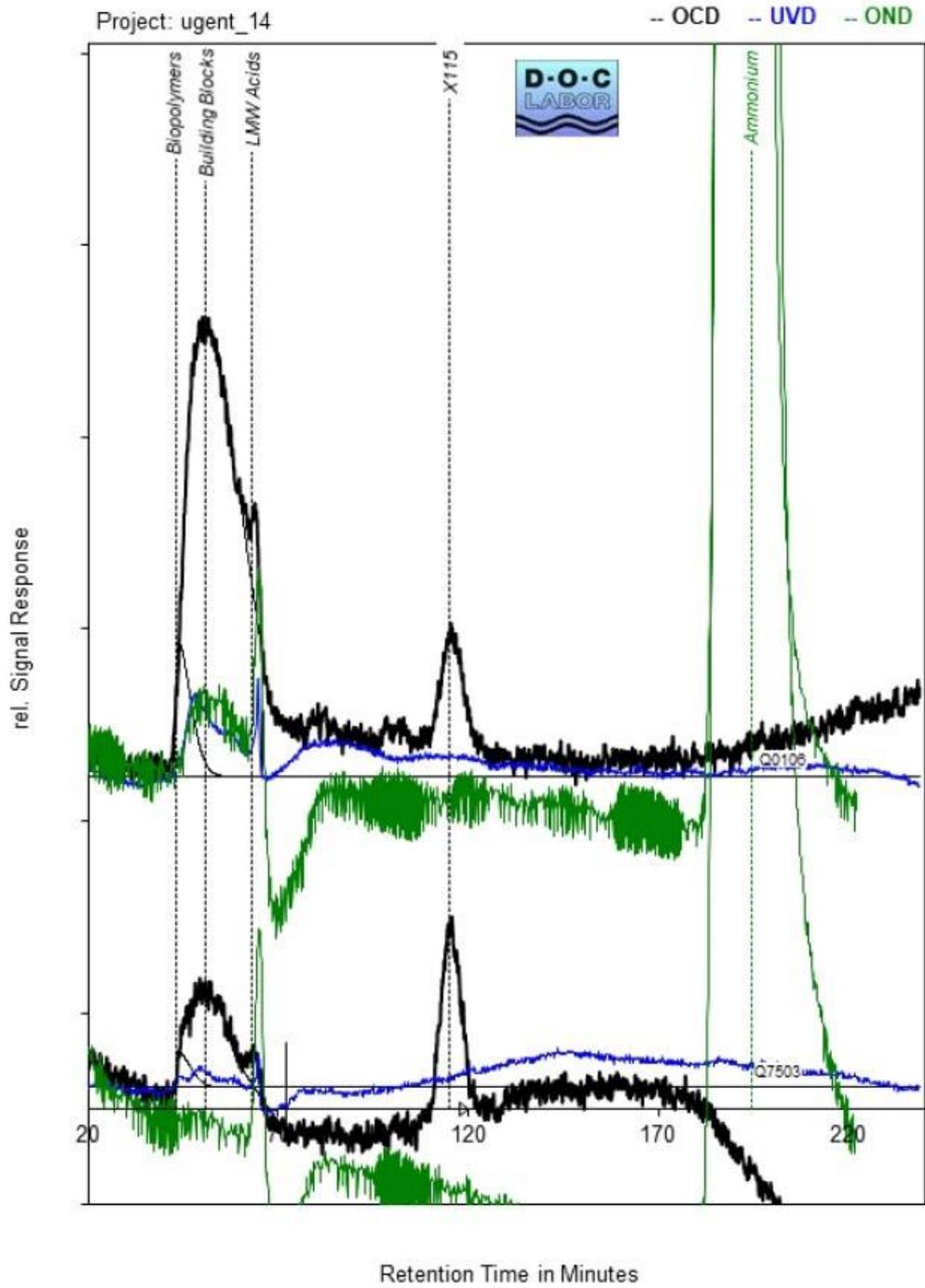


Figure A.2: Chromatogram of the LC-OCD analysis of Q7503 and Q0106.

APPENDIX B

COMPLETE CHARACTERISATION OF THE SAMPLES

Table B.1: Complete characterisation of the Biesbosch water.

	First sample of Biesbosch water BB1	Second sample of Biesbosch water BB2
Properties		
pH	7.99	7.86
Turbidity (NTU)	0.58	1.17
Conductivity ($\mu\text{S}/\text{cm}$)	406	464
TOC (mg/L)	1.075	3.78
IC (mg/L)		
Li ⁺	ND	ND
Na ⁺	30.2	36.26
K ⁺	4.44	4.76
Ca ²⁺	34.74	19.76
Mg ²⁺	6.58	9.04
NH ₄ ⁺	ND	ND
F ⁻	0.22	0.27
Formate	ND	ND
Acetate	ND	0.89
NO ₂ ⁻	ND	ND
Cl ⁻	50.76	54.45
Propionate	ND	ND
Br ⁻	ND	0.2
NO ₃ ⁻	9.66	11.63
SO ₄ ²⁻	46.99	49.79
PO ₄ ³⁻	ND	ND
ICP-OES		
Cu	<LOD	-
Fe	0.018	-
Ca	47	-
Mg	7.44	-
Zn	<LOD	-
Cr	<LOD	-
Ni	0.01	-
Pb	<LOD	-
Cd	<LOD	-
Mn	<LOD	-
B	<LOD	-
Be	<LOD	-
Ba	<LOD	-
Co	<LOD	-
Na	30.72	-
K	6.32	-
Al	<LOD	-
Bi	<LOD	-
Ga	<LOD	-
Li	0.015	-
Se	0.061	-
Sr	0.165	-
Te	<LOD	-
Tl	<LOD	-
As	<LOD	-
P	<LOD	-
Ti	<LOD	-
Si	1.594	-
In	<LOD	-
Sb	<LOD	-
V	0.024	-

