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CERAMIC NANOFILTRATION FOR DIRECT FILTRATION OF MUNICIPAL SEWAGE

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Franca KRAMER

Master of Civil Engineering, Delft University of Technology, the Netherlands
born in Leidschendam, the Netherlands

This dissertation has been approved by the

promoter   prof. dr. ir. Luuk Rietveld
copromotor   dr. ir. Bas Heijman

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CONTENT

SUMMARY

'Rien dans la vie n'est à craindre, tout doit être compris. C'est maintenant le moment de comprendre davantage, afin de craindre moins.'

'Nothing in life is to be feared, it is only to be understood. Now is the time to understand more, so that we may fear less.'

Marie Curie

SUMMARY

There is an urgent need for alternative water sources worldwide due to population growth, water scarcity, and climate change. Reclamation of municipal sewage reclamation for irrigation water, industry water, and, in some countries even, drinking water is an upcoming trend in water treatment (Bixio et al., 2005; Raffin et al., 2013; Rietveld et al., 2011; Wielemaker et al., 2018). Using municipal sewage as water source has the advantage of keeping the water cycles small, also because water is mainly needed in places where municipal sewage is available: places where people work and live. Furthermore, municipal sewage is a source of nutrients and organics with a high recovery potential.

In this research, a concept is proposed to directly treat municipal sewage with ceramic nanofiltration (NF) as pretreatment for reverse osmosis (RO). Ceramic NF membranes were chosen because of their high mechanical strength and high chemical and thermal resistance (Weber et al., 2003). These membranes are expected not to be damaged by high pressures, high temperatures, and high concentration of chemicals, which enables vigorous chemical cleaning of the membranes. Furthermore, the lifetime of the membrane is over 15 years, when applied for drinking water purposes, and their material is recyclable (Heijman, 2007; Lee et al., 2015; Samaei et al., 2018; Shang, 2014). Ceramic membranes are prone to less irreversible fouling than polymeric membranes (Lee et al., 2013; Zhao et al., 2018), which makes this technology suitable for direct treatment of municipal sewage.

Research on ceramic NF membranes is limited in literature and treatment of municipal sewage using ceramic NF as pretreatment of RO has not been reported yet. Just as, information on the robustness, organic and ion rejection, and methods to control fouling on the membrane surface, which is essential in order to enable direct ceramic NF of municipal sewage. Therefore, the purpose of this research was to study the potential of the application of ceramic NF for treatment of municipal sewage. This was divided into four research questions.

1. What is the feasibility of the sewer mining concept, presented above, in terms of water production, organic matter and ion retention, and biofouling potential?
2. What is the quality and long-term robustness of commercially manufactured ceramic NF membranes?
3. What is the influence of multivalent counter ions and organic fouling on the membrane surface on the phosphate retention in ceramic NF?
4. What is the most efficient way to control organic fouling during ceramic NF when treating municipal sewage?

First, raw municipal sewage was treated by ceramic NF in preliminary pilot study. The filtration lasted for five days without intermediate cleaning of the membranes. After filtration, the membranes were successfully cleaned using chemical cleaning: 93% of the organic fouling was removed from the membrane surface. The chemical cleaning consisted of treatment of sodium hypochlorite (0.1% for 45 min) to remove organic fouling, followed by hydrochloric acid (0.1 mol·L^{-1} for 15 min) treatment for removal of salts. On average 80% of the organic matter was rejected by ceramic NF. While the phosphate retention varied. No conclusive cause for this varying retention was found in this part of the research.

To determine the possibility of treating municipal sewage with ceramic NF as pretreatment for RO, the fouling potential was measured using the Membrane Fouling Simulator (Vrouwenvelder et al., 2006, 2007). The fouling potential was as low as Dutch drinking water, making ceramic NF suitable as pretreatment for RO.

Second, the quality and long-term robustness of ceramic NF membranes was studied. An extension to a commonly used molecular weight cut-off (MWCO) method was developed to be able to quantify defects in membranes and to determine the MWCO accurately. It was found that the quality of the membranes was more accurately determined using this extended method than the original method. Therefore, this method was further used to study the quality of a broad range of commercial ceramic membranes: both tubular and disc membranes from various suppliers. The quality of the membranes was tested by determining the (i) hydraulic permeability, (ii) molecular weight cut-off, and (iii) quantitative defects. The results showed that all batches showed variations in quality and membranes with defects.

Furthermore, the robustness of tubular ceramic NF membranes was studied by monitoring long-term exposure to sodium hypochlorite, most commonly used for removal of organic fouling from ceramic membranes (Cui et al., 2013; Lee et al., 2015; Xu et al., 2013; Zebić Avdičević et al., 2017). In this study, long-term was the equivalent one year filtration including chemical treatment. It was demonstrated that the ceramic NF membranes were negatively affected by this long-term treatment and the glass end seal layer on the membranes was damaged by sodium hypochlorite exposure. The separation layer in these membranes was not notably compromised.

Third, the influence of pH, multivalent counter ions, and membrane fouling on phosphate retention was studied. Various experiments were performed to analyse the phosphate retention and the membrane charge. Streaming potential measurements were executed to be able to calculate the zeta potential and the membrane charge, in order to gain insight in the electrostatic interactions on the membrane surface. The phosphate retention during ceramic NF of a salt solution increased from 76% to 99% with the pH that ranged from 5 to 9. Furthermore, magnesium ions and organic fouling had a large influence on the phosphate retention. At pH 7, the phosphate

retention decreased from 92% to 42-43% due to the presence of either magnesium ions or organic fouling.

