Scaling of reverse osmosis permeate

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Bachelor Thesis
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Second supervisor: Bas Heijman
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TU Delft Delft University of Technology
Challenge the future

Acknowledgement

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Bas Heijman who was my secondary supervisor helped me in situations where me and Amir could not figure it out.

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Abstract

Reverse Osmosis is a possible process production of drinking water from saline or freshwater, in which water is forced through a semi permeable membrane resulting in production of pure water with very low ion concentrations. This water is then remineralized to prevent corrosion and make it suitable for consumer usage. It is reported that at higher temperatures, for instance in boilers, scaling occurs in an earlier stage in drinking water produced by RO than water produced with conventional water treatment plant. Presumed is that the absence of certain materials removed by RO during filtration is the cause of this early scaling. One of these substances is humic acids.

In this research the effect of addition of several concentration of HA on scaling is measure at high temperature and calcium concentration of approximately 20mg/l and 40mg/l. The results show that dosing of at least 3 mg/L of humic acids can significantly reduce scaling in RO permeate water. In water with lower Ca^{2+} concentrations no scaling was measured thus the experiment was repeated with a higher initial Ca^{2+} concentration.

Contents

1

Introduction

Water, the element of life, covers 71% of the earth's surface. Yet only 2.5% of this water is freshwater from which 0.6% is accessible for use and the rest being located at the poles [**1**]. Safe drinking water is essential for the survival of humans and other species. Access to safe drinking water has improved over the last decades in almost every part of the world, but approximately one billion people still lack access to safe water and over 2.5 billion people lack access to adequate sanitation **[2]**. With the increasing world population, climate change, and industrialisation of developing countries, the global demand of freshwater continues to grow. Therefore to meet the growing demand of fresh water, it is of utmost importance to find a safe and efficient method to turn sea water and brackish water into fresh water. One of these methods is Reverse Osmosis (RO), which uses membrane technology to clear water from impurities.

1.1. Membrane Operation

Membrane operations are processes which separate the salts from the solutions and are classified based on their driving force into four categories: Electrical forces, pressure forces, separation by concentration and heat gradients. The pressure driven membranes can be categorized based on their rejection ability into four categories: Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO)**[3]**. MF and UF use microporous membranes to remove particulate matter simply by sieving on the size of the particles. Together with the particulate matter, turbidity and microorganisms are also removed. However, these two systems do not remove dissolved particles such as ions. RO and NF do remove these dissolved particles because of their semi-permeable membranes and diffusion controlled separation process. NF removes almost all types of particles, except for the monovalent ions whilst RO removes even most of the monovalent particles, such as natrium (Na^+) and kalium (K^+), leaving pure water as permeate. Figure 1 shows the rejection potential of different type of membranes.

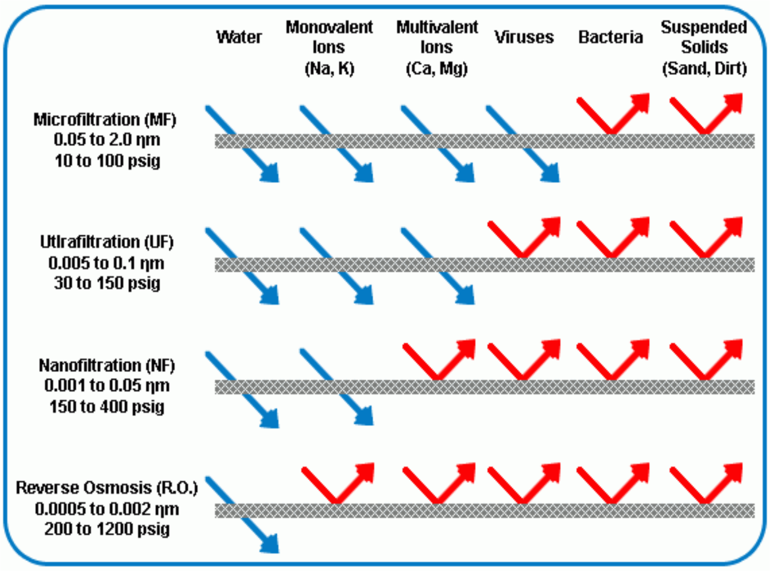


Figure 1: Membrane filtration characteristics

1.2. Reverse Osmosis

Osmosis is a natural phenomenon in which a solvent (usually water) passes through a semipermeable barrier or a membrane from the side with lower solute concentration to the higher solute concentration**[4]**. This is shown in the left picture of Figure 2.

