A New Concept of Ultrafiltration Fouling Control: Backwashing with Low Ionic Strength Water
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A New Concept of Ultrafiltration Fouling Control: Backwashing with Low Ionic Strength Water

Proefschrift

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op gezag van de Rector Magnificus prof. ir. K.C.A.M. Luyben,
voorzitter van het College voor Promoties,

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Chapter 1

Introduction
**1.1 Ultrafiltration (UF) in water treatment**

Because of the excellent quality of the permeate of membrane filtration, it has become increasingly popular in water treatment. Moreover, the number of installation all over the world has increased dramatically over the past decades. Membrane filtration consists of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). MF and UF are low pressure membranes, while NF and RO are high pressure membranes with smaller pore sizes than MF and UF.

In Figure 1.1, an overview of different membrane filtration processes and sizes of compounds removed is shown. In practice, UF is mainly used for the removal of bacteria, turbidity, micro-organisms and viruses (Jacangelo et al. 1995). The successful removal of suspended solids for UF is at least 99%. The removal of bacteria, micro-organisms and viruses is up to 99.99% (MWH 2005). However, the removal of dissolved organics is limited for UF.

![Figure 1.1: Overview of different membrane filtration processes and sizes of compounds removed](image)

NF and RO require high quality feed water, but conventional treatments (such as coagulation and sand filtration) cannot guarantee a stable supply of high quality feed water. Therefore, due to the high removal of suspended solids by UF, it has recently been used as a pretreatment for NF and RO to reduce their fouling.
**Filtration process**

In terms of flow configuration, UF is usually divided into inside-out and outside-in filtration. Inside-out means the active membrane surface is on the inner side of the capillary fibers and the permeate is collected outside of the membrane fibers (as shown in Figure 1.2) The outside-in means that the active surface is outside of the capillary fibers. Inside-out UF is used in surface water treatment. Outside-in UF is often used in membrane bioreactors (MBR) in order to prevent the blocking of fibers with small diameters by the activated sludge.

![Principle of inside-out filtration](image)

Within the inside-out configuration, there are two ultrafiltration modes: cross flow and dead-end. In practice, the dead-end mode is normally applied. As shown in Figure 1.3, feed water is pushed through the UF membrane by pressure. The rejected suspended solids, micro-organisms and viruses remain on the membrane surface, causing membrane fouling. As a result, the resistance of the membrane...
increases and the flux decreases. In full-scale treatment plants, flux is constant, so the transmembrane pressure (TMP) has to be increased to overcome the increased membrane resistance.

**Fouling**

The increase in resistance is due to the deposition of rejected substances, which is generally called fouling. Fouling can be subdivided into different mechanisms:

- Pore blocking
- Adsorption in pores
- Cake layer filtration

Pore blocking describes the fouling caused by the substances that have a similar diameter as the membrane pore size. These substances seal the membrane pores and do not accumulate on each other. Adsorption in pores is caused by substances smaller than the pore size. These substances reach the pores and deposit on the pore wall and accumulate on each other. Cake layer filtration
describes the deposition of substances with diameters larger than the pores. They accumulate on the membrane surface without entering the pores.

**Cleaning (hydraulic and chemical)**

Because of the fouling, UF membranes have to be cleaned periodically to reduce the resistance of membranes. There are two ways to reduce the resistance: 1) hydraulic and 2) chemical cleaning. Hydraulic cleaning includes forward flushing with feed and backwashing with permeate, as shown in Figure 1.4. Chemical cleaning consists of chemical-enhanced backwashing (CEB) and cleaning in place (CIP). CEB is a combination of a normal backwash with chemical dosing, and the membranes are normally soaked in a chemical solution for 10 minutes before rinsing with clean water. Compared to CEB, CIP has a much longer soaking period (normally 24 hours but sometimes up to one week).

![Figure 1.4: Different hydraulic cleanings](image)

Figure 1.5 describes the definitions of filtration cycles and different types of fouling related to cleanings. During the constant flux filtration, TMP increases due to the fouling. After a hydraulic backwash, part of the fouling is removed, causing a reduction in increased TMP. This part of fouling is called hydraulically reversible fouling. On the other hand, the unreduced TMP is caused by the so-called hydraulically irreversible fouling. Because the hydraulically irreversible fouling accumulates over time, a CEB is necessary at a certain point. TMP after a CEB can be significantly reduced, and this reduction is due to the removal of fouling during CEB, called CEB reversible fouling. The fouling that remains after CEB is CEB irreversible fouling. In this case, CIP is normally conducted to recover the permeability of membranes.
In the past decades, membrane filtration (especially low pressure membrane: microfiltration and ultrafiltration), has become increasingly popular in drinking water treatment. That is because membrane filtration is a promising process as a first step in surface water treatment. For example, ultrafiltration (UF) can achieve a better removal of particles and microorganisms than conventional treatments (Laine et al. 2000). However, fouling is the challenge hindering the application of UF (Cho et al. 2000, Hong and Elimelech 1997, Jermann et al. 2008, Jermann et al. 2007).

Fouling results in the increase of energy consumption, in water loss due to hydraulic backwash, in the use of chemicals for cleaning, and eventually in a too early replacement of membranes. Natural organic matter (NOM) is thought to be the main fouling contributor (Dong et al. 2007, Fan et al. 2001). Furthermore, many
researchers have reported that NOM fouling is influenced by some external factors, such as pH and ionic strength (Hong and Elimelech 1997, Katsoufidou et al. 2007, Song and Singh 2005). Hong and Elimelech systematically investigated the impact of pH, ionic strength and concentration of divalent ions on NOM fouling of nanofiltration (NF) with humic acid model compounds, and reported that the NOM fouling of NF increases when the pH of feed water is low (4 in their study), when ionic strength increases, and when the concentration of calcium increases (Hong and Elimelech 1997). They argued that the negatively charged NOM compounds are protonated at low pH values, so they become less negatively charged which can reduces the repulsion force between them and negatively charged NF membranes. When the feed water contains a high ionic strength, the negative charge of NOM compounds and NF membrane is screened by monovalent cations in water, which refers to ‘charge-screening effect’. When the concentration of calcium in the feed water is high, the NF fouling becomes sever due to not only the charge-screening effect, but also the Ca-bridging effect. Some recent studies also indicate the impact of these factors on the fouling of UF membranes (Wang and Waite 2008).

Different pretreatments have been investigated to control membrane fouling, such as powder activated carbon adsorption, lime softening, ion exchange, conventional media filtration and coagulation with inorganic and/or polymeric coagulants (Kabsch-Korbutowicz et al. 2008, Kweon and Lawler 2004, Lee et al. 2000, Nguyen and Roddick 2010, Zheng et al. 2010). In-line coagulation is the most commonly used pretreatment for ultrafiltration of surface water. Kabsch-Korbutowicz claimed that in-line coagulation resulted in a better removal of NOM and less membrane fouling (Kabsch-Korbutowicz 2006a, b).

However, the problem with in-line coagulation is that a large amount of backwash-derived waste sludge containing dosed coagulants is produced. Since in Western Europe the backwash waste sludge with coagulant has to be treated before its discharge, it represents additional cost for the membrane treatment plant. Panglisch calculated the cost of the biggest UF treatment plant in the Germany and
reported that the backwash waste sludge cost can be up to 20% of the total cost of the whole plant (Panglisch et al. 2008).

Therefore, a new fouling control method is required. Demineralized water (low ionic strength water with a conductivity lower than 1 µS/cm) backwashing has been found to be a potential method to control the UF fouling (Li et al. 2009). It was believed that the demineralized water backwashing can create a low ionic strength environment near the membrane surface, and thus restore the reduced repulsion forces between negatively charged NOM and membranes caused by charge screening effect during filtration. Consequently, the backwash with demineralized water is more efficient than permeate. However, this method is not adequately confirmed by experiments. Furthermore, the mechanisms of demineralized water backwashing are not clear.

1.3 The DEMIFLUSH project

Objectives

The DEMIFLUSH project is launched to develop this new fouling control method for real application. Therefore, demineralized water backwashing (the DEMIFLUSH concept) is systematically investigated in this dissertation.

The objectives of this dissertation are:

- Prove the effectiveness of the DEMIFLUSH concept on UF fouling control
- Demonstrate the mechanisms of the DEMIFLUSH concept
- Evaluate the possibility of its implement in full scale plants

Dissertation outline

Chapter 1 briefly introduces this dissertation.

Chapter 2 describes the improvement of the DEMIFLUSH concept on UF fouling control at a pilot scale. The possible substances responsible for this improvement are also discussed, providing indication for further investigation explained in Chapter 3.
Chapter 3 describes the impact of the backwash water composition on UF fouling control. Three main components present in UF permeate but not in dematerialized water are investigated separately to understand their influences on fouling control. Mono- and divalent cations, not present in demineralized water, are responsible for the improvement of the DEMIFLUSH concept, and corresponding hypotheses related to these components (the charge screening and calcium bridging effects) are reviewed.

Chapter 4 explains the dominant mechanism of the DEMIFLUSH concept. Both the charge screening and calcium bridging effect are discussed.

Chapter 5 discusses the effectiveness of the DEMIFLUSH concept on different fractions of natural organic matter (NOM). This chapter illustrates the effectiveness of this concept on different NOM fractions in natural surface water via LC-OCD analysis. Furthermore, the effectiveness of this concept on model compounds representing different fractions is also described.

Chapter 6 describes the application of the DEMIFLUSH concept on seawater treatment (the other chapters focus on surface water treatment). The improvement of the DEMIFLUSH concept on UF fouling control of seawater treatment, the influence of season and backwash duration on the effectiveness of this concept are discussed in this chapter.

Chapter 7 provides practical experiences of the application of the DEMIFLUSH concept at a pilot scale. It describes the consistency results achieved between the pilot installation and a full-scale plant, and illustrates the success of the DEMIFLUSH concept in practice. Furthermore, this chapter also demonstrates the benefits of this concept in terms of cost.

Chapter 8 describes the general conclusions and recommendations for further research.
1.4 References


Chapter 2

Effectiveness of demineralized water backwashing

This chapter is based on the following published papers:

2.1 Introduction

As mentioned in Chapter 1, a lot of studies have been conducted to control the NOM fouling of ultrafiltration membranes. Many research has shown that NOM fouling is influenced by some external factors, such as pH, multivalent cations and ionic strength (Hong and Elimelech 1997, Katsoufidou et al. 2007, Song and Singh 2005, Wang and Waite 2008)

However, all these studies focus on the influence of these factors on formation of fouling. Only limited studies considering their corresponding effect on UF membrane fouling control are available. Abrahamse and her colleagues investigated the effectiveness of backwashing with Milli-Q water on UF membrane fouling control with small scale membrane modules (with a surface area of 0.0125 m$^2$), and found that backwashing with Milli-Q water is much better than with normal UF permeate (the normal operation procedure in UF plants) in terms of the recovery of membrane permeability (Abrahamse et al. 2008). They attributed this to the reduction of ionic strength and Ca-bridging effect due to absence of mono- and divalent cations and NOM compounds in Milli-Q water. However, this study was carried out at a very small scale. It is not clear whether the same case would be observed in a UF membrane with a higher surface area.

The objective of this chapter is to investigate the effectiveness of backwashing with demineralized water on a pilot scale. Backwashing with demineralized water is likely to dilute the ion concentration on the membrane surface which will increase the repulsion force between NOM and the membrane. Compared with normal backwashing with UF permeate (containing the same amount of cations as UF feed water), it can remove the fouling layer from membrane surface more efficient. Furthermore, the influence of monovalent cations is also investigated by backwashing with NF permeate.
2.2 Material and methods

2.2.1 Feed water

In this pilot scale study, two types of feed water were used: untreated Schie canal water and ion exchange pretreated Schie canal water. The Schie canal water was continuously pumped from the canal and no pre-filtration was used. The concentrations of metal ions were checked using a flame Atomic Absorption Spectroscopy (AAS), and the dissolve organic carbon (DOC) was determined with a Shimadzu TOC-V series TOC analyzer. The water quality of two types of feed water is shown in Table 2.1. Effluent of IEX show a very high sodium concentration, but that is probably because the sample was taken at the early stage of this study, the dosage of NaHCO$_3$ for pH adjustment after IEX column 1 is not optimized yet (too much NaHCO$_3$ in the column 2). When the dosage is optimized, the sodium concentration in IEX effluent should be about 100 mg/l, based on the theoretical calculation (4 mmol/l NaHCO$_3$ dosed). There is no clear explanation regarding the increase of Aluminum, Manganese and Iron. It might be due to the impurity in the columns or the pipes.

2.2.2 Backwash water

Three different types of backwash water were prepared: 1) demineralized water, 2) UF permeate and 3) NF permeate. The water quality of these backwash waters is shown in Table 2.2.

2.2.3 Chemical solution

Because enhanced chemical backwash was incorporated in long-term experiments, chemical solution with a pH of 12 was prepared by dosing NaOH in demineralized water.
2.2.4 Membrane

Two similar polymeric hollow fiber ultrafiltration membrane modules were used in this study. The characteristics of modules are shown in Table 2.3. These membranes are made of a mixture of polyethersulfone (PES) with a small amount of polyvinylpyrrolidone (PVP).

2.2.5 Ion exchange (IEX) setup

In order to investigate the impact of monovalent ions on the fouling control efficiency of ultrafiltration, a fluidized Pseudo-moving ion exchange system, consisting two columns, was used as a pretreatment of ultrafiltration (as shown in Figure 2.1). In this system, two columns are placed in series. After breakthrough occurs in the first column, the second column takes care of the polishing. Therefore, the effluent of this system is free from divalent cations. When the first column is saturated with divalent cations, it is regenerated and connected after the second column after regeneration. Each column is 2.5 m high and its inner diameter is 19 cm, the flow rate of this system is 3.6 m/h. Weak acid cation resin, Amberlite IRC86 from Rohm & Haas Company, was used in this study. Its capacity is 4.1 eq/l. Because hydrogen ions were released from the resin, the pH of effluent of IEX column 1 decreased from 8.1 (raw surface water) to about 4. The reduction of pH hindered the process in column 2 (resin works properly at a pH > 4.8), so 4 mmol/l NaHCO₃ was dosed in the effluent of column 1 as a buffer.

Some studies indicated that fouling of nanofiltration membrane becomes more serious when the pH of feed water is low, e.g., (Hong and Elimelech 1997). That is because the carboxyl functional groups of the NOM molecules can be protonated with hydrogen ions in water. Consequently, the Nom molecules become less negatively charged and easier to deposit on the negatively charged membrane. Therefore, when the ion-exchange pretreated water was used as the feed water of ultrafiltration, 1.8 mmol/l NaOH was dosed in feed water to increase its pH to around 7, which originally was about 4 after the pretreatment of ion exchange.
2.2.6 Ultrafiltration setup and filtration protocol

An Ultrafiltration setup from Kiwa Water Research was used in this study for dead-end fouling experiments. This setup consists of two parallel centrifugal feed pumps, two centrifugal backwashing pumps and two chemical dosing pumps, enabling parallel experiments. There are two sieves (0.5 mm) before the feed pumps to retain large suspended solids that can block membrane fibers (Heijman et al. 2007). Permeate was collected in a storage vessel. Transmembrane pressure (TMP) and flow rates of feed and permeate were measured with precision manometers (Endress and Hauser) and logged every eight seconds. Afterwards, the respective graphs as a function of time were automatically plotted on computer.

This setup works automatically based on the following program settings: 1) 15-minute filtration at a constant flux of 65 l/(m².h); 2) one-minute backwashing at a constant flux of 130 l/(m².h); 3) enhanced chemical backwashing with NaOH at a
pH of 12. Enhanced chemical backwash is composed of 30-second backwashing with chemical solution, 15-minute soaking and 20-second normal backwashing.

![Figure 2.2: Scheme of ultrafiltration pilot setup](image)

<table>
<thead>
<tr>
<th>Water quality parameter</th>
<th>Raw water</th>
<th>Effluent of IEX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho phosphate (mg/l)</td>
<td>0.65</td>
<td>0.56</td>
</tr>
<tr>
<td>Silicate (mg/l)</td>
<td>7.5</td>
<td>6</td>
</tr>
<tr>
<td>Sulphate (mg/l)</td>
<td>154</td>
<td>176</td>
</tr>
<tr>
<td>Aluminum (µg/l)</td>
<td>5.9</td>
<td>10</td>
</tr>
<tr>
<td>Barium (µg/l)</td>
<td>16</td>
<td>1.3</td>
</tr>
<tr>
<td>Calcium (mg/l)</td>
<td>150</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Potassium (mg/l)</td>
<td>18</td>
<td>9.4</td>
</tr>
<tr>
<td>Magnesium (mg/l)</td>
<td>26</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Manganese (µg/l)</td>
<td>0.99</td>
<td>13</td>
</tr>
<tr>
<td>Sodium (mg/l)</td>
<td>92</td>
<td>290</td>
</tr>
<tr>
<td>Iron (mg/l)</td>
<td>&lt;0.05</td>
<td>0.1</td>
</tr>
<tr>
<td>DOC (mg/l)</td>
<td>15</td>
<td>16</td>
</tr>
</tbody>
</table>
Table 2.2: Composition of backwash water

<table>
<thead>
<tr>
<th></th>
<th>DOC (mg/l)</th>
<th>Ca (mmol/l)</th>
<th>Conductivity (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Demineralized water</td>
<td>&lt;0.5</td>
<td>&lt;0.01</td>
<td>1</td>
</tr>
<tr>
<td>UF permeate</td>
<td>16</td>
<td>3.15</td>
<td>980</td>
</tr>
<tr>
<td>NF permeate</td>
<td>N/A</td>
<td>&lt;0.01</td>
<td>600</td>
</tr>
</tbody>
</table>

Table 2.3: Characteristics of membrane modules

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane material</td>
<td>PES/PVP</td>
</tr>
<tr>
<td>Molecular weight cut-off</td>
<td>100K Da</td>
</tr>
<tr>
<td>Filtration mode</td>
<td>Inside-out</td>
</tr>
<tr>
<td>Internal fiber diameter (mm)</td>
<td>0.8</td>
</tr>
<tr>
<td>Length of module (cm)</td>
<td>100</td>
</tr>
<tr>
<td>Surface area (m²)</td>
<td>2.4</td>
</tr>
</tbody>
</table>

2.3 Results and Discussion

2.3.1 Influence of backwashing with demineralized water

Figure 2.3 shows the TMP as a function of time in short-term for four conditions (as shown in Table 2.4). For condition 1 (Schie water is feed water and UF permeate is backwash), increase in TMP is the fastest, from 0.4 bar to almost 1.4 bar within 2.3 hours. On the other hand, either removing divalent cations from feed water or backwashing with demineralized water can substantially reduce the speed of increase in TMP (the speed of fouling). Furthermore, when both removing divalent cations and backwashing demineralized water were applied (condition 4), it displays the lowest increase in TMP. Based on this figure, backwashing with demineralized water is as good as removal of divalent cations from the feed with respect to fouling control.
Table 2.4: Different filtration conditions applied in this study

<table>
<thead>
<tr>
<th>Condition No.</th>
<th>Feed water</th>
<th>Backwash water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Schie water</td>
<td>UF permeate</td>
</tr>
<tr>
<td>2</td>
<td>IEX pretreated water</td>
<td>UF permeate</td>
</tr>
<tr>
<td>3</td>
<td>Schie water</td>
<td>demineralized water</td>
</tr>
<tr>
<td>4</td>
<td>IEX pretreated water</td>
<td>demineralized water</td>
</tr>
</tbody>
</table>

Figure 2.3: TMP as a function of time in short-term for four conditions

Figure 2.4 shows the TMP as a function of time in long-term for backwashing with two types of water: demineralized water and normal UF permeate. Raw schie water is used in this experiment as feed water. From the beginning of experiment until the 48th hour, the membrane was backwashed with demineralized water. After the 48th hour, the membrane was backwashed with normal permeate. The improvement of backwash with demineralized water can be seen. For BW with demineralized water, TMP increased 0.5 bar within 48 hours. Given the benefit of chemical cleaning, the increment of TMP was only 0.2 bar. In contrast, for BW of permeate, the TMP increased by 0.6 bar within 4 hours. It is corresponding to the short-term results.
Backwash with demineralized water was able to remove the fouling more efficiently than backwash with permeate. This is probably due to the absence of multivalent cations (Ca$^{2+}$, Mg$^{2+}$, Ba$^{2+}$), monovalent cations (Na$^+$, K$^+$) and organic substances in demineralized water. Multivalent cations can bridge negatively charged membranes and negatively charged natural organic matter (NOM), compacting the fouling layer on the surface of the membranes.

Multivalent cations on membrane surface are the most important factors in fouling, because they are the bridge between the negatively charged membrane and NOM. The concentration of multivalent cations is lower during the BW with demineralized water; therefore, it is easier to remove the fouling layer with the same backwash velocity. During the BW with permeate the concentration of multivalent ions is the same as the feed water as the UF cannot reject multivalent ions therefore fouling was more significant.

![Figure 2.4](image_url): TMP as a function of time at 65 l/(m2.h) for untreated Schie water, with two different backwash periods: demineralized water 0-48th hour and permeate 48th-52nd hour (no in-line coagulation was used)
2.3.2 Influence of backwashing with NF permeate

Backwashing with demineralized water and permeate of nanofiltration were compared in the experiment with a constant flux of 42 l/(m².h). In this experiment ion exchange was used as pretreatment. Figure 2.5 shows the results and it should be considered in three parts: 1) 0-10 hours; 2) 10-32 hours; 3) 32-52 hours. The membrane is backwashed with demineralized water in part one and three, and it is backwashed with permeate of nanofiltration in part two.

![Figure 2.5: TMP as a function of time at 42 l/(m².h) for IEX pretreated Schie water, with three different backwash periods, demineralized water 0-10th hour and 32nd-52nd hour, NF permeate 10th-32nd hour](image)

In part one, TMP remained stable, which suggested that the BW of demineralized water successfully prevented the formation of fouling. However, the TMP started to increase when permeate of nanofiltration was used for the backwash. When demineralized water was used again for the backwash in part three, the TMP of the system decreased and became stable again.

As most of the multivalent cations and organic matter were rejected in the NF, the possible fouling factor in the NF permeate was monovalent cations, such as Na⁺, K⁺. Although monovalent cations cannot bridge NOM and membrane material, they can reduce the electrostatic repulsion force by decreasing the zeta potential.
around NOM and the membrane. The zeta potential is an important factor in the formation of a fouling layer, and Hong and Elimelech reported for nanofiltration that the higher the ionic strength of the solution, the more serious membrane fouling becomes (Hong and Elimelech 1997).

2.4 Conclusions

The impact of different backwash waters on UF fouling control has been investigated at a pilot scale in this study. Two types of feed water (raw canal water and ion-exchange pretreated canal water), three types of backwash water (demineralized water, UF permeate and NF permeate) were tested in this study. Results show that ion-exchange pretreatment can substantially prevent the UF fouling. Furthermore, regarding the three types of backwashing, demineralized water is the best option for backwash of UF. That is probably due to the absence of multivalent cations and monovalent cations, reducing the charge screening effect and Ca-bridging effect between the negatively charged membrane and NOM, leading to a restoration of repulsion force and consequently an easy removal of fouling layer.

2.5 References


Chapter 3

Impact of backwash water composition

This chapter is based on the following published paper:
3.1 Introduction

In last chapter, it has been proved that demineralized water backwashing can substantially improve the ultrafiltration fouling control. Although it indicated that the monovalent cations, such as sodium play an role on reducing fouling control efficiency, but as the water compositions of normal backwash water (UF permeate) and demineralized water are totally different, it is not clear which component in the backwash water actually reduce the fouling control efficiency.

At least three types of substances in backwash water can affect fouling control efficiency: divalent cations (calcium), monovalent cations (sodium), and organic matter. Many studies have investigated the impact of these substances on the fouling of UF membranes when they are present in the feed water (Abrahamse et al. 2008, Ahn et al. 2008, Costa et al. 2006, Hong and Elimelech 1997, Jermann et al. 2007, Katsoufidou et al. 2007, Singh and Song 2007, Song and Singh 2005, Ven et al. 2008, Yamamura et al. 2007). Hong and Elimelech (Hong and Elimelech 1997) systematically investigated the role of chemical and physical interactions in the NOM fouling of nanofiltration membranes, and they found that this fouling is low when the feed water has a low ionic strength, contains low levels of divalent cations, and has a high pH. It is believed that the presence of divalent cations (calcium) in the feed water significantly reduces the charge of the membrane and NOM, not only by effective charge screening but also by complex formation, whereby calcium can simultaneously bind to the carboxyl functional groups of the membrane and NOM molecules through specific complex formations, thereby enhancing membrane fouling. Jermann et al. (Jermann et al. 2007) investigated the impact of molecular interactions between different NOM compounds on ultrafiltration fouling mechanisms. An aggravated fouling was also observed with the presence of calcium in a humic acid feed solution, and the fouling was found to be irreversible. The impact of calcium on fouling was attributed to: the reduction of electrostatic repulsion between membranes and NOM molecules (due to a screening of the membrane and NOM surface charge); complexation between the membrane and the NOM molecules; and/or, complexation among the NOM
molecules themselves. Several studies also indicate an increase in fouling with an increase in the calcium concentration (Song and Singh 2005, Ven et al. 2008, Yamamura et al. 2007).

In contrast to these findings, Katsoufidou et al. (Katsoufidou et al. 2007) showed that with an increase in calcium concentrations, the fouling of UF membranes by alginate becomes more reversible. However, at a concentration of 2 mM calcium, irreversible fouling was not found. They argued that this was caused by the formation of a highly permeable hydrogel layer which forms when calcium binds to alginate.

