Sustainable design of the ammonium removal process by ion-exchange

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I declare that I have prepared this Master Thesis self-dependent according to section 16 of the Examination Regulation of the Master Programme Transnational ecosystem-based Water Management (TWM) published at 9 August 2005 at the Faculty of Biology and Geography at the University of Duisburg-Essen.

I declare that I did not use any other means and resources than indicated in this thesis. All external sources of information have been indicated appropriately in the text body and listed in the references.

Delft, September 29, 2016

Ekaterina Isupova
Abstract

In the coming years the groundwater increases in salinity, nutrients and unknown organic micro pollutants. The drinking water company Oasen conducts research on a new approach based on Reverse Osmosis (RO) membranes to face these future challenges. RO reduces the amount of the treatment steps which company has now and filters known and unknown substances. However RO membranes do not remove all ammonium from the groundwater. To meet the target concentration of ammonium of 0.03 mg/l an extra treatment step is needed. This research investigates removal of ammonium by ion-exchange with synthetic resins with an gel structure and Na-ionic form. The aim of this study is to find an optimal resin for design of an ion exchange treatment in terms of operating capacity and sustainability.

A pilot study was conducted with two coarse and two fine resins. The experiment demonstrates that the smaller beads resins behave different. One of the resin was highly compacted and cannot be used in the given operational conditions. However another fine resin showed higher operating capacity than coarse resins due to higher amount of active sides ready for ion exchange. Furthermore the data received from the experiment was scaled up to a functional unit of one year, equal to a production of 2400000 m$^3$ of water. The contribution of different resins to climate change and freshwater eutrophication was assessed by means of a life cycle assessment. In this assessment four aspects were considered: the amount of the consumed energy, the amount of the used resins, the amount of the produced waste water and the amount of the used salt by four different resins. The results showed that the contribution to climate change and freshwater eutrophication is linked to the amount of the used salt. Other parameters contribute significantly less, because the resin is used throughout 10 years, the energy used by Oasen is a wind energy and the main waste is NaCl which does not contribute much to climate change or eutrophication.

From this point it can be concluded that fine resin has a higher operating capacity, uses less salt and therefore contributes less to climate change and freshwater eutrophication.
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1 Introduction

Much research in recent years has focused on climate change and rapid rise of temperature (Grassl 2011). As a consequences of climate change the salinity of surface waters is increasing (Bonte and Zwolsman 2010). Climate change is often linked with population grow and urbanisation. It leads to an increase of nutrients concentration and other known and unknown pollutants in water. For example organic micro pollutants (Schwarzenbach et al. 2006). This creates a challenge for drinking water companies. They want to ensure high quality of drinking water (Drinkwaterbesluit 2016). This study looks how drinking water company Oasen deals with these problems. Oasen uses river bank infiltrate and faces these problems with water.

Traditionally it still uses a conventional water treatment scheme which is not a "state-of-the-art" process anymore. The conventional scheme is shown in figure 1. This water treatment scheme developed historically by adding new treatment steps when new pollutants were discovered. Nowadays new threats appear in water, it is of utmost importance to keep drinking water free from these threats.

![Figure 1: Conventional production scheme](image)

AER and RSF - aeration and Rapid Sand Filtration (biological iron removal); PS - Pellet Softening; COF - Carry over filter; GAC - Granular Activated carbon; UV - Disinfection with UV; CWR - Collection in clean water reservoir.

To fulfill this task drinking water company Oasen conducts research on another water treatment scheme. This scheme is based on Reverse Osmosis filtration (further RO). An example of a treatment scheme based on RO which Oasen foresees is shown in figure 2. This scheme based on RO can remove most of the known and unknown substances from the water. It is a promising technology which can replace many steps of a conventional water treatment process. It can mitigate the future threats as increasing salinity of ground water, nutrients concentration and organic micro-pollutants. Furthermore, it is important that a new scheme contributes as little as possible to climate change to make it sustainable.
1.1 Problem definition

Although RO membranes remove a lot of substances from the water, ammonium is still present in the effluent in concentration of 0.1-0.2 mg/l. This concentration is higher than the target concentration of 0.03 mg/l set by the company (Ruepert 2016). Even though the ammonium concentration does not exceed the Dutch standards for drinking water of 0.2 mg/l (Drinkwaterbesluit 2016), the concentration target for the new treatment plant is significantly lower for the several reasons.

First, the water quality should not be worse than after a conventional process implemented now. The drinking water produced by the current treatment plants has a concentration of ammonium below 0.03 mg/l. Therefore a new scheme should produce water with concentration of ammonium below 0.03 mg/l.

Second, ammonium (NH$_4^+$) can convert into nitrite (NO$_2^-$) in distribution system (WHO 2003) and cause health problems. That is why water quality standards for nitrite in water is more strict. The allowed concentration of nitrite is 0.05 mg/l (0.001 mmol). As a precaution it is assumed that all present NH$_4^+$ can be converted into NO$_2^-$, then the maximum concentration of ammonium must be 0.02 mg/l (0.001 mmol).

Third, the laboratory equipment has the detection limit for ammonium of 0.03 mg/l (Ruepert 2016). Therefore the target concentration is set less than 0.03 mg/l.

1.2 Previous research

To remove ammonium after RO filtration and reach the target concentration, the RO permeate requires an extra treatment step shown by the question mark in figure 2. This research focuses on removal of ammonium from
RO permeate by ion-exchange with synthetic resins in gel form and Na ionic form.

Different methods to remove ammonium from water were considered by Oasen. Among these were:

- biological conversion of ammonium into nitrate
- stripping of ammonia
- ion-exchange
- electrodeionisation
- double-pass RO step

From these, the ion exchange method was chosen because of the following reasons. Biological conversion can not be used because this method reintroduces nutrients in water and provokes bacteria growth, which is undesired after RO filtration. Biological removal of ammonium can be done through the nitrification process from ammonium to nitrite and then to nitrate in the presents of the bacteria *Nitrosomonas* spp. and ammonia oxidizing archaea *Nitrospira* spp. (Vet et al. 2009).

Stripping ammonia is inefficient with low ammonium concentrations (De Moel, Verberk, and Dijk 2006). This method requires high pH and it needs extra usage of chemicals (O’Farrel et al. 1972).

Ion-exchange, double pass RO and electrodeionisation are best suited for ammonium removal. A preliminary cost analyses was performed and ion exchange has been chosen, because of its performance and low cost (Ruepert 2016). In the electrodeionisation (EDI) the driving force to move ions is created by the cathode and anode. The process consumes more energy when it is with small concentration of ions (Meyer et al. 2005). RO membrane technology requires high amount of energy therefore double RO would be very expensive.

To investigate an optimal design in terms of operating capacity and sustainability of an ion exchange treatment step Oasen conducted research on different media. Zeolites and synthetic resins were studied as filling for the ion-exchange columns. The zeolites showed significantly lower operating capacity (Ekovati 2014, Wu and Wang 2015). From the synthetic resins with gel and macro-porous structure, the gel-structured resins showed a greater operating capacity. This is due to the lower cross-linking which allows ions to reach the active sides easier (Papapostolou 2015, Ruepert 2016). The resins with the Na and H ionic forms showed insignificant difference in operating capacity. However the Na-form was recommended
for further investigation because it can be regenerated by NaCl, whereas H-form resin requires HCl (Ruepert 2016). NaCl is safer for operators and environment than HCl.