The pressure requires to achieve osmotic equilibrium is known as the osmotic pressure.
The reverse of this process is called reverse osmosis (right picture of Figure 2). It is a separation process that uses pressure to force solvent (water) through the membrane, which retains the solute (contaminate) on one side and allows the pure solvent (water) to pass to the other side. This process makes it possible to convert brackish or seawater into drinking water.

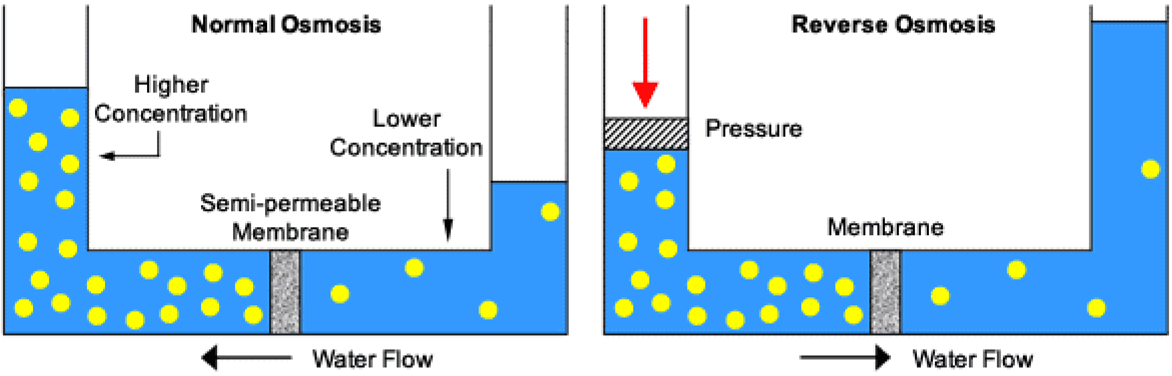


Figure 2: Principle of osmosis and reverse osmosis

1.3. RO Treatment Plant

Reverse osmosis has become important as an energy and operating cost saving process for brackish water and seawater compared to other desalination processes**[5]**. The membrane-based RO-treatment plant consists of three parts; pretreatment, RO-unit and post treatment.