However, most of the previous studies have focused on the impact of divalent cations, monovalent cations and organic matter on UF fouling when they are present in the feed water. Limited literature is available regarding the impact of these substances in backwash water. Since backwashing with demineralized water has been proven to be a good method to control UF fouling (Abrahamse et al. 2008), it is important to understand the mechanisms behind this and to understand which components in normal backwash water (i.e., UF permeate) decrease the efficiency of fouling removal, compared to demineralized water. Therefore, the objective of this chapter is to investigate the separate impacts of divalent and monovalent cations (calcium and sodium) and NOM in backwash water on the foulant removal of UF membranes. Moreover, online streaming potential measurements were conducted out to study the influence of different types of backwash water on the charge of the UF membrane surface, in order to elucidate the mechanisms by which backwashing with demineralized water improves fouling control.

This chapter will thus be divided into three major sections:

1. A study of the impact of mono- and divalent cations in backwash water on UF fouling control;
2. A study of the impact of organic matter in backwash water on UF fouling control; and,
3. A study of the effects of different types of backwash water on the UF membrane’s surface charge (and the charge in the membrane’s pores).

3.2 Material and methods

3.2.1 Impact of cations in backwash water

3.2.1.1 Feed water

Most research on UF membrane fouling has been conducted with artificial water types containing commercial model organic compounds such as humic acid and sodium alginate (Katsoufidou et al. 2007, Ven et al. 2008, Yuan and Zydney 1999). However, the question is how representative these commercial compounds are for the natural organic matter in natural water. In this study, the goal was to mimic real situations. Therefore, 400 liters of raw surface water (batch 1) was taken from the Schie Canal in summer (Delft, the Netherlands) and used in this study as the feed water for the ultrafiltration. The surface water was stored in a climate-controlled room with a constant temperature of 12 °C to limit the biological activity. The quality of feed water and permeate was determined with single analysis and listed in Table 3.1. For each UF experiment, 35 liters of feed water was taken from the climate-controlled room and put in an 80-liter feed vessel equipped with a stirring device. The feed water was used at room temperature (19-20 °C) for the UF experiments.

3.2.1.2 Backwash water

Backwash water with different concentrations of monovalent and divalent cations was prepared by adding calcium (as CaCl₂·2H₂O) and sodium (as NaCl) to demineralized water (NaCl and CaCl₂ were obtained from Sigma-Aldrich and were both reagent grade). The concentrations of calcium and sodium were checked
using a flame Atomic Absorption Spectroscopy (AAS) after dosing. Six different types of backwash water were used, with different concentrations of divalent and monovalent cations (as shown in Table 3.1). 3 mmol/l Ca is often observed in Schie canal water, so this concentration was used in this study. In order to see the impact of a higher concentration, 6 mmol/l was tested as well to see the impact of a high calcium concentration. Because divalent cations have stronger influences on electrical double layer, the tested concentrations for sodium were doubled.

3.2.1.3 Chemical cleaning solution

Because all cation experiments were carried out with a single membrane module, a chemical cleaning was conducted after each experiment. The chemical solution used in this study was a combination of 0.4 g/l NaOH and 120 mg/l NaOCl. After each experiment, the fouled membrane was backwashed with the chemical solution for 5 minutes, and then it was soaked for 15 minutes before a thorough rinsing with demineralized water. If one chemical cleaning was not sufficient to recover the membrane’s initial permeability, another chemical cleaning was conducted. All the cation experiments were started with an initial transmembrane pressure (TMP) around 130 mbar at a flux of 85 l/(m².h).

Table 3.1: Water quality of feed, permeate and backwash water used in three different experiment runs

<table>
<thead>
<tr>
<th>Cation experiments</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>Conductivity (µS/cm)</th>
<th>Ca²⁺ (mmol/l)</th>
<th>Na⁺ (mmol/l)</th>
<th>DOC (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed (Schie water batch 1)</td>
<td>8.1</td>
<td>9.15</td>
<td>882</td>
<td>2</td>
<td>2.5</td>
<td>25</td>
</tr>
<tr>
<td>Backwash water 1 (UF permeate 1)</td>
<td>8.1</td>
<td>0.155</td>
<td>878</td>
<td>2</td>
<td>2.5</td>
<td>16</td>
</tr>
<tr>
<td>Backwash water 2</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Backwash water 3</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>3</td>
<td>&lt;0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Backwash water 4</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>6</td>
<td>&lt;0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Backwash water 5</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>&lt;0.1</td>
<td>6</td>
<td>0.5</td>
</tr>
<tr>
<td>Backwash water 6</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>&lt;0.1</td>
<td>12</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Feed (Schie water batch 2)</strong></td>
<td>8.5</td>
<td>4.5</td>
<td>836</td>
<td>2.5</td>
<td>2.5</td>
<td>20</td>
</tr>
<tr>
<td><strong>UF permeate</strong></td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>2.5</td>
<td>2.5</td>
<td>18.9</td>
</tr>
<tr>
<td><strong>UF permeate after dialysis</strong></td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>0.5</td>
<td>0.37</td>
<td>17</td>
</tr>
<tr>
<td><strong>Demineralized water</strong></td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Feed (UTwente water)</strong></td>
<td>7.7</td>
<td>N/A</td>
<td>N/A</td>
<td>1.9</td>
<td>1.4</td>
<td>13</td>
</tr>
<tr>
<td><strong>UF Permeate 3</strong></td>
<td>8</td>
<td>N/A</td>
<td>N/A</td>
<td>1.88</td>
<td>1.4</td>
<td>11.6</td>
</tr>
</tbody>
</table>

SPC: streaming potential coefficient. DOC: dissolve organic carbon; N/A: Not available

3.2.1.4 Membrane

A commercially available, polymeric hollow fiber ultrafiltration membrane module (RX-300, X-Flow) was used in this study. The characteristics of this membrane module are shown in Table 3.2. These membranes are made of a mixture of polyethersulfone (PES) with a small amount of polyvinylpyrrolidone (PVP). Based on the streaming potential measurements, van der Ven (Ven 2008) reported that the streaming potential coefficient of the same ultrafiltration membrane was
constant at -24 mV/bar in a pH range between 3.5 and 10 by using an electrolyte solution of 10 mmol/l KCl; the charge of the membrane, therefore, is negative at the pH of the feed water (around 8).

Table 3.2: Characteristics of RX-300 membrane module provided by manufacturer

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of membrane fiber</td>
<td>UFC M5 0.8</td>
</tr>
<tr>
<td>Membrane material</td>
<td>PES/PVP</td>
</tr>
<tr>
<td>Molecular weight cut-off</td>
<td>100K Da</td>
</tr>
<tr>
<td>Filtration mode</td>
<td>Inside-out</td>
</tr>
<tr>
<td>Internal fiber diameter (mm)</td>
<td>0.8</td>
</tr>
<tr>
<td>Length of module (cm)</td>
<td>30</td>
</tr>
<tr>
<td>Number of fibers</td>
<td>120</td>
</tr>
<tr>
<td>Surface area (m²)</td>
<td>0.07</td>
</tr>
</tbody>
</table>

3.2.1.5 Ultrafiltration setup and filtration protocol

Many studies on UF fouling control are conducted in a constant-pressure mode and/or only one filtration cycle is carried out (Hong and Elimelech 1997, Jermann et al. 2007, Katsoufidou et al. 2007). However, because all full-scale ultrafiltration plants are operated under a constant-flux mode and with a regular backwash, the results from these experiments are not representative for full-scale operations. Therefore, the ultrafiltration setup used in this study (Figure 3.1) was designed for constant-flux experiments (Heijman et al. 2007). Feed water flows via the grey and dark lines for filtration as shown in the Figure 3.1. Furthermore, backwashing was incorporated in the setup (backwash water is used to flush the membrane via the dotted and dark lines in Figure 3.1), and software was added to run the setup continuously with a program of several operational cycles of filtration and backwashing. The constant flux of the setup was maintained by a Verder VG 1000 Basic gear pump which was controlled by a flow meter (Endress & Hauser). Flow rate, temperature and TMP were continuously logged with a time interval of 8
seconds during the experiments. Flow rate and TMP were also measured with Endress & Hauser equipment.

All experiments were carried out in a dead-end operation mode. Before each experiment (and after each chemical cleaning), the setup was thoroughly flushed with demineralized water in filtration mode and backwash mode to remove the chemical residues and air in the system. Afterwards, the setup was operated at a flux of 85 l/(m².h) for half an hour to determine the initial permeability of the membrane. Each fouling experiment, with a different type of backwash water used each time, consisted of 14 operational cycles. Each cycle was composed of three phases: 1) filtration at a flux of 85 l/(m².h) for 15 minutes; 2) purging the setup at a flow of 4 l/h for one minute to clean the tubes before backwashing; 3) backwashing at a flux of 170 l/(m².h) for one minute. All these setting points were programmed into the setup’s controller before starting the experiment. The duration of each experiment (the full 14 cycles) was about 4 hours. After the experiment, the setup was shut down and all logged data were taken from the logger for analysis.

Figure 3.1: Scheme of the ultrafiltration setup [22]
3.2.2 Impact of NOM in backwash water

3.2.2.1 Feed water

A new batch of 300 liters of Schie Canal water (batch 2) was taken in autumn for the NOM experiments. Because a different batch of raw water was taken than the batch used in the cation experiments, the feed water composition is not exactly the same (due to seasonal varieties). However, since each batch was used to make a relative comparison of the influence of a single component in the backwash water, the difference between the two batches is not relevant. The water quality of the second batch of raw water is listed in Table 3.1.

3.2.2.2 Backwash water

To study the influence of the NOM in backwash water on UF fouling control, three types of backwash water were compared: 1) UF permeate; 2) demineralized water; and, 3) UF permeate after dialysis. UF permeate after dialysis (as shown in Table 3.1) was prepared using a 20-hour dialysis. Five liters of UF permeate was poured into dialysis bags (Spectrum Europe BV, the Netherlands) with a molecular weight cut-off (MWCO) of 3.5 kDa and the filled bags were put in a vessel with 80 liters of demineralized water. The demineralized water in the vessel was recirculated with an aquarium pump. The ions in the UF permeate diffused through the dialysis bags into the demineralized water, until equilibrium was reached. Most of the organic matter in the UF permeate was retained in the dialysis bags, because its molecular weight was higher than the MWCO of the bags. The water remaining in the dialysis bags was then used for backwashing.
3.2.2.3 Chemical cleaning

A new membrane module was used after each experiment and therefore no chemical cleaning (see section 3.2.1.3 above) was carried out.

3.2.2.4 Membrane

The same type of hollow fiber ultrafiltration membrane modules (X-Flow UFC M5, see Table 3.2) was used in this set of experiments.

3.2.2.5 Setup and filtration protocol

The UF setup was already described in section 3.2.1.5. Moreover, most of these settings were the same as in the experiments studying the influence of cations. The only differences were the operational flux and the backwash flux: in this set of experiments, the fluxes for filtration and backwashing were 120 l/(m².h) and 240 l/(m².h), respectively. Since several trial experiments did not show efficient fouling (85 l/(m².h)), a higher flux was used in these experiments to ensure a high enough increase in TMP.

3.2.3 Measurements of streaming potential

The charge of the membrane surface can be quantified using the zeta potential. Based on the well-known Helmholtz-Smoluchowski equation, the zeta potential can be calculated from streaming potential measurements. Because the emphasis of this experiment is to evaluate the changes in the membrane charge under two different backwash conditions, the exact values of the zeta potential are not necessary, only the relative changes. Therefore, the streaming potential coefficient (SPC) was used in this study to evaluate the change in membrane charge (Equation 3.1).
$$SPC = \frac{\Delta \phi}{\Delta P}$$  
Eq. 3.1

Where, $\Delta \phi$ and $\Delta P$ are the voltage and pressure differences between two measuring points in units of mV and bar, respectively.

3.2.3.1 Feed water

Raw natural water on the campus of the University of Twente was used in this study as feed water. The water quality of the raw water is listed in Table 3.1.

3.2.3.2 Backwash water

The purpose of the SPC’s determination is to demonstrate that backwashing with demineralized water can maintain the original negative charge of the UF membrane (improving fouling control), so only two types of backwash water were compared. They were UF permeate and ultrapure water (demineralized water purified by a Synergy Water Purification System from Millipore).

3.2.3.3 Membrane

Since the experimental setup is not designed for an X-Flow RX-300 membrane module, two homemade membrane modules containing RX-300 hollow fibers were prepared. Ten one-meter fibers were potted in an 8 mm PVC pipe (using a polyurethane potting resin) to represent one module with a surface area of 0.025 m$^2$. 
3.2.3.4 Determination of SPC

The SPC over the membrane’s surface (axial SPC) and through its pores (radial SPC) was determined. Five pressure differences between two measuring points were applied by using five different flow rates. Under each pressure difference, the streaming potential between the measuring points was measured using a Keithley 2000 multimeter with two homemade Ag/AgCl electrodes. By plotting the streaming potential as a function of pressure a linear relationship was obtained. The slope of this line was the SPC.

3.2.3.5 Filtration/streaming potential setup and filtration and streaming potential measuring protocol

The experimental setup, as shown in Figure 3.2, was designed for long-term and automated process operations (Ven et al. 2008). It can be operated under constant pressure and in a constant-flux mode. The system contains a feed pump and a backwash pump (Ismatec, Reglo-Z). Feed and backwash flows are measured by two mass flow controllers (Bronkhorst, NL, Cori-Flow M53C and M54C). The internal PID controllers of these two instruments directly control the pumps to achieve a constant flux. During the streaming potential measurements, a background electrolyte solution for the measurements is taken from the backwash tank. By opening solenoid valves 4 and 5 (Plast-o-matic), as shown in Figure 3.2, the streaming potential of the UF membrane surface can be measured. On the other hand, the streaming potential measurements of the membrane pores are enabled by opening valves 3 and 5.
Twenty-five liters of raw water was taken from a campus pool and filtered with a coarse (40 micron) metal filter. The membrane module was thoroughly rinsed with ultrapure water before use (under the filtration and backwash mode). Afterwards, the permeability of the membrane was determined with ultrapure water. Following this, the SPC of the clean membrane surface and its pore walls was determined. Streaming potential measurements were carried out in a 1 mmol/l KCl background electrolyte solution in ultrapure water. The pH and conductivity of this solution were 6.5 and 178.8 µS/cm, respectively. A fouling experiment was conducted after the determination of their initial streaming potentials. The fouling experiment consisted of 14 cycles, each cycle had a 15-minute filtration at a flux of 120 l/(m².h) and a one-minute backwash at a flux of 240 l/(m².h). After the fouling experiments, the SPC of the fouled membrane surface and its pore walls was again determined.
3.3 Results and discussion

3.3.1 Impact of mono- and divalent cations in backwash water on UF fouling control efficiency

In field practice, most UF membranes are hydraulically cleaned by reversing the water flow after a short period of filtration (backwashing). The part of the fouling that can be removed by a hydraulic backwash is defined as reversible fouling. On the other hand, the fouling that cannot be removed by a hydraulic backwash and remains on the membranes after backwashing is defined as hydraulically irreversible fouling.

The term “fouling control efficiency” refers to the extent of the recovery of the membrane’s permeability by means of hydraulic backwashing (i.e., high fouling control efficiency corresponds to a high recovery of membrane permeability after consecutive backwashings). Since one usually distinguishes reversible and irreversible fouling, high fouling control efficiency in this study refers to a low irreversible fouling after consecutive backwashings.

3.3.1.1 Effect of backwashing with demineralized water

In Figure 3.3, the increase in relative TMP (TMP/TMP₀) as a function of time is plotted for a constant flux experiment when backwashed with UF permeate and demineralized water. It is clear from this graph that the relative TMP only increased slightly when backwashed with demineralized water. However, when backwashed with UF permeate, the measured relative TMP increased much faster. This indicates that higher fouling control efficiency can be achieved by backwashing with demineralized water, which agrees with the finding of Abrahamse et al. (Abrahamse et al. 2008). The increased fouling control efficiency when backwashed with demineralized water compared with backwashing with UF permeate can result from the absence of either monovalent cations, divalent
cations, or the NOM in the demineralized water compared to UF permeate. The increase in TMP for backwashing with UF permeate is a bit higher than that of backwashing with synthetic sodium spiked demineralized water. That is probably because of the presence of calcium in UF permeate which has a stronger influence on the electrical double layer and consequently the charge of NOM and UF membranes than sodium.

![Figure 3.3: Relative TMP as a function of time for two different backwash waters in cation experiments: demineralized water and UF permeate](image)

**3.3.1.2 Impact of monovalent cations in backwash water on fouling control**

Three types of backwash water were compared in this study: demineralized water, demineralized water with 6 mmol/l Na\(^+\) added, and demineralized water with 12 mmol/l Na\(^+\) added. In Figure 3.4, the relative TMP as a function of time for constant flux experiments is plotted for these three types of water. Only a minor increase in irreversible fouling (a 30% relative TMP increase, from 1 to 1.3) could be observed.
when backwashed with demineralized water, indicating high fouling control efficiency. For the water types containing NaCl, however, the relative TMP after several backwashes increased by 130% within 14 operational cycles for both types of backwash water with sodium.

The UF membrane used in this study is negatively charged at the feed water pH, due to the dissociation of carboxyl functional groups on the membrane surface. A large number of NOM molecules present in the feed water are also negatively charged at the feed water pH. Both calcium and sodium ions are present in the feed water. Calcium can either bridge the negatively charged membrane and NOM molecules, or screen their negative charge by compressing their electrical double layers. However, since sodium is monovalent, it is not capable of bridging the negatively charged UF membrane and the negatively charged NOM via complexation. Therefore, the most logical explanation for the decrease in permeability during the filtration phase, when Na$^+$ is present in the water, is a charge-screening effect of the negatively charged UF membrane and the negatively charged NOM, due to the compression of their electrical double layers in the presence of Na$^+$. As a result of this charge screening, the electrostatic repulsion force between the UF membrane and the NOM is reduced, thereby enhancing deposition of NOM molecules on the membrane’s surface (Figure 3.5a).

When backwashing the fouled membrane with backwash water containing high concentrations of sodium (Figure 3.5b), the compressed electrical double layer formed during the filtration phase is maintained during the backwash and, therefore, the adhesion between the NOM fouling layer and the membrane is maintained. In this case, a vigorous agitation is required to remove it from the membrane surface, and the hydraulic forces induced by the backwash are not sufficient to remove this layer. However, when the membrane is backwashed with demineralized water (Figure 3.5c), the sodium concentration in the NOM fouling layer on the membrane surface is lowered and a lower sodium concentration is established, leading to a relaxation of the compressed electrical double layer. The negative charge of the
membrane and the NOM and the electrostatic repulsion force between the two are restored, resulting in an easier removal of the fouling layer.

There is a change in TMP increase tendency at the 10th cycle between two sodium added demineralized water (Figure 3.4). The increase tendency for 6 mmol/l sodium added water is a bit higher than that for 12 mmol/l sodium added, which is not matched with the hypothesis. However, that might be due to the reduction of colloids in feed water. There was a weekend break between experiments of backwashing with 6 and 12 mmol/l sodium added demineralized water. There might be some biological activities happened during the weekend and reduce the amount of foulants in feed water, leading to the change in TMP increase. The absolute value of the negative membrane charge (determined by measurements of zeta potential) increases with the dilution of the background electrolyte solution, indicating that the membrane charge decreases with increasing ionic strength (and thus the sodium concentration). However, this increase is not linear and the increase in the membrane charge might be low for sodium concentrations around 5 mmol/l and 10 mmol/l. Consequently, in terms of the fouling control efficiency, there is no big difference between backwashing with 6 mmol/l and 12 mmol/l sodium solution.

Since UF membranes cannot reject sodium, the sodium concentration in the UF permeate is equal to that in the feed water. Therefore, when the UF membranes are used as a pretreatment for seawater or brackish water desalination, the sodium concentration in the permeate is very high and this can seriously affect the fouling control efficiency in these applications, if the permeate is used as backwash water.
Figure 3.4: The relative TMP as a function of time during constant flux fouling experiments for the three types of backwash water: demineralized water, demineralized water with 6 mmol/l Na\(^+\), and demineralized water with 12 mmol/l Na\(^+\).
Figure 3.5: Proposed mechanism regarding charge-screening effect caused by sodium ions in: a) filtration; b) backwash with Na\(^+\) solution; c) backwash with demineralized water.
3.3.1.3 Impact of divalent cations in backwash water on fouling control

Again, three types of backwash water (demineralized water, demineralized water with 3 mmol/l Ca$^{2+}$ added and demineralized water with 6 mmol/l Ca$^{2+}$ added) were compared for their effect on fouling control efficiency. Figure 3.6 displays the relative TMP as a function of time for constant flux fouling experiments using the three types of backwash water. As before, when the membrane is backwashed with demineralized water, the relative TMP after several backwashings only slightly increases. However, its increases for backwash waters containing 3 and 6 mmol/l Ca$^{2+}$ are 150% and 180%, respectively. The presence of calcium ions in backwash water, therefore, appears to reduce the UF fouling control efficiency.

![Figure 3.6: The relative TMP as a function of time during constant flux fouling experiments for three types of backwash water: demineralized water, demineralized water with 3 mmol/l Ca$^{2+}$, and demineralized water with 6 mmol/l Ca$^{2+}$]
Figure 3.7: Proposed mechanisms caused by calcium ions in: a) filtration; b) backwash with Ca\(^{2+}\) solution; c) backwash with demineralized water

The thickness of a diffuse double layer of particles and the membrane surface can be determined. Not only the concentration of the electrolyte in solution, but also the valence of the electrolyte in solution influence the charges of the membrane and
the NOM particles. At a constant electrolyte concentration, compression of the electrical double layer increases with increasing valence of ions in the electrolyte solution. Therefore, as shown in Figure 3.7a, divalent cations have a stronger influence than monovalent cations on the compression of the electrical double layer, and thus the charge-screening effect becomes more severe. As a result, the electrostatic repulsion force between the membrane and NOM decreased even more when Ca\(^{2+}\) was present in the feed water. Moreover, it is likely that calcium ions also cause complexation of NOM macromolecules and bridging between NOM molecules and the membrane surface. The negatively charged functional groups of the membrane and the NOM can be bound by calcium via a complexation during the filtration phase, which is generally called a ‘Ca-bridging effect’. These deposited NOM molecules form a compact fouling layer on the membrane surface, which is difficult to reverse by backwashing.

In Figure 3.7b, the process of backwashing with a solution containing Ca\(^{2+}\) is displayed. The bound NOM fouling layer is not removed by backwashing. The presence of calcium ions in the backwash water maintains the charge-screening effect and the Ca-bridging effect between the membrane and the NOM, and acts against the hydraulic shearing force of the backwash. Therefore, the adhesion force between the membrane’s surface and the NOM is maintained, leading to a less efficient NOM fouling removal. When the membrane is backwashed with demineralized water (Figure 3.7c), the calcium concentration near the membrane surface is lowered, thus reducing the charge screening and restoring the electrostatic repulsion force between the membrane and the NOM molecules. Some of the calcium ions contributing to the Ca-bridging effect and the complexation between NOM molecules are also removed when backwashed with demineralized water. The main findings of this study can be used to improve the fouling control strategies as full-scale.
3.3.2 Impact of organic matter in backwash water

Figure 3.8 shows the relative TMP as a function of time during constant flux fouling experiments using three different types of backwash water: demineralized water, the UF permeate and the UF permeate after dialysis (containing mainly organic matter). The composition of backwash water is displayed in Table 3.1. The relative TMP increased by 80% after 14 cycles when backwashed with demineralized water, a higher increase than in the previous experiments (30%). This is probably due to the higher flux used in this set of experiments compared to the cation experiments. When the membrane was backwashed with the UF permeate, the relative TMP after several backwashings increased by 500% after 14 cycles, which is also higher than in the previous experiments (also probably caused by the higher operating flux). Surprisingly, when the membrane was backwashed with UF permeate after dialysis, (which contains a limited amount of calcium and sodium ions, but most of the organic matter present in the UF permeate), the increase in the relative TMP was similar to the increase when backwashed with demineralized water. Based on the findings of cation experiments in section 3.1, the presence of calcium and sodium ions was found to reduce the fouling control efficiency. However, calcium (0.50 mmol/l) and sodium (0.37 mmol/l) ions in the UF permeate after dialysis are much lower than the values in cation experiments: 3 & 6 mmol/l for calcium and 6 & 12 mmol/l for sodium. There might be critical cation concentrations in backwash water regarding the fouling control. On the other hand, because the organic matter in the UF permeate can pass through the membrane, the organic matter does not cause pore blocking or fouling of the membrane. Furthermore, because of the low concentration of cations in the backwash water, the adsorption of these small NOM molecules on the membrane surface via complexation can also be neglected. Therefore, it can be concluded that organic matter in the UF permeate alone does not result in irreversible fouling.
3.3.3 Effect of backwash water composition on UF membrane surface and pore wall charge

The improved fouling control when backwashed with demineralized water and the impact of different components (i.e., mono- and divalent ions and NOM molecules) in backwash water on fouling control efficiency have been investigated and proven. The main explanation for the improvement in fouling control when backwashed with demineralized water was said to be the recovery of the negative charge of the UF membrane during a backwash. In order to confirm this explanation, measurements of streaming potential were carried out.
Table 3.3: Streaming potential coefficients of the UF membranes under different conditions

<table>
<thead>
<tr>
<th></th>
<th>ultrapure water</th>
<th>UF permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before fouling experiment</td>
<td>After the 14th backwashing</td>
</tr>
<tr>
<td>SPC along fiber (mV/bar)</td>
<td>-17.7</td>
<td>-18.0</td>
</tr>
<tr>
<td>SPC through pore (mV/bar)</td>
<td>-47.8</td>
<td>-47.6</td>
</tr>
</tbody>
</table>

Table 3.3 shows the streaming potential coefficients of the UF membrane before the constant flux fouling experiments and after backwashings at the 14th cycle of the fouling experiments with the UF permeate and ultrapure water as backwash waters. The initial SPC through pore is rather different between the ultra pure water and UF permeate backwashing experiments. It might be due to the left negatively charge residuals during membrane manufacturing, which was not flushed out during the pre-cleaning before experiments. When backwashed with UF permeate, both the SPCs over the membrane surface and through the membrane pore wall become less negative. The SPC of the membrane's surface increases from -19.5 to -14.1 mV/bar after 14 operational cycles, while the increase in the SPC through the membrane's pore wall is even higher, from -66.3 to -35.4 mV/bar. The reason for this is that the fouled membrane is covered by a negatively charged NOM fouling layer whose negative charge is reduced by the cations in feed water, and backwashing with the UF permeate could not remove this layer. Consequently, the membrane charge after the 14-cycle fouling experiment becomes less negative compared to the clean membrane charge. In contrast to the UF permeate, backwashing with ultrapure water was able to remove the NOM fouling layer by decreasing the concentration of cations near the membrane surface, thus restoring the negative charge of the UF membrane. The SPC of the membrane after a backwashing at the 14th cycle of the fouling experiment is almost identical to that of the clean membrane. Therefore, it can be concluded that the negative charge of the UF membrane can be recovered by backwashing with ultrapure water.
3.4 Conclusions

The experiments’ results confirm that backwashing of UF membranes with demineralized water is much more efficient than with UF permeate, in terms of the removal of irreversible fouling. Both sodium and calcium ions in backwash water reduce the fouling control efficiency of the UF membrane, and calcium ions have a double stronger impact on fouling control than sodium ions at the same concentration. That is probably because their presence in the backwash water maintains the charge-screening effect, preventing the restoration of the electrical repulsion force between the UF membrane and NOM. Since calcium has a stronger impact on electrical double layer, its influence on fouling control is stronger than sodium. Furthermore, the presence of calcium ions can result in calcium complexation with the membrane and the NOM. The finding about the impact of sodium ions on fouling control is useful when backwashing with demineralized water is applied on UF pretreatment of RO desalination. On the other hand, the organic matter itself in backwash water does not influence the removal of irreversible fouling. Measurements of the streaming potential also confirmed that the charge of the UF membrane becomes less negative when it is backwashed with the UF permeate, while backwashing with ultrapure water can maintain the original negative charge of the UF membrane. This is essential to prevent the NOM fouling.