Other research outside the company were mainly focused on ion exchange for removing other ions (Millar et al. 2016) or ammonium ions but with significantly higher concentration (Millar et al. 2016, Sica et al. 2014). The process of ion exchange is based on equilibrium and column behavior (Millar et al. 2016). For the small concentration the process is influenced by operating conditions and resin behavior. This study investigates ammonium removal after RO filtration with small ammonium concentrations and special respect to water quality and resin characteristics.

1.3 Aim

The aim of this study is to find an optimal resin for design of an ion exchange treatment after RO filtration by considering two parameters: operating capacity and sustainability.

First, the best performing resin in terms of operating capacity was determined. The resins were tested in a pilot unit. The new pilot was improved in comparison with previous research by including a buffer tank, where water was collected, and a pump. It provided a stable flow of the permeate to supply columns and reduced inaccuracies which were a problem in the previous research (Papapostolou 2015).

Secondly, the most sustainable resin was determined by means of life cycle assessment. The most sustainable resin in this case means the resin that least of all contributes to climate change and freshwater eutrophication. Because of high inaccuracy in previous research it was not possible to make a conclusion about sustainability (Papapostolou 2015).

1.4 Research questions

The following research questions were investigated in this study:

- What is an optimal resin to use in the ion exchange treatment with the given water quality and operating conditions?
  1. What is the operating capacity after regeneration of the resins?
  2. How much energy do resins use?
  3. How much waste salt do the resins create per litre?
  4. What is the cost of the resins per litre?
5. Which resin contributes least of all to climate change and freshwater eutrophication?

6. Which resin gives optimal combination of these parameters?

### 1.5 Research approach

To answer the research questions the research was conducted according to the following flowchart figure 3.

![Flowchart](image)

**Figure 3: Research approach**

### Lay out of the report

The report continues with a description of the theory in Chapter 2. It will be referred to when the results are explained in the final part of the report. Next in Chapter 3 the materials and methods are described. Chapter 4 presents the results of the experiments. Chapter 5 describes the discussion about the performances of the resins for ammonium removal. The report is concluded by Chapter 6 presenting the conclusions and recommendations for further research.
2 Theoretical background

2.1 Ion exchange definition

Ion exchange is a process of the exchanging of ions between a solution and a solid material. The solid material is called an ion exchanger. The unwanted cations or anions in the solution are absorbed on the ion exchanger and replaced by equivalent quantities of the other ions with the same charge from the ion exchanger (Dardel and Arden 2001).

One of the possible ion exchangers is resin. A resin is a polymeric matrix with functional groups of the negative charge and ions of the positive charge. The ions are mobile and able to exchange (A+). Schematic process of the cation exchange process are shown in figure 4. The functional groups of resin are connected with each other (or cross linked) and form a polymeric matrix with pores. During ion exchange process ions (A+) can easily move in these pores (Crittenden 2005). Water contains (B+ X-), where B+ is unwanted cation. When water goes through the resin, the following process happened: first, the A+ moves to the solution and X-moves inside of the resin. The driving force of this diffusion is concentration differences. Because of these movements, the solution get more positive charged and the resin more negatively charged. It creates an electrical potential differences. Then, B+ moves to the resin and replace A+ stochiometrically. Finally X- goes back to the solution and bands with A+. The system of the resin and solution is now electrically balanced (Crittenden 2005).

The exchange process can be represented by the following formula:

\[ R-A + B^+ \leftrightarrow R-B+A^+ \]

The exchange process for the Na-form resin and solution which contains ammonium is represented by the following formula:

\[ R-Na + NH_4^+ \leftrightarrow R-NH_4+Na^+ \]

2.2 Resins and Resins properties

Structure

The polymeric matrix of the resin is made of chains of polymers. These chains of polymers are sewed with each other (or crosslinked) by the divinylbenzene (DVB) (Crittenden 2005). A resin which has equally distributed crosslinks and pores is called gel resin. The resin where the crosslinks are disturbed not equally and with clear macro-pores is called macroporous resin.
Degree of cross-linking and porosity

Then greater the degree of crosslinking then more it is resistant to the oxidation and mechanical stress. The less crosslinking, the easier it is to reach the ions for the exchange process (Dardel and Arden 2001). Gel resin has 4-10% of DVB cross-linking (Crittenden 2005). Macro-porous resin has 20-25% DVB cross-linking. The presents of macropores in the structure means that large ions can also be exchanged. The operating capacity is small because the resin has a small amount of functional groups (Crittenden 2005).

2.3 Engineering properties of resins

The two most important engineering parameters are capacity of the resin and selectivity. The capacity of the resin is how many ions can be exchanged by resin per resin volume. Selectivity gives the information about what ions among the present ions in the water are preferred more by resin.

Exchange Capacity

Capacity is the amount of active sides which can be exchanged on the resin (Crittenden 2005). **Theoretical capacity** is a theoretical amount of the ions which can participate in the exchange process. It is expressed...
in equivalents per unit volume of wet resin and represents the number of active sites available for exchange (Dardel and Arden 2001).

Operating capacity In practice not all ions can be exchanged. That capacity is called operating capacity (Ruepert 2016). It is a part of the total capacity which can be used in the operation and depends on the following operational conditions (Crittenden 2005, Dardel and Arden 2001).

- concentration and type of ions to be absorbed (water quality);
- service flow rate (SFR):
- temperature;
- depth of resin bed
- type, concentration, and quantity of solution for regeneration

Selectivity
Resins have a preference to one type of ions to another one. It is called selectivity. The resins select based on electromagnetic strength of ions. The order of preferences for cation is shown below. The ions on the left are more preferred by the resin than the ions on the right (Crittenden 2005).

\[
\text{Ba}^{2+} > \text{Pb}^{2+} > \text{Ca}^{2+} > \text{Ni}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{H}^+
\]

Particle size
There are two important dependencies on the particle size of resins. Firstly, a larger size of resin beads slows the rate of ion exchange. It becomes difficult to reach the active sides in sides of the beads. The process goes on the surface of the beads and smaller beads have a higher ration of surface to volume. Second, greater size of beads decreases the pressure loss through the resin bed (Crittenden 2005, Dardel and Arden 2001).

2.4 Regeneration method
There are two types of the regeneration cocurrent and countercurrent. In this work the countercurrent operation was used.
Countercurrent operation

Countercurrent regeneration is a regeneration where the solution for regeneration is applied in the opposite direction from the direction of the treated water (Crittenden 2005). This method is preferred when a high quality water is required and a leakage is not allowed. In the countercurrent regeneration less amount of chemicals are used for regeneration and therefore it provides less waste water. During this operation countercurrent flow creates turbulence and it can disturb the regeneration, what is why the resin bed should be packed before regeneration.

Regeneration requirements

- regenerant concentration
- regenerant flow rate
- contact time

The concentration for regeneration influences the operating capacity. The smaller concentration of solution for regeneration than than smaller operating capacity. Figure 5 shows a recommendation for the salt concentration to achieve a certain operating capacity (Ruepert 2016).