Fourth, since knowledge on fouling control methods for ceramic NF membranes using high organic load waste streams is limited, several fouling control methods were studied. The well-known fouling control methods for polymeric UF and MF membranes, hydraulic backwash and forward flush, were studied on ceramic NF membranes. In addition, a precoat method was combined with a chemical reaction to aid the detachment of the formed cake layer. During the experiments, the ceramic NF membranes were damaged on the edges due to the hydraulic sheer force during hydraulic backwash needed for sufficient flow. Therefore, it was concluded that hydraulic backwash could not be used as fouling control method of the ceramic NF membranes. Forward flush was able to maintain the flux high, but the relative production downtime was also high. The highest flux was maintain when applying reaction based precoat. Two reactions were tested of which a calcium carbonate reaction with citric acid was more effective than a Fenton reaction.

Overall, it can be concluded ceramic NF has potential for direct treatment of municipal sewage, as pretreatment for RO, regarding water production and the low fouling potential of the produced water of the ceramic NF. However, the quality of the ceramic NF membranes was not sufficient to use these membranes for this purpose on a large scale. The quality of pristine membranes varied within one batch and the long-term treatment using chemicals damaged the glass seal edge of the membranes.

Figure 1: Pristine ceramic nanofiltration membranes in the laboratory of the Fraunhofer institute.

SAMENVATTING

'Rien dans la vie n'est à craindre, tout doit être compris. C'est maintenant le moment de comprendre davantage, afin de craindre moins.'

'Niets in het leven hoeft gevreesd te worden, alles moet begrepen worden. Nu is het moment om meer te begrijpen, zodat we minder hoeven te vrezen.'

Marie Curie

SAMENVATTING

Klimaatverandering, wereldwijde populatiegroei en waterschaarste vergroten de noodzaak om het gebruik van alternatieve waterbronnen te onderzoeken. Een opkomende trend in de waterzuivering is het terugwinnen van gemeentelijk rioolwater als bron voor irrigatiewater, industriewater en in sommige landen zelfs drinkwater (Bixio et al., 2005; Raffin et al., 2013; Rietveld et al., 2011; Wielemaker et al., 2018). Het voordeel van deze recycling is dat de watercycli klein gehouden kunnen worden. Aangezien de vraag naar schoonwater in praktijk voornamelijk nodig is op plaatsen waar gemeentelijk rioolwater aanwezig is, dus waar mensen werken en leven. Daarnaast bevat gemeentelijk rioolwater een bron van nutriënten en organisch materiaal wat via deze methoden gemakkelijk herwonnen kan worden.

In dit onderzoek wordt een concept gepresenteerd, waarmee gemeentelijk rioolwater direct behandeld wordt met keramische nanofiltratie als voorzuivering voor omgekeerde osmose (ofwel *reverse osmosis*). Voor dit concept zijn keramische nanofiltratie membranen gekozen om hun mechanische sterkte en hoge chemische en thermische resistentie (Weber et al., 2003). Naar verwachting zouden deze membranen niet beschadigen bij hoge druk, hoge temperatuur en hoge concentraties chemicaliën, waardoor intensieve chemische reinigingen toegepast kunnen worden op deze membranen. Verder bestaan keramische membranen uit duurzaam materiaal: het is recyclebaar en de levensduur van de membranen is langer dan 15 jaar wanneer ze gebruikt worden voor drinkwater zuivering (Heijman, 2007; Lee et al., 2015; Samaei et al., 2018; Shang, 2014). Bovendien zijn keramische membranen minder vatbaar voor het ontstaan van onomkeerbare vervuiling op het membraanoppervlak dan polymere membranen (Lee et al., 2013; Zhao et al., 2018). Hierdoor is deze technologie zeer geschikt is voor directe behandeling van gemeentelijk rioolwater.

In de literatuur zijn weinig onderzoeken beschreven over keramische nanofiltratie en over de toepassingen van gemeentelijk rioolwaterzuivering is niets te vinden. Net als informatie over de robuustheid, het tegenhouden van organisch materiaal en ionen en daarnaast methodes om vervuiling op het membraan te bedwingen. Deze informatie is essentieel voor het mogelijk maken van rioolwater behandeling met deze membranen. Het doel van dit onderzoek was om de potentie te onderzoeken voor behandeling van gemeentelijk rioolwater met keramische nanofiltratie met de onderstaande vier belangrijkste onderzoeksvragen:

1. Wat is de haalbaarheid van het hierboven gepresenteerde *sewer mining* concept betreffend water productie, organisch materiaal en ionen verwijdering en biologische vervuilingspotentiaal?
2. Wat is de kwaliteit en de robuustheid op lange termijn van de commercieel gefabriceerde keramische membranen?

3. Wat in de invloed van multivalente counter ionen en organische vervuiling op de membraanoppervlak op de fosfaatverwijdering tijdens keramische nanofiltratie?
4. Wat is de meest efficiënte manier om organische vervuiling op het membraanoppervlak te bedwingen?