3.5 Reference


Experimental and molecular modeling study. Journal of Membrane Science 309, 128-140.


Chapter 4

Mechanisms of demineralized water backwashing

This chapter is based on the following published paper:
4.1 Introduction

In the previous study on the influence of backwash water composition on fouling control (Li et al. 2009), it became clear that the presence of monovalent and divalent cations in backwash water reduces the fouling control efficiency. Both the elimination of the charge screening effect and the breakdown of the calcium bridging effect are possible mechanisms to explain this improvement. However, there is no scientific evidence to show that both the elimination of the charge screening effect and the breakdown of the calcium bridging effect are really involved in this phenomenon. If both mechanisms are involved, it is also valuable to know which one is the dominant mechanism. The charge screening effect is related to the well known DLVO theory in colloidal chemistry, named after Derjaguin, Landau, Verwey and Overbeek. Nevertheless, there is not a clear relationship describing the impact of electrolyte pH, concentration and valence on the charge of UF membranes and the corresponding consequences on fouling control. Furthermore, there is also no study regarding the adsorption of calcium on UF membranes, its consequent bridging effect between NOM and membranes, and the possibility of the breakdown of Ca-bridging with demineralized water backwash. The objectives of this study are: firstly, to characterize the membrane charge under different electrolyte conditions; secondly, to investigate the calcium adsorption on membranes and its reversibility with demineralized water backwash by measuring the zeta potentials of membranes under different situations (e.g., before and after a continuous filtration with CaCl₂ solution); lastly, to use the characterization results of the fouling experiments to identify the mechanism related to backwashing with demineralized water.
4.2 DLVO theory and hypotheses

4.2.1 DLVO theory

The DLVO theory describes the interaction forces between charged surfaces. In the framework of the DLVO theory, the interaction energy between two charged surfaces is composed of van der Waals attraction and electrical double layer repulsion. The potential energy between spherical compounds and flat membranes can be calculated with Derjaguin's approximation via surface integration (Bhattacharjee and Elimelech 1997a). The integrated solutions for this specific application are described in the following sections.

van der Waals (VDW) attraction

\[ U_{VDW} = -\frac{A_H a}{6D} \]  
Eq.4.1

Where \( U_{VDW} \) is the attractive van der Waals energy (J), \( A_H \) is the Hamaker constant (J), \( a \) is the diameter of the spherical NOM compounds (m) and \( D \) is the distance between spherical compounds and the membrane surface (m).

Electrical double layer (EDL) interaction

\[
U_{EDL} = \pi \varepsilon_0 \varepsilon_r a \left( \frac{K_B T}{\nu e} \right)^2 \left( \psi_s^2 + \psi_p^2 \right) \times 
\left[ \frac{2\psi_s \psi_p}{\psi_s^2 + \psi_p^2} \ln \left( \frac{1 + \exp^{-\kappa D}}{1 - \exp^{-\kappa D}} \right) + \ln \left( \frac{1 - \exp^{-\kappa D}}{1 - \exp^{-2\kappa D}} \right) \right] 
\]  
Eq.4.2

Where \( U_{EDL} \) is the repulsive electrical double layer energy (J), \( \varepsilon_0 \) is the vacuum permittivity (8.85 x 10^{-12} \, \text{CV}^{-1} \text{m}^{-1}) , \( \varepsilon_r \) is the relative permittivity of the background solution (80 for water), \( \nu \) is charge number of counter ions to the considered
surface, \( e \) is the elementary charge \((1.60 \times 10^{-19} \text{ C})\), \( K_B \) is Boltzmann constant \((1.38 \times 10^{-23} \text{ J/K})\), \( T \) is the absolute temperature (K), \( \psi_s \) is the zeta potential of spherical NOM compounds (V), \( \psi_p \) is the zeta potential of the membrane surface plate (V), \( \kappa \) is the inverse Debye screening length (m\(^{-1}\)).

Therefore, the total interaction energy between spherical NOM and membranes is:

\[
U_{DA} = U_{VDW} + U_{EDL}
\]

**Eq.4.3**

Where \( U_{DA} \) is the total interaction energy (J), including attractive van der Waals energy and repulsive electrical double layer energy

**Influence of electrolyte condition on zeta potential**

As shown in Eq.4.2, the electrical double layer repulsion is influenced by the zeta potential of membranes and NOM. Eq.4.4 describes the potential of substances at a specific distance away from their surface. This potential is a function of inverse Debye screening length and distance away from the surface. The zeta potential is the potential of substances at the shear plane. Although different electrolytes give small changes at the location of the shear plane, the location of the shear plane is actually determined by surface roughness and counter ion size in electrolytes. The surface roughness of NOM and new and fouled membranes were kept constant in the experiments, and the ionic radii for sodium (1.02 Angstrom) and calcium (1 Angstrom) are similar (Shannon 1976). Therefore, the location of the shear plane is considered to be constant here.

\[
\psi = \psi_0 \exp(-\kappa x)
\]

**Eq.4.4**

Where \( \psi \) is the potential at a specific distance from the surface (V), \( \psi_0 \) is the surface potential (V) and \( x \) is the specific distance (m).

In another words, the zeta potential of considered compounds/membranes depends on the surface potential \( \psi_0 \), and the inverse Debye screening length \( \kappa \). \( \psi_0 \) depends on the amount of acidic functional content of the NOM and membranes.
Since the inverse Debye screening length depends on ionic strength (as shown in Eq.4.5), the ion valence and concentration can influence the inverse Debye screening length, and consequently the zeta potential and interaction energy. The zeta potential becomes less negative with the increase in electrolyte concentration and valence (Koper 2007).

\[
\kappa = \sqrt{\frac{1000N_Ae^2}{\varepsilon_0\varepsilon_rK_BT}2I}
\]

Eq.4.5

Where \( N_A \) is the Avogadro number \((6.0\times10^{23} \text{ mol}^{-1})\) and \( I \) is the ionic strength \((\text{Mol/l})\), \( \varepsilon_0, \varepsilon_r, e \) and \( K_B \) are identical as Eq.4.2.

The calculation of \( U_{VDW} \) and \( U_{EDL} \) is described in the following section. First of all, the values for \( N_A, \varepsilon_0, \varepsilon_r, e \) and \( K_B \) are known constants as shown in Eq.4.5. Ionic strength \((I)\) can be determined based on the electrolytes used for zeta potential measurements, and then the corresponding \( \kappa \) can be determined. \( U_{VDW} \) and \( U_{EDL} \) can then be determined with Eq.4.1 and Eq.4.2. The missing parameters for the calculation are \( \nu, T, A_H, \psi_s, \psi_p, D \) and \( a \). The parameter \( \nu \) is the charge number of counter ions to the considered surfaces, it is 1 and 2 for monovalent and divalent electrolytes, respectively. The Hamaker constant \((A_H)\) used in this study is \( 1.4 \times 10^{-20} \text{J} \). That is because the size of colloidal and macromolecular NOM compounds is in nano-scale, and according to literature the Hamaker constant for organic carbon in water is around \( 1 \times 10^{-20} \text{J} \) (Petosa et al. 2010). Considering the mixed nature of surface water consisting of also relatively large colloidal compounds, \( 1.4 \times 10^{-20} \text{J} \) is applied here.

The distance between the colloidal NOM compounds and the membrane \((D)\) and the diameter of spherical colloidal NOM compounds \((a)\) are two parameters that need to be assumed to complete the calculation of \( U_{VDW} \) and \( U_{EDL} \). Because colloidal NOM compounds are generally compounds or particles which deposit on the membrane surface and/or block the membrane pores and thereby build up membrane fouling layer, the focus of the demineralized water backwash is the
removal of colloidal NOM foulants with a diameter similar with the pore size of the membranes. Considering that the pore size of UF membranes is around 30 nm, the diameter of spherical NOM compounds (a) is assumed to be 30 nm. In terms of the distance D, if the colloidal NOM foulants is reversible with demineralized water backwashing, it probably in the secondary energy minimum according to the DLVO theory. The exact value will be assumed in the later section based on the exact zeta potential of the two considered charged surfaces.

4.2.2 Hypotheses for demineralized water backwash

Because the UF membranes used in this study and the NOM in surface water are (usually) negatively charged, the presence of cations in feed water can enhance UF fouling through two mechanisms: charge screening and calcium bridging effects. The charge screening effect involves both monovalent and divalent cations, and the strength of this effect relates with the DLVO theory. The higher electrolyte valence and concentration, the stronger the charge screening effect is. Consequently, the total interaction energy between NOM and membranes becomes more attractive. Therefore, NOM easily fouls the membranes. In addition to the charge screening effect, due to the double valences of calcium, it probably bridges the negatively charged NOM and membranes through bindings of acidic functional groups on NOM and membranes. In that case, the fouling of UF membranes can be enhanced as well. The complexation of natural organics with calcium may lead to stable complexes or aggregation according to Liao and Randtke (Liao and Randtke 1986). In that case, the fouling is further enhanced after backwashes when the following NOM interacts with NOM foulants on the membranes via calcium.

One possible mechanism of demineralized water backwashing is the reduction of the charge screening effect. According to the DLVO theory, the charge screening effect can be changed by varying the ionic environment. When the UF membranes are backwashed with demineralized water, the cation concentration near the membrane surface is reduced by the demineralized water. Consequently, the
charge screening effects on NOM foulants and membranes are reduced and repulsion between NOM foulants and membranes is restored, improving the removal of foulants by backwashing. However, when the membranes are backwashed with UF permeate, the charge screening effects on foulants and membranes are maintained because the cation concentration in UF permeate is similar with that near the membrane surface. Therefore, there is no improvement on foulant removal. If the charge screening effect is the only mechanism behind demineralized water backwash, backwashing with two types of solutions having the same impact on interaction energy would show identical fouling control efficiency.

Another possible mechanism of demineralized water backwashing is the breakdown of the calcium bridging effect. Calcium interacts with natural organics in two manners: site specific weak and strong bindings (Leenheer et al. 1989). Weak binding is present in all molecules and increases with carboxylic acid content and the structural arrangement of these groups, whereas strong binding is very specific to organic components and is not always present. Cabaniss and Shuman reported that about 50% of fulvic acid in a natural environment may be associated with calcium and magnesium, but that such associations may be broken down during extraction process (Cabaniss and Shuman 1988a, b). By applying demineralized water backwashes, some of the calcium bridges may be broken down due to the difference of calcium concentration between demineralized water and the membrane surface. Since this concentration difference leads to a demand for equilibrium, in the case of weak bindings, calcium may be extracted and diffuse into the demineralized water. However, this difference in concentration is not expected to occur when the membrane is backwashed with UF permeate.

According to the DLVO theory, if there is no calcium adsorption/bridging, the zeta potentials of membranes should be identical for measurements with the same electrolyte solution (the same strength of the charge screening effect). Therefore, the zeta potentials of a membrane can be measured at three moments: 1) before and 2) after calcium adsorption, and 3) after demineralized water backwash. If a less negative zeta potential is observed after calcium adsorption, it is caused by
the calcium adsorption/bridging. If a more negative zeta potential is observed after demineralized water backwash, the adsorbed calcium is removed by the backwash.

4.3 Material and Methods

4.3.1 Characterization of NOM

A Nano Zetasizer from Malvern Company was used to assess the zeta potentials of organic matter components. This equipment is capable of measuring the zeta potentials of particles with a diameter between 3.8 nm and 100 µm; thus, dissolved NOM compounds (diameter < 0.45 µm) can be measured. In principle, by applying an electric field, NOM compounds with a zeta potential will migrate toward the electrode of an opposite charge with a velocity proportional to the magnitude of the zeta potential. The velocity of the movement is measured using laser Doppler velocimetry (LDV), and converted into a zeta potential through calculations applying dispersant viscosity and the Smoluchowski theory.

Table 4.1: Different electrolyte conditions for zeta potential measurements of Schie water NOM and UF membranes

<table>
<thead>
<tr>
<th>Electrolyte No.</th>
<th>pH</th>
<th>KCl (mmol/l)</th>
<th>NaCl (mmol/l)</th>
<th>CaCl₂ (mmol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>7</td>
<td>5</td>
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</tr>
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<td>9</td>
<td>7</td>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>7</td>
<td>25</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>7</td>
<td>50</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Raw surface water (Schie canal water in Delft, the Netherlands) was used to investigate the zeta potential of NOM compounds. At first, a filtration experiment with demineralized water backwashes was conducted and the backwash wastewater was collected during the experiment. Since demineralized water contains no ions, the backwash wastewater only consisted of rejected Schie water NOM. Afterwards, the 500 ml of collected backwash wastewater from demineralized water backwashes was divided into 16 samples and adjusted to electrolyte conditions 1-6 and 12-21 (Table 4.1).

On the one hand, because KCl is a standard electrolyte used in SurPAAS, KCl was used to investigate the influence of pH on the zeta potentials of the NOM compounds. On the other hand, since the Na\(^+\) and Ca\(^{2+}\) are common cations found in natural surface water, NaCl and CaCl\(_2\) electrolyte solutions were used to investigate the influence of electrolyte concentrations and valences on the zeta potentials.

### 4.3.2 Characterization of membranes

In this study, the zeta potentials of membrane were determined with a commercial analyzer, SurPAAS, from Anton Paar Company. This analyzer measures the streaming potential coefficient (SPC) of target surfaces and then calculates the
corresponding zeta potential using Eq.4.6. The streaming potential coefficient equals \( \Delta \Phi / \Delta P \). By flushing the target surface with electrolyte solution, potential and pressure differences over the surface are created. The values of \( \Delta \Phi \) and \( \Delta P \) were measured by electrodes and pressure meters installed at both ends of the target surface. Since the focus of this study is the interaction between the NOM compounds and active membrane surfaces, the zeta potential along membrane fibers were determined, instead of the zeta potential through membrane.

\[
\frac{\Delta \Phi}{\Delta P} = \frac{\varepsilon \varepsilon_0 \zeta}{\eta \cdot EC}
\]

Eq.4.6

where, \( \Delta \Phi \) is the measured potential difference along membrane fibers (V), \( \Delta P \) is the respective measured pressure difference along membrane fibers (Pa), \( \zeta \) is the zeta potential of the measured surface (V), \( \eta \) is the dynamic viscosity of the solution (Pa*s), EC is the conductivity of the solution (S*m\(^{-1}\)).

The influence of pH on the zeta potential was investigated at a constant electrolyte concentration for both new and fouled membranes (electrolyte 1-6). The new membranes were characterized under different KCl and CaCl\(_2\) concentrations (electrolyte 7-11 and 17-21). In order to confirm the similar effect of monovalent electrolytes on the zeta potential and demonstrate that results obtained from NaCl and KCl are comparable, characterization of the fouled membranes included NaCl, KCl and CaCl\(_2\) electrolytes (electrolyte 1-21).

### 4.3.3 Impact of calcium adsorption on zeta potentials of membranes

Table 4.2 shows the different measuring moments of zeta potentials for a new membrane and a fouled membrane regarding the impact of calcium adsorption. All the zeta potentials of membranes were measured with 1 mmol/l KCl electrolyte solution. The membranes were flushed with electrolyte for 5 minutes to remove contaminants before real zeta potential measurements.
Table 4.2: Conditions of zeta potential measurements regarding the impact of Ca adsorption

<table>
<thead>
<tr>
<th></th>
<th>New membrane</th>
<th>Fouled membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moment of zeta potential</td>
<td></td>
<td></td>
</tr>
<tr>
<td>measurement 1</td>
<td>Before a 2-hour continuous filtration with 5 mmol/l CaCl₂</td>
<td>After a 2-hour continuous fouling experiment and rinsing with demineralized water</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moment of zeta potential</td>
<td></td>
<td></td>
</tr>
<tr>
<td>measurement 2</td>
<td>After a 2-hour continuous filtration with 5 mmol/l CaCl₂</td>
<td>After a 2-hour continuous filtration with 5 mmol/l CaCl₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moment of zeta potential</td>
<td></td>
<td></td>
</tr>
<tr>
<td>measurement 3</td>
<td>N/A</td>
<td>After a 8-minute demineralized water backwash</td>
</tr>
</tbody>
</table>

4.3.4 Fouling experiments based on the results of characterization

4.3.4.1 Feed and backwash water

Raw surface water was taken from the Schie canal in Delft as feed water. The water was stored in a refrigerator at a temperature of 4°C without prefiltration. The water quality is shown in Table 4.3.

Four types of backwash water were used: 1) UF permeate, 2) demineralized water with 2 mmol/l CaCl₂, 3) demineralized water with 10 mmol/l NaCl and 4) demineralized water. The water quality is shown in Table 4.3. Ten mMol/L NaCl and 2 mmol/l CaCl₂ were also used for backwashing, since these concentrations have shown similar interaction energy between NOM compounds and UF membranes (similar charge screening effect).
Table 4.3: Water qualities of feed and backwash water

<table>
<thead>
<tr>
<th></th>
<th>DOC (mg/l C)</th>
<th>pH</th>
<th>Na⁺ (mmol/l)</th>
<th>Ca²⁺ (mmol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schie canal water (Feed)</td>
<td>25</td>
<td>7.1</td>
<td>2.56</td>
<td>2.92</td>
</tr>
<tr>
<td>UF permeate</td>
<td>23</td>
<td>7.0</td>
<td>2.48</td>
<td>2.87</td>
</tr>
<tr>
<td>2 mmol/l CaCl₂</td>
<td>&lt;0.1</td>
<td>6.9</td>
<td>N/A</td>
<td>2</td>
</tr>
<tr>
<td>10 mmol/l NaCl</td>
<td>&lt;0.1</td>
<td>6.9</td>
<td>9.95</td>
<td>N/A</td>
</tr>
<tr>
<td>Demineralized water</td>
<td>&lt;0.1</td>
<td>7</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

4.3.4.2 Membrane module

Similar self prepared membrane modules used in the study of Chapter 3 is applied in this chapter as well. It contains. Two 30 cm UFC M5 0.8mm hollow fibers (X-FLOW Company) were potted in an 8 mm PVC pipe (using a polyurethane potting resin), providing a surface area of 0.0015 m² for each module. The characteristics of the membrane fibers are listed in Table 4.4.
4.3.4.3 Ultrafiltration setup

The UF setup (Figure 4.1) was designed for constant flux experiments. The constant feed and backwash flow were maintained during the experiments with a DUAL syringe pump system and one single syringe pump (New Era Pump Systems, Inc.), respectively. Two solenoid valves (Burkert Fluid Control Systems) were applied to control the direction of the water flow. The syringe pumps and solenoid valves were controlled by a programmable logic controller (PLC), so the setup could be run automatically and continuously. As shown in Table 4.5, four operational phases were developed for this setup: 1) Forward flush 1 (feed side), 2)
Filtration, 3) Forward flush 2 (permeate side) and 4) Backwash. Forward flush 2 (permeate side) was programmed to ensure that the membrane fibers were completely surrounded by demineralized water before a demineralized water backwash. Two digital pressure meters were used to measure the pressure of feed water during filtration and backwash. Since the pressures of the permeate and backwash waste stream were equal to atmospheric pressure, the pressure exhibited by the two pressure meters was the transmembrane pressure (TMP). The TMP values were uploaded to the computer every 8 seconds.

Table 4.4: Characteristics of membrane fibers provided by manufacturer

<table>
<thead>
<tr>
<th>Membrane material</th>
<th>PES/PVP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight cut-off</td>
<td>100 kDa</td>
</tr>
<tr>
<td>Filtration mode</td>
<td>Inside-out</td>
</tr>
<tr>
<td>Internal fiber diameter (mm)</td>
<td>0.8</td>
</tr>
<tr>
<td>Length of module (cm)</td>
<td>35</td>
</tr>
<tr>
<td>Surface area of module (m²)</td>
<td>0.0015</td>
</tr>
<tr>
<td>Module diameter (mm)</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 4.5: Operational phases of UF setup

<table>
<thead>
<tr>
<th>Forward flush 1 (feed side)</th>
<th>Valve 1</th>
<th>Valve 2</th>
<th>Filtration Pumps</th>
<th>Backwash Pump</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtration</td>
<td>Open</td>
<td>Close</td>
<td>On</td>
<td>Off</td>
</tr>
<tr>
<td>Forward flush 2 (permeate side)</td>
<td>Open</td>
<td>Close</td>
<td>Off</td>
<td>On</td>
</tr>
<tr>
<td>Backwash</td>
<td>Close</td>
<td>Open</td>
<td>Off</td>
<td>On</td>
</tr>
</tbody>
</table>
4.3.4.4 Filtration protocol

All experiments were carried out in a dead-end operation mode. Before each experiment, the setup was thoroughly flushed with demineralized water in both filtration and backwash modes to remove chemical residues and air in the system. Afterwards, the setup was operated with demineralized water at a flux of 120 l/(m$^2$.h) for half an hour to determine the initial permeability of each membrane. Each fouling experiment consisted of 9 operational cycles. Each cycle was composed of three phases: 1) Filtration at a flux of 120 l/(m$^2$.h) for 15 minutes, 2) Forward flush of permeate side for 30 seconds, 3) Backwashing at a double filtration flux for one minute. Fouling experiments were conducted for the different types of backwash water shown in Table 4.3 to compare their fouling control efficiency.

4.4 Results and discussion

4.4.1 Zeta potentials of NOM

4.4.1.1 Impact of pH

The zeta potentials of Schie water NOM as a function of pH are shown in Figure 4.2. The zeta potentials of Schie water NOM became more negative with an increase in pH. That is (probably) because the carboxyl functional groups of NOM compounds were protonated by hydrogen ions at low pH values. The carboxyl functional groups are the negatively charged components of the NOM compounds. After protonation, the NOM compounds became less negatively charged. However, the concentration of hydrogen ions decreased with the increase in pH, leading to less protonation and consequently more negative zeta potentials of the NOM compounds. Furthermore, the zeta potential of the NOM at pH 3 was around -17 mV (not yet reaching its isoelectric point (IEP)); thus, this type of NOM is highly negatively charged. The zeta potentials are influenced by the structure of the NOM compounds.
compounds. There might be high levels of negative functional groups in the Schie water NOM. Because the analyzed Schie water NOM is a mixture of different fractions of NOM, the reason for such a highly negative charge needs a further research.

4.4.1.2 Impact of electrolyte concentration and valence

As shown in Figure 4.3, the NOM compounds also became less negatively charged when the electrolyte concentration increased for both monovalent and divalent electrolyte solutions. That is because there were more cations available for negative charge screening when the electrolyte concentration increased. Although the increase in electrolyte concentration could reduce the negative charge of membranes for both types of electrolyte solutions, NaCl and CaCl$_2$ showed a different negative charge reduction under an equal concentration difference. CaCl$_2$ showed a much greater reduction of the membranes’ negative charge than NaCl did.