![Figure 5: Operating capacity versus concentration of NaCl](image-url)
2.5 Operation until the breakthrough

The breakthrough point is the moment when the unwanted ions first appear in the effluent of the column. Leakage is the appearance of the unwanted ions in the low concentrations in the effluent of the column. Figure 6 shows a plot of leakage in percent of the feed concentration of unwanted ion versus volume of the feed water passed through the resin. The concentration of unwanted ions reaches steadily the concentration in the feed water. It means there is no possible exchange anymore and resin is exhausted completely. Starting from the breakthrough point the unwanted ion is present in effluent in the low concentration. The operation is stopped before it reaches a target concentration.

![Figure 6: Total and operating capacity](image)

2.6 Life Cycle Assessment

Life Cycle Assessment (LCA) is a method to quantify and compare the environmental impacts of the products through the whole life cycle of these products (Rebitzer et al. 2004). The product is considered from the raw material extraction and product production to its disposal. All used natural resources and produced emissions during the life cycle are quantified. Further the emissions and resources are reclassified to the environmental problems. LCA is used to compare and determinate which of the products or services are more "environmentally friendly" (Baumann and Tillman 2004).
3 Materials and Methods

To be able to answer the research questions an experiment with different resins was conducted. This experiment was done on the specifically designed pilot unit fed by RO permeate and treated on the different resins. In the following chapter the working of the pilot unit, the measurements methodology and data analysis will be explained.

3.1 Ion exchange pilot unit

The idea and design of the pilot unit was done together by engineering company Ovivo and Oasen. Figure 7a shows the empty pilot unit and ammonium analyzer 7b. Schematic figures 8 and 9 demonstrate front and rear views of the pilot unit and its parts.

![ion exchange pilot unit](image1)

![Analyzer](image2)

Figure 7: Set up

The experiment was conducted in the following way. RO permeate was collected in a buffer tank (1). Then water was pumped to the four columns (2) by a pump (4). The pump worked automatically and switched off when the water levels in the buffer tank were to low. Flows in the were controlled by valves (5) operated manually. On the top and bottom of the columns manometers (7) were installed to check the pressure drop during the experiment. Flow was recorded by a digital panel(9). Concentration of ammonium was recorded by another digital panel on the ammonium analyser. It was also possible to take water samples from the samples points (8). Codes of the samples are XKMFIEX00A, XKMFIEX01Z, XKMFIEX02Z, XKMFIEX03Z, XKMFIEX04Z. After a treatment cycle resins in
Figure 8: Front view

Figure 9: Rear view
columns required regeneration with solution of NaCl. The solution was prepared in brine tank (3). Flowmeters (6) showed flows of the solution and water pumped through the columns. There were also pressure vessel and air pump (not on the picture). They were added to the installation later to control the amount of water and brine for regeneration. Next to the pilot unit an ammonium analyzer was placed. Water samples from each of the columns were sent to the ammonium analyzer to analyze concentration of ammonium in the water. Appendix A contains a description of the pilot unit operation and regeneration.

3.2 Tested water

To know how well resins remove ammonium it is necessary to have data on the ammonium concentration of influent and effluent. The feed water of ion exchange pilot unit was a permeate from RO membranes filtration. This water contained ammonium in the range between 0.1 to 0.2 mg/l. Data collected by the Vites laboratory during a period of the experiment. The median value of 0.18 mg/l was taken for the further calculation. Figures 10a and 10b contain statistical analysis of water quality data and show a median value of ammonium and other ions concentration. Water after treatment on different resins was analyzed by ammonium analyzer and recorded. pH of the tested water was in the range between 5 to 6 pH.

![Figure 10: Concentration of ammonium and other ions in the feed water](image-url)
### 3.3 Types of resins

To remove ammonium from the water the pilot unit columns were filled with four different resins. The resins were chosen based on the previous research. All four resins were of the gel structure and Na-ionic form. DOW chemical company supplied a fine resin Monosphere C400L (further C400L) and a coarse resin MarathonC. Lanxess supplied a fine resin Lewatit MDS 1368 NA (further MDS1368) and a coarse resin Lewatit S 1668 (further S1668). Table 1 contains a summary of the resin characteristics from the biggest to the smallest beads size. The resins were placed into the columns in the same order. Figure 11 shows four tested resins.

Table 1: Characteristics of tested resins based on factsheets of suppliers

<table>
<thead>
<tr>
<th>No.</th>
<th>Supplier</th>
<th>Name</th>
<th>Ionic form</th>
<th>Structure</th>
<th>Mean particle size, ( \mu m )</th>
<th>Theoretical total capacity, eq/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lanxess</td>
<td>Lewatit S 1668</td>
<td>Na</td>
<td>Gel</td>
<td>620 ± 50</td>
<td>2.2</td>
</tr>
<tr>
<td>2</td>
<td>DOW</td>
<td>Marathon C</td>
<td>Na</td>
<td>Gel</td>
<td>585 ± 50</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>DOW</td>
<td>Monosphere C400L</td>
<td>Na</td>
<td>Gel</td>
<td>400 ± 50</td>
<td>2.2</td>
</tr>
<tr>
<td>4</td>
<td>Lanxess</td>
<td>Lewatit MDS 1368 Na</td>
<td>Na</td>
<td>Gel</td>
<td>320 ± 30</td>
<td>1.8</td>
</tr>
</tbody>
</table>

### 3.4 Measurements

To analyse the margin of error of the measurements done, the following measurements and parameters were considered: ammonium concentration, flow, pressure and the length of columns. Further the detection limits, measurement ranges and accuracy classes of the used instruments are described below.

The ammonium concentration in the effluents was measured automatically by the analyser Appalikon Alert Ion Analyzer Model 200Z. Samples were sent to the analyzer every 15 minutes from each column consequently. It means one sample was taken from each of the columns every hour. Results were recorded by the digital panel. The ammonium analyzer detection limit is 0.01 mg/l \( \text{NH}_4^+ \) with an accuracy 5 %.. As an extra measure
before regeneration of resins ammonium concentration was measured by a cuvette test Hach Lange LCK 304. By the measurements of the analyzer were validated if it is corresponded with data on the screen. The detection range of the cuvettes test is 0.02-2.5 mg/l NH$_4^+$ . Precision is 10 % of a limit value. In addition, the Vitens laboratory took samples of the feed water and columns effluent three times per week during the time of the experiment. The lab determined ammonium concentration in water samples by using the AquaKem 600. The detection limit is 0.03 mg/l NH$_4^+$ . Water flows through columns were measured by watermeters Elster KSM-20-165, accuracy 2 %. Water flows for regeneration were measured by flowmeters Gemü, for H$_2$O 805/25/D, with measurement range 100 to 1000 l/h and for NaCl 25 % 855/20/D with measurement range 50 to 550 l/h and accuracy of 1 % of end value and 3 % of measured value. Pressure was measured by manometers Wika with measurement range of 0-6 bar and a scale of 0.2 bar and accuracy class 1.6. Length of bed volume was measured by a roll-meter of length 2 m with scale 1 mm and accuracy class II.