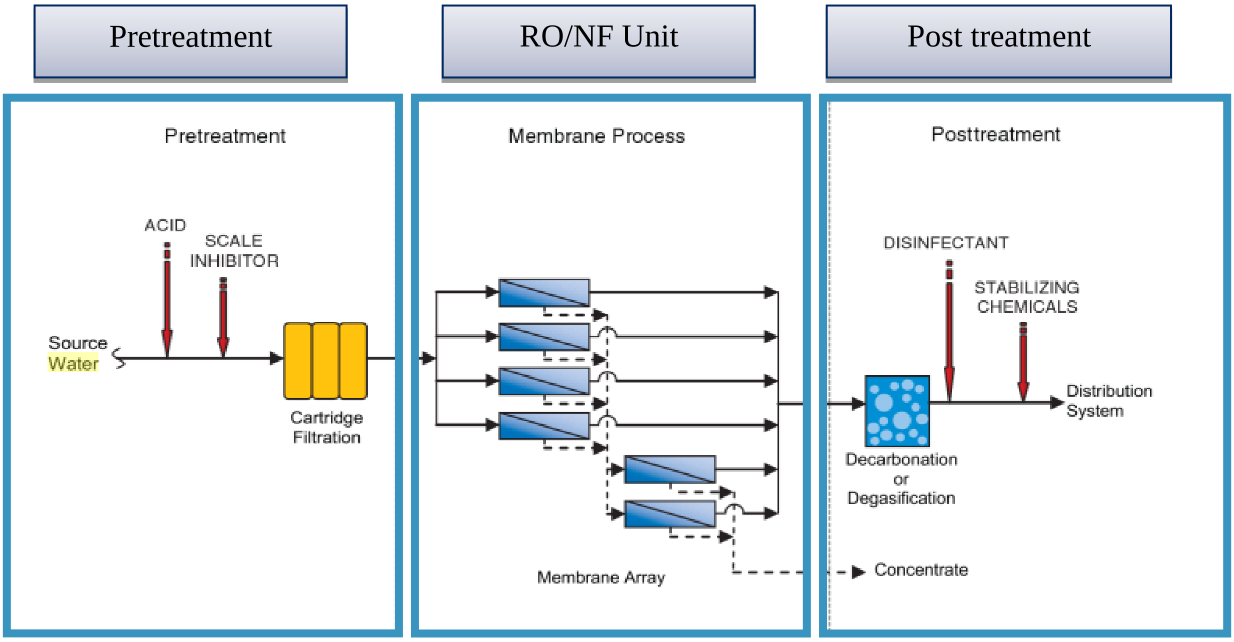


Figure 3: RO treatment plant

Pretreatment

The primary aim of pretreatment is to remove all the organic, colloidal and biological matter from the feed water before it enters the RO module. Pretreatment provides an increase of efficiency and life expectancy for the RO-elements by minimizing fouling, scaling and degradation of the membrane**[6]**.

RO-unit

After the pretreatment step, the feed water is ready to enter the RO-unit. It enters the RO-unit with a certain concentration C_f and flow Q_f. The water that is pressed through the membrane is called the permeate (Q_p). The permeate contains only a part of monovalent ions of the feed water and all other materials are removed from it (C_p). The rejected part is called ‘rejection’ or ‘concentration’ and has a flow Q_c and a concentration C_c. In the RO-unit the following flow and mass balances are applicable:

Flow balance: $Q_{f} = Qp + Q_c$

Mass balance: $Q_f * C_f = Q_{p*} C_p + Q_{c*} C_c$

This is shown in Figure 4.

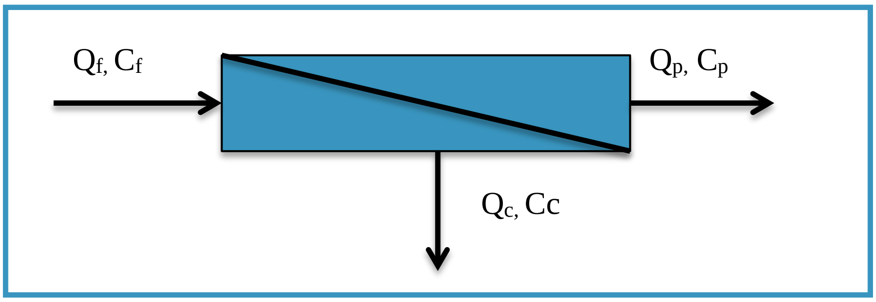


Figure 4: Mass and flow balance RO-unit

Post-treatment

Before the pure water is distributed to the consumers, some post-treatment step has to be applied on the produced water from reverse osmosis membrane, such as stabilization and remineralisation in order to be able to produce drinking water conform the drinking water regulations. Ions such as calcium or/and magnesium are added into permeate to prevent the corrosion of the pipes and provide healthy water to consumer. The amount of Ca^{2+} and Mg^{2+} expressed in mmol/l is called the total hardness. According to the

Water Supply Act the total hardness should be between 1-2.5 mmol/l**[7]**. Furthermore, the remineralized water has to be disinfected to prevent regrowth of bacteria inside the transportation pipelines. The materials used for remineralization are not pure and generally contain some impurities. When the permeate passes through these materials or when these materials are added into the permeate water, the permeate water can be infected by impurity of these materials. By passing the time and changing the conditions, for instance during transportation in pipelines, biological growth can occur and therefore water can be contaminated. Therefore, a disinfection step such as UV-disinfection is required after remineralization**[7]**.
Corrosiveness of water is often characterised by Langelier saturation index (LSI). If the LSI is negative, the water is corrosive to calcium carbonate. For LSI equal to zero, the water is non-aggressive and no deposition layer will be formed. Positive LSI can result in deposition of calcium carbonate**[7]**.
The aim of remineralisation of RO permeate is to produce a slightly positive LSI to prevent pipe corrosion and to have a fine precipitation layer for additional protection**[7]**.

1.4. Remineralization Process

There are several remineralisation processes of which the dissolution of calcium carbonate with carbon dioxide in water is the most effective and widespread**[8]**. In order to attain the required amount of calcium ions, the permeate water goes through a calcium carbonate column and CO_2 is added. The chemical reaction which occurs when the permeate passes through the column is as follows:

$CaCO_3 + CO_2 + H_20 \text{-->} 2\ HCO_3\text{-} + Ca^{2+}$

1.5. Objective of the Study

Water attained from a reverse osmosis treatment has shown to have earlier scaling under higher temperatures than water from conventional treatment plants that has the same Ca^{2+} concentration. Presumed is that the absence of materials removed by RO, such as humic acids, sodiumbicarbonate and trisodiumphosphate is the main cause of earlier scaling occurance. This study will focus on the effect of humic acids as an anti-scalant.