This phenomenon can be explained by the DLVO theory, since the location of the zeta potential measurement is fixed (fixed $x$ in Eq.4.4), the zeta potential depends on the surface potential ($\psi_0$) of substances and an inverse Debye screening length ($\kappa$). The surface potential relates to the acidic functional content, if the number of functional groups is not changed (for example reduced by calcium adsorption), the surface potential is constant. Therefore, zeta potentials of specific substance vary with the inverse Debye screening length, which depends on the ionic strength as shown in Eq.4.5. Based on the theoretical calculation of ionic strength using Eq.4.7, 1.5 mmol/l CaCl$_2$ has a similar ionic strength to 5 mmol/l NaCl (Table 4.6), and thus the inverse Debye screening length for both cases should be identical. Consequently, a similar zeta potential for both situations should be expected, according to Eq.4.4. However, it was not as expected; the measured zeta potential at 1 mmol/l CaCl$_2$ was similar to the one at 5 mmol/l NaCl (Figure 4.3). That is probably because a small amount of Ca$^{2+}$ adsorbed onto the NOM during the zeta
potential measurement (which took more than half an hour) via the acidic functional
groups on membranes, reducing the surface potential of NOM ($\psi_0$).

$$I = \frac{1}{2} \sum_i Z_i M_i$$  \hspace{1cm} \text{Eq.4.7}

Where $I$ is the ionic strength, $Z_i$ is the valence of ion type $i$ and $M_i$ is the mole
concentration of ion type $i$ in units of Mol/l.

Table 4.6: Ionic strengths of 1 and 1.5 mmol/l CaCl$_2$ and 5 mmol/l NaCl electrolytes

<table>
<thead>
<tr>
<th>Cation concentration (mmol/l)</th>
<th>Cation valence</th>
<th>Anion concentration (mmol/l)</th>
<th>Anion valence</th>
<th>Ionic strength (mmol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl$_2$</td>
<td>1.0</td>
<td>2</td>
<td>2.0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>2</td>
<td>3.0</td>
<td>1</td>
</tr>
<tr>
<td>NaCl</td>
<td>5.0</td>
<td>1</td>
<td>5.0</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 4.2: Zeta potentials of Schie water NOM at different pH values, measured with 1 mMol/L KCl
electrolyte solution
4.4.2 Zeta potentials of membranes

4.4.2.1 Impact of pH

Figure 4.4 shows the zeta potentials of new and fouled membranes at different pH values (all these zeta potentials were measured with 1 mmol/l KCl electrolyte solution). It is clear that the membranes used in this study are negatively charged at a neutral pH of 7. Furthermore, the zeta potentials of both new and fouled UF membranes become more negative with an increase in pH. At a low pH, the membrane was positively charged, while it became negatively charged when the pH was higher than 4.5; thus, the IEP for fouled membranes is pH 4.5. The influence of pH on the zeta potential (charge) of membranes is dramatic.
However, the zeta potentials of new membranes were more negative than they were for fouled membranes, but were still negative (around -14 mV), even at pH 4. The same type of membrane fibers were also used by van der Ven, and a constant negative streaming potential within the whole pH range was reported (van der Ven 2008). The difference between the zeta potential of new and fouled membranes indicates that foulants reduce the negative charge of membranes, probably due to the adsorption of NOM and calcium during filtration, changing the surface properties of fouled membrane.

![Figure 4.4: Zeta potentials of new and fouled membranes at different pH values, measured with 1 mmol/l KCl electrolyte solution](image)

4.4.2.2 Impact of electrolyte concentration and valence

**New membrane**

The zeta potentials of a new membrane under different electrolyte conditions (electrolyte valence and concentration) are shown in Figure 4.5. Zeta potentials of new membranes became less negative with the increase in cation concentration for
both types of cation. In addition, divalent cations showed a much bigger influence on the reduction of the negative zeta potential than monovalent cations did. That is because of the higher charge screening efficiency of divalent cations. Similar to the NOM results, similar zeta potential of the membrane should occur at 1.5 mmol/l CaCl$_2$ and 5 mmol/l NaCl as well according to the DLVO theory since they have a similar ionic strength (Table 4.6). However, a greater influence of calcium on the zeta potential was also observed. As explained in Section 4.4.1.2, calcium adsorption during measurement with calcium electrolytes is probably the reason for this.

Although the impact of cations on NOM and new membranes was similar, the exact zeta potential values under the same electrolyte concentrations were different. That is because the zeta potential also depends on the surface potential of substances (as shown in Eq.4.4). Surface potential depends on the acidic functional content of substances. Since the amount of this content is probably different on membranes and NOM, their surface potentials are different as well. Consequently, zeta potentials are different under the same electrolyte conditions.

Figure 4.5: Zeta potential of a new UF membrane as a function of electrolyte concentration for two types of electrolyte solutions: KCl and CaCl$_2$ at pH 7
Fouled membrane

Figure 4.6 shows the zeta potentials of fouled UF membranes under different electrolyte concentrations for three types of electrolyte solutions: KCl, NaCl and CaCl$_2$ at a pH of 7. Although the zeta potentials are not identical as in the characterization of NOM and new membranes, the tendency of zeta potential variation under different conditions is similar to those of NOM and new membranes.

According to the trend line, the membrane reached its IEP at a concentration around 8 mmol/l CaCl$_2$. On the other hand, the membrane reached its IEP at concentrations of 40 and 45 mmol/l for KCl and NaCl electrolytes, respectively. KCl and NaCl electrolyte solutions have a similar trend line concerning the zeta potential as a function of their concentration. That is because both of them are monovalent ions, which has a similar effect on the electrical double layer on the membrane surface.

Figure 4.6: Zeta potential of a fouled UF membrane as a function of electrolyte concentration for three types of electrolyte solution: KCl, NaCl and CaCl$_2$ at pH 7
The zeta potentials of fouled membranes were less negative than those of new membranes. That is probably because of the adsorption of calcium and NOM molecules on the membranes, reducing the zeta potential of membranes (Figure 4.4). Because there are calcium ions and NOM compounds in surface water, calcium is expected to adsorb on membranes, making surface of membranes less negatively charged. Furthermore, the zeta potential of NOM in the Schie canal water was -12.5 mV at pH 8 and 960 µS/cm, while the zeta potential of a new membrane at the same condition was between -15 and -16 mV. Therefore, if the NOM compounds are adsorbed on the membranes, the zeta potential of the membrane could be reduced as well.

By varying the distance between the colloidal NOM and membranes, a graph of interaction energy versus distance is obtained as Figure 4.7. According to this figure, the secondary energy minimum is at a distance around 30 nm, so the distance between the colloidal NOM foulant and membranes is assumed to be this value. At this distance, interaction energy based on the zeta potentials of fouled membranes was calculated with Eq.4.1-4.3 and 4.5 for different electrolyte situations. For example, using 1 mmol/L CaCl$_2$ electrolyte, the ionic strength is 0.0035 M (as shown in Table 4.6), and the corresponding inverse Debye screening length was calculated to be $1.77 \times 10^8$ m$^{-1}$ with Eq.4.4. The measured zeta potentials of the NOM and membranes at 20°C with 1 mmol/L CaCl$_2$ electrolyte were -18.5 and -5.5 mV, respectively (as shown in Figure 4.3 and 4.6).

Putting all experimentally determined values together with the known constants in Eq 1 and 2, $U_{VDW}$ and $U_{EDL}$ can be obtained, and consequently the total interaction energy ($U_{DA}$) can be determined with Eq.3. Therefore, the $U_{DA}$ for 1 mmol/L CaCl$_2$ is $19 \times 10^{-21}$ J (4.64 kT) with a $U_{VDW}$ of $-2.33 \times 10^{-21}$ J and a $U_{EDL}$ of $21.4 \times 10^{-21}$ J. The corresponding interaction energy of different electrolyte situations is calculated and shown in Figure 4.8. In this Figure, positive interaction energy indicates the repulsive interaction between membranes and NOM compounds, while negative interaction energy reveals attractive interaction between them. The increase in both divalent and monovalent cation concentration reduces the repulsive interaction.
energy between membranes and NOM, and the interaction energy translates into attractive interaction at a specific concentration. The attractive interaction energy of both CaCl$_2$ and NaCl solutions supports the argument about the enhancement of membrane fouling with a presence of cation in feed water (Hong and Elimelech 1997, Li et al. 2009b). This specific concentration is different for divalent and monovalent cations, and the one for calcium is much lower than for sodium. In terms of NaCl electrolyte, the interaction energy for the colloidal compounds with diameters around 30 nm becomes repulsive when concentration is lower than 8 mmol/L NaCl. The interaction energies between NOM and membranes for both 2 mmol/L CaCl$_2$ and 10 mmol/L NaCl solutions are attractive and at the same level (around -0.35 kT).

When membranes are backwashed with demineralized water, the cation concentration near the membrane surface is almost zero. As seen in Figure 4.8, the interaction energy between the membrane and the NOM is repulsive, enhancing the backwash efficiency. On the other hand, the interaction energy is still attractive if the backwash water is UF permeate because the cation concentration near the membrane surface does not change, containing about 3 mmol/l Ca$^{+2}$ and 2.5 mmol/l Na$^{+}$.

Since the hydraulically irreversible fouling cannot be completely prevented even with demineralized water backwashing, the fouling control of UF membranes by backwashing is more related to how to control the buildup of hydraulically irreversible fouling on slightly fouled membrane as opposed to new membrane. Therefore, the results of the zeta potential characterization of fouled membranes and their corresponding calculated interaction energy were applied to the fouling experiments to assess whether the charge screening effect is the dominant mechanism behind demineralized water backwashing.
Figure 4.7: Variation of interaction energy between colloidal NOM compounds and membranes versus the distances between them

Figure 4.8: Calculated interaction energy between spherical NOM compounds and membrane surfaces at different electrolyte concentrations for both NaCl and CaCl₂ solutions (the distance between NOM compounds and membranes, diameter of NOM compounds and the Hamaker constant (A_H) are assumed to be 30 nm, 30 nm and $1.4 \times 10^{-20}$ J, respectively)
4.4.3 Adsorption of calcium on the UF membranes

The zeta potential of the membrane after calcium adsorption became significantly less negative, with a difference up to more than 4 mV (as shown in Figure 4.10). The observed less negative zeta potentials demonstrated that a certain amount of calcium adsorbed on the membranes and consequently influenced the charge of membranes.

Regarding the effectiveness of the demineralized water backwashing on the fouling caused by calcium adsorption, Figure 4.10 shows the zeta potential of fouled membrane under three conditions: 1) before calcium adsorption (freshly fouled membrane), 2) after calcium adsorption (fouled membrane after a 2-hour filtration with 5mmol/l CaCl$_2$ solution), and 3) fouled membrane after a 2-hour filtration with 5mmol/l CaCl$_2$ solution and an 8-minute demineralized water backwash. Although the zeta potentials of the fouled membrane after a demineralized water backwash became slightly more negative than those values after the calcium adsorption, the zeta potential after demineralized water backwash was still obviously less negative than the original negative zeta potential of freshly fouled membrane. Therefore, it is clear that (at least) part of the adsorbed calcium could not be removed from the membrane even with demineralized water backwashing. This part of calcium makes the surface charge of a fouled membrane less negative, and consequently makes the membrane more easily fouled by the NOM again in the next filtration cycles. That is probably the reason why a certain amount of hydraulically irreversible fouling was observed even when demineralized water backwashing was applied in the Schie canal water filtration in the past (Li et al. 2010a, Li et al. 2009).
Figure 4.9: Zeta potential of a new membrane as a function of pH for two situations: before and after 2-hour calcium adsorption

Figure 4.10: Zeta potential of a fouled membrane as a function of pH for three situations: before calcium adsorption experiment, after 2-hour calcium adsorption experiment, and after calcium adsorption and 8-minute demineralized water backwash
4.4.4 Fouling experimental results

4.4.4.1 Clean water permeability of membrane modules

Each experiment was conducted with a new membrane module. All the self-prepared membrane modules were tested with demineralized water to determine their clean water permeability; the TMP of modules in this test were used as the \( \text{TMP}_0 \) of modules (0.095 ± 0.005 bar at a flux of 120 l/(m\(^2\).h)).

![Figure 4.11: Normalized TMP as a function of time for four backwash waters: 1) Demineralized water, 2) Demineralized water with 2 mmol/l Ca\(^{2+}\), 3) Demineralized water with 10 mmol/l Na\(^+\), and 4) UF permeate (with 3 mmol/l Ca\(^{2+}\) and 2.5 mmol/l Na\(^+\)](image)

4.4.4.2 Comparison of fouling control efficiency

As shown in Figure 4.11, demineralized water exhibits the lowest increase in \( \text{TMP}/\text{TMP}_0 \) within 2.5 hours. According to the characterization results of fouled membrane, similar interaction energy was calculated for the electrolyte solutions
with 2 mmol/L Ca\(^{2+}\) or 10 mmol/l Na\(^+\) by applying Eq.4.1-4.3 (Figure 4.8). If eliminating the charge screening effect is the dominant mechanism of demineralized water backwashing, then backwashing with these two types of water should show a similar fouling control efficiency. In Figure 4.11, the increase rates in TMP/TMP\(_0\) of these two backwash waters are higher than the demineralized water, showing the impact of cations in backwash water on fouling control. Although the control efficiency of 10 mmol/l Na\(^+\) is slightly higher than 2 mmol/l Ca\(^{2+}\) (a bit lower increase in TMP/TMP\(_0\)), they are on a similar level. The higher fouling removal for 10 mmol/L Na\(^+\) was probably caused by the breakdown of a small amount of weak calcium bridging. Therefore, reduction of the charge screening effect plays a dominant role on the fouling removal of demineralized water backwashes.

UF permeate showed the highest increase in TMP/TMP\(_0\) in Figure 4.11, which is almost 6 times higher than demineralized water. That is because of the composition of the UF permeate. The UF permeate contained around 3 mmol/l Ca and 2.5 mmol/l Na, so it present a stronger potential for maintaining the charge screening effect during its backwash than any other backwash waters used in this study. The improvement of demineralized water backwash observed here corresponds to the previous findings of the authors (Abrahamse et al. 2008, Li et al. 2010a, Li et al. 2010b, Li et al. 2009).

### 4.5 Conclusions

The hypotheses of demineralized water backwashing were investigated in this study, including the charge screening and the calcium bridging effects. By determining the zeta potential of the membranes and the NOM compounds at different conditions, the impact of pH and electrolyte valence and concentration on their charge was assessed. Furthermore, the adsorption of calcium on the membranes and the NOM compounds was also illustrated.

Results showed that a membrane became less negatively charged when the pH decreased and the concentration of electrolyte increased, consistent with the
findings of other researchers. That is because the negatively charged functional
groups on the membrane surface were protonated by hydrogen ions at low pH
values, and the negative charge of membranes were screened by more cations
when the electrolyte concentration was high. Furthermore, divalent cation has a
much stronger effect on the increase of membrane zeta potential than monovalent
cations. Although similar tendencies were observed for new and fouled membranes
at different conditions, the zeta potential of fouled membranes is less negative than
of new membranes at the same electrolyte condition. That is probably because the
NOM molecules are adsorbed on the membrane surface.

Calcium ions indeed adsorbed on either new or fouled membranes, and bridged
NOM and membranes afterwards. However, the interaction of calcium with fouled
membranes is more substantial than with new membranes. Demineralized water
backwashing showed the best fouling control, while the UF permeate showed the
lowest foulants removal. The 2 mmol/l CaCl₂ and 10 mmol/l NaCl solutions showed
the same interaction energy between the NOM and membranes. Although 10
mmol/l NaCl solution displayed a slightly better fouling control, both solutions
exhibited a similar level of fouling control efficiency. This indicates that the charge
screening effect played a dominant role in the membrane fouling and fouling
control by demineralized water backwashing. The small difference of backwash
efficiency between 2 mmol/l CaCl₂ and 10 mmol/l NaCl was probably caused by
the breakdown of weak calcium bridging connections. However, most of the fouling
caued by calcium bridging is difficult to remove even with a demineralized water
backwash.

4.6 References

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Membrane Science 323(1), 153-158.


Chapter 5

Influence on fouling of different NOM fractions

This chapter is based on the following paper:
5.1 Introduction

In our previous studies, experimental results have shown that demineralized water backwashing substantially improves the fouling control of ultrafiltration for natural surface water. This is because demineralized water backwashing eliminates (at least partly) the charge screening and Ca-bridging effects, restoring the negative charges of both the UF membrane and natural organic matter (NOM) (Li et al. 2009b).

Hong and Elimelech (1997) systematically investigated the impact of ionic strength, pH and calcium concentration in the feed water on the fouling of nanofiltration membranes. They reported that membrane fouling increases with an increase in ionic strength of the feed water. This was attributed to the charge screening effect of cations (both monovalent and divalent) on the negatively charged NOM and NF membranes (Hong and Elimelech 1997). Pontié et al. (1998) reported the same impact of ionic strength on PES UF membranes (Pontié et al. 1998). In addition to the contribution to the charge screening effect, calcium also aggravates fouling via the calcium bridging effect.

However, it has to be noted that even with demineralized water backwashes, not all the foulants can be hydraulically flushed away. Due to the complex nature of NOM, it is difficult to distinguish which fraction of NOM is sensitive to the demineralized water backwash. Nevertheless, this information is important to understand fouling control. To address this issue, tests with natural water and model compounds were conducted for this study. Several model organic compounds have been widely used to mimic different NOM fractions in membrane fouling research.

Sodium alginate (SA) has been used as a model to mimic polysaccharides in many studies since it behaves similarly to extracellular polymeric substances (EPS) during filtration (Ang and Elimelech 2007, de Kerchove and Elimelech 2007, Katsoufidou et al. 2007, Lee et al. 2006, Ye et al. 2005). Suwannee River humic acid (SRHA) has been used as a model compound for humic substances in many
fouling studies as well, because it is isolated from natural water, thereby better representing reality (Jermann et al. 2007). Bovine serum albumin (BSA) has been widely used as a model compound to represent protein fouling in UF membranes, especially in wastewater treatment (Li et al. 2007). In this study, these compounds were used to test demineralized water backwashing effectiveness.

The objective of this study is to investigate the effectiveness of demineralized water backwashing on different fractions of NOM via LC-OCD analysis, and compare the LC-OCD results with tests using different model compounds representing different fractions of NOM. By comparing the results of natural surface water and model compounds, a better understanding of demineralized water backwashing is expected and its effectiveness for the removal of different fractions of NOM can be assessed.

5.2 Material and Methods

5.2.1 Feed water

5.2.1.1 Natural water types

Two types of surface water were used in this study: 1) Schie Canal water (Delft, the Netherlands) and 2) Biesbosch reservoir water. Schie Canal water was taken in January 2010, while Biesbosch reservoir water was taken in March 2010. In order to prevent any changes in feed water quality, all water samples were freshly taken and stored in a refrigerator and used for experiments within two days. The water quality of the two water types is shown in Table 5.1. Schie Canal water was characterized by LC-OCD as well to understand fraction composition of NOM in Schie Canal water. Furthermore, permeate and backwash wastewater were also analyzed with LC-OCD for experiments with Schie Canal water using both demineralized water and UF permeate backwashes.
5.2.1.2 Model compound solutions

Three types of model compounds (representing different fractions of NOM) were prepared. These are Suwannee River humic acid (SRHA) from the international humic substances society (IHSS), sodium alginate (SA) and bovine serum albumin (BSA) from the Aldrich Company.

SA is produced from brown algae, with a molecular weight of 12-80 kDa. Moreover, SA is a straight-chain, hydrophilic, colloidal, polyuronic acid composed primarily of anhydro-β-D-mannuronic acid residues with 1→4 linkage. It is negatively charged at neutral pH (Jermann et al. 2007). SRHA is isolated from the Suwannee River by XAD-8 resin adsorption. It is well-characterized, with a clear charge density and a low molecular weight between 1000 and 5000 Da (Thorn et al. 1989). The properties of SRHA are given in Table 5.2. BSA is a single polypeptide chain, consisting of around 583 amino acid residues and no carbohydrates. The molecular weight of BSA is around 66 kDa. BSA can cross-link with Ca$^{2+}$ via its free thiol-groups (Kelly and Zydney 1994).

A concentration of 20 mg/l was used for the SA and BSA solutions because that is the concentration at which fouling can be observed in a relatively short time. Van de Ven and his colleague used a concentration of 50 mg/l SA in their study to get sufficient fouling (van de Ven et al. 2008). As for the SRHA, 5 mg/l is a common concentration in surface water, so that is what was used in this study.
Table 5.2: Characteristics of humic acid from IHSS

<table>
<thead>
<tr>
<th>Acidic Functional Groups of IHSS Suwannee River sample</th>
<th>Carboxyl (meq/g C)</th>
<th>Phenolic (meq/g C)</th>
<th>Q_1</th>
<th>LogK_1</th>
<th>n_1</th>
<th>Q_2</th>
<th>LogK_2</th>
<th>n_2</th>
<th>N</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.13</td>
<td>3.72</td>
<td>9.7</td>
<td>4.35</td>
<td>3.3</td>
<td>4.5</td>
<td>10.4</td>
<td>1.7</td>
<td>171</td>
<td>0.08</td>
<td></td>
</tr>
</tbody>
</table>

Note: Q_1 and Q_2 are the maximum charge densities of Carboxyl and Phenolic binding sites, Log K_1 and Log K_2 are the mean log K values for proton binding by these two types of sites, and n_1 and n_2 are empirical parameters that control the width (in log K) of proton binding sites. N is the number of fitted titration data points, and RMSE is the root mean-square error for fitting a modified Henderson-Hasselbalch equation to the data (Ritchie and Perdue 2003)

Table 5.3: Water quality of model solutions

<table>
<thead>
<tr>
<th>DOC (mg/l)</th>
<th>pH</th>
<th>Na (mmol/l)</th>
<th>Conductivity (µS/cm)</th>
<th>Ca (mmol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium alginate 1</td>
<td>20</td>
<td>7.35</td>
<td>-</td>
<td>7.1</td>
</tr>
<tr>
<td>Sodium alginate 2</td>
<td>20</td>
<td>7.35</td>
<td>2</td>
<td>450</td>
</tr>
<tr>
<td>Sodium alginate 3</td>
<td>20</td>
<td>7.35</td>
<td>2</td>
<td>234</td>
</tr>
<tr>
<td>Humic acid 1</td>
<td>5</td>
<td>4.28</td>
<td>-</td>
<td>20.1</td>
</tr>
<tr>
<td>Humic acid 2</td>
<td>5</td>
<td>4.3</td>
<td>2.5</td>
<td>719</td>
</tr>
<tr>
<td>Bovine serum albumin 1</td>
<td>20</td>
<td>7.1</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Bovine serum albumin 2</td>
<td>20</td>
<td>7.1</td>
<td>3</td>
<td>720</td>
</tr>
</tbody>
</table>

The different tested water qualities are listed in Table 5.3. Although the concentrations of different model compound solutions were different, it did not limit the comparison between the UF permeate backwash and the demineralized water backwash within the specific type of model compound solution. Within the experiments of a specific model compound, DOC concentration was constant. The main focus of this study was to understand which compound is sensitive to the demineralized water backwash, so the concentration difference of model compounds was not a problem.
In order to investigate the impact of cations (both divalent and monovalent) on the membrane fouling of model compounds, \( \text{CaCl}_2 \) and \( \text{NaCl} \) were dosed in the model compound solutions.

### 5.2.2 Backwash water

Two types of backwash water were compared: 1) demineralized water and 2) UF permeates, since the main goal of this paper was to determine the effectiveness of demineralized water backwashing on different fractions of NOM and corresponding different model compounds.

### 5.2.3 Membrane

Similar self-prepared hollow fiber ultrafiltration membrane modules as the one specified in Chapter 4 were used.

Depending on the experiments, modules with different surface areas were used in this study. Modules used for SA, BSA and natural waters were five-fiber modules with a surface area of 0.00375 m\(^2\), while the modules used for SRHA were one-fiber modules with a surface area of 0.00075 m\(^2\). Due to the limited quantity of SRHA model compounds, fewer fibers were put in the modules for experiments so that one experiment would consume less water. Although the surface area of modules used for SRHA experiments is different from the modules used for the rest of the experiments (experiments for SA, BSA and natural waters), the critical issues for the fouling formation are feed water concentration and flux. All fouling experiments with the same specific type of feed water (model compound or natural water) were conducted with the same membrane modules, feed water concentrations and flux. Furthermore, different model compounds were not cross compared. Therefore, the difference in surface area did not influence the comparison of different backwashes within one type of feed water.
5.2.4 Filtration setup and protocol

The same ultrafiltration setup as the study of chapter 4 was used in this study as well. The detail description can be seen in Material and Methods section of Chapter 4.

Before each experiment, the setup was thoroughly flushed with demineralized water in both filtration and backwashing modes to remove the chemical residues and air in the system. Afterwards, the setup was operated with demineralized water at a flux of 120 l/(m$^2$.h) for half an hour to determine the initial permeability of each membrane module.

All fouling experiments were carried out in the same mode for several filtration cycles. Each filtration cycle is composed of three phases: 1) Filtration (15 minutes); 2) Forward flush of permeate side before backwashing (30 seconds); 3) Backwashing at a double filtration flux (one minute).