### 3.5 Analysis

To make conclusions about resin performance the measured parameters were analyzed. In this paragraph processing of data on operating capacity and sustainability are described.
Data on operating capacity

To calculate operating capacity it is necessary to know the following parameters: flow ($Q$), volume of resin in each of the columns ($V$), concentration of the ammonium in the influent ($C_{in}$), ammonium concentration in the effluent ($C_{out}$) and breakthrough time ($t_{br}$). Figures 12a, 12b show initial data for calculation ammonium operating capacity ($OC_{NH4}$) and total operating capacity ($OC_{tr}$). The calculation was done by formula:

$$OC = \frac{Q}{V} \int_{t=0}^{t_{br}} \Delta C(t)dt$$

(1)

There are two types of operating capacity: operating capacity for ammonium ($OC_{NH4}$) and total operating capacity ($OC_{tr}$). Operating capacity for ammonium was calculated by using difference of concentration of ammonium in influent and effluent:

$$\Delta C = C(NH^+_4)_{in} - C(NH^+_4)_{out}$$

(2)

Total operating capacity was calculated by using the sum of difference of all ions ($K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, NH^+_4$) concentration in influent and effluent:

$$\Delta C = C(ions)_{in} - C(ions)_{out}$$

(3)

The flow ($Q$) for calculation in the 1st, 2nd and 3d columns were used 1098, 1111, 989, 682 l/h according the flow in Appendix D. The 4th column could not produced a bigger flow because of the small beads or resin created high resistance to flow.

The volume ($V$) of resin bed was calculated to be 0.02 m$^3$ as a height was 1 m and diameter 0.16 m.

Time when the resins reached their breakthrough points was obtained from the experiment. During the experiment, the time in hours and the concentration of ammonium were recorded and plotted. From these plots the breakthrough time was determined. It was set at the time when the ammonium concentration was higher then 0.03 mg/l. Breakthrough times were determined for resin by using data from the last operation cycle. Then the leakage time for each resin was determined.

Operating capacity for ammonium (further in the text just operating capacity) was calculated by formula 1 as follow. First, operating capacity was calculated with the assumption that the concentration of ammonium in effluent is equal to zero ($C(NH^+_4)_{out}=0$ mg/l). This operating capacity is equal to the red area in Figure 13. In practice concentration of ammonium was equal zero until the leakage time point ($t_{leak}$) and then raised until 0.03
In:
\[ C(\text{NH}_4^+)=0.18 \text{ mg/l} \]
\[ C(\text{K}^+)=0.23 \text{ mg/l} \]
\[ C(\text{Ca}^{2+})=0.17 \text{ mg/l} \]
\[ C(\text{Mg}^{2+})=0.02 \text{ mg/l} \]
\[ C(\text{Fe}^{2+})=0.01 \text{ mg/l} \]

V=0.02 m³
Q=1 m³/h

Out:
\[ C(\text{NH}_4^+)=0 \text{ mg/l} \]
\[ C(\text{K}^+)=0 \text{ mg/l} \]
\[ C(\text{Ca}^{2+})=0 \text{ mg/l} \]
\[ C(\text{Mg}^{2+})=0 \text{ mg/l} \]
\[ C(\text{Fe}^{2+})=0 \text{ mg/l} \]

(a) Operating capacity ammonium
(b) Total operating capacity

Figure 12: Initial data

mg/l. It means that operating capacity has an error which is equal a grey figure area in Figure 14. It is assumed to be an area of triangle.

Figure 13: Operating capacity calculation

The error was calculated by the following formula:

\[ \varepsilon = \frac{1}{2} \left( t_{br} - t_{leak} \right) C_{br} \]
\[ C_{in}(t_{br} - t_0) \]

\[ (4) \]

The error turned out to be in the range between 0.2 to 0.9% for all breakthrough curves and was not included in the further calculation of operating capacity.
The operating capacity was not measured directly and it was influenced by the measurement errors of the measured values. It was calculated from the flow \(Q\), volume \(V\), concentration \(C\) and time \(t\). The error of the operating capacity was calculated as following:

\[
\frac{\Delta OC}{OC} = |\frac{\Delta Q}{Q}| + |\frac{\Delta V}{V}| + |\frac{\Delta C}{C}| + |\frac{\Delta t}{t}| + \varepsilon
\]  \hspace{1cm} (5)

There were median values used for the flow and for the ammonium concentration. The deviation was determined by the median absolute deviation. This method did not included outliers and made the calculation more robust.

Life Cycle Assessment

To make a choice about the optimal resin in terms of sustainability life cycle assessment (LCA) was used. Assessment was performed by using LCA software SimaPro. This software contains worldwide scientific based data on processes and products and measures environmental impacts across the whole life cycle of the focused process. This study focused on the ion exchange treatment phase of the RO based scheme of water treatment. Steps following before and after the ion exchange treatment step were left out of the scope and were not considered in the LCA. The system boundaries are shown in Figure 15. Within ion exchange treatment the following steps were included: energy consumption, chemicals used for regeneration, materials used for treatment process, chemicals and materials transport from a production side to water treatment plant, and waste
production. To determine the contribution of emissions to the environmental impacts the ReCiPe midpoint method was used. Midpoints are the impacts that in the end contribute to the endpoint impacts. The following impact categories were selected for analysis: climate change, freshwater eutrophication as they are causes of increasing salinity of water and the amount of nutrients in the water. Climate change is described in kgCO$_2$eq due to emissions of greenhouse gasses (CO$_2$, CH$_4$, N$_2$O). Freshwater eutrophication is described in kgP$_{eq}$ due to P emissions.

![Figure 15: System boundaries](image)

The data was put in SimaPro for calculation according to the functional unit. The functional unit was chosen of a year of production or 2.400.000 m$^3$ of water. Inventory table further contains all inputs for the Life Cycle Assessment.

**Scale up**

To be able to perform a life cycle assessment for the ion exchange process data from the pilot study was scaled up to the functional unit. The capacity of the full scale plant is 2400000 m$^3$/year or 274 m$^3$/h. According to Oasen the full scale plant will have 3+1 vessels with diameter of 1.7 m and resin bed height of 1.5 m. Three columns are in operation, the fourth is used in the period of regeneration. Than volume of one column is:
\[ V = \pi \times \left( \frac{D}{2} \right)^2 \times H \]  
(6)

\[ V = 3.14 \times \left( \frac{1.7}{2} \right)^2 \times 1.5 = 3.4 \text{ m}^2 \]

\[ V_{\text{tot}} = V \times 4 \text{ to buy} \]  
(7)

\[ V_{\text{tot}} = 3.4 \times 4 = 13.6 \text{ m}^3 \]

\[ V_{\text{tot}} = V \times 4 \text{ to use} \]  
(8)

\[ V_{\text{tot}} = 3.4 \times 3 = 10.2 \text{ m}^3 \]

\[ \text{SFR} = \frac{Q}{V_{\text{tot}}} \]  
(9)

\[ \text{SFR} = \frac{274 \text{ m}^3/\text{h}}{10.2 \text{ m}^3} = 27 \text{ BV/h} \]

The surface flow rate (SFR) used in the pilot study was 50 BV/h. It is on the high end of the possible range of SFR at which damage to resin could occur. It was used to decrease the time required to perform the pilot study. For the full scale design a SFR of 27 BV/h will be used.

**Data on energy consumption**

To calculate energy consumption it is necessary to know pressure loss in each columns. For this purpose a flow test was performed for bed height 1 m. The pressure at the entrance and exit of the resin bed were measured and then calculated a pressure drop (\( \Delta P \)):

\[ \Delta p = p_{\text{top}} - p_{\text{bottom}} \]  
(10)

Figure 23 shows pressure drops recorded from flow test for different linear flows.