Table B.2: Complete characterisation of Q8870.

Q8870	
Properties	
pH	7.25
Turbidity (NTU)	3.48
Conductivity ($\mu\text{S}/\text{cm}$)	3000
TOC (mg/L)	5.32
IC (mg/L)	
Li ⁺	ND
Na ⁺	716.1
K ⁺	41.9
Ca ²⁺	86.8
Mg ²⁺	50.7
NH ₄ ⁺	45.1
F ⁻	1.3
Formate	ND
Acetate	91
NO ₂ ⁻	ND
Cl ⁻	1038.1
Propionate	ND
Br ⁻	4.7
NO ₃ ⁻	5.3
SO ₄ ²⁻	199.2
PO ₄ ³⁻	ND
ICP-OES	
Fe	0.009
Ca	106
Mg	59.3
Zn	0.533
Cr	-
Ni	-
Pb	-
Cd	-
Mn	-
B	-
Be	-
Ba	-
Co	-
Na	386
K	20.9
Al	-
Bi	-
Ga	-
Li	0.0217
Se	<LOD
Sr	0.659
Te	-
Tl	-
As	-
P	0.0377
Ti	-
Si	3.75
In	-
Sb	-
V	0.144

Table B.3: Complete characterisation of Q8860 and NQ8860.

	Q8860	NQ8860
Properties		
pH	7.76	7.83
Turbidity (NTU)	1.02	26.3
Conductivity ($\mu\text{S}/\text{cm}$)	2860	2800
TOC (mg/L)	3.544	2292
IC (mg/L)		
Li ⁺	ND	-
Na ⁺	499.4	-
K ⁺	18.4	-
Ca ²⁺	162.2	-
Mg ²⁺	30.7	-
NH ₄ ⁺	ND	-
F ⁻	<LOD	<LOD
Formate	ND	56
Acetate	ND	329.6
NO ₂ ⁻	ND	ND
Cl ⁻	825	235.7
Propionate	ND	1889.3
Br ⁻	4	ND
NO ₃ ⁻	7.5	ND
SO ₄ ²⁻	137.3	0.432
PO ₄ ³⁻	ND	ND
ICP-OES		
Cu	<LOD	-
Fe	<LOD	17.5
Ca	71.5822	24.4
Mg	60.02	14.2
Zn	0.2154	0.473
Cr	<LOD	-
Ni	<LOD	-
Pb	<LOD	-
Cd	<LOD	-
Mn	<LOD	-
B	<LOD	-
Be	<LOD	-
Ba	<LOD	-
Co	<LOD	-
Na	454.5	663
K	21.06	8.69
Al	<LOD	-
Bi	<LOD	-
Ga	<LOD	-
Li	0.2076	0.007
Se	<LOD	<LOD
Sr	0.533	0.168
Te	<LOD	-
Tl	<LOD	-
As	<LOD	-
P	<LOD	0.0882
Ti	<LOD	-
Si	3.0992	1.69
In	<LOD	-
Sb	<LOD	-
V	0.1217	<LOD

Table B.4: Complete characterisation of Q8835.

Q8835	
Properties	
pH	12.95
Turbidity (NTU)	25.3
Conductivity ($\mu\text{S}/\text{cm}$)	16222
TOC (mg/L)	173.46
IC (mg/L)	
Li ⁺	ND
Na ⁺	1598.8
K ⁺	ND
NH ₄ ⁺	ND
F ⁻	ND
Formate	90.4
Acetate	237.6
NO ₂ ⁻	ND
Cl ⁻	32.4
Propionate	69.2
Br ⁻	ND
NO ₃ ⁻	27.2
SO ₄ ²⁻	186.4
PO ₄ ³⁻	42.8
ICP-OES	
Cu	<LOD
Fe	<LOD
Ca	1.298
Mg	0.3729
Zn	<LOD
Cr	<LOD
Ni	<LOD
Pb	<LOD
Cd	<LOD
Mn	<LOD
B	<LOD
Be	<LOD
Ba	<LOD
Co	<LOD
Na	1956.8
K	2.356
Al	<LOD
Bi	<LOD
Ga	<LOD
Li	0.904
Se	0.0622
Sr	<LOD
Te	<LOD
Tl	<LOD
As	<LOD
P	0.578
Ti	<LOD
Si	0.746
In	<LOD
Sb	<LOD
V	<LOD

Table B.5: Complete characterisation of Q1811 and NQ1811.