Table 5.4: Experimental conditions for natural water

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Feed water</th>
<th>Backwash water</th>
<th>Filtration flux l/(m$^2$.h)</th>
<th>Backwash flux l/(m$^2$.h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 1</td>
<td>Schie Canal</td>
<td>Demineralized water</td>
<td>120</td>
<td>240</td>
</tr>
<tr>
<td>Experiment 2</td>
<td>Schie Canal</td>
<td>UF permeate</td>
<td>120</td>
<td>240</td>
</tr>
<tr>
<td>Experiment 3</td>
<td>Biesbosch reservoir</td>
<td>Demineralized water</td>
<td>120</td>
<td>240</td>
</tr>
<tr>
<td>Experiment 4</td>
<td>Biesbosch reservoir</td>
<td>UF permeate</td>
<td>120</td>
<td>240</td>
</tr>
</tbody>
</table>

The experimental conditions for the different fouling experiments are shown in Tables 5.4 and 5.5. Before conducting all the experiments, some trial experiments were conducted to determine the flux required to get sufficient fouling within the
required time period. For the experiments of natural water, SRHA and BSA, 120 l/(m².h) were required. However, filtering the SA solution showed a much faster increase in TMP within each filtration cycle. In order to prevent exceeding the maximum pressure of UF system, a filtration flux of 60 l/(m².h) was applied in the experiments using SA solution. Because the main comparison was within the specific model compound, the difference of flux between SA and the other types of feed water did not cause any problem.

Table 5.5: Experimental conditions for model-compound water

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Feed water</th>
<th>Backwash water</th>
<th>Filtration flux l/(m².h)</th>
<th>Backwash flux l/(m².h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Sodium alginate 1</td>
<td>Demineralized</td>
<td>60</td>
<td>120</td>
</tr>
<tr>
<td>6</td>
<td>Sodium alginate 1</td>
<td>UF permeate</td>
<td>60</td>
<td>120</td>
</tr>
<tr>
<td>7</td>
<td>Sodium alginate 2</td>
<td>Demineralized</td>
<td>60</td>
<td>120</td>
</tr>
<tr>
<td>8</td>
<td>Sodium alginate 2</td>
<td>UF permeate</td>
<td>60</td>
<td>120</td>
</tr>
<tr>
<td>9</td>
<td>Sodium alginate 3</td>
<td>Demineralized</td>
<td>60</td>
<td>120</td>
</tr>
<tr>
<td>10</td>
<td>Sodium alginate 3</td>
<td>UF permeate</td>
<td>60</td>
<td>120</td>
</tr>
<tr>
<td>11</td>
<td>Humic acid 1</td>
<td>Demineralized</td>
<td>120</td>
<td>240</td>
</tr>
<tr>
<td>12</td>
<td>Humic acid 1</td>
<td>UF permeate</td>
<td>120</td>
<td>240</td>
</tr>
<tr>
<td>13</td>
<td>Humic acid 2</td>
<td>Demineralized</td>
<td>120</td>
<td>240</td>
</tr>
<tr>
<td>14</td>
<td>Humic acid 2</td>
<td>UF permeate</td>
<td>120</td>
<td>240</td>
</tr>
<tr>
<td>15</td>
<td>Bovine serum albumin 1</td>
<td>Demineralized</td>
<td>120</td>
<td>240</td>
</tr>
</tbody>
</table>
5.3 Results

5.3.1 Surface water filtration experiments

Figure 5.1 shows the TMP as a function of time during the experiments with Schie Canal water. As shown in this figure, TMP increased steadily during each operational cycle. During a backwash, some of the foulants are removed (hydraulically reversible fouling), but some foulants still remain on the surface (hydraulically irreversible fouling). Since not all the foulants are removed, the initial TMP of every new operational cycle steadily increased over time.

Different backwash waters showed different effectiveness on UF fouling control. For example, in experiments of Schie Canal water, demineralized water backwashing resulted in an increase of 0.03 bar in the initial TMP of each cycle (initial TMP was 0.1 bar at the beginning of the experiment, and became 0.13 bar at the 18th cycle). However, UF permeate backwashing resulted in an increase of 0.1 bar in TMP. Although the fouling potential of Schie Canal water in this study was lower than in our previous study, the increased backwash efficiency of demineralized water backwashing is consistent with the results of previous studies (Li et al. 2009b).
The increase in TMP during filtration of the raw Schie Canal water is lower in this study than what was reported in a previous study conducted during summer (Li et al. 2009b). This is mainly because the experiments in this study were conducted in winter, whereas the Schie Canal water has a higher fouling potential in summer.

This increase in backwash efficiency is mainly due to the reduction of the charge screening effect. Zeta potential measurements showed that the average zeta potential of the organic compounds present in Schie Canal water is -12.5 mV. The zeta potential of the UF membranes used is negative as well, around -15 mV at pH 7 (measured with 1 mmol/l KCl electrolyte solution). Van de Ven measured the streaming potential coefficient of the same type of membrane and also reported a negative charge (van de Ven et al. 2008).

Since the charge of NOM and UF membranes are negative, the presence of cations in water can screen the negative charge by compressing the electrical double layers, and thus make NOM easily deposit on the membranes. This is the
charge screening effect involving both monovalent and divalent cations. Divalent cations have a much stronger ability to compress electrical double layers according to the DLVO theory, and thus a higher charge reduction than monovalent cations at the same concentration. In addition to the contribution to the charge screening effect, calcium can also bind the negatively charged NOM with membranes through the carboxyl functional groups on them. Therefore, NOM can easily deposit on UF membranes via the “calcium bridge”. After the formation of the first fouling layer, calcium also bridges the new NOM onto the existing NOM fouling layer via the bridging effect. Consequently, the thickness of the fouling layer steadily increases.

In terms of fouling control with backwashes, the presence of cations in backwash water could maintain the charge screening of the negative charges of the NOM and membranes, maintaining reduced electrostatic repulsion between them. Consequently, backwash was not that effective, resulting in an increase in irreversible NOM deposition on the membranes. When the membrane is backwashed with demineralized water, the cation concentration around the membrane is reduced, restoring the repulsive force between the negatively charged NOM and membranes, and resulting in an efficient backwash. However, UF permeate contains almost the same cation concentration as the feed water. Therefore, the cation concentration near the membrane remained unchanged when UF permeate was used for backwashing, and the repulsive force was not completely restored, resulting in a less efficient backwash.

LC-OCD analyses were conducted to investigate the rejection of different fractions of NOM and their reversibility during different backwashes. Figures 5.2 and 5.3 show the OCD signal responses for the 1) demineralized water backwash experiment and 2) UF permeate backwash experiment, respectively. Furthermore, a mass balance calculation was conducted for the two commonly reported NOM fractions that cause fouling: biopolymers and humic substances, as shown in Table 5.6. Because there was always feed water inside the fibers before a backwash, the remaining feed water (from the inside of fibers to the backwash wastewater collecting point) can contaminate the backwash wastewater samples. Therefore, in
order to eliminate the impact of remaining feed water, this contamination was taken into account for the mass balance calculation.

OCD signal responses as a function of elution time for feed water, permeate and backwash wastewater of demineralized water are shown in Figure 5.2. Since the demineralized water contains no NOM, the measured NOM in the backwash wastewater was all the foulants flushed off. Although there was contamination from the remaining feed water in the fibers, this contamination was a small amount and identical for both types of backwash. In Figure 5.3, OCD signal responses as a function of elution time for feed water, permeate and foulants flushed off by the UF permeate are shown. Because UF permeate contains a substantial amount of NOM, the curve of the foulants flushed off was obtained by using the OCD response of NOM in backwash wastewater subtracting the OCD responses of NOM in permeate. Again, the foulants flushed off shown in the OCD graph include the contamination of the remaining feed water.

Figures 5.2 and 5.3 show that some biopolymers, humic substances and low molecular weight (LMW) substances are rejected by the UF membrane. Therefore, they are the potential foulants that increase transmembrane pressure (TMP). The interesting observation is that quite an amount of biopolymers was flushed off during backwash: 82.2% and 88.2% of biopolymers were flushed off for UF permeate and demineralized water, respectively. It means that, although some biopolymers are rejected by the UF membrane and increase the TMP, biopolymer fouling has a relatively high reversibility via hydraulic backwashes. This result corresponds to our previous results for sodium alginate (SA), which showed a high fouling reversibility of hydraulic backwashes (either UF permeate and demineralized water) as well.

However, demineralized water and UF permeate showed different effectiveness on their removal of deposited humic substances. UF permeate flushed off a limited amount of deposited humic substance (16.5%), but demineralized water backwashing was able to remove 71.9%.
It should be noted that, according to the LC-OCD analysis of natural water, even with demineralized water backwashing, not all the deposited natural biopolymers and humic substances could be removed. The mechanism of demineralized water backwashing mainly involves the reduction of the charge screening effect. The fouling of unremoved biopolymers and humic substances is probably related to some other mechanisms, such as hydrophobicity interactions and calcium bridging effect.

![Signal response (OCD) as a function of elution time for samples in demineralized water backwash experiments: feed, permeate and backwash wastewater (foulants flushed off)](image-url)

Figure 5.2: Signal response (OCD) as a function of elution time for samples in demineralized water backwash experiments: feed, permeate and backwash wastewater (foulants flushed off)
Figure 5.3: Signal response (OCD) as a function of elution time for samples in UF permeate backwash experiments: feed, permeate and foulants flushed off (backwash wastewater with subtraction of UF permeate).

Table 5.6: Mass balance calculation for biopolymers and humic substances

<table>
<thead>
<tr>
<th></th>
<th>&gt;&gt;20.000 Da</th>
<th>-1000 Da</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Biopolymer</td>
<td>Humic substances</td>
</tr>
<tr>
<td>Feed</td>
<td>0.451</td>
<td>8.394</td>
</tr>
<tr>
<td>Permeate</td>
<td>0.14</td>
<td>7.916</td>
</tr>
<tr>
<td>Backwash waste, UF permeate</td>
<td>1.808</td>
<td>8.49</td>
</tr>
<tr>
<td>Backwash waste, Demineralized water</td>
<td>1.808</td>
<td>3.479</td>
</tr>
</tbody>
</table>

Fixed values for both backwashes

<table>
<thead>
<tr>
<th></th>
<th>Time of one filtration cycle (min)</th>
<th>Flow of filtration (ml/min)</th>
<th>Time of one backwash (min)</th>
<th>Flow of backwash (ml/min)</th>
<th>Fouling on membrane within one cycle (mg)</th>
<th>Volume of remained feed (ml)</th>
<th>Contamination of remained feed (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF permeate backwash</td>
<td>15</td>
<td>7.5</td>
<td>1</td>
<td>15</td>
<td>0.035</td>
<td>2.754</td>
<td>0.001</td>
</tr>
<tr>
<td>Demineralized water backwash</td>
<td>15</td>
<td>7.5</td>
<td>1</td>
<td>15</td>
<td>0.035</td>
<td>2.754</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Note: The calculation based on one cycle (15 minutes filtration and 1 minute backwash)

Fouling experiments were also carried out with water from the Biesbosch Reservoir in the Netherlands. Although the zeta potential of the natural organic matter in the
Biesbosch water was not measured, surface water NOM is usually negatively charged. Since the same negatively charged UF membrane was used for the Biesbosch water experiments as in the previous experiments, it was expected that fouling would be influenced by charge screening and the calcium bridging effect here as well. Figure 5.4 shows the TMP as a function of time for ultrafiltration of the Biesbosch water using two different backwash waters: 1) UF permeate and 2) demineralized water.

Experiments with Biesbosch Reservoir water were carried out in a longer time range (24 hours) than the previous experiments. This was partly because of the relatively low DOC concentration of Biesbosch Reservoir water, but also the purpose of investigating the longer-term effect of demineralized water backwashing. Within the first three hours of operation, the two different backwash water types did not result in a significant difference on the effectiveness of fouling control. Development of hydraulically irreversible fouling is a gradual process and, as such,
it takes time for the demineralized water backwash to show its improvement on the irreversible fouling.

After 4 hours, however, the effectiveness of demineralized backwashing began to show: the initial TMP of a new filtration cycle increased from 0.1 up to around 0.4 bar when the membrane was backwashed with UF permeate. However, when the membrane was backwashed with demineralized water, the increase in initial TMP of each cycle was only 0.05 bar (increase from 0.1 to 0.15 bar). Therefore, demineralized water backwashing is also effective for Biesbosch Reservoir water treatment.

Results from natural surface water are consistent with the results in our previous publications (Li et al. 2009b). It is clear that backwashing with demineralized water improves the UF membrane fouling control efficiency, which can be explained by the charge screening effect of cations and the calcium bridging effect.

### 5.3.2 Synthetic solutions fouling experiments

#### 5.3.2.1 SA

Figure 5.5 shows the increase in TMP as a function of time for filtrating pure SA solution (20 mg/l) at a flux of 60 l/(m$^2$.h) with two different backwashes: 1) UF permeate and 2) demineralized water. TMP increased dramatically within one filtration cycle, from around 0.05 bar to 0.3 bar. The main fouling mechanism of sodium alginate ultrafiltration is reported to be cake layer formation in another study (Wang and Waite 2008). Because of the long-chain structure and high molecular weight of SA, SA molecules deposit on the membrane surface, covering the pores. With the increase in SA molecules, a cake layer is formed and thus increases the filtration resistance. Consequently, an increase in TMP was observed. However, most of the fouling was reversible with both UF permeate and demineralized water backwashes.
Figure 5.5: TMP as a function of time for filtrating SA solution (no ions) and backwashing with 1) UF permeate and 2) demineralized water

Figure 5.6: TMP as a function of time for filtrating SA solution with 2 mmol/l CaCl₂ and backwashing with 1) UF permeate and 2) demineralized water
Contrary to what was expected, a significantly lower fouling potential was observed when calcium was added to the SA solution (Figure 5.6). Apparently, fouling was dramatically decreased by adding calcium ions to a pure SA solution. In the presence of calcium ions, SA forms a highly organized gel layer with a structure resembling an egg-box (Grant et al. 1973), where calcium binds preferentially to the carboxylic functional groups of alginates and forms bridges between molecules. The reason for less fouling is probably due to chelating and aggregation effects of calcium with sodium alginate. Due to this aggregation, the size of the SA colloids increases, leading to a relatively more porous fouling layer on the membrane surface, and thus less build-up of TMP. This finding corresponds to a few studies about less fouling being observed with calcium addition (Katsoufidou et al. 2007, Listiarini et al. 2009, van de Ven et al. 2008), although other studies showed the contrary (Ang and Elimelech 2007, de Kerchove and Elimelech 2007, Lee and Elimelech 2006).
However, when sodium instead of calcium was added to the SA solution as feed water, a much higher increase in TMP within each operation cycle was observed. As shown in Figure 5.7, TMP increased from 0.06 bar up to around 0.5 bar in most cycles. This is because the presence of sodium in the feed water shielded the negatively charged SA molecules (van de Ven et al. 2008), compressing the electrical double layers of SA molecules and membranes and thus reducing the electrostatic repulsion between them. Because of their straight-chain structure, rejected SA molecules formed a more compact fouling layer when there were sodium ions in the feed water than when no ions were added. In contrast to calcium, sodium does not seem to have a chelating effect (since it cannot form intermolecular bridges).

Although the increase in TMP was higher when sodium was added to the SA solution, the fouling was still reversible for both demineralized water and UF permeate backwash, no matter which type of SA feed solution was used. The explanation is that the SA molecules formed a cake layer on the membrane surface instead of being adsorbed on the surface or in the pores. It is believed that cake layer fouling is more reversible than adsorptive fouling (Bessiere et al. 2005, Jermann et al. 2007).

5.3.2.2 SRHA

Figure 5.8 shows TMP as a function of time for filtrating the pure SRHA solution and SRHA solution with 2 mmol/l Ca and 2.5 mmol/l Na. Although the DOC concentration of SRHA is lower than SA (still comparable with Biesbosch Reservoir water used in this study), SRHA solution with 2 mmol/l Ca and 2.5 mmol/l Na (mimicking natural water) showed a high fouling potential. The presence of Ca and Na in feed water resulted in a more severe membrane fouling, similar to other studies (Hong and Elimelech 1997, Jermann et al. 2007, Li et al. 2009b). The SRHA and UF membranes are negatively charged. Because both calcium and sodium ions screen the negative charge of the SRHA molecules and membranes
via the charge screening effect, the SRHA molecules easily deposited/adsorbed onto membranes. In addition to the charge screening effect, SRHA molecules and membranes have the potential to react with multivalent cations by bridging via their carboxyl functional groups. Some studies have reported that the presence of calcium in SRHA solution can deteriorate the fouling of ultrafiltration (Hong and Elimelech 1997, Jucker and Clark 1994). That deterioration was attributed to the bridging effect of calcium between NOM and UF membranes via carboxyl functional groups binding, which enhanced the adsorption of NOM molecules onto the membranes.

Figure 5.9 shows TMP as a function of time for filtrating SRHA solution with 2 mmol/l Ca and 2.5 mmol/l Na in two backwash situations: 1) UF permeate and 2) demineralized water. In contrast to what is observed in surface water experiments, demineralized water backwashing did not improve the fouling control of SRHA solution with 2 mmol/l Ca and 2.5 mmol/l Na. That is probably because of the strong calcium bridging effect between SRHA molecules and membranes. Calcium can interact with NOM and membranes via functional group bindings (Leenheer et al. 1989). Binding is present in all molecules and increases with carboxylic acid content and the structural arrangement of these groups (Schäfer 2001). By interacting with both SRHA molecules and membranes, the calcium bridge is formed. Although the interaction can be broken, the extraction process normally involves decreasing pH to 2-3 and/or using extractants like EDTA. Therefore, it is difficult to break down the bridge connection with only demineralized water backwashing.
Figure 5.8: TMP as a function of time for filtrating HA solution (no ions) and HA solution with 2 mmol/l Ca & 2.5 mmol/l Na, both backwashed with demineralized water.

Figure 5.9: TMP as a function of time for filtrating HA solution with 2 mmol/l Ca & 2.5 mmol/l Na, and backwashed with 1) demineralized water and 2) UF permeate.
Furthermore, the low reversibility of SRHA fouling is also in contrast to the fouling of SA. That is probably because the fouling caused by SRHA is more closely related to the adsorption of molecules than the cake layer formation due to the reduction of the charge screening effect. Adsorptive fouling is most irreversible among different membrane fouling mechanisms.

The deposition of humic substances on the membrane surface involved the calcium bridging effect between the membrane and humic substances and also calcium complexation between humic substances. In order to illustrate this interaction and the corresponding reversibility of demineralized water backwashing, zeta potential measurements were conducted on a new membrane under different conditions. First the zeta potential of this new membrane was measured. Afterwards, the membrane was fouled by a 2-hour continuous filtration with 5 mg/l SRHA, and subsequently the zeta potential of the fouled membrane was measured. Next, the SRHA fouled membrane was used for a 2-hour filtration of 5 mmol/l CaCl$_2$ solution, and the zeta potential of the membrane was measured again after calcium adsorption. Finally, the SRHA fouled and calcium-adsorbed membrane was backwashed with demineralized water for 8 minutes and then its zeta potential was measured.

Table 5.7 shows the results of zeta potentials under different condition. The zeta potential of a new membrane is -15 mV. After the SRHA adsorption on the membrane, the zeta potential of the fouled membrane became -10 mV, indicating the deposition of SRHA on the membrane. Afterwards, due to the calcium adsorption onto the fouled membrane, the zeta potential of the membrane was further reduced to -5 mV. After a demineralized water backwash, although the zeta potential became a bit more negative (-5.5 mV), it was still far less negative than the values of new and freshly fouled membranes. The less negative zeta potential after a demineralized water backwash clearly showed calcium stuck on the membrane. Therefore, demineralized water backwashing is not effective for (at least most of) fouling caused by calcium bridging effect SRHA and calcium ions.
Table 5.7: Zeta potentials of an SRHA fouled membrane under different conditions

<table>
<thead>
<tr>
<th></th>
<th>Zeta potentials (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>New membrane</td>
<td>-15</td>
</tr>
<tr>
<td>SRHA fouled membrane</td>
<td>-10</td>
</tr>
<tr>
<td>SRHA fouled and Ca-adsorbed membrane</td>
<td>-5</td>
</tr>
<tr>
<td>After demineralized water backwashing</td>
<td>-5.5</td>
</tr>
</tbody>
</table>

Note: Zeta potentials were measured at pH 7 with 1mmol/l KCl electrolyte solution

5.3.2.3 BSA

Figure 5.10 shows the TMP as a function of time for four experiments: 1) UF of BSA (no ions) with demineralized water backwash; 2) UF of BSA (no ions) with UF permeate backwash; 3) UF of BSA with 2 mmol/l Ca and 3 mmol/l Na, with demineralized water backwash and 4) UF of BSA with 2 mmol/l Ca and 3 mmol/l Na, with UF permeate backwash. All experiments were conducted at a constant flux of 60 l/(m².h).

When pure BSA solution was filtrated, the initial TMP of each new cycle increased significantly over the course of the experiment, indicating irreversible fouling. Moreover, demineralized water backwashing did not result in a significant improvement of the fouling control.

When calcium was added to the feed solution, a significant improvement in the fouling was observed, similar to what was observed for the SA. Again, the lesser fouling is probably because of the chelating and aggregation effect of calcium, leading to an increased size of the BSA colloids and thus a more porous, less compact cake layer.

The UF membranes fouled with BSA showed a small improvement in fouling when backwashing with demineralized water, but the extent was much lower than that of natural waters. This indicates that the BSA fouling layer is not highly reversible with
demineralized water backwash, which is similar to the observations for SRHA and in contrast to the observations for SA. This is probably because the BSA molecules were strongly adsorbed onto the membranes like the SRHA. Moreover, the amino functional groups of the protein might bind to the PES membranes. Although the PES membrane used was mixed with polyvinylpyrrolidone (PVP) to increase its hydrophilicity, it is probably still not sufficient to prevent protein adsorption. BSA might adsorb on some less hydrophilic locations of the membranes due to its hydrophobicity. Marchese et al. (2003) also reported that there was BSA adsorption on the PES membrane even with polyvinylpyrrolidone (PVP) addition, although the mixing of PVP with PES membrane can increase the hydrophilicity of UF membranes and reduce the adsorption of protein due to hydrophobic attractive forces (Marchese et al. 2003).

![Figure 5.10: TMP as a function of time for four different experiments: 1) filtrating solution containing 20 mg/l BSA with 2 mmol/l Ca and 3 mmol/l Na, and backwashing with UF permeate; 2) filtrating solution containing 20 mg/l BSA with 2 mmol/l Ca and 3 mmol/l Na, and backwashing with demineralized water; 3) filtrating solution containing 20 mg/l BSA, and backwashing with demineralized water; 4) filtrating solution containing 20 mg/l BSA, and backwashing with UF permeate](image)
5.4 Discussion

Results from the synthetic solution are completely different from what we found in natural surface water, and each synthetic compound showed a different fouling behavior. Of course, the NOM in natural surface water is a mixture of different organic substances including polysaccharide, protein and humic substances. SA, BSA and SRHA are each only one type of substances, so it is difficult to use one of them to illustrate all the NOM fouling mechanisms. That is also the reason why the same influence of calcium on membrane fouling was not observed in the tests with SA and BSA solution. Based on the LC-OCD analysis, biopolymers (polysaccharide and protein) are a small fraction of the total NOM compounds. In the natural water treatment, biopolymers might show the same reaction to calcium as SA and BSA, but their influence was very likely covered by the major fraction of NOM compounds (humic substances) showing high fouling potential with the addition of calcium.

All these model compound solutions also exhibited different effects on the backwashing of demineralized water, which has been shown to be effective on fouling control for natural surface water. Considering the LC-OCD analysis results of Schie Canal NOM compounds, although biopolymers are rejected by the membranes and also very likely to form a fouling layer on the membrane surface, this fouling layer is reversible via hydraulic backwashes. Since SA is one type of polysaccharide, belonging to biopolymers, it should be possible to flush away this foulant via hydraulic backwashes as well, no matter what kind of backwash water is used. The results of SA are indeed inconsistent with the LC-OCD analysis results of Schie Canal water NOM compounds.

On the other hand, BSA is one type of protein belonging to biopolymers. Although LC-OCD results of Schie Canal water showed that demineralized water backwashing substantially removed a large amount of biopolymers, it was not effective on all biopolymers: 18% and 12% of biopolymers were not removed by UF
permeate and demineralized water backwashes, respectively. BSA might be in the 12% of biopolymers not removed by demineralized water backwashing.

The SRHA used in this study is humic substances, and it was difficult to remove with demineralized water backwashing as well. According to the LC-OCD analysis of Schie Canal water, this fraction of NOM compounds can be removed up to around 70% with demineralized water backwashing. However, similar to biopolymers, not all the humic substances could be removed by a demineralized water backwash. SRHA appears in the remaining 30% which is not sensitive to demineralized water.

Although a single model compound cannot represent natural water types (due to different fouling mechanisms involved), a mixture probably can solve this problem. Moreover, all these model compounds are still useful for the investigation of specific fouling mechanisms.

5.5 Conclusions

In this study, the effectiveness of demineralized water backwash on ultrafiltration fouling control was compared for different natural waters and model compounds representing different fractions of NOM. Results of natural waters show that demineralized water backwash remove more foulants from membranes than UF permeate backwash, identical with the authors’ previous findings (Li et al. 2010, Li et al. 2009a, Li et al. 2009b). LC-OCD analysis of Schie Canal water showed that biopolymers can be flushed away by hydraulic backwashes of both demineralized water and UF permeate. Furthermore, compared to almost zero removal of humics and LMW substances by UF permeate backwashes, demineralized water backwashing was able to remove a substantial amount of humics, and a small amount of LMW substances.

The organic model compounds showed different fouling from natural waters. SA and BSA showed less fouling when Ca was added to the feed water, which is
probably due to the calcium chelating and aggregation effect. SRHA showed more fouling with calcium addition, similar to that observed in natural waters.

Concerning the demineralized backwash, SA fouling showed a high reversibility no matter what kind of backwash water was used. This was because the main fouling mechanism for SA is cake layer formation, which is usually more reversible than adsorption. These results are also consistent with the LC-OCD analysis of Schie Canal water. However, not all biopolymers were removed by hydraulic backwashes, a low fouling reversibility was observed for BSA, and it may be in the part of unremoved biopolymers with demineralized water.