Linear velocity (\( u_s \)):

\[ u_s = \frac{Q}{A_{\text{tot}}} \]  
(11)
\[ u_s = \frac{274 \, m^3/h}{8.8 \, m^2} = 40 \, m/h \]

By using linear approximation pressure drops for calculated for linear flow of 40 m/h and bed height of 1.5 m.

Than using these pressure drops (\( \Delta p \)) the power consumption (\( P \)), [W] was calculated by the following formula:

\[ P = \frac{Q \times \Delta p}{3600} \quad (12) \]

The energy consumption (\( E \)), [kWh/year] was calculated by the following formula:

\[ E = \frac{P \times 365 \times 24}{1000} \quad (13) \]

**Data on salt consumption**

To calculate salt consumption of resin the following formulas were used:

Overall cycle time (\( t_{cyc} \)) is a time till the breakthrough \( BV_{br} \).

\[ t_{cyc} = \frac{BV_{br}}{SFR} \quad (14) \]

Salt loading rate (\( SLR \)) was calculated for three different regeneration concentration of NaCl (\( C_{NaCl} \)): 140, 100, 60 g/l. In the pilot study regeneration flow (\( Q_{reg} \)) of 450 l/h and contact time (\( t_{cont} \)) of 20 min were used.

\[ SLR = \frac{C_{NaCl} \times Q_{reg} \times t_{cont}}{V} \quad (15) \]

\[ SLR = \frac{140 \, g/l \times 450 \, l/h \times 20 \, min}{0.02 \, m^3 \times 60 \, min} = 1050 \, kg \, NaCl/m^3 \, resin \]

\[ SLR = \frac{100 \, g/l \times 450 \, l/h \times 20 \, min}{0.02 \, m^3 \times 60 \, min} = 750 \, kg \, NaCl/m^3 \, resin \]

\[ SLR = \frac{60 \, g/l \times 450 \, l/h \times 20 \, min}{0.02 \, m^3 \times 60 \, min} = 450 \, kg \, NaCl/m^3 \, resin \]

Number of regeneration for each column per year (\( k \)):

\[ k = \frac{(365 \, d/yr)(24 \, h/d)}{t_{cyc}} \quad (16) \]
Annual salt quantity for regeneration ($M_{NaCl}$)

$$M_{NaCl} = (V_{tot} * S LR) * k$$  \hfill (17)

The error of the salt consumption calculation was influenced by the measured values. It was calculated from the measured values as saturated salt concentration ($C_{NaCl}$), total flow ($Q_{tot}$), salt flow ($Q_{NaCl}$), time (t) and volume (V). The error of the salt consumption was calculated as following (due):

$$\frac{\Delta M_{NaCl}}{M_{NaCl}} = |\frac{\Delta C_{NaCl}}{C_{NaCl}}| + |\frac{\Delta Q}{Q}| + |\frac{\Delta V}{V}| + |\frac{\Delta t}{t}|$$  \hfill (18)

Accuracy of saturated salt concentration is assumed to be 0 as it is achieved without making any precision measurements based on the physical properties.

Flow for regeneration was measured by the flowmeter for the saturated salt solution and then after the salt and water mixed by the flowmeter for the total flow. As it was measured twice the error was calculated as follows:

$$\frac{\Delta Q}{Q} = \frac{Q_{NaCl}}{(Q_{tot} + Q_{NaCl})^2} * (\Delta Q_{tot} + \Delta Q_{NaCl})$$  \hfill (19)
4 Results

The results are summarized in this chapter. Calculation of operating capacity and comparison of the theoretical, total and operating capacity is shown. The life cycle assessment of the ion exchange water treatment and its contribution to climate change and freshwater eutrophication is depicted below.

4.1 Data on operating capacity

To be able to compare the resins and choose the one for the future use operating capacity was calculated for each resin based on the breakthrough curves. Breakthrough curves show how concentration of ammonium in the effluent changes when the bed volumes (BV) of water passed through. Breakthrough curves, ammonium concentration versus BV, are shown in figure 16. Breakthrough curves where ammonium concentration plotted versus time are shown in Appendix B.

![Breakthrough curves](image.png)

Figure 16: Breakthrough curves

Horizontal line on the plots is target ammonium concentration of 0.03 mg/l in the effluent. When the line crosses the breakthrough curve the
Resin is exhausted and requires regeneration. In production the process is stopped. In the experiment the curves often went further. Single outliers appear in the curves when the columns are closed during regeneration of another column. The ammonium ions are collected at the bottom and the first sample after regeneration will be with the high concentration. For each column at least three good cycles of data were collected.

Based on the breakthrough curves time was determined and than operating capacity for each cycle was calculated. Breakthrough time and operating capacity are shown in Table 2.

Table 2: Operating and total capacity

<table>
<thead>
<tr>
<th>No reg.</th>
<th>Breakthr. time, h</th>
<th>Op. capacity, eq/l</th>
<th>Total op. capacity, eq/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column1 - Lewatit S1668</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>291</td>
<td>0.14</td>
<td>0.37</td>
</tr>
<tr>
<td>4</td>
<td>246</td>
<td>0.13</td>
<td>0.33</td>
</tr>
<tr>
<td>5</td>
<td>219</td>
<td>0.12</td>
<td>0.32</td>
</tr>
<tr>
<td>Column2 - DOW Marathon C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>242</td>
<td>0.14</td>
<td>0.36</td>
</tr>
<tr>
<td>2</td>
<td>241</td>
<td>0.12</td>
<td>0.32</td>
</tr>
<tr>
<td>4</td>
<td>213</td>
<td>0.12</td>
<td>0.31</td>
</tr>
<tr>
<td>Column3 - DOW Monosphere C400L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>310</td>
<td>0.18</td>
<td>0.47</td>
</tr>
<tr>
<td>2</td>
<td>285</td>
<td>0.15</td>
<td>0.40</td>
</tr>
<tr>
<td>4</td>
<td>318</td>
<td>0.16</td>
<td>0.42</td>
</tr>
<tr>
<td>Column4 - Lewatit MDS 1368Na</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>475</td>
<td>0.14</td>
<td>0.38</td>
</tr>
<tr>
<td>2</td>
<td>343</td>
<td>0.12</td>
<td>0.31</td>
</tr>
<tr>
<td>3</td>
<td>311</td>
<td>0.11</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Operating capacity for each cycle is shown in figure 17. The first operating capacity was higher than the operating capacity of the following cycles for all four columns. The resins ‘S1668’ and ‘Marathon C’ showed almost the same operating capacity. The ‘C400L’ resin has the highest operating capacity and the ‘MDS1368’ has the smallest.

Except ammonium there were other ions in the feed water (Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe²⁺). Amount of these ions is shown in figure 18a and 18b. They were included in the calculation of the total operating capacity. Results are shown in figure 19. Total operating capacity was higher than operating capacity for ammonium in 2.5 times for all four resins.
Figure 17: Operating capacity

Figure 18: Concentration of other ions
To choose between resins the suppliers provided information on the theoretical capacity. The comparison of theoretical, total and operating capacity is in figure 20. Theoretical capacity is significantly higher than total capacity and operating capacity calculated at the given operating conditions. The relative difference between theoretical capacity and total capacity is 14.5; 15.5; 19; 15.6% for 'S1668', 'Marathon C', 'C400L', 'MDS1368' respectively. The relative difference between theoretical capacity and operating capacity is 5.5; 6; 7.3; 6.1% for 'S1668', 'Marathon C', 'C400L', 'MDS1368' respectively. The relative differences are shown in figure 21.