2

Methodology

In order to study the effects of humic acids on scaling , the experimental conditions should remain constant. Therefore variables such as the pH and temperature of the RO permeate, and contamination by salts in humic acids

2.1.1 Preparation of humic acids

Humic acid is a principal component of humic substances, which are the major organic constituents of soil (humus), peat and coal. It is produced by biodegradation of dead organic matter. It is not a single acid; rather, it is a complex mixture of many different acids. Humic acids can form complexes with ions that are commonly found in the environment creating humic colloids**[9]**. Humic acids are commonly used as a fertilizer in agriculture. Humic acids used in this experiment are a byproduct of wastewater treatment plants, thus are cheap to purchase. A downside however is that these humic acids are contaminated with various salts originating from the waste water treatment plant. In order to remove these salts as much as possible we use membrane dialysis.

2.1.2 Dialysis Setup

Dialysis is the process of exchanging of solutes through a semipermeable membrane. Through diffusion dissolved substances will move from an area of high concentration to an area of low concentration.
At our disposal we have a 3500 Dalton MWCO Spectra/Por® dialysis tubing membrane. The molecular weight cut-off (MWCO) refers to the lowest molecular weight solute that is 90% retained by the membrane.

For our setup we have a sample containing 100 mL of untreated humic acids. The buffer solution (called the dialysate) consists of Ultra Pure Water that contains no ions and minerals

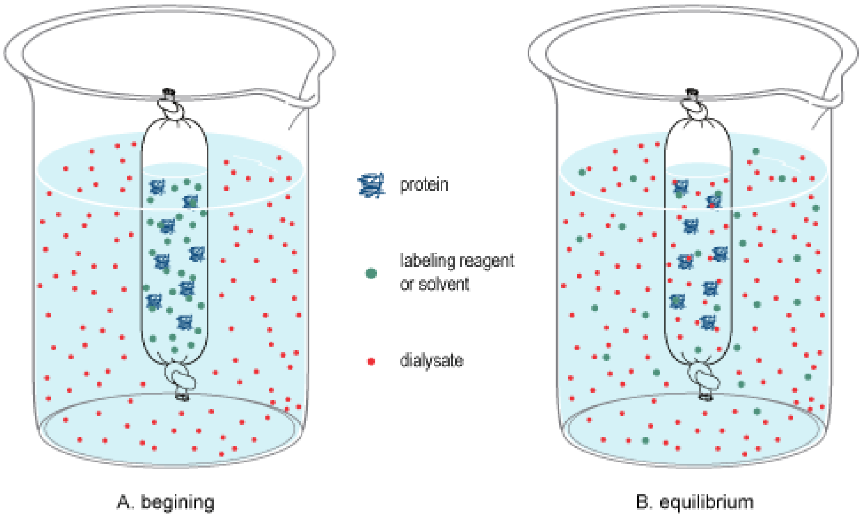


Figure 5: A typical dialysis setup

Due to the pore size of the membrane, large molecules in the sample cannot pass through the membrane whilst small molecules will diffuse freely across the membrane until equilibrium is reached. By replacing the dialysate with fresh dialysate one can reduce the concentration of these small molecules even further.
We repeated this process of replacing the dialysate with fresh dialysate until no change in the concentration of salts in the dialysate was observed. The concentration of salts is measured with an electrical conductivity meter (EC-meter) by measuring the conductivity of dissolved salts.

At the start our 100 mL sample of untreated humic acid had an electrical conductivity of 800 µS/cm. After a period of a week at the end of dialysis the sample only had 120 µS/cm. In comparison, tap water has a conductivity of 300-600 µS/cm and Ultra Pure water which was used as a dialysate has a conductivity of 1 µS/cm.