	Q1811	NQ1811
Properties		
pH	10.14	10.97
Turbidity (NTU)	2.84	2.75
Conductivity ($\mu\text{S}/\text{cm}$)	1467	915
TOC (mg/L)	647.4	356.4
IC (mg/L)		
Li ⁺	ND	-
Na ⁺	294.8	-
NH ₄ ⁺	ND	ND
F ⁻	0	-
Formate	ND	ND
Acetate	814	427.6
NO ₂ ⁻	ND	ND
Cl ⁻	17.7	9
Propionate	154.8	64.7
Br ⁻	ND	ND
NO ₃ ⁻	ND	ND
SO ₄ ²⁻	6	10.1
PO ₄ ³⁻	24.8	31.9
ICP-OES		
Cu	<LOD	-
Fe	<LOD	0.025
Ca	0.158	0.197
Mg	0.373	0.023
Zn	<LOD	<LOD
Cr	<LOD	-
Ni	<LOD	-
Pb	<LOD	-
Cd	<LOD	-
Mn	<LOD	-
B	<LOD	-
Be	<LOD	-
Ba	<LOD	-
Co	<LOD	-
Na	423.38	207
K	0.628	4.12
Al	<LOD	-
Bi	<LOD	-
Ga	<LOD	-
Li	0.031	0.002
Se	<LOD	0.01
Sr	<LOD	<LOD
Te	<LOD	-
Tl	<LOD	-
As	<LOD	-
P	3.4	16.4
Ti	<LOD	-
Si	0.84	0.26
In	<LOD	-
Sb	<LOD	-
V	<LOD	<LOD

Table B.6: Complete characterisation of Q7503 and NQ7503.

	Q7503	NQ7503
Properties		
pH	9.45	9.42
Turbidity (NTU)	0.61	0.34
Conductivity ($\mu\text{S}/\text{cm}$)	11.7	15.42
TOC (mg/L)	0.26	0.142
IC (mg/L)		
Li ⁺	ND	ND
Na ⁺	<LOD	2.07
K ⁺	0.622	0.396
Ca ²⁺	0.467	0.244
Mg ²⁺	0.182	0.164
NH ₄ ⁺	2.51	1.23
F ⁻	<LOD	<LOD
Formate	0.21	ND
Acetate	0.147	ND
NO ₂ ⁻	ND	ND
Cl ⁻	ND	0.064
Propionate	ND	ND
Br ⁻	ND	ND
NO ₃ ⁻	ND	0.029
SO ₄ ²⁻	0.029	0.085
PO ₄ ³⁻	ND	ND
ICP-OES		
Cu	<LOD	-
Fe	<LOD	0.291
Ca	0.0199	0.104
Mg	<LOD	0.0084
Zn	<LOD	0.0168
Cr	<LOD	-
Ni	<LOD	-
Pb	<LOD	-
Cd	<LOD	-
Mn	<LOD	-
B	<LOD	-
Be	<LOD	-
Ba	<LOD	-
Co	<LOD	-
Na	<LOD	0.62
K	<LOD	0.014
Al	<LOD	-
Bi	<LOD	-
Ga	<LOD	-
Li	0.0202	<LOD
Se	<LOD	<LOD
Sr	<LOD	<LOD
Te	<LOD	-
Tl	<LOD	-
As	<LOD	-
P	<LOD	<LOD
Ti	<LOD	-
Si	<LOD	<LOD
In	<LOD	-
Sb	<LOD	-
V	<LOD	0.0095

Table B.7: Complete characterisation of Q0106.

Q8870	
Properties	
pH	9.27
Turbidity (NTU)	0.78
Conductivity ($\mu\text{S}/\text{cm}$)	7.55
TOC (mg/L)	0.45
IC (mg/L)	
Li ⁺	ND
Na ⁺	0.13
K ⁺	0.308
Ca ²⁺	0.429
Mg ²⁺	0.183
NH ₄ ⁺	1.023
F ⁻	ND
Formate	ND
Acetate	ND
NO ₂ ⁻	ND
Cl ⁻	0.068
Propionate	ND
Br ⁻	ND
NO ₃ ⁻	ND
SO ₄ ²⁻	ND
PO ₄ ³⁻	ND
ICP-OES	
Cu	<LOD
Fe	<LOD
Ca	0.03
Mg	<LOD
Zn	<LOD
Cr	<LOD
Ni	<LOD
Pb	<LOD
Cd	<LOD
Mn	<LOD
B	<LOD
Be	<LOD
Ba	<LOD
Co	<LOD
Na	<LOD
K	<LOD
Al	<LOD
Bi	<LOD
Ga	<LOD
Li	<LOD
Se	<LOD
Sr	<LOD
Te	<LOD
Tl	<LOD
As	<LOD
P	<LOD
Ti	<LOD
Si	<LOD
In	<LOD
Sb	<LOD
V	<LOD