Next step of the experiment was to know operating capacity for the 'Marathon C' and 'C400L' with regenerations by different concentration of NaCl. The breakthrough curves for the concentration of 140 g/l, 100 g/l and 60 g/l are shown in figure 22. For 'Marathon C' the breakthrough curves were very close to each other. For 'C400L' the breakthrough for the 100 g/l concentration appeared earlier than for the 140 g/l concentration. The breakthrough curve for the 60 g/l was interrupted because of malfunction of the analyzer. During maintenance of the analyzer the pilot unit stayed still and after that the concentration of ammonium was scattered and located in between of the breakthrough curves for the 140 and 100 g/l. The operating capacity based on these curves was calculated. The results are shown in table 3.
Lewatit S1668  DOW Marathon C  DOW Monosphere C400L  Lewatit MDS1368Na
0  0.5  1  1.5  2  2.5
Operating capacity, [eq/l]

Comparison of operating capacity

Figure 20: Comparison of operating, total and theoretical capacity

Lewatit S1668  DOW Marathon C  DOW Monosphere C400L  Lewatit MDS1368Na
10  20  30  40  50  60  70  80  90  100
Relative difference theoretical capacity, total capacity and operating capacity

Figure 21: Relative difference between theoretical, total and operating capacity

35
Figure 22: Breakthrough curves with different regeneration concentrations

Table 3: Operating and total capacity for different concentration

<table>
<thead>
<tr>
<th>g/l</th>
<th>Breakthr. time, h</th>
<th>Op. capacity, eq/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Column 2 - DOW Marathon C</td>
</tr>
<tr>
<td>140</td>
<td>213</td>
<td>0.12</td>
</tr>
<tr>
<td>100</td>
<td>209</td>
<td>0.11</td>
</tr>
<tr>
<td>60</td>
<td>204</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Column 3 - DOW Monosphere C400L</td>
</tr>
<tr>
<td>140</td>
<td>318</td>
<td>0.16</td>
</tr>
<tr>
<td>100</td>
<td>272</td>
<td>0.14</td>
</tr>
<tr>
<td>60</td>
<td>292</td>
<td>0.15</td>
</tr>
</tbody>
</table>
The operating capacity error was calculated based on the error of the measured values as flow, concentration, volume and time. It is in the range between 16.7 to 28.2%. The errors for four resins for each cycle are shown in Appendix C.
4.2 Life cycle assessment

To compare resins by sustainability data from the pilot unit was scaled up and used for the life cycle assessment in SimaPro.

To get data on the energy consumption a flow test was performed. The results of the flow test is shown in figure 23. The lines show flow rate versus pressure drop for the bed height of 1 m for four different resins. The coarse resins ‘S1668’ and ‘Marathon C’ have smaller pressure drop than fine resin ‘C400L’ and ‘MDS1368’. The ‘S1668’ and ‘Marathon C’ performed performed very similar. The resin ‘MDS1368’ had higher pressure drop than the resin ‘C400L’.

![Figure 23: Results of the flow test](image)

By using linear approximation the pressure drops were determined for the linear flow of 40 m/h and bed eight of 1.5 m. Results on the power and energy consumption used by different resins for the full scale plant per year are shown in table 4.
Table 4: Energy consumption for the full scale plant

<table>
<thead>
<tr>
<th>Resin</th>
<th>Flow ( Q, \text{ m}^3/\text{h} )</th>
<th>( \Delta p ) (at ( Q ), bar)</th>
<th>( P, \text{ W} )</th>
<th>Energy consumption, kWh/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lewatit S1668</td>
<td>274</td>
<td>1.1</td>
<td>( 0.84 \times 10^4 )</td>
<td>( 7.33 \times 10^4 )</td>
</tr>
<tr>
<td>DOW MarathonC</td>
<td>274</td>
<td>1.1</td>
<td>( 0.84 \times 10^4 )</td>
<td>( 7.33 \times 10^4 )</td>
</tr>
<tr>
<td>DOW Monosphere C400L</td>
<td>274</td>
<td>2.1</td>
<td>( 1.6 \times 10^4 )</td>
<td>( 14 \times 10^4 )</td>
</tr>
<tr>
<td>Lewatit MDS1368Na</td>
<td>274</td>
<td>4.9</td>
<td>( 3.73 \times 10^4 )</td>
<td>( 32.7 \times 10^4 )</td>
</tr>
</tbody>
</table>

With a higher operating capacity, a lower frequency of regeneration can be applied. Different number of regeneration per year with different regeneration concentrations use different amount of salt. The results for the salt consumption for three scenarios of 140 g/l, 100 g/l and 60 g/l are shown in table 5.

Table 5: Salt quantity for resins with regeneration by different concentration

<table>
<thead>
<tr>
<th>Resin</th>
<th>No reg. per year</th>
<th>Scenario 1: 140 g/l, kg</th>
<th>No reg. per year</th>
<th>Scenario 2: 100 g/l, kg</th>
<th>No reg. per year</th>
<th>Scenario 3: 60 g/l, kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>( 2.14 \times 10^5 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>( 2.14 \times 10^5 )</td>
<td>23</td>
<td>( 1.76 \times 10^5 )</td>
<td>23</td>
<td>( 1.06 \times 10^5 )</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>( 1.60 \times 10^5 )</td>
<td>17</td>
<td>( 1.3 \times 10^5 )</td>
<td>16</td>
<td>( 0.73 \times 10^5 )</td>
</tr>
<tr>
<td>4</td>
<td>22</td>
<td>( 2.36 \times 10^5 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Comparison of the salt and energy consumption by different resins per 1 m\(^3\) of produced water is shown in figure 24. The resins 'S1668' and 'Marathon C' performed very similar. The resin 'MDS1368' had the highest energy consumption and highest salt consumption. The resin 'C400L' consumed less salt than other resins. It also required less energy than the resin 'MDS1368' but more than the resins 'S1668' and 'Marathon C'.

The salt consumption was calculated with accuracy of 6.8 to 8.1 %.
The errors of the measured values are shown in Appendix.

Waste water produced by the ion exchange treatment step included NaCl in the amount as it is requited for regeneration and ammonium. The waste water went to the waste water treatment plant.