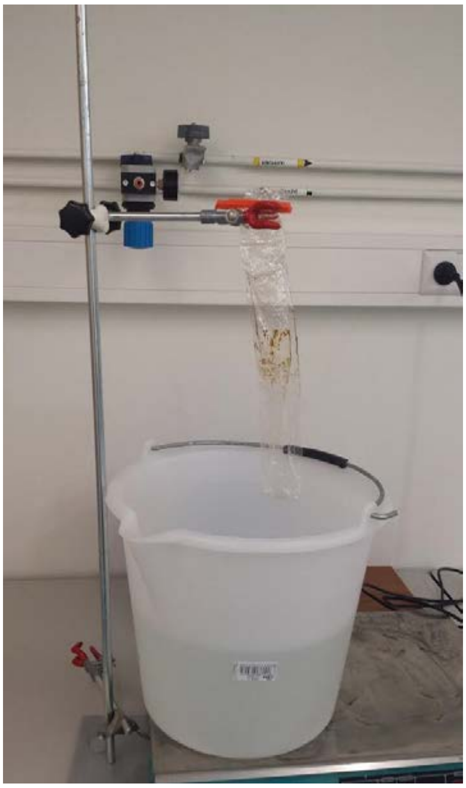


Figure 6: The dialysis membrane after emptying

2.2. TOC measurement

After dialysis the sample is then put through a Total Organic Carbon (TOC) analyser to measure its organic carbon content. This is done by first removing the inorganic carbon and then measuring the leftover (organic) carbon. Since this process is done by purging an acidified sample, it’s more accurate to call it the leftover carbon as non-purgable organic carbon (NPOC).

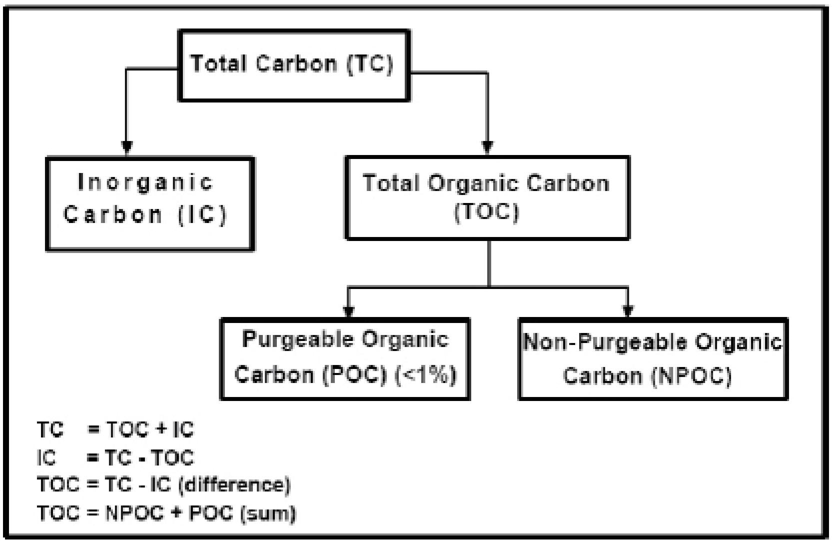


Figure 7: A carbon component Flow chart

The NPOC measured from the untreated humic acid sample contained 800 mg/L organic carbon. The sample which was treated with dialysis contained 200 mg/L. this means that

2.3. Preparation of water samples

The water that is going to be used is Ultra Pure Water from the TU delft waterlab. This water is pure water with very little traces of ions. In order to stabilize its pH a buffer solution will be added to the water.

$CaCl_2 + 2\ NaHCO_3 \leftrightarrows 2\ Na^+ + 2\ Cl^- + CaCO_3 + H_2CO_3$

The sodium bicarbonate will act as a buffer solution whilst the calcium chloride will disassociate into calcium and chloride ions providing us with the necessary Ca^{2+} concentration of water.
Concentration of Ca 20 and 40mg/l.

2.4. Experiment set-up

The experiment will be done by filling six bottles of 1 litre prepared solution and varying dosage of humic acids. We will also add 1mmol of calcium carbonate in each bottle so it can act as a surface for calcium to precipitate on. A 7th bottle filled with regular tap water will be used as a controlling sample.
The bottles will be heated to 90° C and we will take samples every half hour for the first 2 hours. After that we will take samples twice a day for a period of 6 days. One at 20 degree.