No improvement in fouling control for SRHA was observed when demineralized water was used for the backwash. This is probably because the calcium bridging between SRHA and membranes is difficult to break down.

5.6 References


membrane system for drinking water production. DESALINATION 145(1-3), 237-245.


Chapter 6

Seawater application

This chapter is based on the following paper:

6.1 Introduction

Recently, UF is also used as a pre-treatment for reverse osmosis.

In the past, conventional pre-treatments were used for seawater RO systems. Most of these need to be well designed and operated so that they can provide feed water with high enough quality to the RO systems. Otherwise, the RO systems can be fouled quickly and frequent chemical cleanings are required, thereby leading to a short RO membrane lifetime. However, upsets in the performance of a conventional system can still lead to excessive levels of solids causing RO membrane fouling. RO membranes require an influent water quality with a 15-min silt density index (SDI) lower than 3 to ensure a stable operation (Chakravorty and Layson 1997). However, this low SDI value is not always achieved by conventional pre-treatments, especially when the water quality of raw seawater changes over the seasons with algal blooms during spring, for example (Lorain et al. 2007).

In the past decade, many researchers have investigated the possibility of using UF membranes as a pre-treatment for RO desalination or water reclamation, and all have reported the success of the UF pre-treatment (Brehant et al. 2003, Jezowska et al. 2009, Knops et al. 2007, Laine et al. 2000, Lorain et al. 2007, Van Hoof et al. 1999, Van Hoof et al. 2001, Yan et al. 2010). The advantage of UF pre-treatment is that UF provides stable high-quality influent water for RO systems, regardless of seasonal variations. Several studies have investigated the use of hollow fiber UF membranes (similar to this study) as a pre-treatment of seawater reverse osmosis (SWRO). Ahmad et al. (1993) showed that, compared to conventional pre-treatment, the inside-out hollow fiber UF process is an easy-to-use and robust alternative (Al-Ahmad and Aleem 1993). Hoof et al. (1999) carried out a pilot test in Addur using an X-Flow hollow fiber UF membrane as pre-treatment for half a year, and results showed that the UF permeate had stable SDI values as low as 1.5 (Van Hoof et al. 1999). Merrilee and James (2004) successfully supplied a UF–SWRO system to a United Arab Emirates system that treats about 11.4 million liters of
seawater a day with UF to supply 3.8 million liters to the SWRO system (Galloway and Mahoney 2004).

However, the fouling of UF membranes is a challenge for the widespread application of UF in seawater desalination as well. This is actually happening at a desalination demonstration plant of Evides Water Company at Jacobahaven, Zeeland, The Netherlands, a location where this study was conducted. Coagulation is being used by this plant to control the fouling of UF membranes. Coagulation has been proven to be a good method to control the UF fouling in seawater desalination by some researchers (Brehant et al. 2003, Yang and Kim 2009, Zeng et al. 2009).

Although coagulation is normally selected for UF fouling control, the disposal of high coagulant-concentrated backwash wastewater is a serious issue that can result in a significant cost.

The application of the DEMIFLUSH concept is investigated in this chapter. In the past, experimental results have shown that demineralized water backwashing substantially improved the fouling control of natural surface water ultrafiltration (Li et al. 2010a, Li et al. 2010b, Li et al. 2009). Similar results were also reported by Abrahamse and her colleagues (Abrahamse et al. 2008). That is because of the reduction of charge screening and Ca-bridging effects around both negatively charged UF membranes and natural organic matter (NOM) (Li et al. 2009).

Seawater has a high concentration of monovalent ions, so it is possible to apply the DEMIFLUSH concept to the seawater ultrafiltration and achieve good UF fouling control. However, no study has been conducted yet to investigate the feasibility of backwashing UF membranes with demineralized water to control fouling. Since SWRO permeate has a similar quality as demineralized water and is available in desalination plants, it is easy to make use of some of the SWRO permeate for this purpose. In this paper, a study is presented that analyzes ultrafiltration fouling control of seawater with the DEMIFLUSH concept at conditions
closely resembling an actual plant operation (constant flux with an increasing feed pressure as a means to compensate for the increasing filtration resistance). Furthermore, by dosing different amounts of NaCl in the demineralized water, the impact of monovalent cations on UF fouling control was also investigated. At the end, a long-term experiment incorporating chemical cleaning was conducted to check the effectiveness of SWRO permeate backwashing on fouling control and the reproducibility of two different backwashes (UF and SWRO permeate backwashes).

6.2 Material and methods

6.2.1 Feed water

Twenty liters of raw seawater were taken from Scheveningen beach in The Hague and from the Evides desalination plant at Jacobahaven, Zeeland, the Netherlands. The seawater was stored in a refrigerator at a temperature of 4 degrees Celsius without pre-filtration. The water quality is shown in Table 6.1.

<table>
<thead>
<tr>
<th></th>
<th>DOC (mg/l)</th>
<th>Conductivity (µS/cm)</th>
<th>Phytoplankton (n/ml)</th>
<th>Ca (mmol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheveningen beach</td>
<td>2.427</td>
<td>34700</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Jacobahaven February</td>
<td>1.97</td>
<td>43600</td>
<td>600</td>
<td>9.75</td>
</tr>
<tr>
<td>Jacobahaven April</td>
<td>2.46</td>
<td>41400</td>
<td>12000</td>
<td>9.25</td>
</tr>
</tbody>
</table>

6.2.2 Backwash water

Two types of backwash water were used for Scheveningen beach in this study: 1) UF permeate and 2) demineralized water. The water quality is shown in Table 6.2.
Table 6.2: Water quality of backwash water

<table>
<thead>
<tr>
<th></th>
<th>DOC (mg/l)</th>
<th>Conductivity (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF Permeate</td>
<td>2.34</td>
<td>30350</td>
</tr>
<tr>
<td>Demineralized water</td>
<td>0.43</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Four types of backwash water were used in the short-term (7 hours) experiments at Jacobahaven: 1) UF permeate, 2) demineralized water with 5 mmol/l NaCl, 3) demineralized water with 50 mmol/l NaCl, and 4) demineralized water. The water quality is shown in Table 6.3. Five mmol/l NaCl was used for backwashing, since this concentration is similar to the concentration used in investigations of monovalent cations’ influence on canal water UF fouling control (Li et al. 2009). On the other hand, according to previous results of canal water treatment, 50 mmol/l NaCl was sufficient to compress the electrical double layer of UF membranes fouled by canal NOM compounds, and thus a zeta potential close to zero. Although the zeta potential also depends on the amount of calcium, type and amount of NOM fouling on a membrane, 50 mmol/l NaCl might also reduce the zeta potential of the membrane and NOM compounds to a low level in a seawater application. Therefore, this is the concentration that was used in this study. Two types of backwash water were used in the long-term (more than 50 hours) experiments at Jacobahaven, and their water qualities are shown in Table 6.4.

Table 6.3: Water quality of backwash water in short-term experiments

<table>
<thead>
<tr>
<th></th>
<th>DOC (mg/l)</th>
<th>Conductivity (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF Permeate</td>
<td>1.7</td>
<td>38000</td>
</tr>
<tr>
<td>5 mmol/l NaCl</td>
<td>&lt;0.3</td>
<td>0.59</td>
</tr>
<tr>
<td>50 mmol/l NaCl</td>
<td>&lt;0.3</td>
<td>4.5</td>
</tr>
<tr>
<td>Demineralized water</td>
<td>&lt;0.3</td>
<td>&lt;0.6</td>
</tr>
</tbody>
</table>
6.2.3 Chemical cleaning

No chemical cleaning was carried out in the short-term experiments because each experiment was conducted with a new self-prepared membrane module.

During the long-term experiments, membranes were chemically cleaned with 1000 mg/l NaOCl solution using the following procedure:

1. Membranes were put in a vessel with 2 liters 1000 mg/l NaOCl solution for a two-hour soaking
2. Membranes were thoroughly rinsed with demineralized water (the outside of the module and the outside of the membrane fibers as well)
3. Membrane was flushed with demineralized water for 15 minutes with a combination of forward flushing and backwashing
4. Afterwards, the clean membrane permeability was determined at a flux of 120 l/(m².h).
5. After that, the cleaned membrane was used again.

6.2.4 Membrane module

Self-prepared membrane modules containing UFC M5 0.8 mm hollow fibers (X-FLOW Company) were prepared (same modules as used in studies of Chapter 4 and 5). The surface area of these modules is 0.0015 m².
6.2.5 Ultrafiltration setup

The same ultrafiltration setup described in Chapter 4 and 5 is also used in this chapter.

6.2.6 Filtration protocol

All experiments were carried out in a dead-end operation mode. Before each experiment (and after each chemical cleaning), the setup was thoroughly flushed with demineralized water in filtration mode and backwash mode to remove the chemical residues and air in the system. Afterwards, the setup was operated with demineralized water at a flux of 180 l/(m²·h) for half an hour to determine the initial permeability of each membrane. Each fouling experiment, with a different type of backwash water used each time, consisted of more than 10 operational cycles. Each cycle was composed of three phases: 1) filtration for 15 or 30 minutes; 2) forward flush of permeate side for 30 seconds to clean the modules before backwashing; 3) backwashing at a double filtration flux for one or two minutes (exact duration for different experiments is clarified in the coming paragraphs). Six groups of comparison experiments were conducted. Group 3 was conducted with seawater from Scheveningen beach in July; groups 1-2 and 4-5 were conducted with seawater from Jacobahaven in February (low fouling period), and group 6 was conducted with seawater from Jacobahaven in April (high fouling period). The details of each group of experiments are summarized in Table 6.5.
<table>
<thead>
<tr>
<th>Feed water (Seawater location and time)</th>
<th>Backwash water</th>
<th>Filtration flux $l/(m^2.h)$</th>
<th>Filtration duration (min)</th>
<th>Backwash flux $l/(m^2.h)$</th>
<th>Backwash duration (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 1 Jacobahaven in February</td>
<td>1) Demineralized water <em>4hours/</em> 2) UF permeate <em>3hours</em></td>
<td>180</td>
<td>15</td>
<td>360</td>
<td>1</td>
</tr>
<tr>
<td>Experiment 2a Jacobahaven in February</td>
<td>Demineralized water</td>
<td>180</td>
<td>30</td>
<td>360</td>
<td>2</td>
</tr>
<tr>
<td>Experiment 2b Jacobahaven in February</td>
<td>UF permeate</td>
<td>180</td>
<td>30</td>
<td>360</td>
<td>2</td>
</tr>
<tr>
<td>Experiment 3a Scheveningen beach in July</td>
<td>Demineralized water</td>
<td>180</td>
<td>15</td>
<td>360</td>
<td>2</td>
</tr>
<tr>
<td>Experiment 3b Scheveningen beach in July</td>
<td>UF permeate</td>
<td>180</td>
<td>15</td>
<td>360</td>
<td>2</td>
</tr>
<tr>
<td>Experiment 4a Jacobahaven in February</td>
<td>Demineralized water</td>
<td>180</td>
<td>15</td>
<td>360</td>
<td>1</td>
</tr>
<tr>
<td>Experiment 4b Jacobahaven in February</td>
<td>UF permeate</td>
<td>180</td>
<td>15</td>
<td>360</td>
<td>1</td>
</tr>
<tr>
<td>Experiment 4c Jacobahaven in February</td>
<td>Demineralized water</td>
<td>180</td>
<td>30</td>
<td>360</td>
<td>1</td>
</tr>
<tr>
<td>Experiment 4d Jacobahaven in February</td>
<td>UF permeate</td>
<td>180</td>
<td>30</td>
<td>360</td>
<td>1</td>
</tr>
<tr>
<td>Experiment</td>
<td>Location</td>
<td>Conditions</td>
<td>Time (min)</td>
<td>Temperature (°C)</td>
<td>pH</td>
</tr>
<tr>
<td>------------</td>
<td>----------</td>
<td>------------</td>
<td>------------</td>
<td>-----------------</td>
<td>----</td>
</tr>
<tr>
<td>4e</td>
<td>Jacobahaven in February</td>
<td>Demineralized water</td>
<td>240</td>
<td>30</td>
<td>480</td>
</tr>
<tr>
<td>4f</td>
<td>Jacobahaven in February</td>
<td>UF permeate</td>
<td>240</td>
<td>30</td>
<td>480</td>
</tr>
<tr>
<td>5a</td>
<td>Jacobahaven in February</td>
<td>Demineralized water</td>
<td>180</td>
<td>30</td>
<td>360</td>
</tr>
<tr>
<td>5b</td>
<td>Jacobahaven in February</td>
<td>Demineralized water with 5 mmol/l NaCl</td>
<td>180</td>
<td>30</td>
<td>360</td>
</tr>
<tr>
<td>5c</td>
<td>Jacobahaven in February</td>
<td>Demineralized water with 50 mmol/l NaCl</td>
<td>180</td>
<td>30</td>
<td>360</td>
</tr>
<tr>
<td>5d</td>
<td>Jacobahaven in February</td>
<td>UF permeate</td>
<td>180</td>
<td>30</td>
<td>360</td>
</tr>
<tr>
<td>6a</td>
<td>Jacobahaven in April</td>
<td>Demineralized water</td>
<td>180</td>
<td>30</td>
<td>360</td>
</tr>
<tr>
<td>6b</td>
<td>Jacobahaven in April</td>
<td>UF permeate</td>
<td>180</td>
<td>30</td>
<td>360</td>
</tr>
<tr>
<td>6c</td>
<td>Jacobahaven in April</td>
<td>1) UF permeate_12 hours/ 2) SWRO permeate_12 hours/ 3) UF permeate_12 hours/ 4) SWRO permeate_12 hours</td>
<td>120</td>
<td>30</td>
<td>240</td>
</tr>
</tbody>
</table>
6.3 Results and discussion

6.3.1 Clean membrane permeability

Before each fouling experiment, the clean membrane permeability was tested. For all the self-prepared membrane modules used in this study, their TMPs from clean water tests at a flux of 180 l/(m².h) were 0.13 ± 0.01 bar, corresponding to permeability of 1384 ± 100 l/(m².h.bar).

6.3.2 Effect of DEMIFLUSH on seawater UF fouling control

Five liters of raw seawater were taken from the Evides desalination demonstration plant (Jacobahaven, Zeeland, The Netherlands) during the low fouling period. The increase in TMP for demineralized water backwash and UF permeate at a filtration flux of 180 l/(m².h) is given in Figure 6.1 (Experiment 1). The UF membrane was backwashed with demineralized water in the first 4 hours, and then UF permeate was used for backwashing in the following 2.5 hours. Following a one-minute demineralized water backwash, the initial TMP of each filtration cycle (proportionally related to the increase in hydraulically irreversible fouling) increased from 0.13 to 0.165 bar over 4 hours. On the other hand, the increase in initial TMP of each cycle for the UF permeate backwash was 0.05 bar (from 0.17 to 0.225) over 2.5 hours. The slope of the increase in initial TMP (reflecting the rate of irreversible fouling formation) is plotted in Figure 6.2, showing that the rate of fouling increase for UF permeate backwashing (0.0193) is almost two times higher than that for demineralized water backwashing (0.0108).
The backwash water was switched from demineralized water to UF permeate

Figure 6.1: TMP as a function of time for demineralized water and UF permeate backwash, one cycle consisting of 15-minute filtration at a flux of 180 l/(m²·h) and a 1-minute backwash at a double filtration flux (Seawater was taken during low fouling period from Zeeland, the Netherlands)

Figure 6.2: Slope of hydraulically irreversible fouling for demineralized water backwash and UF permeate at a flux of 180 l/(m²·h) (Seawater was taken during low fouling period from Zeeland, the Netherlands)
Experimental results showed that demineralized water backwashing substantially improved the seawater UF fouling control. There is a change in the slope of irreversible fouling after switching the type of backwash water shown in Figure 6.2. At first glance, this might have nothing to do with switching the type of backwash water, and the change in slope might be due to the nature of irreversible fouling formation for the specific feed water. In this case, a smooth change would be expected. However, the change in slope started immediately after switching the backwash water. Therefore, the reason for this change is more strongly related to the switching of the backwash water. Furthermore, the results from two parallel experiments with new membranes confirmed the improvement of backwashing with demineralized water, as shown in Figure 6.3 (Experiment 2a and 2b). The increase in irreversible TMP for demineralized water backwashing was from around 0.13 to 0.16 bar, while the irreversible TMP increased from around 0.13 to almost 0.30 bar for the UF permeate backwash within the same operation time. In this comparison, all of the experimental conditions are identical for both types of backwash (the
membranes used were new and the same feed water was used): the differences observed between different backwash waters can really be attributed to the type of backwash water.

Seawater from another location (Scheveningen, the Hague, the Netherlands) was also tested under the same conditions as in experiments 2a and 2b. The TMP as a function of time for experiments 3a and 3b is shown in Figure 6.4. These two experiments were conducted at a constant flux of 180 l/(m²·h) and with 2-minutes backwashing. The reason for conducting 2-minute backwashes was to ensure that the membrane was thoroughly backwashed with demineralized water and reached a low ion concentration during backwashing. Figure 6.4 shows that the TMP of the first cycle for both backwashes increased rather quickly. Nevertheless, a hydraulic backwash recovered most of the membrane permeability. Furthermore, the maximum TMP of the second cycle was much lower than the first cycle. That is probably because there was air in the filtration system which was not flushed away in the air removal step before the fouling experiments. From the second cycle on, filtration worked properly, and consequently, the TMP increased steadily. When the membrane was backwashed with UF permeate, the TMP increase in each cycle became progressively greater and with an increasing number of filtration cycles. The hydraulically irreversible fouling (the TMP at the start point of each cycle) increased from 0.16 bar up to around 0.32 bar. Although there was still a certain amount of TMP increase after each backwash for the demineralized water backwash, from 0.16 bar up to 0.2 bar, it is lower than the UF permeate backwash. Therefore, demineralized water backwashing can substantially improve the UF fouling control for seawater filtration as well, similar to the previous findings in canal water treatment (Li et al. 2009).
Figure 6.4: TMPs as a function of time for backwashing with UF permeate and demineralized water, one cycle consisting of 15-minute filtration at a flux of 180 l/(m².h) and a 2-minute backwash at a double filtration flux (Seawater was taken during low fouling period from the Scheveningen beach, the Hague, the Netherlands)

The mechanisms behind the DEMIFLUSH concept probably include charge screening and calcium-bridging effects. During filtration of seawater, the negatively charged natural organic matter (NOM) in seawater can easily deposit on the negatively charged UF membrane due to the compressed electrical double layers of NOM and membranes under a high salinity condition, and thus a reduced repulsion force between them. Consequently, NOM fouling of UF membranes develops over time. On the other hand, the presence of calcium in seawater not only screens the negative charge of NOM and membranes like monovalent cations, but also probably bridges the negatively charged NOM and UF membranes together through bridging with their acidic functional groups. When UF membranes are backwashed with UF permeate, since the UF permeate leaves almost all of the cations in the feed water, the concentration of cations on the membrane surface is not changed during backwash. The charge screening effect and calcium bridging effect are probably maintained, against the hydraulic force of backwashing.
Therefore, some of the foulants are not flushed away. However, when UF membranes are backwashed with demineralized water, the cation concentration near the membrane surface can be substantially reduced and, consequently, the repulsion force between NOM and UF membranes can be restored, enhancing the efficiency of hydraulic backwashes.

Since demineralized water backwash probably removed more foulants than the UF permeate did, a higher permeability of the UF membranes was recovered after a backwash, contributing to a steadier filtration for the next cycle. However, due to more foulants remaining on the membrane after a UF permeate backwash, some of the membrane pores are blocked over time, leading to a less effective membrane area. Because all experiments were constant flow experiments, the same amount of feed water passed through the less effective area, increasing the actual effective flux. Therefore, as shown in Figure 6.4, the increase in TMP within each filtration cycle for backwashing with UF permeate was more rapid than its previous cycle (except for the first two cycles which might have been influenced by air).

6.3.3 Impact of backwash duration on the effectiveness of demiflush

Although a 1-minute backwash showed a slight improvement with demineralized water backwashing (as shown in Figures 6.1 and 6.2), the improvement was not as obvious as what has been reported in surface water treatment (Li et al. 2010a, Li et al. 2010b, Li et al. 2009). Therefore, the duration of backwashing is probably a parameter which needs to be adjusted. To address this issue, experiments 4a-4f were conducted with seawater at Jacobahaven, and the results are shown in the Figures 6.5 and 6.6. Figure 6.5 depicts the TMP increase as a function of time for demineralized water and UF permeate backwashing for the first two stages. These two stages are: 1) a 15-minute filtration at a flux of 180 l/(m².h) and a one-minute backwashing at a flux of 360 l/(m².h), 4-hour operation; 2) a 30-minute filtration at a
flux of 180 l/(m²·h) and a one-minute backwashing at a flux of 360 l/(m²·h), 3-hour operation. Figure 6.6 shows the last stage: a 30-minute filtration at a flux of 240 l/(m²·h) and a two-minute backwashing at a flux of 480 l/(m²·h), 5-hour operation. When the UF membrane was backwashed for one minute in the first two stages, the improvement on UF fouling control with demineralized water backwashing is not as obvious when compared to UF permeate backwashing. Although the TMP for backwashing with UF permeate is slightly higher than with demineralized water over the whole 7-hour operation, the slopes of increases in hydraulically irreversible fouling are identical for both kinds of backwashes. However, when the duration of the backwash was extended to 2 minutes, the improvement with demineralized water backwashing is clear, even at a higher filtration flux of 240 l/(m²·h), as shown in Figure 6.6. The improvement of 2-minute demineralized water backwashing is clear as well at the filtration flux of 180 l/(m²·h) for both seawater at Jacobahaven and Scheveningen beach, shown in Figures 6.3 and 6.4, respectively.

Therefore, results showed that a 2-minute demineralized water backwash is better than 1-minute to improve the fouling control of seawater if backwash flux is two times higher than filtration flux. That is probably because of the high salinity of seawater, with dilution and dispersion occurring during the backwashes: backwash water enters the feed side of the membrane along the whole length of fibers and dilutes the cation concentration of the remaining feed water. Due to the much higher salinity of seawater than surface water, more water is required to reach the same cation concentration level for seawater application. Furthermore, dispersion happens all the time when water with two different concentrations is mixed. When surface water was treated, the amount of demineralized water within a one-minute backwash probably is sufficient to limit the effect of dispersion. However, due to the high salinity of seawater, more demineralized water is necessary in this case to limit the effect of dispersion. Under the same backwash flux as surface water treatment, a longer backwash time is necessary then, and important for a successful demineralized water backwash. While it may not be cost-effective to backwash the membranes with demineralized water for 2 minutes, the duration of filtration can be extended as in the conducted experiments. In surface water
treatment, filtration protocol of a 15-minute filtration with a 1-minute backwash was applied, while a new filtration protocol of a 30-minute filtration with a 2-minute backwash was used for most experiments in this study. In terms of the recovery, both surface water treatment and seawater treatment were identical. Moreover, the consumption of demineralized water can be further optimized in the future.

Figure 6.5: TMP as a function of time for demineralized water and UF permeate backwash, (Seawater was taken during low fouling period from Zeeland, the Netherlands). In the first 4-hour operation, filtration is 15 minutes at 180 l/(m².h) flux; in the last three hours, filtration is 30 minutes at 360 l/(m².h) flux, backwashes are one minute at a double filtration flux for both
Figure 6.6: TMP as a function of time for demineralized water and UF permeate backwash, one cycle consisting of 30-minute filtration at a flux of 240 l/(m².h) and a 2-minute backwash at a double filtration flux (Seawater was taken during low fouling period from Zeeland, the Netherlands)

6.3.4 Impact of monovalent cations on the effectiveness of backwashing

Based on previous experience, the presence of monovalent cations in backwash water plays an important role in UF fouling control (Li et al. 2009). Due to the high salinity of seawater, in theory the impact of monovalent cations is profound for seawater UF fouling. Two types of backwash solutions with two different NaCl concentrations were prepared for fouling experiments (experiments 5a-5d). Seawater at Jacobahaven during a low fouling period was used in these experiments. Experiments with demineralized water and UF permeate backwash were compared in terms of fouling control efficiency. The increase in TMP as a function of time for all mentioned backwash waters is depicted in Figure 6.7. The demineralized water backwash shows the lowest increase in TMP, while the highest increase is caused by the UF permeate backwash. The main observation from this figure is that the fouling control efficiencies of two types of NaCl solutions
are between demineralized water and UF permeate. The difference between 5 and 50 mmol/l NaCl backwash water is small. Although the TMP increase in each filtration cycle for 5 mmol/l NaCl backwash is higher than that for 50 mmol/l NaCl, the irreversible fouling control efficiency (TMP after each backwash) for these two types of backwash water is similar. This indicates that the UF fouling control efficiency becomes worse when there are monovalent cations in the backwash water, but the fouling control efficiency does not decrease with an increase in the concentration of monovalent cations above 5 mmol/l, similar to the results with Schie canal water (Li et al. 2009). In terms of charge screening, 50 mmol/l NaCl solution was a relatively high concentration, and might make the zeta potential of the membrane much less negative (close to zero). Therefore, this solution might show a similar fouling control efficiency as UF permeate if the charge screening effect is the only mechanism of demineralized water backwashing. However, backwashing with UF permeate showed the worst fouling control efficiency. Since the seawater contains 390 mg/l Ca and UF membranes cannot reject calcium ions, there are also calcium ions in the UF permeate. The absence of calcium in the NaCl solution showed better foulant removal, indicating that the impact of calcium on fouling is partly related to the Ca-bridging effect.