Data on salt and energy consumption, amount waste water, amount of resin and also distance from the production sides for transportation was summarized in inventory table 6. For the further use as inputs for the life cycle assessment.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lewatit S1668</th>
<th>DOW Marathon C</th>
<th>DOW Monosphere C400L</th>
<th>Lewatit MDS 1368Na</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of resin, m$^3$</td>
<td>13.6</td>
<td>13.6</td>
<td>13.6</td>
<td>13.6</td>
<td>Life time - 10 years</td>
</tr>
<tr>
<td>Amount of resin, kg</td>
<td>$1.1\times10^3$</td>
<td>$1.1\times10^3$</td>
<td>$1.1\times10^3$</td>
<td>$1.1\times10^3$</td>
<td>Density: 840; 820; 830; 840 g/l</td>
</tr>
<tr>
<td>Distance, km</td>
<td>620</td>
<td>1122</td>
<td>1122</td>
<td>620</td>
<td>Lewatit - Bitterfeld, DOW - Fombio, Italy</td>
</tr>
<tr>
<td>Amount of salt, scenario 1</td>
<td>$2.14\times10^5$</td>
<td>$2.14\times10^5$</td>
<td>$1.6\times10^5$</td>
<td>$2.36\times10^5$</td>
<td>Salt concentration 140 g/l</td>
</tr>
<tr>
<td>Amount of salt, scenario 2</td>
<td>-</td>
<td>$1.76\times10^5$</td>
<td>$1.3\times10^5$</td>
<td>-</td>
<td>Salt concentration 100 g/l</td>
</tr>
<tr>
<td>Amount of salt, scenario 3</td>
<td>-</td>
<td>$1.06\times10^5$</td>
<td>$0.73\times10^5$</td>
<td>-</td>
<td>Salt concentration 60 g/l</td>
</tr>
<tr>
<td>Distance, km</td>
<td>151</td>
<td>151</td>
<td>151</td>
<td>151</td>
<td>AkzoNobel</td>
</tr>
<tr>
<td>Energy for operation, kWh</td>
<td>$0.92\times10^5$</td>
<td>$0.92\times10^5$</td>
<td>$1.75\times10^5$</td>
<td>$4.8\times10^5$</td>
<td>Pump efficiency 80%, wind energy</td>
</tr>
<tr>
<td>Waste water, amount of salt, kg</td>
<td>$2.14\times10^5$</td>
<td>$2.14\times10^5$</td>
<td>$1.6\times10^5$</td>
<td>$2.36\times10^5$</td>
<td>The same as amount of salt for regeneration</td>
</tr>
<tr>
<td>Waste water, amount of NH$_4^+$, kg</td>
<td>439</td>
<td>432</td>
<td>431</td>
<td>426</td>
<td></td>
</tr>
</tbody>
</table>
The environmental impacts of climate change freshwater eutrophication are modeled by the SimaPro software and shown in figure 25a and 25b. The contribution to both categories were almost the same for the resins 'S1668' and 'Marathon C'. The 'MDS1368' had the highest impact and the 'C400L' had the smallest impact. The energy contributed very little. The salt production and transport showed the biggest contribution to the impacts. The resin contributed a little bit different to climate change for the resins 'S1668' and 'MDS1368' and resins 'Marathon C' and 'C400L'.

![Figure 25: Environmental impacts: Climate Change and Freshwater eutrophication](image)

Environmental impacts of the process with salt concentration of 140, 100, 60 g/l are shown in figure 26. The contribution to climate change and freshwater eutrophication is in proportion to the amount of salt used. The reduction of impacts is not linear because amount of salt is reduced not linearly. The amount of salt per regeneration is reduced but operating capacity also reduced and number of regeneration per year is increased.

### 4.3 Cost analysis

In addition conclusion about the costs of the process has to be done. The results for the cost analysis are shown in figure 27. The cost analysis the same functional unit was used as for the life cycle assessment. The price for the resins 'S1668', 'Marathon C' and 'C400L' was 2000 €/m³ and for the resin 'MDS1368' it was 10000 €/m³, NaCl cost 0.25 €/kg and energy cost 0.11 €/kWh. The costs of the process with 'S1668', 'Marathon C' and
Figure 26: Comparison of environmental impacts with different concentration of regeneration

'C400L' resins are comparable. The treatment with the resin 'MDS1368' is the most expensive.

Figure 27: Costs
5 Discussion

The interpretation of the results of the experiment on the pilot unit and life cycle assessment will be discussed below. Additionally limitations of the research will be mentioned in this chapter.

The results of the experiment on operating capacity were calculated based on the data from the breakthrough curves. They show the following trends. The tested coarse resins 'S1668' and 'Marathon C' demonstrated similar operating capacity. The fine resin 'C400L' had higher operating capacity than the coarse resins 'S1668' and 'Marathon C'. This is due to the fact that the small beads resin has higher surface area of the beads in comparison with bigger beads resin. Therefore the fine resin has more active sides with sodium for the ion exchange process. The 'MDS1368' resin showed lower operating capacity than other tested resins. This is because the small beads were highly compacted. Thereby preventing ammonium from going inside the resin to exchange with sodium.

The operating capacity of the first breakthrough runs was higher than the operating capacity for the next cycles for all four resins. This might be because the resin is more selective to other ions present in the water, such as Ca²⁺, Mg²⁺, Fe²⁺ and K⁺ ions. The selectivity is based on the electromagnetic strength of ions. After the resin exchanges sodium to calcium some of the calcium ions stay bonded to the resin even after regeneration. The operating capacity of the next breakthrough cycles depends on the salt concentration for regeneration. Higher concentrations of salt will increase the likelihood of release of bonded ions. If the salt concentration, during multiple regenerations, is the same, the breakthrough runs will have the same operating capacity.

The theoretical capacity, given by the suppliers, differs from the results of the experiment for coarse resins 'S1668' and 'Marathon C'. The resin 'C400L' demonstrated the highest theoretical and operating capacity. The 'MDS1368' resin demonstrated the smallest theoretical and operating capacity. The coarse resins 'S1668' and 'Marathon C' had the same capacity. In practice even though the theoretical capacity of the resin 'S1668' was higher, the operating capacity was in the range of 5.5 - 7.3 % from the theoretical capacity and did not significantly differ for different suppliers. The total operating capacity including some other ions was higher than operating capacity for ammonium. It was in the range of 14.5 - 19 % from the theoretical capacity. It can be assumed that the operating capacity for other not tested resins will be in the same range if feed water quality and salt concentration for regeneration are the same with this experiment.
The sustainability of the process was assessed based on the contribution to climate change and freshwater eutrophication. The water treatment process included energy and salt consumption, waste water, resin production and transport of materials. The fine resins 'C400L' and 'MDS1368' consumed more energy than coarse resins 'S1668' and 'Marathon C' because the small beads resins create higher pressure drop in the column than the resin with the bigger beads. The resin 'MDS1368' consumed even more energy than the fine resin 'C400L' because of very compacted resin bed. It may be that there is a threshold of the beads size for the given operational conditions, related to the height of the resin bed and the flow rate. The flow rate in the full scale plant will not change the behavior of the resin as the nominal flow rate (27 BV/h) and maximum flow rate (40 BV/h) in the full scale plant are both lower than in the experiment (50 BV/h). The bed height for the full scale plant is designed of 1.5 m. It is higher than the tested height bed of 1 m. It is therefore recommended to test the resin 'C400L' with the higher resin bed to exclude the opportunity that it will be compacted as the resin 'MDS1368'.

According to the life cycle assessment the salt production and salt transportation contribute the most of the other process for climate change and freshwater eutrophication. The resin 'C400L' uses less salt for regeneration because it needs less frequent regeneration. The other resins with the smaller operating capacity require more salt for regeneration per year. The contribution to the environmental impacts correlated with salt consumption. As Oasen uses wind energy this energy contributes very small to the environmental impacts. The resin production and transport does not contribute a lot to environmental impacts because of long life time of 10 years. In addition cost of the process was calculated. The salt cost contributes significantly to the costs of the whole ion-exchange process.

As the salt is important, an experiment with different salt concentration was conducted. The breakthrough curves did not show significant reduction of the operating capacity. It can be explained by two ways. First, there was more than enough salt for regeneration for all three regeneration because the contact time is quite long. In this case it is recommended to reduce the contact time and see how the operating capacity will change. Second, the cycles were repeated only once due to limited amount of time, thus operating capacity was not yet established. In this case it would be better to repeat the experiment with different concentrations several times.