2.4. Ion chromatography

The waterlab at the TU Delft has as a Methrohm IC chromatograph, which consists of an auto-sampler, an anion system, a cation system and a computer with MagIC Net software. Ion chromatography can be used to separate and measure inorganic and short-chain organic anions and cations. The measurement of cations and anions can be done independently from each other in different machines. In this study only the cation machine is needed to measure the Ca^{2+} concentration of vial samples. The separation of ions is possible due to their affinity. A HPLC pump pushes eluent at high pressure and with an accurate flow rate through the column. At the end of the column, a conductivity detector measures the signal produced by each separated ion species. Each signal peak represents a certain concentration. The mentioned auto-sampler is able to measure a maximum of 56 samples at a time. This happens automatically with the present needle. A solution of 3mMol nitric acid (HNO3) is used for cleaning of the column after each measurement. For calibration of the system and controlling of the IC measurements 3 vials of known concentrations are used. These are called ‘standards’ and are in our case Ca^{2+} concentrations of 1, 10 and 50 mg/L. The other 53 remaining vials are samples taken from the heated bottles and some blank vials to control the measurements and to prevent any contamination. The results can be put in tables and graphs for further analyses to find the solution to the scaling problem.

The measurements are done in two separate groups at two weeks for a total of 182 samples. The dissolved Ca concentration is measured for 91 samples with initial concentration of approximately 20mg/l (first group) and 91 samples with initial concentration of 40mg/l. The samples were taken throughout a period of 6 days, then they were diluted and their calcium concentration was measured using a IC-chromatograph.

3

Results

3.1. Experiments week 1

In the first week of experiments humic acids were dosed in quantities of ranging from 1 mg/L to 10 mg/L. One sample dosed with 1 mg/L humic acid was not heated and used as a controlling sample. Furthermore a sample with drinking water was also heated to show scaling properties in normal drinking water.

The humic acids used in this experiment all went through a dialysis membrane filtration as mentioned in chapter 2.