6.3.5 Effect of season

Experiments were conducted in two periods with seawater at Jacobahaven: a low fouling period (February) and a high fouling period (April). The results of the low fouling period have been displayed in Figures 6.1-6.7. In Figure 6.1, the increase in TMP at the beginning of each cycle for demineralized water backwashing is around 0.05 bar in a 7-hour operation, while the corresponding value for UF permeate backwashing is 0.15 bar over the same period of operation. However, the same difference in TMP increase can be observed in Figure 6.8 (experiments 6a and 6b), which is based on a lower constant flux (120 l/(m².h)) of the high fouling period than that at the flux (180 l/(m².h)) of the low fouling period. Since a higher flux normally causes more fouling, these results show that fouling of the UF
membranes was more severe in April (the high fouling period). This is probably because the algae bloom happened in spring, which is indicated in Table 6.1. Other researchers also reported the impact of algae bloom in spring on the fouling of seawater UF membranes (Lorain et al. 2007).

Figure 6.7: TMP as a function of time for 1) demineralized water backwash, 2) demineralized water with 50 mmol/l NaCl solution, 3) demineralized water with 5 mmol/l NaCl solution and 4) UF permeate, one cycle consisting of 30-minute filtration at a flux of 180 l/(m².h) and a 2-minute backwash at a double filtration flux (Seawater was taken during low fouling period from Zeeland, the Netherlands)
6.3.6 Long-term operation

Before the long-term fouling experiment, the clean membrane permeability was tested, and the clean water permeability for the new membrane was $1333.3 \pm 60$ l/(m$^2$.h.bar). The clean water permeability of the membrane after each chemical cleaning is shown in Table 6.6.

Table 6.6: Clean water permeability of M4 after each chemical cleaning

<table>
<thead>
<tr>
<th>Cleaning</th>
<th>Cleaning 1</th>
<th>Cleaning 2</th>
<th>Cleaning 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean water permeability</td>
<td>1200</td>
<td>1043.5</td>
<td>923</td>
</tr>
<tr>
<td>l/(m$^2$.h.bar)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 6.9 shows the TMP as a function of time for four different backwashing phases (experiment 6c). These phases are: 1) 10-hour UF permeate backwash; 2) 10-hour SWRO permeate backwash; 3) 10-hour UF permeate backwash and 4) 10-hour SWRO permeate backwash. There was a chemical cleaning between every two phases. It is clear from Figure 6.9 that the fouling of the UF membrane can be much better controlled when it is backwashed with SWRO permeate. The increases in TMP caused by hydraulically irreversible fouling for UF permeate backwashing were around 0.3 bar. On the other hand, the increases in TMP for the first and second SWRO permeate backwash were 0.05 and 0.08 bar, respectively. The reason for the difference between the two RO permeate backwashes is probably due to the difference in the initial membrane permeability. Since the chemical cleaning before the second RO permeate backwash was not that successful, the initial membrane permeability before the second RO backwash was not as high as that of the new membrane and the membrane before the first SWRO
permeate backwash, as shown in Table 6.6. Even though the initial membrane permeability was lower than before and the fouling control efficiency of the second SWRO backwashing was not as high as the first one, the SWRO permeate backwashing still showed a much better fouling control efficiency than the other two UF permeate backwashes. These results confirm the improvement of demineralized water backwashing/ SWRO permeate on the fouling control of seawater UF.

6.4 Conclusions

Demineralized water backwashing can substantially improve seawater UF fouling control, similar to the previous findings in surface canal water. However, the duration of a successful demineralized water backwash should be extended from one to two minutes. This is due to the high salinity of seawater and thus more demineralized water was required to dilute the seawater and limit a higher dispersion effect of seawater than surface water. Monovalent cations in backwash water showed their impact on the fouling control efficiency, indicating the existence of a charge screening effect. However, UF permeate backwashing showed an even worse fouling control than the 50 mmol/l NaCl solution. Therefore, the Ca in UF permeate probably diminishes the fouling control efficiency not only by maintaining the charge screening effect but also the Ca-bridging effect between the membranes and the NOM compounds. Furthermore, the different UF membrane fouling behaviors in winter and spring indicated the impact of a seasonal influence on UF membrane fouling. In spring, the membrane showed more fouling probably due to the algae bloom which is widely considered an important fouling factor. The results of the long-term experiment reconfirmed the effectiveness of backwashing with SWRO permeate on the fouling control of seawater UF. Since it is very easy to access SWRO permeate in a UF-RO desalination plant, this approach can be implemented easily.
6.5 References


Chapter 7

Practical experience of the DEMIFLUSH concept

This chapter is based on the following paper:
S. Li, S.G.J. Heijman, J.Q.J.C. Verberk, G.L. Amy and J.C. van Dijk, Practical experience of backwashing with SWRO permeate for UF fouling control, will be submitted to Desalination
7.1 Introduction

In our previous studies, backwashing with demineralized water (the DEMIFLUSH concept) has been proven successful to control fouling of ultrafiltration (UF) for both surface water and seawater treatments (Li et al. 2010a, Li et al. 2010b, Li et al. 2009b). The absence of cations in demineralized water establishes a cation-free environment near the negatively charged UF membrane surface during backwashes, eliminating the charge screening effect formed during filtration. Therefore, a restored repulsion force between negatively charged membranes and NOM compounds is achieved, enhancing the backwash efficiency.

However, this concept has not been tested with standard modules used in full-scale plants. Membrane modules used in the previous experiments include modules with a surface area of $3.75 \times 10^{-3}$, $7 \times 10^{-2}$ and 2.4 m$^2$. All these modules are much smaller than the surface area of standard modules (40 m$^2$). In order to show that the DEMIFLUSH concept can also improve the fouling control in a realistic situation, tests with standard modules were conducted on a pilot scale. Since the quality of SWRO permeate is similar to demineralized water in terms of the low concentration of cations, SWRO permeate was applied for backwashing in this study. Furthermore, because the settings of small-scale experiments require too much SWRO permeate (13.3% of produced water), which makes the DEMIFLUSH concept not economically feasible, the consumption of SWRO permeate was also optimized by extending the duration of filtration cycle in this study. Although the consumption optimization can be conducted at all scale experiments, the greater the scale the more demineralized water/SWRO permeate is consumed in the pipeline system. Therefore, it is better to optimize the SWRO permeate consumption with standard modules at a scale representing full-scale plants.

Although both seawater and surface water applications of the DEMIFLUSH concept need to be investigated at this pilot scale, seawater application was considered first in this study. That is because the DEMIFLUSH concept is more
convenient and economically feasible for implementation in a desalination plant with both UF and RO systems.

In this study, the applicability of results between the DEMIFLUSH pilot (one standard module used) and the demonstration plant of Evides Water Company was experimentally determined, and effectiveness of the DEMIFLUSH concept on standard modules was investigated as well.

### 7.2 Material and methods

Pilot tests were conducted near a desalination demonstration plant of Evides Water Company in the Netherlands at Oosterschelde, a North Sea estuary. Raw seawater (same as the desalination plant) was used in the DEMIFLUSH pilot as feed water, so that the results between the pilot and the desalination plant were comparable.

#### 7.2.1 Feed water

Seawater was continuously taken from the desalination demonstration plant of the Evides Company within the period from January to March, and May to June 2011. The raw seawater was pre-filtered in the desalination plant with a 50 micron strainer to remove the large particles, and then delivered to the DEMIFLUSH pilot by gravity. The water quality of the seawater is shown in Table 7.1.

<table>
<thead>
<tr>
<th>Table 7.1: Water quality of seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>January-March</td>
</tr>
<tr>
<td>May-June</td>
</tr>
</tbody>
</table>
7.2.2 Backwash water

Two types of backwash water were compared: 1) demonstration plant SWRO permeate and 2) pilot UF permeate. The water quality is shown in Table 7.2.

Table 7.2: Water quality of backwash water for seawater treatment

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Ca (mmol/l)</th>
<th>Na (mmol/l)</th>
<th>DOC (mg/l)</th>
<th>Conductivity (µS/cm);20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF permeate</td>
<td>7.92</td>
<td>9</td>
<td>369.5</td>
<td>1.7</td>
<td>N/A</td>
</tr>
<tr>
<td>SWRO permeate</td>
<td>5.84</td>
<td>0.02</td>
<td>0.78</td>
<td>&lt; 0.1</td>
<td>205</td>
</tr>
</tbody>
</table>

7.2.3 Membrane

Standard XIGA modules (equipped with UFC M5 0.8 fibers) from Norit X-Flow were used in this study. The characteristics of this membrane fiber are same as for the modules used in the previous studies which have been described in detail previously (Abrahamse et al. 2008, Li et al. 2010a, Li et al. 2009a, Li et al. 2010b, Li et al. 2009b). These membranes are made of a mixture of polyethersulfone (PES) with a small amount of polyvinylpyrrolidone (PVP). The dimensions of a standard XIGA module are shown in Table 7.3.

Table 7.3: Dimensions of a standard XIGA module

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter of module (cm)</td>
<td>19</td>
</tr>
<tr>
<td>Length of module (m)</td>
<td>1.5</td>
</tr>
<tr>
<td>Surface area (m²)</td>
<td>40</td>
</tr>
</tbody>
</table>

7.2.4 Chemical cleaning

Chemical enhanced backwashing consisted of two parts. The first part was the alkaline chemical cleaning with 200 mg/l NaOH and 250 mg/l NaOCl, and the second part was the acidic cleaning with 450 mg/l HCl. Dosing of chemicals continued for 2.5-minute at a 60 l/(m².h) flux, and then the membrane was soaked
in chemical cleaning solution for ten minutes. After soaking, the membrane was rinsed with SWRO permeate for two minutes at a flux of 165 l/(m².h).

### 7.2.5 DEMIFLUSH pilot and filtration protocol

Figures 7.1 and 7.2 show the flow scheme of the DEMIFLUSH pilot and its pictures, respectively. In this pilot, there are five possible operation phases: 1) forward flush with raw water, 2) forward flush with SWRO permeate, 3) filtration with raw water, 4) backwash with UF permeate and 5) backwash with SWRO permeate. In addition to the fouling control with DEMIFLUSH, in-line coagulation is also incorporated in this pilot but was not used during the current experiments. Therefore, the combination of coagulation and DEMIFLUSH can be utilized when desired. This pilot is fully automated and remote-controllable.

All experiments were carried out in a dead-end operation mode. Depending on the experiments conducted, different operation conditions were applied. Each fouling experiment, with one type of backwash medium (either UF permeate or SWRO permeate), consisted of more than one operational cycle. Each cycle was composed of filtration and backwashing. When the permeability of the membrane decreased to 200 l/(m².h.bar), a chemically enhanced backwash was conducted (same as at the desalination demonstration plant). Details of the experiments conducted are listed in Table 7.4.

The experiments focused on:

1. Comparing the performance of the DEMIFLUSH pilot and the Evides desalination plant, with identical operation conditions (both backwashing with UF permeate).
2. Comparing the SWRO permeate backwash and UF permeate backwash with the DEMIFLUSH pilot.
Table 7.4: Experimental conditions of the DEMIFLUSH pilot

<table>
<thead>
<tr>
<th>Time Period</th>
<th>Feed media</th>
<th>Filtration flux (l/(m².h))</th>
<th>Filtration time (min)</th>
<th>Backwash media</th>
<th>Backwash flux (l/(m².h))</th>
<th>Backwash time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan-Feb 2011 (low fouling)</td>
<td>Strained seawater</td>
<td>55</td>
<td>90</td>
<td>UF permeate</td>
<td>265</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Strained seawater</td>
<td>55</td>
<td>90</td>
<td>SWRO permeate</td>
<td>265</td>
<td>45</td>
</tr>
<tr>
<td>Mar 2011 (more fouling)</td>
<td>Strained seawater</td>
<td>55</td>
<td>45</td>
<td>UF permeate</td>
<td>265</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Strained seawater</td>
<td>55</td>
<td>45</td>
<td>SWRO permeate</td>
<td>265</td>
<td>45</td>
</tr>
<tr>
<td>May-June 2011 (high fouling)</td>
<td>Strained seawater</td>
<td>55</td>
<td>45 or 50</td>
<td>UF permeate</td>
<td>265</td>
<td>90 or 60</td>
</tr>
<tr>
<td></td>
<td>Strained seawater</td>
<td>55</td>
<td>45 or 50</td>
<td>SWRO permeate</td>
<td>265</td>
<td>90 or 60</td>
</tr>
</tbody>
</table>
Figure 7.1: Flow scheme of the DEMIFLUSH pilot
Figure 7.2: Pictures of the DEMIFLUSH pilot
7.3 Results

7.3.1 Reproducibility of results from the DEMIFLUSH pilot

Figure 7.3 shows permeability as a function of the date for UF permeate backwash experiments conducted from January to the beginning of March 2011. Operation details of these experiments are shown in Table 7.4.

Each line in this figure represents the permeability decline of one operation run. Most of the initial permeabilities are between 350-400 l/(m².h.bar), except the last two runs which started from 300 l/(m².h.bar). The relatively low permeability was because of an insufficient CEB. However, considering the permeability decline rate (fouling rate), all the tested runs showed a similar decline rate (similar slope in the figure). Therefore, the results obtained from the DEMIFLUSH pilot are reproducible.

7.3.2 Comparability between the DEMIFLUSH pilot and the demonstration plant

All experiments’ settings were identical between the Evides desalination demonstration plant and the DEMIFLUSH pilot. In order to show a clearer permeability decline of UF permeate backwash over time, data from 20 Jan to 25 Jan 2011 is plotted in Figure 7.4.

There was a 30-hour blank interval between the first and second run due to a stoppage of the seawater supply. Before each run, a CEB was conducted to recover the permeability of the membrane. The initial permeability of the first run (400 l/(m².h.bar)) was higher than the other two runs (330 l/(m².h.bar)). That is probably because the soaking time of CEB before the first run was longer than the other two runs. The chemical soaking time for the first run was 5 hours, and for the other two runs 10 minutes. For the 5-hour soaking time, NaOCl probably had more
sufficient time to break down the foulants on the membrane, and thus more permeability was recovered.

In this figure (Figure 7.4), the permeability decline rate is seen as similar for all three runs, consistent with the results shown in Figure 7.3. The comparison in performance between the DEMIFLUSH pilot and the demonstration plant is shown in Table 7.5. Taking the second run as an example, the initial permeability of this run was 330 l/(m².h.bar), and this run reached the set permeability for CEB (200 l/(m².h.bar)) within 25 hours. In this case, the permeability decline rate during filtration was around 5.2 l/(m².h².bar). On the other hand, based on the results obtained from the demonstration plant, a similar permeability decline rate was observed in the plant as well, around 5.5 l/(m².h².bar). Therefore, the results of the DEMIFLUSH pilot are applicable to the demonstration plant.

<table>
<thead>
<tr>
<th></th>
<th>Permeability pre-CEB [l/(m².h.bar)]</th>
<th>Permeability post-CEB [l/(m².h.bar)]</th>
<th>Permeability decline rate [l/(m².h.bar)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desalination plant</td>
<td>200*</td>
<td>350-400*</td>
<td>5.5*</td>
</tr>
<tr>
<td>DEMIFLUSH pilot</td>
<td>200</td>
<td>330-400</td>
<td>5.2</td>
</tr>
</tbody>
</table>

* Data provided by the Evides Water Company
Figure 7.3: Permeability as a function of the date for the experiments of backwashing with UF permeate from 27 January to 3 March 2011 (90 min filtration at 55 l/(m².h) flux followed by 45 s backwash at 265 l/(m².h) flux)

Figure 7.4: Permeability as a function of date for the experiment with UF permeate backwashes from 19 January to 25 January 2011 (90 min filtration at 55 l/(m².h) flux followed by 45 s backwash at 265 l/(m².h) flux)
7.3.3 Effectiveness of backwashing with SWRO permeate

7.3.3.1 Low fouling period

The improvement of SWRO permeate backwashing was investigated. Figure 7.5 displays the permeability as a function of the date for experiments with UF and SWRO permeate backwashes, which were operated at 55 l/(m².h) for 90 min per filtration cycle and 265 l/(m².h) for 45 seconds per backwash. Results show that the duration of one run with a UF permeate backwash was around 24 hours, while the duration of the SWRO permeate backwash was up to 48 hours. Therefore, backwashing with SWRO permeate can improve the UF fouling control at a pilot scale.

Figure 7.6 shows another comparison between UF and SWRO permeate backwashes conducted in March 2011. In these experiments, the duration of one filtration cycle was 45 minutes, shorter than the 90 minutes of results shown in Figure 7.5, but the remaining settings were identical. The duration of the SWRO permeate backwash exhibited a slower permeability decline rate than the UF permeate backwash, as well. Therefore, the effectiveness of SWRO permeate backwashing on UF fouling control of seawater was confirmed.

The backwash duration and backwash flux were identical for SWRO permeate backwash experiments in both cases. However, in Figure 7.6, the improvement of SWRO permeate was obtained at a filtration cycle of 45 minutes, while the improvement was obtained at a filtration cycle of 90 minutes in Figure 7.5. The consumption of SWRO permeate was reduced in this way. Because the SWRO permeate is expensive, the less SWRO permeate consumed the more economically feasible the application of DEMIFLUSH will be. Considering the filtration flux of 55 l/(m².h), the backwash time of 45 seconds and the backwash flux of 275 l/(m².h), the required SWRO permeate as a percentage of produced UF permeate within one operation cycle is 91.6% for 45-min and 95.8% for 90-min filtration.
Therefore, the SWRO permeate consumption can be reduced significantly, reducing the cost of application of the DEMIFLUSH concept. However, because these experiments were conducted during a low fouling period of the tested seawater (January-March), it needs to be confirmed again during the high fouling period. In the high fouling period, the Evides plant had to incorporate in-line coagulation to control the UF fouling. If the same optimization results could be obtained in high fouling period, the DEMIFLUSH concept probably can replace in-line coagulation as a fouling control method.

When the SWRO permeate is used for backwashing, the waste sludge from the backwash contains only salt and organic substances originally from the sea. Therefore, it should be possible to discharge it back into the sea and thus the coagulant dosing and waste sludge treatment facilities are no longer necessary. Both capital and maintenance costs can be saved in this case, making the application of DEMIFLUSH more economically feasible. Of course, it depends on the consumption of SWRO permeate as well. If too much SWRO permeate is required, then it is still not cost effective. However, application of the DEMIFLUSH concept is still environmentally friendly, with respect to the possible elimination of disposal of backwash waste sludge.
Figure 7.5: Permeability as a function of date for experiments with UF and SWRO permeate backwashes (90 min filtration at 55 l/(m².h) flux followed by 45 sec backwash at 265 l/(m².h) flux).

Permeability decline rate:
- UF Permeate 5.2 L/(h².m².bar)
- SWRO permeate 1.5 L/(h².m².bar)

Figure 7.6: Permeability as a function of date for experiments with UF and SWRO permeate backwashes (45 min filtration at 55 l/(m².h) flux followed by 45 sec backwash at 265 l/(m².h) flux).
7.3.3.2 High fouling period

Figure 7.7 and 7.8 show the experimental results of pilot tests in the high fouling period (from May to June of 2011). As shown in these two figures, the recovery of UF for UF permeate backwashing were 77.8 %, which means 22.2% of UF permeate was used for backwashing. When the membrane was backwashes with UF permeate, TMP increased sharply all the time. On the other hand, the recoveries of UF for the SWRO permeate backwashing in Figure 7.7 and 7.8 are 84% and 91%, respectively. At these two recoveries, less amount of water was used for backwashing, but the fouling control efficiencies were still satisfactory (stable TMP after a small initial increase).

These two figures indicated that the SWRO permeate (almost demineralized water) backwashing can control the UF fouling in high fouling period as well. In terms of the usage of SWRO permeate, the amount can be reduced to 9% of the production of UF until this moment (91% recovery). Unfortunately, because the high fouling period is gone after June 2011, further optimization could not be continued. The consumption of SWRO permeate may be reduced further. This should be investigated in the high fouling period next year at the same location. If the same high recovery 95.8% as low fouling period is achievable, the application will be more realistic.
Figure 7.7: TMP as a function of date for experiments with UF and SWRO permeate backwashes (UF permeate backwashing experiments were conducted at 77.8% recovery, with 45 min filtration at 55 l/(m².h) flux and followed by 2 min backwash at 265 l/(m².h) flux; SWRO permeate backwashing experiment was conducted at 84% recovery)
Figure 7.8: TMP as a function of date for experiments with UF and SWRO permeate backwashes (UF permeate backwashing experiments were conducted at 77.8% recovery, with 45 min filtration at 55 l/(m².h) flux and followed by 2 min backwash at 265 l/(m².h) flux; SWRO permeate backwashing experiment was conducted at 91% recovery)

7.3.3.3 Cost estimation

Cost estimation based on the highest recovery achieved in both low and high fouling periods is calculated in this section.
This estimation is based on the cost calculation of the largest UF plant in Germany, which consist of a drinking water production line and also a backwash wastewater treatment line. As shown in Table 7.6 and 7.7, the backwash wastewater treatment investment cost is about 20% (5,080,000 €) of the total cost of this plant (25,480,000 €). Considering construct a small plant with a capacity of 1000 m$^3$/day, the cost is divided by 87. Because directly divided by 87 according to the capacity normally underestimate the cost of a small plant, a compensation factor 1.5 is applied (as shown in Table 7.6 and 7.7). Therefore, the investment costs of drinking water production and backwash wastewater treatment line for a 1000 m$^3$/day plant are 353,100 and 87,600 euro, respectively.

Table 7.6: Investment cost of a 1000 m$^3$/day demo plant based on the largest German UF plant (only the drinking water production line, not including backwash water treatment)

<table>
<thead>
<tr>
<th>Drink water producing line</th>
<th>Largest plant in Germany</th>
<th>Demo plant (Scaled down by /87)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (m$^3$/day)</td>
<td>87000</td>
<td>1000</td>
</tr>
<tr>
<td>Building (T€)</td>
<td>5900</td>
<td>68</td>
</tr>
<tr>
<td>Process-technology (without membranes) (T€)</td>
<td>8600</td>
<td>99</td>
</tr>
<tr>
<td>Membranes (T€)</td>
<td>3000</td>
<td>35</td>
</tr>
<tr>
<td>Electrical components (T€)</td>
<td>1600</td>
<td>18.4</td>
</tr>
<tr>
<td>Additional cost (T€)</td>
<td>1300</td>
<td>15</td>
</tr>
<tr>
<td>Total cost (T€)</td>
<td>20400</td>
<td>235.4</td>
</tr>
<tr>
<td>Compensation factor (-)</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>Cost of Demo plant (T€)</td>
<td></td>
<td>353.1</td>
</tr>
</tbody>
</table>
Considering the highest UF recovery by applying demineralized water backwashing until now (91%), 90 m³ of SWRO permeate or demineralized water are required for one backwash. Since the price of SWRO permeate is varying between 0.7-1 US$/m³, taking the currency exchange rate into account, a price of 0.5 €/m³ SWRO permeate is used in this estimation. The extra cost per year of applying demineralized water backwashing is calculated. Table 7.9 shows the extra cost for when demineralized water backwashing is applied for 3, 6 and 9 months within a year.

Table 7.10 shows the saved cost by applying demineralized water backwashing. If the investment cost is split into 10 years, the investment cost is 8760 €/y. because no coagulation is used, 2400 €/y is saved by applying demineralized water backwashing as well. In total, 11200 €/y can be saved. Compared with the extra cost caused by demineralized water backwashing, at 91% UF recovery, this technique is economically feasible when it is applied no more than half year. If it has to be applied the whole year, it will be more expensive than in-line coagulation pre-treatment.

However, the consumption of demineralized water is not perfectly optimized yet. If the consumption can be further reduced, to 5% of the production for example, the application of demineralized water backwashing will be economically feasible even for 12 month operation.
Table 7.8: Constants used for cost estimation

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrafiltration recovery</td>
<td>91%</td>
</tr>
<tr>
<td>Price of RO permeate</td>
<td>0.5</td>
</tr>
<tr>
<td>Required RO permeate for per Demi backwashing</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 7.9: Extra cost of the application of the demineralized water backwashing

| Extra cost of Demiflush (needed for 3 months per year) (T€/y) | 4.1 |
| Extra cost of Demiflush (needed for 6 months per year) (T€/y) | 8.1 |
| Extra cost of Demiflush (needed for 9 months per year) (T€/y) | 12.2 |

Table 7.10: Saved cost with demineralized water backwashing

<table>
<thead>
<tr>
<th></th>
<th>Coagulation</th>
<th>Demiflush</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment cost (assumed used for 10 years) (T€/y)</td>
<td>8.8</td>
<td>0</td>
</tr>
<tr>
<td>Operational cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coagulants (T€/y)</td>
<td>2.4</td>
<td>0</td>
</tr>
<tr>
<td>Chemical for cleaning (T€/y)</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Sum (T€/y)</td>
<td>11.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Saved cost by Demiflush (T€/y) 11.2

7.4 Conclusions

Results in the previous studies with small-scale membrane modules are confirmed again with a standard UF membrane module during a low fouling period. SWRO permeate (having similar qualities as demineralized water) backwashing substantially improved the seawater UF fouling control. The effectiveness of SWRO permeate backwashing on UF fouling control was observed at recoveries of
95.8% and 91% during low and high fouling periods, respectively. Furthermore, the results of the DEMIFLUSH pilot were similar to the Evides desalination plant having the same operational settings, suggesting that the results obtained from the DEMIFLUSH pilot are applicable to full-scale plants. Cost estimation based on 91% recovery showed that application of demineralized water backwashing is economically feasible when it is needed for no more than half year. However, it probably can be extended to a whole year when the consumption of demineralized water is further optimized.