Om te beginnen werd er een voorstudie uitgevoerd in een pilot proefopstelling, waarbij gemeentelijk rioolwater door middel van keramische nanofiltratie is behandeld. Vijf dagen kon de filtratie onophoudelijk voortduren zonder dat het tussendoor schoonmaken van de membranen nodig was. De membranen werden succesvol schoongemaakt na filtratie met behulp van chemische reiniging: 93% van de organische vervuiling was verwijderd van het membraan. Tijdens deze chemische reiniging werden de membranen behandeld met natrium hyperchloriet (0.1% voor 45 min) om organische vervuiling te verwijderen, gevolgd door zoutzuur (0.1 mol·L⁻¹ voor 15 min) om zouten te verwijderen. Verder bleek gemiddeld 80% van het organische materiaal verwijderd te zijn tijdens keramische nanofiltratie. Dit terwijl de fosfaatverwijdering varieerde tijdens verschillende metingen. Er werd geen sluitende conclusie gevonden voor de variatie van deze verwijdering in dit deel van het onderzoek.

Vervolgens werd het vervuilingspotentiaal (ofwel *fouling potential*) van keramische nanofiltratie na behandeling van gemeentelijk rioolwater gemeten met behulp van de Membrane Fouling Simulator (Vrouwenvelder et al., 2006, 2007), om de haalbaarheid van voorbehandeling met omgekeerde osmose te onderzoeken. Het vervuilingspotentiaal bleek even laag als Nederlands drinkwater, waardoor keramische nanofiltratie geschikt lijkt als voorzuivering voor omgekeerde osmose.

In tweede instantie werd de kwaliteit en de robuustheid van keramische nanofiltratie membranen op lange termijn onderzocht. Een toevoeging aan de veel gebruikte *moleculair weight cut-off* (MWCO) methode werd ontwikkeld om de defecten in membranen te kunnen kwantificeren en de MWCO accuraat te kunnen bepalen. Met behulp van deze toevoeging kan de kwaliteit van de membranen meer accuraat bepaald worden in vergelijking met de oorspronkelijke methode. Daarom werd deze methode ook gebruikt om de kwaliteit van een breed spectrum commercieel gefabriceerde keramische membranen te bepalen: zowel voor cilindervormige als disc membranen van verschillende leveranciers. De kwaliteit van de membranen was getest door middel van het bepalen van de (i) hydraulische permeabiliteit, (ii) MWCO en (iii) kwantiteit van de defecten. In alle partijen werden variaties aangetoond in de kwaliteit en defecten in een of meer membranen.

Bovendien werd de robuustheid van de cilindervormige keramische nanofiltratie membranen onderzocht door de membranen voor lange termijn bloot te stellen aan natrium hyperchloriet. In dit geval betekent lange termijn een periode vergelijkbaar

met een jaar filtreren inclusief chemische reinigingen. Chemische reiniging met natrium hyperchloriet is de meest gebruikte methode om keramische membranen schoon te maken (Cui et al., 2013; Lee et al., 2015; Xu et al., 2013; Zebić Avdičević et al., 2017). Dit experiment maakte duidelijk dat de keramische nanofiltratie membranen aangetast werden door de lange blootstelling aan natrium hyperchloriet. Nader onderzoek heeft aangetoond dat de glazen beschermingslaag aan de uiteinden van het membraan beschadigd was, terwijl de scheidingslaag niet noemenswaardig aangetast was.

Op de derde plaats werd de invloed van pH, multivalente counter ionen en organische vervuiling op het membraanoppervlak op de fosfaatverwijdering onderzocht. Verschillende experimenten werden uitgevoerd om de fosfaatverwijdering en de lading op het membraanoppervlak te analyseren. Streaming potentiaal metingen werden uitgevoerd om de zeta potentiaal te kunnen bepalen en dus de lading van het membraan, om meer inzicht te krijgen in de elektrostatische interacties op het membraanoppervlak. Tijdens keramische nanofiltratie van een zoutoplossing was de fosfaatverwijdering tussen de 76% en 99% te zijn, oplopende met de pH van 5 tot 9. Bovendien hadden magnesium ionen en organische vervuiling veel invloed op de fosfaatverwijdering. Bij pH 7 degradeerde de fosfaatverwijdering van 92% naar 42-43% door de aanwezigheid van zowel magnesium ionen als organische vervuiling op het membraan.

In vierde instantie werden verschillende methodes om organische vervuiling op het membraanoppervlak te bedwingen getest, aangezien kennis over vervuiling beheersingsmethodes tijdens keramische nanofiltratie om afvalstromen met een hoge organische lading te behandelen gelimiteerd is. Terugspoelen en vooruit spoelen zijn de meest gebruikte methodes tijdens polymere ultra- en microfiltratie. In dit onderzoek werden deze methodes ook getest voor keramische nanofiltratie. Daarnaast werd ook een precoat methode gecombineerd met een chemische reactie om het loskomen van de cake laag van het membraanoppervlak makkelijker te maken.

Tijdens de hydraulische terugspoel experimenten werden de keramische nanofiltratie membranen beschadigd aan de uiteinden van het membraan. Dit werd veroorzaakt door de schuifkracht die nodig was om voldoende flow door het membraan te krijgen. Daaruit kan geconcludeerd worden, dat hydraulisch terugspoelen niet gebruikt kan worden als vervuiling beheersingsmethode voor keramische nanofiltratie. Vooruitspoelingen zorgden ervoor dat de flux hoog gehouden werd, maar de netto productie tijd was laag tijdens deze aanpak. De flux bleef het hoogst tijdens filtratie met toepassing van reactie gedreven precoat. Twee reacties werden getest waarvan een calcium carbonaat reactie met citroenzuur het meer effectief bleek dan een Fenton reactie.