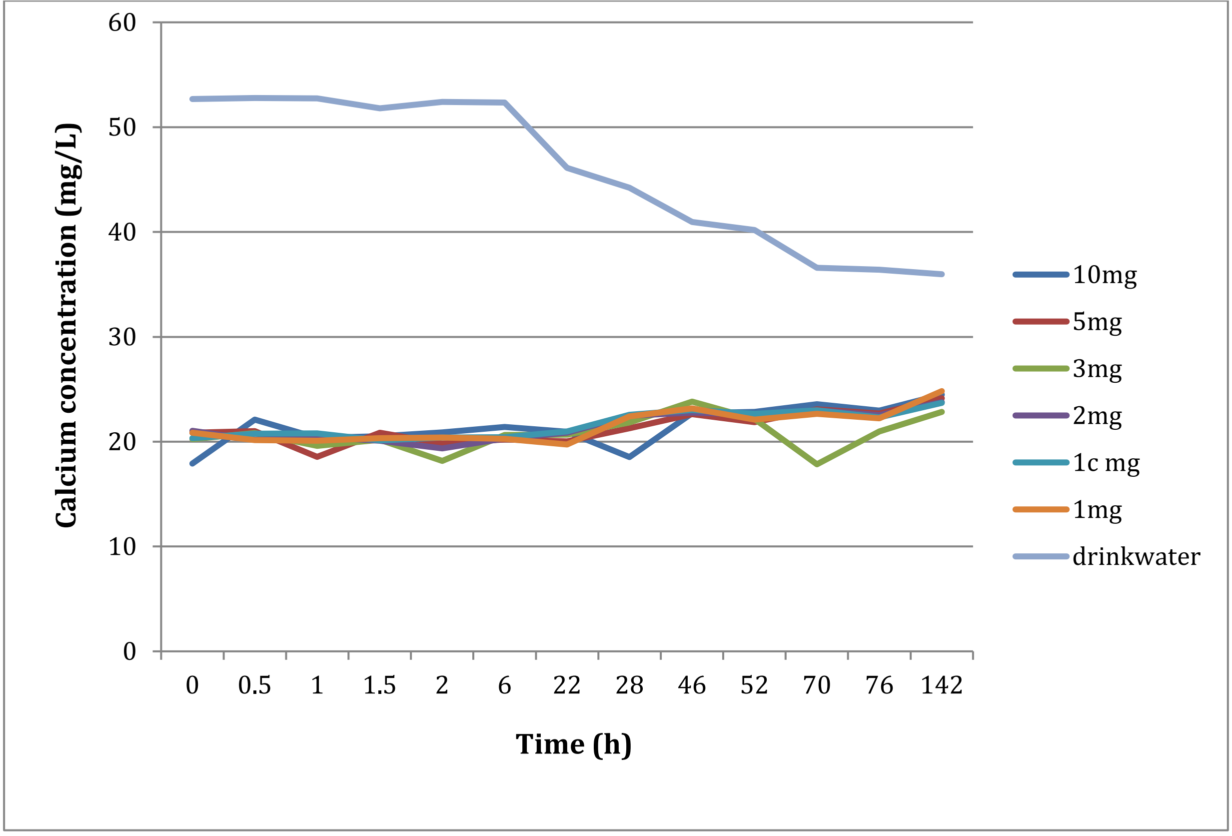
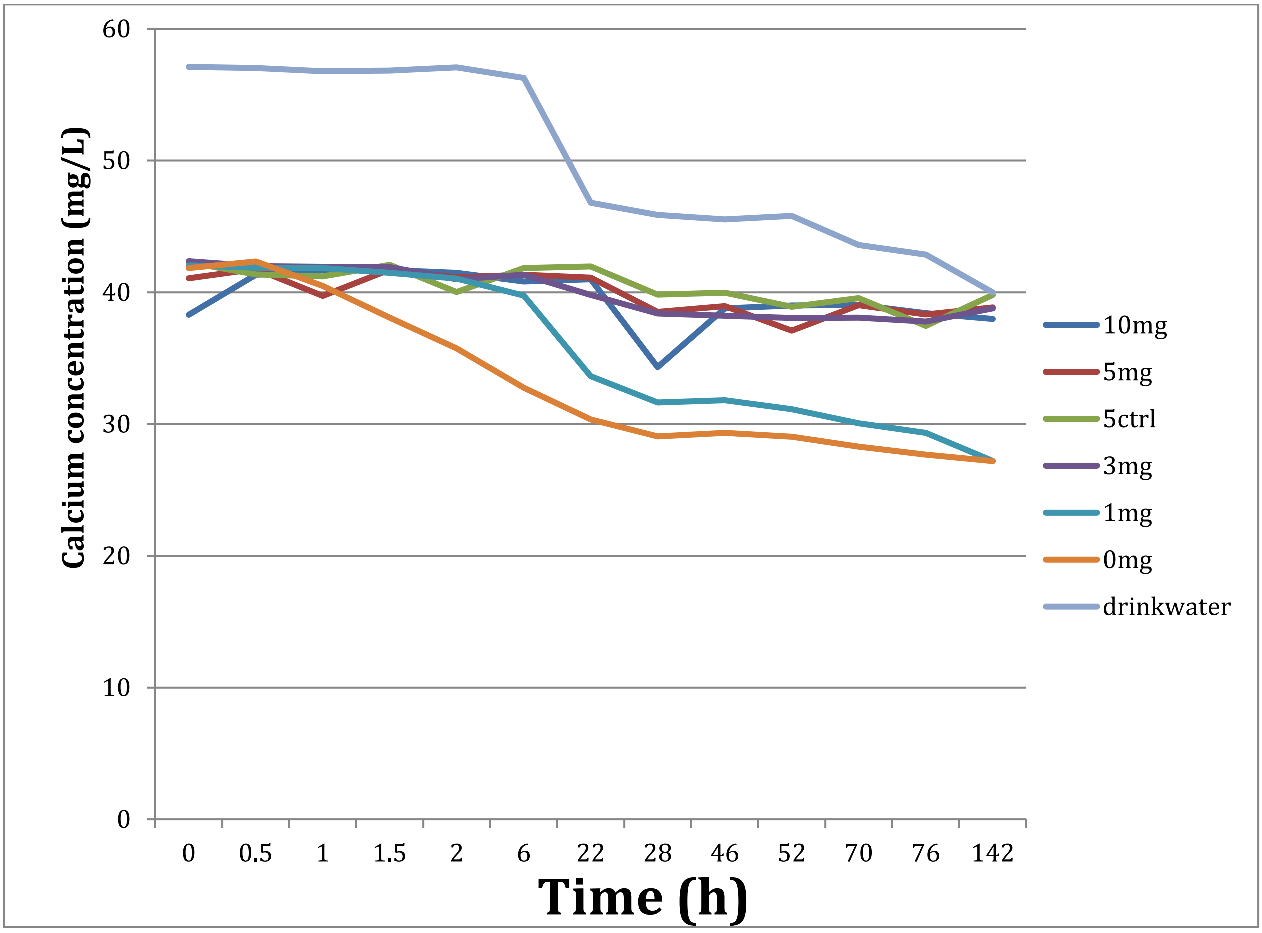


Figure 8: Graph of week 1 of experiments

As seen in figure 8 the sample with drinking water clearly shows scaling occurring after around 22 hours of heating. What can also be observed is that due to the low amount of calcium in the samples no scaling takes place.