7.5 References


Chapter 8

General conclusions and recommendations
8.1 General conclusions

This dissertation introduced a new fouling control method for ultrafiltration: demineralized water backwash (the DEMIFLUSH concept). Compared to the conventional fouling control method based on coagulation, it has the following potential benefits:

- No coagulant dosage
- Easy disposal of backwash waste sludge
- Less cost of the sludge treatment

In a pilot test using UF membranes with a surface area of 2.4 m², the improvement of demineralized water backwash on UF fouling control was observed for the first time in surface water treatment (Li et al. 2010a). During filtration, cations in feed water can enhance the fouling via the charge screening and calcium bridging effects (Hong and Elimelech 1997). During UF permeate backwash, three types of substances in backwash water are hypothesized to be responsible for the fouling. These substances are monovalent cations, divalent cations and organic substances. However, demineralized water contains none of these substances, so the hypothesized mechanisms of the DEMIFLUSH concept related with these substances are:

- Reduction of the charge screening effect (caused by both monovalent and divalent cations);
- Breakdown of the calcium-bridging effect; and,
- No further adsorption of organic substances during backwashes.

Chapter 3 describes the impact of cations and organic substances on fouling control (Li et al. 2010b, Li et al. 2009). Results show that backwash water containing only organic substances isolated from UF permeate displayed a fouling control similar to that of demineralized water. Therefore, the presence of only organic substances in UF permeate does not reduce the backwash efficiency. Because the hypothesis regarding DEMIFLUSH and organic substances was based on the assumption that organic substances reduce the fouling control
efficiency, this mechanism can be eliminated. However, the combination of organic substances and cations might still enhance the adsorption of organic substances on membranes during backwashes. On the other hand, the presence of either monovalent or divalent cations (adding either NaCl or CaCl$_2$ to demineralized water for backwashes) reduces the fouling control efficiency of backwashes. Therefore, these cations are responsible for the low efficiency of backwashing with cation containing solutions (for instance UF permeate). Considering the hypotheses, both reduction of the charge screening and breakdown of the calcium bridging effects are related to the presence of cations.

To demonstrate the validity of these two hypotheses of the DEMIFLUSH concept, Chapter 4 describes the relationship between the ionic environment and the charge of membranes and NOM via zeta potential measurements. Results show that the zeta potentials of UF membranes and NOM become less negative when the pH decreases and the electrolyte concentration and valence increases, generally consistent with the DLVO theory. Divalent cations have a stronger charge screening effect than monovalent cations due to their stronger ability to compress the electrical double layer of membranes and NOM. By backwashing with demineralized water, a cation-free environment is established and the negative charge of membranes and NOM is recovered. Consequently, the repulsion between membranes and NOM is restored, and the backwash becomes more efficient. Based on the DLVO theory, there is similar interaction energy between membranes and NOM at the electrolyte conditions of 2 mmol/l CaCl$_2$ and 10 mmol/l NaCl. Furthermore, the fouling experiment results show that these two solutions have a similar efficiency on fouling control, although the efficiency for 10 mmol/l NaCl is slightly higher. *Therefore, reduction of the charge screening effect is the dominant mechanism of the DEMIFLUSH concept.*

On the other hand, results show that calcium also adsorbs on the membranes via the bridging effect. After a 2-hour continuous filtration with 5 mmol/l CaCl$_2$ solution, the zeta potentials of membranes become less negative. However, by conducting a demineralized water backwash, the negative zeta potential of membranes was only
slightly recovered, but still was less negative than the one without calcium adsorption. Therefore, the calcium bridging effect cannot be mostly broken down with only demineralized water backwashes. *Fouling caused by the calcium bridging effect is mostly irreversible even with the DEMIFLUSH concept.*

After an explanation of the dominant mechanism of the DEMIFLUSH concept, Chapter 5 describes the influence of the DEMIFLUSH concept on different fractions of NOM from surface water. According to the LC-OCD analyses of Schie canal water, some biopolymers and humic substances are rejected by the UF membranes during filtration, so these components are the potential foulants. By conducting a hydraulic backwash (regardless of whether the backwash media is UF permeate or demineralized water), most of the biopolymers were removed from the membranes. Therefore, although the fouling of biopolymers increases the resistance of filtration, this fouling is highly reversible. Experiments with sodium alginate (representing biopolymers) confirm this high reversibility as well. However, compared to the low removal of humic substances with UF permeate backwashes, the DEMIFLUSH concept is especially effective on the removal of humic substances. Mass balance calculations show that more than 70% of humic foulants are removed by demineralized water backwashes. *Therefore, the improvement of the DEMIFLUSH concept is mainly due to the enhanced removal of humic substances during backwashes.*

The application of the DEMIFLUSH concept on seawater treatment is described in Chapter 6. Due to the high salinity of seawater, the improvement of the DEMIFLUSH concept based on the DLVO theory can be expected. *As expected, this concept also substantially improves the control of UF fouling in seawater treatment.* However, more demineralized water is consumed in the seawater application than the surface water application, since more demineralized water is required to dilute the high salt concentration of seawater and limit the dispersion effect near the membranes.

*To summarize, the DEMIFLUSH concept is applicable to UF fouling control for both surface water and seawater treatment.* Therefore, pilot tests with SWRO permeate
(similar quality as demineralized water) backwashes were conducted with a standard membrane module to investigate the feasibility of this concept in practice and optimize the consumption of SWRO permeate. Chapter 7 describes some experiences during the pilot tests (only performed during low fouling periods until now). SWRO permeate backwashing also substantially improved the UF fouling control in the pilot tests. In low fouling periods, the recovery of UF can be increased up to 95.8% under conditions of maintaining good fouling control. In high fouling period, the recovery can be up to 91% until now (not perfectly optimized yet). Cost estimation based on 91% recovery showed that application of demineralized water backwashing is economically feasible when it is needed for no more than half year. However, it probably can be extended to a whole year when the consumption of demineralized water is further optimized.

Based on the results of the pilot tests during a low fouling period, the DEMIFLUSH concept has the potential to replace coagulation as a fouling control method. Coagulation is often used as a pretreatment of UF, but the disposal of coagulant-containing sludge is problematic. Considering the possible elimination of coagulation and sludge treatment system, application of the DEMIFLUSH concept can be more cost-effective than coagulation. However, it will only become practice if the results of pilot tests can be reproduced during high fouling periods as well.

8.2 Recommendations

Since SWRO permeate and demineralized water are expensive to use, the consumption of both should be further optimized to increase the recovery of UF. There are two potential ways to reduce their consumption:

1. Reduce the backwash frequency or backwash duration; and,
2. Combine the SWRO permeate/demineralized water forward flush and normal UF permeate backwash.

The function of SWRO permeate/demineralized water forward flush is to establish the cation-free environment and restore the repulsion force between foulants and
membranes, and then remove them with normal UF permeate backwashes. In this case, the consumption of SWRO permeate/demineralized water can be reduced dramatically.

8.3 References


Appendix 1 Preparation of home made membrane modules

1. **Hot-melt adhesive:**
   Hot-melt adhesive (hot glue) is used for potting self-prepared membrane modules.

2. **Potting:**
   - Cut transparent PVC pipes and fibers
   - One membrane module is composed of 6 parts: two short 8-mm transparent PVC pipes (4 cm), two Festo T-joint connecters, one long 8-mm transparent PVC pipe (length depends on the operator's demand), capillary membrane fibers (the length of fibers should be 3-4 cm longer than the total length of pipes)
   - Connect the PVC pipes and Festo T-joint as the following Figure 1
   - Push the fibers in the module
   - Inject hot-melt gel in one end of modules (with hot-melt piston gun)
   - When the gel is dry after around 10 minutes, cut the pipe at the position shown in Figure 1b
   - Repeat the above steps 4 and 5 for the other end of the module
Figure 1: Schematic instruction of membrane module potting

1a: Resin injection for potting

1b: Vertically standing of membrane module for resin drying

1c: Finished membrane module

Cut the membrane at this position when the resin is dry after one day

Silicon gel
Appendix 2 Zeta potential measurement of hollow fiber membrane with EKA (Anton Paar)

Since the EKA is not designed for hollow fiber membrane measurement, the original cells cannot be used in this case. Therefore, a hollow fiber membrane module (as shown in Figure 1) should be prepared first for this measurement. The procedure of preparing this kind of hollow fiber module is described in ‘preparation of home made membrane modules’.

![Figure 1: home made hollow fiber membrane module](image)

The configuration of this kind of membrane module makes the flow of electrolyte solution possible for either along the surface of membrane (green arrows) or through the membrane (red arrows). There are 4 openings on this module (as shown in Figure 1). When the flow direction of electrolyte solution is determined, the unused openings should be blocked with Festo valves.
For example, if the zeta potential of membrane surface is measured, the opening 2 and 3 should be blocked. The electrodes on the Electronic kinetic Analyzer (EKA) are connected to the opening of 1 and 4. In order to prevent the electrolyte solution passes through the membrane and consequently influences the measurement, the same electrolyte solution should be filled in the outside of membrane fibers by injecting electrolyte from opening 2 to 3 (before they are blocked by valves).

After that, the electrodes of the EKA will be fitted on the membrane module. Because the difference of diameter between membrane module and the electrode of EKA, some tube transactions are necessary. As shown in Figure 2-4, first, two plastic tubes with a 8mm inner diameter will be put on both ends of the membrane module to increase the diameter of the module’s both ends. Secondly, two soft tubes will be used to connect the electrodes and the membrane module. In order to make sure that there is no leakage, two metal rings with screw will be used to tighten the connections (See Figure 4).

When all the mentioned steps have been done, the membrane module is ready to be measured with EKA. After this, the measuring program should be set. The procedure for measurement with cyringical cell is suitable for hollow fiber membrane, and the Helmholtz-Smoluchowski equation should be used for the zeta potential calculation. The rest settings can be the same as other measurements. For example, the electrolyte solution depends on what kind of electrolyte the operator wants to use. From here on, the operator can start the measurement by following the instruction of EKA user manual.
Figure 2: tube transaction 1 to fit the electrode of EKA on membrane module_1

Figure 3: tube transaction 1 to fit the electrode of EKA on membrane module_2
Figure 4: tube transaction 2 to fit the electrode of EKA on membrane module
Ultrafiltration (UF) is a proven technology in water treatment nowadays. However, fouling remains a major challenge in the operation of UF, especially in regard to colloidal NOM fouling. In general, a number of colloidal NOM fouling mechanisms may occur, such as adsorption, gel formation. Colloidal NOM fouling is influenced by multivalent cations, ionic strength and pH. In order to control membrane fouling, different pretreatments such as powder activated carbon adsorption, lime softening, ion exchange, conventional media filtration and coagulation with inorganic and polymeric coagulant have been investigated. In-line coagulation is the most commonly used pretreatment for UF of surface water. However, the problem with in-line coagulation is that a large amount of backwash-derived waste sludge containing dosed coagulants is produced. Since the backwash waste sludge with coagulant has to be treated before its discharge (especially in Western Europe), this option creates additional cost for the membrane treatment plant (up to 20% of the total cost of the whole plant). This dissertation investigates the technical possibility of controlling the UF fouling by backwashing with low ionic strength water (deionized water in the Netherlands), in order to reduce the ionic strength and the amount of multivalent cations and thus reduce NOM fouling. Chapter 1 briefly introduces this dissertation.

The effectiveness of deionized water backwashing is generally investigated on a pilot scale (with a 2.4 m² membrane) in Chapter 2. Results show that regarding the removal of NOM foulants via hydraulic backwashes, deionized water is better than UF and NF permeate. That is probably due to the absence of cations, reducing the charge screening effect and/or Ca-bridging effect between the negatively charged membrane and NOM, leading to a restoration of repulsion force and consequently an easy removal of fouling layer. However, it is not clear which components in backwash water lead to the low foulant removal in this chapter. Therefore, Chapter 3 investigates the influence of backwash water composition on fouling control. Different amount of CaCl₂ and NaCl was dosed in deionized
water to test their effect on fouling control. It became clear that the presence of monovalent and divalent cations in backwash water reduces the fouling control efficiency. Moreover, by isolating the organic matter in UF permeate for backwashing, it is found that the organic matter in UF permeate itself does not cause fouling problems when they are in backwash water. In terms of the influence of monovalent and divalent cations, both the elimination of the charge screening effect and the breakdown of the calcium bridging effect are possible mechanisms to explain this improvement. Therefore, these two effects are presumed to be the mechanisms of demineralized water backwashing.

The investigation of the hypotheses of demineralized water backwashing is reported in Chapter 4, including the charge screening and the calcium bridging effects. By determining the zeta potential of the membranes and the colloidal NOM compounds at different conditions, the impact of pH and electrolyte valence and concentration on their charge was assessed. Furthermore, the adsorption of calcium on the membranes and the NOM compounds was also illustrated. Results showed that a membrane became less negatively charged when the pH decreased and the concentration of electrolyte increased, proving the presence of the charge screening effect. Furthermore, divalent cation has a much stronger effect on the increase of membrane zeta potential than monovalent cations which is generally in consistent with the DLVO theory. Calcium ions indeed adsorbed on either new or fouled membranes, and bridged NOM and membranes afterwards. However, the interaction of calcium with fouled membranes is more substantial than with new membranes. However, the charge screening effect played a dominant role in the membrane fouling and fouling control by demineralized water backwashing. Most of the fouling caused by calcium bridging is difficult to remove even with a demineralized water backwash.

Chapter 5 illustrates the effectiveness of demineralized water backwashing on ultrafiltration fouling of different fractions of NOM. Results of natural waters show the same fouling removal via demineralized water backwashing as the previous chapters. Furthermore, LC-OCD analysis of Schie Canal water showed that
biopolymers can be flushed away by hydraulic backwashes of either demineralized water or UF permeate. Compared to almost zero removal of humics and LMW substances by UF permeate backwashes, demineralized water backwashing was able to remove a substantial amount of humics, and a small amount of LMW substances.

Fouling of sodium alginate model compound showed a high reversibility no matter what kind of backwash water was used. This is also consistent with the LC-OCD analysis of Schie Canal water. However, not all biopolymers were removed by hydraulic backwashes. A low fouling reversibility was observed for BSA fouling, but BSA may be in the part of unremoved biopolymers with demineralized water. No improvement in fouling control for fouling of Suwannee River humic acid (SRHA) was observed as well when demineralized water was used for the backwash. This is probably because the calcium bridging via carboxyl functional groups is the main mechanism for SRHA fouling, which is difficult to break down.

Since the charge screening effect is the main mechanism of demineralized water backwashing, theoretically speaking, its application on seawater treatment is also possible. Chapter 6 demonstrates that demineralized water backwashing can substantially improve seawater UF fouling control, similar to the previous findings in surface canal water. However, the duration of a successful demineralized water backwash should be extended from one to two minutes. This is due to the high salinity of seawater and thus more demineralized water was required to dilute the seawater and limit a higher dispersion effect of seawater than surface water. Monovalent cations in backwash water showed their impact on the fouling control efficiency, indicating the existence of a charge screening effect. Furthermore, the different UF membrane fouling behaviors in winter and spring indicated the impact of a seasonal influence on UF membrane fouling. In spring, the membrane showed more fouling probably due to the algae bloom which is widely considered an important fouling factor. The results of the long-term experiment reconfirmed the effectiveness of backwashing with SWRO permeate (similar quality as demineralized water) on the fouling control of seawater UF. Since it is very easy to
access SWRO permeate in a UF-RO desalination plant, this approach can be implemented easily.

In order to apply this technique in industry, optimization work was conducted on a pilot scale with a standard membrane element (40 m$^2$) and reported in Chapter 7. Results show that SWRO permeate (having similar qualities as demineralized water) backwashing substantially improved the seawater UF fouling control, consistent with the previous studies with small-scale membrane modules. The effectiveness of SWRO permeate backwashing on UF fouling control was observed at a recovery rate up to 95.8% during a low fouling period. Furthermore, the results of the DEMIFLUSH pilot were similar to the Evides desalination plant having the same operational settings, suggesting that the results obtained from the DEMIFLUSH pilot are applicable to full-scale plants. However, the results of high fouling period are missing. If the optimization results can be repeated in high fouling period as well, the application of SWRO permeate is also economically feasible due to the low consumption of SWRO permeate.

Optimization work should be continued to reduce the consumption of SWRO permeate or demineralized water, since the usage of these water is expensive.
Samenvatting

Ultrafiltratie (UF) is een bewezen technologie in de waterbehandeling. Echter, vervuiling blijft een grote uitdaging in de bedrijfsoering van UF, in het bijzonder met betrekking tot vervuiling door colloïdaal NOM. In het algemeen kan een aantal vervuilingmechanismen met colloïdaal NOM optreden, zoals adsorptie en gelvorming. Vervuiling met colloïdaal NOM wordt beïnvloed door meerwaardige kationen, ionsterkte en pH. Om membraanvervuiling te beheersen zijn verschillende voorbehandelingen onderzocht, zoals adsorptie aan actieve koolpoeder, ontharding, ionenuitwisseling, filtratie met conventionele media en coagulatie met anorganische en polymere coagulant. In-line coagulatie is de meest gebruikte voorbehandeling voor UF van het oppervlaktewater. Het probleem met in-line coagulatie is echter dat bij membraanspoeling een grote hoeveelheid afvalslib wordt geproduceerd dat het gedoseerde coagulant bevat. Omdat het afvalslib met coagulant moet worden behandeld voordat het geloost kan worden (in het bijzonder in West-Europa), brengt deze optie extra kosten met zich mee voor de membraan zuiveringsinstallatie (tot 20% van de kosten van de gehele installatie). Dit proefschrift onderzoekt de technische mogelijkheid van het beperken van UF vervuiling door terug te spoelen met water met lage ionische sterkte (gedemineraliseerd water in Nederland), om de ionische sterkte en het aantal multivalente cationen te verminderen en zo NOM vervuiling te reduceren. Hoofdstuk 1 introduceert kort dit proefschrift.

De effectiviteit van terugspoelen met gedemineraliseerd water is onderzocht op pilotschaal (met een 2.4 m² membraan) in hoofdstuk 2. Uit de resultaten blijkt dat voor de verwijdering van NOM vervuiling met hydraulische terugspoeling, gedemineraliseerd water effectiever is dan UF of NF permeaat. Dat is waarschijnlijk dankzij de afwezigheid van kationen, het verminderen van de heffing screening effect en / of het Ca-bridging effect tussen de negatief geladen membraan en NOM, wat leidt tot een herstel van afstotende kracht en dus een gemakkelijke verwijdering van de vervuilingsslaag.
Het is echter niet duidelijk in dit hoofdstuk welke componenten in het spoelwater leiden tot de lage verwijdering van vervuiling. Daarom wordt in hoofdstuk 3 de invloed onderzocht van spoelwater samenstelling op effectiviteit van verwijdering van vervuiling. Verschillende hoeveelheid CaCl$_2$ en NaCl werden gedoseerd in gedemineraliseerd spoelwater om hun effect op verwijdering van vervuiling te toetsen. Het werd duidelijk dat de aanwezigheid van monovalente en tweewaardige kationen in spoelwater het reinigingsrendement verminderd. Bovendien is door het isoleren van de organische stof in UF permeaat vastgesteld dat de organische stof in het spoelwater zelf geen vervuiling veroorzaakt. Mogelijke mechanismen die deze verbetering verklaren zijn de eliminatie van ladingsafscherming en calciumbrugvorming door monovalente en tweewaardige kationen.

Onderzoek en hypotheses over terugspoelen met gedemineraliseerd water worden gerapporteerd in hoofdstuk 4, inclusief ladingsafscherming en calciumbrugvorming. Door bepaling van het zeta potentieel van de membranen en de colloïdale NOM verbindingen onder verschillende omstandigheden, was de invloed bepaald van pH, elektrolyt valentie en de ladingsconcentratie. Bovendien werd de adsorptie van calcium op de membranen en de NOM verbindingen ook geïllustreerd. Resultaten toonden aan dat een membraan minder negatief geladen werd wanneer de pH verminderd en de concentratie van elektrolyt toenam. Hieruit blijkt de aanwezigheid van ladingsafscherming. Bovendien hadden tweewaardige kationen een veel sterker effect op de toename van het zeta potentieel van het membraan dan eenwaardige kationen, wat overeenstemt met de DLVO theorie. Calciumionen adsorbeerden inderdaad op nieuw of vervuilde membranen, om vervolgens een brug te vormen tussen NOM en het membraan. De interactie van calcium is echter groter bij vervuilde membranen dan bij nieuwe membranen. Ladingsafscherming speelde een dominante rol bij membraanvervuiling en het voorkomen daarvan door met gedemineraliseerd water terug te spoelen. De meeste vervuiling die is veroorzaakt door calciumbrugvorming is lastig te verwijderen, zelfs met terugspoelen met gedemineraliseerd water.
Hoofdstuk 5 illustreert de effectiviteit van gedemineraliseerd water terugspoelen op de vervuiling van UF membranen met verschillende fracties van de NOM. Uit resultaten van experimenten met natuurlijk water bleek de verwijdering van vervuiling door terugspoelen met gedemineraliseerd water even effectief als in vorige hoofdstukken. Ook was aangetoond met een LC-OCD analyse van Schie kanaalwater dat biopolymeren kunnen worden verwijderd door terugspoelen met gedemineraliseerd water en UF permeaat. Terwijl met terugspoelen met UF permeaat geen humuszuren en kleine NOM-componenten konden worden verwijderd, was terugspoelen met gedemineraliseerd water effectief voor de verwijdering van humuszuren en een geringe hoeveelheid van kleine NOM-componenten.

Vervuiling met de modelstof natriumalginaat was in grote mate omkeerbaar, en onafhankelijk van het type spoelwater dat werd gebruikt. Dit is ook consistent met de LC-OCD analyse van Schie kanaal water. Niet alle biopolymeren konden echter worden verwijderd door hydraulische terugspoeling. Vervuiling door BSA was beperkt omkeerbaar, en is deel van de biopolymeren die niet kan worden verwijderd bij terugspoelen met gedemineraliseerd water. Bij het gebruik van Suwannee River humuszuur (SRHA) als modelstof, is geen verbetering waargenomen van verwijdering van vervuiling bij terugspoelen met gedemineraliseerd water. Dit komt waarschijnlijk doordat het voornaamste mechanisme voor SRHA vervuiling de calciumbrugvorming via carboxyl functionele groepen is, en die binding is moeilijk te breken.

Omdat het verminderen van ladingsafscherming het belangrijkste mechanisme van gedemineraliseerd water terugspoelen is, is theoretisch gezien de toepassing ervan op zeewater behandeling ook mogelijk. Hoofdstuk 6 laat zien dat terugspoelen met gedemineraliseerd water de vervuiling van UF membranen aanzienlijk kan verminderen, wat in overeenkomst is met de eerdere bevindingen waarbij oppervlaktewater is gebruikt. Voor een effectieve spoeling met gedemineraliseerd water moet de spoelingduur wel worden verlengd tot twee
minuten (t.o.v. een minuut bij oppervlaktewater). Dit is te wijten aan het hoge zoutgehalte van het zeewater, waardoor meer gedemineraliseerd water nodig was om het zeewater te verdunnen en de hogere zoutdispersie tegen te gaan, vergeleken met oppervlaktewater.

Eenwaardige kationen in het spoelwater beïnvloedden de effectiviteit van de verwijding van vervuiling, wat aantoont dat ladingsafscherming optreedt. Daarnaast bleek UF membraanvervuiling te verschillen per seizoen. In het voorjaar vervuilde het membraan meer, wat waarschijnlijk te wijten is aan algenbloei. De resultaten van een lange termijn experiment met UF membranen bij zeewaterbehandeling herbevestigden de effectiviteit van de terugspoeling met SWRO op verwijdering van vervuiling. SWRO is van vergelijkbare kwaliteit als gedemineraliseerd water. Omdat het zeer eenvoudig is om over SWRO water te beschikken bij een UF-RO ontziltingsinstallatie, kan deze aanpak eenvoudig worden geïmplementeerd.

Om deze techniek toe te passen in de industrie, is optimalisatie onderzoek uitgevoerd op pilotschaal met een standaard membraan element (40 m²), wat is gerapporteerd in hoofdstuk 7. Resultaten tonen aan dat terugspoelen met SWRO permeaat de vervuiling van UF membranen bij zeewaterbehandeling aanzienlijk verminderd, wat in overeenstemming is met de eerdere bevindingen met kleinschalige membraanmodules. De effectiviteit van terugspoelen met SWRO permeaat op verwijdering van vervuiling is waargenomen bij een recovery tot 95,8% tijdens een periode van lage aangroei van vervuiling. De resultaten van de DEMIFLUSH pilotinstallatie waren vergelijkbaar met die van de ontziltingsinstallatie van Evides die met dezelfde operationele instellingen werd bedreven, wat suggereert dat de resultaten van de DEMIFLUSH pilotinstallatie ook van toepassing zijn op full-scale installaties. De resultaten van een periode met hoge aangroei van vervuiling ontbreken echter. Als dezelfde resultaten kunnen worden bereikt in een periode met hoge aangroei van vervuiling, dan zou terugspoelen met SWRO economisch haalbaar zijn vanwege het lage verbruik van SWRO permeaat bij terugspoelen.
Verdere optimalisatie zou zich moeten richten om het verbruik van SWRO permeaat of gedemineraliseerd water te verminderen, omdat de productie van dit water duur is.

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Publications

Published international peer reviewed papers


Submitted international peer reviewed papers


International peer reviewed papers in preparation


Conference proceedings


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