Uiteindelijk kan de conclusie getrokken worden dat keramische nanofiltratie potentie heeft voor het direct behandelen van gemeentelijk rioolwater en als voorzuivering voor omgekeerde osmose, betreffend de waterproductie en de lage biologische vervuilingspotentiaal van het geproduceerde water. Daarentegen is de kwaliteit van de keramische nanofiltratie membranen niet voldoende om deze membranen te gebruiken voor deze toepassing op grote schaal. De kwaliteit van de gloednieuwe membranen varieerde binnen een partij en behandeling met chemicaliën op lange termijn beschadigde de glazen beschermingslaag aan de uiteinden van de membranen.

Figuur 1: Gloednieuwe keramische nanofiltratie membranen in laboratorium van het Fraunhofer instituut.

Chapter 1

INTRODUCTION

'What we know is a drop, what we don't know is an ocean.'

Isaac Newton

INTRODUCTION

General background

Worldwide population growth, water scarcity, and climate change contribute to an urgent need for alternative water sources for irrigation water, industry water, and, in some countries even, drinking water. The implementation of municipal sewage reclamation is an upcoming trend in water treatment (Bixio et al., 2005; Raffin et al., 2013; Rietveld et al., 2011). The use of municipal sewage has the advantage of being available at places where people live and work which is also the location where water is needed: keeping the water circles small. Moreover, more is to gain from municipal sewage: nutrients and energy are abundantly present in this water and could potentially be recovered too (Rulkens, 2006; Wielemaker et al., 2018).

Current water reclamation from sewage consists of conventional sewage treatment followed by e.g. multi-media filtration, microfiltration (MF) or ultrafiltration (UF), and reverse osmosis (RO) (Bartels et al., 2005; Raffin et al., 2013; Shang et al., 2011). In the conventional treatment, municipal sewage is usually led through primary settlers, activated sludge processes, and secondary settlers, whereas the sludge is stabilised in a digester prior to dewatering and disposal (Figure 2) (Shang et al., 2011; Wintgens et al., 2005). However, this conventional, RO-based, water treatment system requires a large footprint and does not make optimal use of energy, water and nutrient reuse (Raffin et al., 2013; Verstraete et al., 2009). Therefore, alternative treatment concepts are needed.

In this thesis, an innovative sewer mining concept is presented and analysed. Sewer mining is a decentralised water reclamation concept, where municipal sewage is considered a resource instead of a waste stream. The sewage flow is (partly) captured and directly treated for on-site usage, usually for non-potable purposes (Butler and Maccormick, 1996). As an example, here a possible, innovative system is described based on a decentralised water treatment using raw municipal sewage for production of demineralised water to nearby located industries (see Figure 1). Firstly, the raw sewage passes a coarse grit and a fine sieve of 1 mm to remove the largest fraction of suspended solids (Ruiken et al., 2013). Then, the water flows directly through a ceramic nanofilter which is the pretreatment step for RO. The debris from the fine sieve and, potentially, the concentrate stream from the ceramic nanofiltration (NF) can be stabilised in anaerobic digester systems where the organic matter is to be converted into biogas. In the meantime, phosphate could be recovered from either the concentrate stream of the ceramic NF or the concentrate stream of the RO.
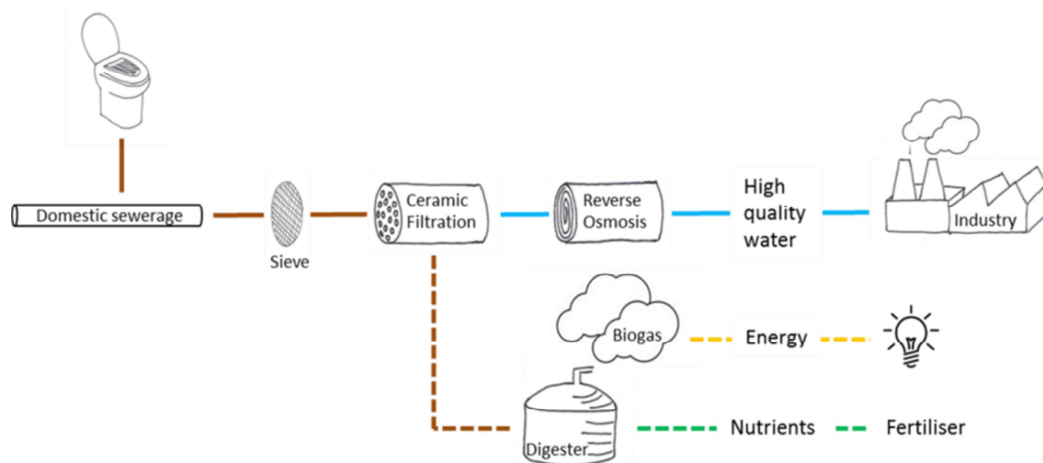
Figure 1: Innovative sewer mining concept for reclamation of high quality water, energy and nutrients from municipal sewage using ceramic NF.

Ceramic nanofiltration

Ceramic membranes are chosen in the concept described above, due to their high mechanical strength and high chemical and thermal resistance (Weber et al., 2003). The membranes are expected not to be damaged by high pressures, high temperatures, or chemicals in high concentrations which enables vigorous chemical cleaning of the membranes. Other benefits are the long life time of the membrane (> 15 years), when applied for drinking water purposes, and the recyclability of the membrane material (Heijman, 2007; Lee et al., 2015; Samaei et al., 2018; Shang, 2014). Moreover, ceramic membranes are prone to less irreversible fouling than polymeric membranes (Lee et al., 2013; Zhao et al., 2018) which makes this technology suitable for direct treatment of municipal sewage.