3.2. Experiments week 2



As expected the sample with no humic acid added to it shows the earliest scaling after just 1 hour without the water even reaching 90°C. The drinking water again shows scaling after 22 hours. Scaling in the sample with 1 mg/L humic acid is significantly delayed. Scaling in all other samples with higher concentrations of humic acids show almost no or negligible amount of scaling thus confirming our hypothesis of humic acids acting as an anti-scalant. Not only do high concentrations of humic acids delay scaling, they complete stop the process from happening.

4

Conclusion

References

[1]

[2]

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Appendix A

Plan van aanpak

Bachelor Eindwerk CTB3000
Naam: Heysem Ugurlu

Studentnummer: 4149793

Onderwerp: Scaling of water permeate by reverse osmosis
Begeleiders:
1^e begeleider: Amir Haidari
2^e begeleider: Bas Heijman

Inleiding

Als onderdeel van de bachelor civiele techniek sluiten we het laatste jaar van onze studie af met een bachelor thesis. Hierbij kies je zelf een onderwerp en moet je je academische vaardigheden die je in al die jaren op de TU hebt opgedaan tentoonstellen. De bedoeling is dat je door zelfstanding te experimenteren, ervaring opdoet en alvast een voorproefje krijgt van wat er te wachten staat in de master. Deze plan van aanpak is opgesteld voor mezelf en mijn begeleiders om een idee te krijgen van wat mijn precieze doelstelling is en het tijdsbestek waarin ik dit voor elkaar wil krijgen.

Doelstelling

Toegang tot schoon drinkwater is één van de belangrijkste levensbehoeften van de mens. Schoon drinkwater is schaars, en wordt met de toenemende wereldbevolking en klimaatverandering nog schaarser. Het vinden van een effectieve manier om schoon en veilig water te krijgen is dus van levensbelang. Reverse Osmosis (RO) is één van die manieren om effectief schoon water te verkrijgen door het ontzouten van zeewater of brak water of zuiveren van rivier water.
Alleen is het probleem dat het water eigenlijk te schoon is. Drinkwater dat door conventionele processen wordt vervaardigd bevat onder andere mineralen en ionen. Het pure water dat door RO wordt voortgebracht kan door het ontbreken van deze stoffen bij hoge temperaturen leiden tot kalkaanslag.
Dit onderzoek heeft als doel een beter idee te krijgen waarom water van RO bij hoge temperaturen leidt tot kalkaanslag.

Literatuur

Over dit onderwerp is er nog niet veel onderzoek naar gedaan. Wel zijn er voorgangers van mij geweest die op de TU Delft een soortgelijk onderzoek hebben gedaan. Dus in zekere zin zal mijn onderzoek een voortgang zijn van waar mijn collega studenten mee zijn begonnen. Ter voorbereiding van dit onderwerp heb ik ook het vak Water Treatment gevolgd. Zo nodig kan ik colleges en slides raadplegen voor extra theoretische achtergrond.

Contact met begeleiders

De bedoeling is dat ik minstens 1x per week met mijn begeleider afspreek. Naast face-to-face ontmoetingen kan ik hem altijd mailen of bellen.

Onderzoek

Het onderzoek dat bij mijn eindwerk hoort, voer ik uit in het waterlab van de TU Delft. De benodigde apparatuur is aanwezig en de cursus lab veiligheid heb ik al gevolgd. Mijn begeleider heeft mij al laten zien welke apparaten ik nodig heb en waar ik ze kan vinden.

Tijdsplanning

Week 1: oriëntatie, lab veiligheid afronden, beginnen met opzet, literatuur review
Week 2 t/m 7
Uitvoeren van experimenten
Week 4
Voorbereiding tussenrapport en tussenpresentaties

Week 7
Eindrapport inleveren ter controle bij begeleider
Week 8
Eindrapport definitief inleveren en eindpresentatie voorbereiden.
Week 9
Eindpresentatie