The life cycle assessment was done for different amount of salt. The contribution to environmental impacts is not linear as the amount of salt is not reducing linear. When the amount of salt per regeneration is reduced, the operating capacity will also be reduced, and the number of regener-
ations per year will increased. It is therefore recommended to continue research with different salt concentration to find a balance between the amount of salt and operating capacity.

An important limitation of this research was the accuracy of the measured values. For calculation of operating capacity there are four measured values: time, concentration of ammonium, flow and Volume of the resin bed. The combined margin of error of these parameters give a margin of 10% of operating capacity. The margin of error could be decreased to below 2.5% by using the recommendation in the conclusion. For calculation of the amount of salt it is important to keep probability of error low to be able to compare between the resins. The error of the salt calculation is in the range of 6.8 to 8.1% which makes the comparison better.

6 Conclusion

The answer to the research question what is an optimal resin to use in the ion exchange treatment with the given water quality and operating conditions is the following. The fine resin has higher operating capacity that coarse resin, but can demonstrate unpredictable behavior, a highly compacted resin bed. The resin with higher operating capacity consumes smaller amount of salt and therefore contributes the least to environmental impacts. The salt cost is also a significant part of the process costs. That is why it is recommended to conducted an extra research on the optimal concentration for regeneration. It can reduce environmental impacts and process costs.

To increase accuracy of the further research calculation it is recommended to measure the concentration of ammonium with the ammonium analyzer with the smaller time intervals.

To reduce amount of salt used it is recommended continue research with salt concentration for regeneration and consider the reuse of the solution after regeneration to dissolve salt for the next regeneration.
Appendices

A Pilot unit operation

The operation of the pilot unit consists of four modes:

1. Operational mode
2. Lifting up
3. Regeneration
4. Rinsing

Operation mode. Four different resins in four columns were tested simultaneously. The tested water was collected in the buffer tank and then it was pumped through the columns downflow. The pump work was automated and managed by the digital control panel. The valves controlled the water flow direction and they were operated manually in the operation mode. The outflow of the system was directed to the sewage system.

Lifting up. To prevent the resin bed from disturbance during regeneration it has to be lifted up. The water was pumped upwards through the columns. The valves were in the regeneration position. The compacted resin bed was not influenced by the turbulent flows and better regenerated. The phase lasted for 3 minutes. When the resin is stable the column is ready for regeneration.

Regeneration mode. Regeneration was completed for one column at the time. During the regeneration of one column other columns are still. The brine was prepared in the separate tank. The air-pump was pumping the brine to the pressure vessel. From the pressure vessel brine was pumped upflow. The phase lasted for 20 minutes.

Rinsing. To remove the extra salt after regeneration the resins was rinsed with clean water. The phases lasted for 30 minutes. When the conductivity of the effluent is less than 1000 $\mu$ Siemens/m the rinsing phase was stopped.

Table 7 contains a summary of the pilot unit operational parameters.
### Table 7: Operational parameters for the pilot study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin</td>
<td>Strong acid cation exchanger</td>
<td>-</td>
</tr>
<tr>
<td>Flow direction</td>
<td>Down flow</td>
<td>-</td>
</tr>
<tr>
<td>Regeneration mode</td>
<td>Countercurrent</td>
<td>-</td>
</tr>
<tr>
<td>Column diameter</td>
<td>0.16</td>
<td>m</td>
</tr>
<tr>
<td>Resin depth</td>
<td>1</td>
<td>m</td>
</tr>
<tr>
<td>Service flow rate</td>
<td>50</td>
<td>BV/h</td>
</tr>
<tr>
<td>Flow rate per column</td>
<td>0.6-1</td>
<td>m3/h</td>
</tr>
<tr>
<td>Column resin volume</td>
<td>0.02</td>
<td>m3</td>
</tr>
<tr>
<td>Regenerant type</td>
<td>NaCl</td>
<td>-</td>
</tr>
<tr>
<td>Regenerant strength</td>
<td>60-140</td>
<td>g/l</td>
</tr>
<tr>
<td>Salt loading rate</td>
<td>450-1050</td>
<td>kg NaCl/m³</td>
</tr>
<tr>
<td>Regeneration flow rate</td>
<td>0.45</td>
<td>m3/h</td>
</tr>
<tr>
<td>Rinse flow rate</td>
<td>0.3</td>
<td>m3/h</td>
</tr>
</tbody>
</table>
B Breakthrough curves

Figure 28: Breakthrough curves: ammonium concentration vs. time

Figure 29: Breakthrough curves with different concentration for regeneration: ammonium concentration vs. time
### Statistics

Table 8: The error margin of the operating capacity in %

<table>
<thead>
<tr>
<th>Regen.</th>
<th>$t_{\text{leak}}$</th>
<th>$t_{\text{break}}$</th>
<th>Conc. ammon. in</th>
<th>Flow</th>
<th>Volume</th>
<th>Capacity</th>
</tr>
</thead>
<tbody>
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<td>Column 1 - Lewatit S1668</td>
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<td></td>
<td></td>
<td></td>
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<td>5.2</td>
<td>6</td>
<td>21.8</td>
</tr>
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<td>0.1</td>
<td>10.6</td>
<td>2.2</td>
<td>6</td>
<td>18.9</td>
</tr>
<tr>
<td>5</td>
<td>0.6</td>
<td>0.1</td>
<td>10.6</td>
<td>3.3</td>
<td>6</td>
<td>20.0</td>
</tr>
<tr>
<td>Column 2 - DOW Marathon C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.9</td>
<td>0.1</td>
<td>10.6</td>
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<td>6</td>
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</tr>
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<td>0.1</td>
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<td>3.1</td>
<td>6</td>
<td>19.8</td>
</tr>
<tr>
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<td>0.1</td>
<td>10.6</td>
<td>3.3</td>
<td>6</td>
<td>20.0</td>
</tr>
<tr>
<td>Column 3 - DOW Monosphere C400L</td>
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<td></td>
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</tr>
<tr>
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<td>2.9</td>
<td>6</td>
<td>19.5</td>
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<tr>
<td>2</td>
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</tr>
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<td>3.3</td>
<td>6</td>
<td>19.9</td>
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<td>2.8</td>
<td>6</td>
<td>19.4</td>
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<td>Column 2 - DOW Marathon C</td>
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</tr>
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<td>2.2</td>
<td>6</td>
<td>18.8</td>
</tr>
</tbody>
</table>
## Table 9: The error margin of the salt consumption

<table>
<thead>
<tr>
<th>Conc. of reg., g/l</th>
<th>Conc. of satur. sol., g/l, %</th>
<th>Flow, %</th>
<th>Volume, %</th>
<th>Time, %</th>
<th>Salt, %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Column 1 - Lewatit S1668</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>0</td>
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<td>6</td>
<td>0.1</td>
<td>8.1</td>
</tr>
<tr>
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<tr>
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<td>8</td>
</tr>
</tbody>
</table>
D  Flow deviation

Figure 30: Flow deviation
Flow deviation

Figure 31: Flow deviation during the experiment with salt concentration of 100 and 60 mg/l
References


Millar, G.J. et al. (2016). “Factors influencing kinetic and equilibrium behaviour of sodium ion exchange with strong acid cation resin”. In: *Separation and Purification Technology* 163, pp. 79–91.