When using ceramic NF for sewage treatment, concentrating, amongst others, organic matter for energy recovery could be maximised during anaerobic treatment, given an advantage over conventional sewage treatment systems where a large part of the organic matter is mineralised to carbon dioxide in the aeration tanks and, subsequently, released to the atmosphere (McCarty et al., 2011; Rulkens, 2006; Verstraete et al., 2009).

For research, ceramic NF membranes with a titanium oxide filtration layer were selected because this material has the highest stability compared to the other, commonly used, materials for ceramic NF such as silicium oxide, zirconium oxide and aluminum oxide (α-Al_2O_3 and γ-Al_2O_3) (Buekenhoudt, 2008).

However, to date, ceramic membranes are less used in water treatment than polymeric membranes, mainly due to their higher price per m^2: 500-2000 USD·m^{-2} compared to 50-400 USD·m^{-2} (Samaei et al., 2018) for the polymeric ones. Therefore, more research on polymeric membranes can be found in literature. However, the layer of the polymeric membranes is sensitive to chemical cleaning with the use of extreme pH, temperature, or chemical concentrations (Ang et al., 2006; Chen et al., 2003; Li and Elimelech, 2004). Therefore, chemical cleaning of polymeric membranes can only be done when low concentrations of chemicals and a long contact time are used. Sayed et al. (2007) studied direct sewage treatment using polymeric NF, but found that the duration of the chemical cleaning was as long as the filtration time, making this concept economically not viable.

Guerra and Pellegrino (2013)developed a techno-economical model to estimate the operating expenses based on experimental data collected from various industrial sewage reclamation plants using ceramic and polymeric UF and MF membranes. They found that at a higher fouling load the costs of ceramic membranes become competitive with polymeric membranes. Therefore, direct sewage treatment using ceramic NF has probably more potential than polymeric NF since these membranes are resistant to chemical cleaning, especially with the commonly used sodium hypochlorite (Cui et al., 2013; Lee et al., 2015; Xu et al., 2013; Zebić Avdičević et al., 2017).

Research on fouling control using ceramic and polymeric NF is limited in literature. However, many alternative fouling control methods are available for polymeric UF and MF for removal of organic fouling. Most commonly used methods for polymeric UF and MF are backwash and forward flush to remove the so-called hydraulic reversible fouling. These methods are used in various forms: e.g. using a combination of backwash and forward flush, cross-flushing with pressure pulsing (Kennedy et al., 1998), air-enhanced backwashing (Remize et al., 2010; Verberk, 2005). These methods cannot be applied for polymeric NF membranes because the pressure needed for the backwash will damage the thin, fragile filtration layer. Therefore, polymeric NF is usually used for drinking water purposes or after proper pretreatment, where fouling control is less imperative. However, since ceramic NF membranes are more robust, the mentioned cleaning measures could have potential for removal of organic fouling on ceramic NF membranes.

Knowledge gaps

Even though ceramic NF membranes are expected to be robust and resistant to high concentrations of chemicals, the reported research to support this is limited. Since sodium hypochlorite is widely used for chemical cleaning in order to remove organic and inorganic fouling from membranes (Cui et al., 2013; Lee et al., 2015; Xu et al., 2013; Zebić Avdičević et al., 2017), there is a need for a long-term robustness study on

the effect of sodium hypochlorite on the ceramic NF membranes. Also because, Buekenhoudt (2008) has described that ceramic NF membranes are vulnerable for instabilities between the different filtration layers, at the glass seal layer, and at places were the membrane is curved (at the edges).

In addition, quality control of the ceramic NF membranes is limited, suppliers usually test only one membrane per batch before distribution, which might not give a good impression of the quality of the entire batch. Therefore, the quality of the individual membranes should be studied in more detail and the variation within one batch should be outlined.

As mentioned above, the most commonly used method to control fouling on ceramic NF membrane is chemical cleaning. However, this method has two disadvantages. First, chemical cleaning, especially using sodium hypochlorite, for removal of organic fouling, impacts the environment, and therefore is less suitable for an innovative, environmental friendly, sewer mining concept. Second, when effective interval flushes could be used a higher flux could be maintained. Thus, more research is needed to find effective and efficient alternative fouling control methods that can keep the flux, and thus the water production, high.

NF has the ability to separate inorganic ions with smaller sizes and hydraulic radii than the pore size due to electrostatic repulsion in certain pH ranges (Tansel et al., 2006). This has been reported in literature for polymeric NF membranes but to a lesser extent for ceramic NF (Kotrappanavar et al., 2011; Nyström et al., 1995; Schaep and Vandecasteele, 2001). Various membrane materials give a different membrane surface charge with varying ion repulsion. Ceramic NF membranes with a titanium oxide filtration layer have a negative charge in the pH range 7-9 (Cui et al., 2013; Puhlfürß et al., 2000), which means the membrane could potentially reject phosphate ions due to electrostatic repulsion. Moreover, Shang et al. (2014) showed that ceramic UF membranes, with a larger pore size than ceramic NF membranes, have a high phosphate retention in clean water, up to 87% for pH 8.5. In order to be able to predict phosphate retention in the sewer mining concept, and thus potential recovery of phosphate, the phosphate retention should also be studied in water loaded with (multivalent) counter ions, organic matter, responsible for a fouling layer on the membrane surface and potentially changing the surface charge.

Main objective & research questions
Based on the above knowledge gaps, the main objective in this thesis is to study the potential of the application of ceramic NF membranes for direct treatment of municipal sewage. Four research questions were formulated in order to investigate this objective in more detail.

1. What is the feasibility of the sewer mining concept, presented above, in terms of water production, organic matter and ion retention, and biofouling potential?
2. What is the quality and long-term robustness of commercially manufactured ceramic NF membranes?
3. What is the influence of multivalent counter ions and organic fouling on phosphate retention in ceramic NF?
4. What is the most economical and sustainable way to control organic fouling during ceramic NF when treating municipal sewage?

How to read this thesis

In this thesis, the four sub-objectives will be discussed in the chapters of this thesis. In Chapter 2, the concept of sewer mining is introduced and the first feasibility experiments are presented. During these experiments the performance of ceramic NF, using fine-sieved municipal sewage, was analysed, as well as the retention of organic matter and ions. To determine the water production and the potential organic matter and ion recovery. Moreover, the biofouling potential of the ceramic NF pretreatment was determined using the Membrane Fouling Simulator (Vrouwenvelder et al., 2010, 2007).

Next, the quality of ceramic NF membranes are reported in Chapter 3. A new extension to a commonly used molecular weight cut-off method was developed to quantify defects in membranes. A broad range of commercial ceramic membranes was investigated with this new approach by determining the (i) hydraulic permeability, (ii) molecular weight cut-off, and (iii) quantitative defects. Moreover, the long-term robustness was studied by exposing ceramic NF membranes to the equivalent of sodium hypochlorite of one year of filtration.

Chapter 4 contains a study on phosphate retention to determine the possibilities for recovery of phosphate from sewage. In this part, the influence of pH, multivalent counter ions, and fouling layer on the membranes surface was analysed. Phosphate retention and zeta potential were measured under various conditions.

Then, various fouling control methods are presented in Chapter 5. The commonly used fouling control methods for polymeric UF and MF membranes, hydraulic backwash and forward flush, were tested using ceramic NF. Furthermore, reaction based pre-coat methods were introduced and analysed.

Finally, the conclusions and outlook of the potential of ceramic NF membranes for treatment of municipal sewage are discussed in Chapter 6. All the references in this book can be found in the chapter Literature behind chapter 6.
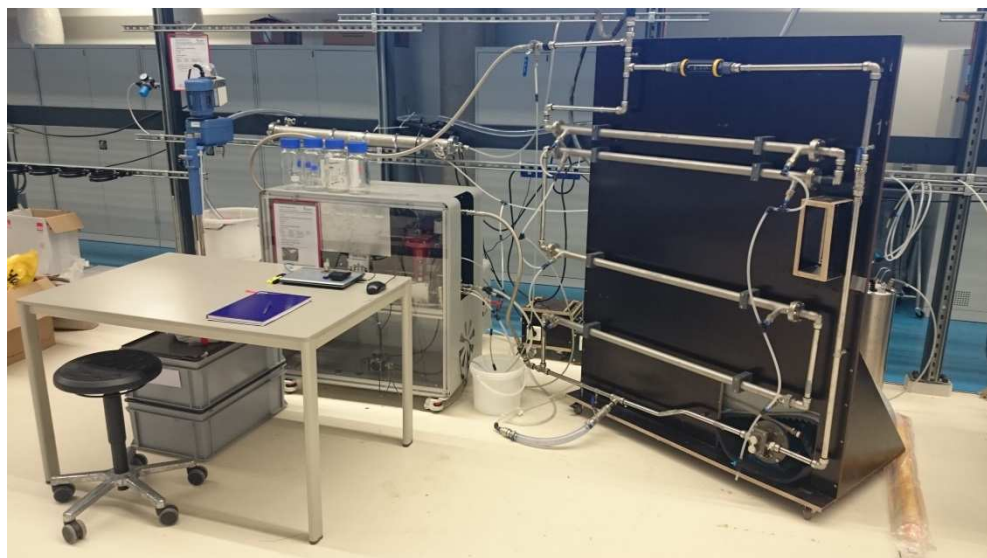
Figure 2: Laboratory set-up with four large ceramic nanofiltration membranes (1200mm long) in the Waterlab at TU Delft.
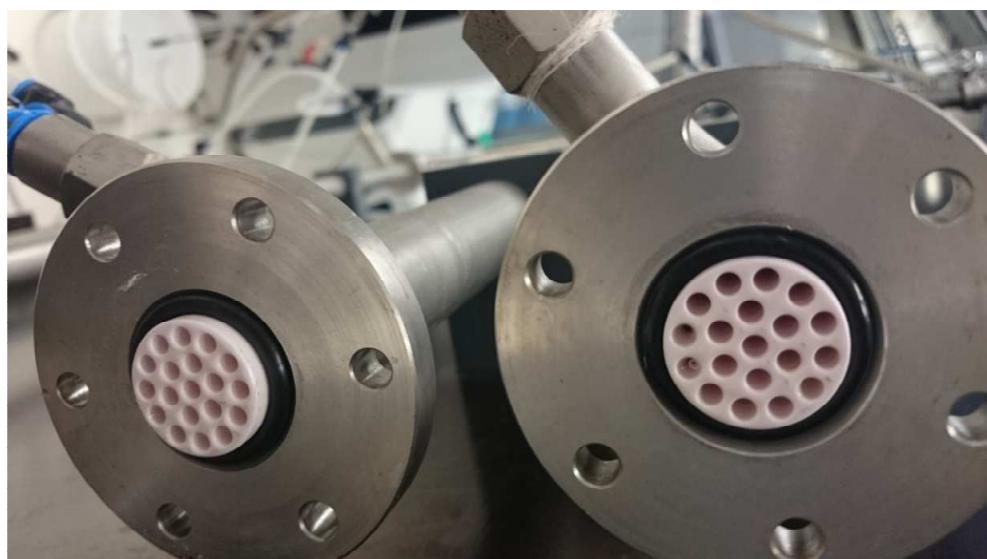

Figure 3:Large ceramic nanofiltration membranes (1200mm long) in their membrane module. The feed side of the membrane is visible just as the O-ring that separates the feed from the permeate.

Chapter 2

DIRECT WATER RECLAMATION FROM SEWAGE USING CERAMIC TIGHT ULTRA- AND NANOFILTRATION

'The first quality that is needed is audacity.'

Winston Churchill

DIRECT WATER RECLAMATION FROM SEWAGE USING CERAMIC TIGHT ULTRA- AND NANOFILTRATION

Abstract

Sewage is a nutrient rich reliable water source that is rather consistent in quality, volume and temperature, and is available in large amounts in urban areas. Decentralised reclamation of water including its constituents from municipal sewage, further referred to as sewer mining, is a concept in which municipal sewage is considered a resource instead of a waste stream.

In this research, water reclamation in the sewer mining concept was studied using ceramic tight ultra- (UF) and ceramic nanofiltration (NF). In our current approach, ceramic membrane filtration is proposed as pretreatment for reverse osmosis (RO) to produce demineralised water for industries from municipal sewage. The objectives of this research are to study (i) the membrane performance, (ii) the organic matter and ion rejection, and (iii) the biofouling potential of RO using permeate water from the ceramic filtration.

The application of ceramic tight UF and ceramic NF for direct treatment of municipal sewage has been demonstrated in this study. The cross flow ceramic tight UF and NF fed with filtered sewage, can be operated for 1- 4 days without any cleaning required. The membrane performance remained high with chemical cleaning with sodium hypochlorite (0.1%) and hydrochloric acid (0.1 mol·L^{-1}) solutions. On average about 81% of organic matter was rejected by both ceramic tight UF and NF membranes. Finally, the pressure drop increase in the MFS fed with ceramic NF permeate was low during an operation of 14 days. These results were comparable with the increase in pressure drop of an MFS fed with Dutch drinking water.

1. Introduction

Sewer mining is a decentralised water reclamation concept, where municipal sewage is considered a resource instead of a waste stream. In this concept, the sewage flow is fully or partly captured and directly treated for on-site usage, usually for non-potable purposes (Butler and Maccormick, 1996). There is a growing interest in the sewer mining concept as a possible economic and sustainable alternative for the currently applied decentralised sewage treatment plants (STPs), while recovering nutrients, water and energy from the sewage flows.

Reclamation of treated sewage for drinking water purposes is a much more difficult approach than for non-potable use due to psychological barriers and the perceived health risk (Rietveld et al., 2011). However, sewer mining is considered a breakthrough approach for the production of industrial water, minimising competitive fresh water claims in urban areas. In northern and central Europe, the majority of fresh water supply is used for industrial water (Wintgens et al., 2002), whereas for many applications, industrial water requires a low salt concentration and low hardness, i.e. demineralised water (Bixio et al., 2005).

Reverse osmosis (RO) is commonly applied to produce demineralised water, considering its high rejection of impurities, manageable costs, and ease of operation (Bartels et al., 2005; Flemming, 1997; Rietveld et al., 2011). However, RO membranes are sensitive to fouling which declines its efficiency, performance and salt rejection. Four types of fouling can be defined; particulate fouling, organic fouling, inorganic fouling (i.e. scaling), and bio-fouling (Pandey et al., 2012). Biofouling is caused by biological growth on the membrane and in the feed spacer. Not only the biofilm itself but also the extracellular polymeric substances (EPS) produced by the micro-organisms, can deteriorate the membrane performance (Herzberg and Elimelech, 2007; Shang et al., 2014b; Vrouwenvelder, 2009). Membrane fouling is directly linked to the feed water quality, therefore extensive pretreatment of RO-feed water is required (Choi et al., 2005; Pandey et al., 2012).

Current RO-based water reclamation consists of conventional sewage treatment followed by multimedia filtration (MMF), microfiltration (MF) or ultrafiltration (UF) and RO (Bartels et al., 2005). In the conventional treatment, municipal sewage is usually led through primary settlers, activated sludge process, secondary settlers, whereas the sludge is stabilised in a digester prior to dewatering and disposal (Figure 1)(Shang et al., 2011; Wintgens et al., 2005). However, the conventional RO-based water recycle technology requires a large footprint and does not make optimal use of energy, water and nutrient reuse (Raffin et al. 2013; Verstraete et al. 2009). Therefore, alternative treatment concepts are in demand.

Ravazzini et al. (2005) and Sayed et al. (2007) suggested to disregard the conventional sewage pretreatment by treating sewage directly with polymeric UF and nanofiltration (NF). However, they found that this process is not economically feasible, due to the duration of the membrane cleaning. The layer of polymeric membranes is very sensitive to chemical cleaning with the use of extreme pH, temperature or chemical concentrations (Ang et al. 2006; Chen et al. 2003; Li and Elimelech 2004). Sayed et al. (2007) found that due to the severe clogging of the membranes using sewage as feed water, chemical cleaning with a duration of 8 hours was required after a filtration time of 8 hours including hydraulic backwashing. This means that the filtration and relative production downtime are similar.

Forward osmosis (FO) is a new technique that can be used as an alternative water reclamation step in the proposed sewer mining concept (Lutchmiah et al., 2014). FO is a membrane separation technique based on osmotic pressure; the feed solution is driven through the membrane by a draw solution that has a higher ion concentration than the feed solution. FO consumes much less energy than other membrane techniques, since osmotic pressure is the driving force and no additional pressure is required (Lutchmiah et al., 2011). The permeate water can be reclaimed with RO, and FO is a suitable pretreatment step for RO (Holloway et al., 2007; Lutchmiah et al., 2014; Xie et al., 2013). However, in order to remove water from sewage, a high ion concentration in the draw solution of FO is required. Due to the high ion concentration, a high pressure RO is necessary, which consumes a lot energy (Holloway et al., 2007). Furthermore, implementation of the FO is limited by its relatively low flux (Qin et al., 2010).

Ceramic tight UF or ceramic NF is considered a potential alternative of interest for water reclamation in the sewer mining concept (Shang et al., 2014b). Ceramic membranes, compared to polymeric membranes, are robust; they have a high mechanical strength, a high chemical and thermal resistance, and a homogeneous distribution of narrow pores (Weber et al. 2003). The membrane is expected not to be damaged by high pressure, high temperatures or chemicals, enabling high pressure backwash and vigorous chemical cleaning of the membrane. Other benefits are the long life of the membrane (> 15 years) and the recyclability of the membrane material. To date, ceramic membranes are less frequently utilised than polymeric membranes due to their higher price per m^2 (Shang et al., 2014b). In literature, conclusive definitions cannot be found to distinguish ceramic UF from ceramic NF. In this research, the following definitions were used based on the molecular weight cut-off (MWCO) of the membranes: ceramic membranes with a MWCO between 500 and 3000 Da are defined as tight UF membranes, and those with a MWCO smaller than 500 Da as NF membranes.

In this chapter, the concept of the production of industrial water from raw sewage in small residential areas using ceramic tight UF or ceramic NF is presented. Figure 1 gives an overview of the concept in which the conventional RO-based water reclamation process is replaced by fine sieves, ceramic filtration and RO. This decentralised water treatment can supply demineralised water to nearby located industries, and the resultant cost saving in water transportation can be expected. In our proposed concept, the raw municipal sewage passes firstly through a course sieve and grit removal followed by a fine sieve of 1 mm to remove the largest fraction of suspended solids (Ruiken et al., 2013). Then the pre-treated sewage is directly subjected to ceramic filtration, which serves as the pretreatment step for RO. The concentrate from the ceramic membrane and the debris from the fine sieve can then be stabilised in anaerobic digester systems in which the organic matter is largely

converted into biogas by, for example, an up-flow anaerobic sludge blanket (UASB) reactor. In conventional STPs, a large part of the organic matter is mineralised to CO_2 in the aeration tanks and subsequently released to the atmosphere. By using ceramic filtration combined with anaerobic digestion of the sewage organic matter, energy recovery from the sewage constituents is maximised (McCarty et al. 2011; Rulkens 2006; Verstraete et al. 2009).
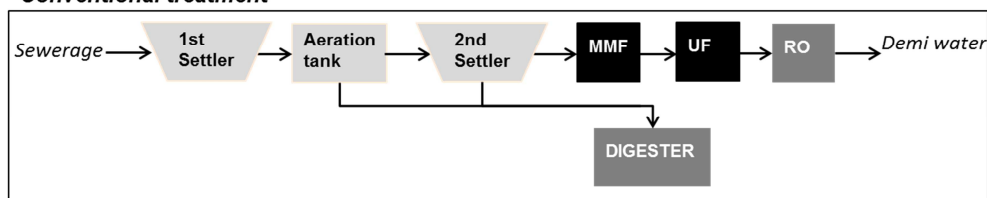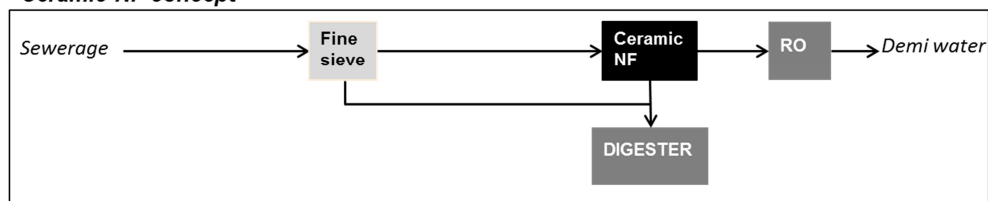

Figure 1: Production of demineralised (demi) water from sewage using conventional treatment and the ceramic filtration concept. Raw municipal sewage first faces course sieve and grit removal before entering the first step of both treatment processes.

Due to the high foulant load of the sewage, fouling in the ceramic membrane and in the subsequent RO membrane is expected to be the main challenge in this ceramic filtration concept. The aim of this chapter is therefore to investigate the feasibility of this concept by determining the (i) performance of ceramic tight UF and ceramic NF in sewage filtration, (ii) rejection of organic matter and ions of the ceramic membrane, and (iii) biofouling potential of the RO with ceramic NF pretreatment. The energy production from the concentrate of ceramic membranes will be studied in the future stages of research, but is not within the scope of this chapter.

2. Materials & Methods

2.1 Performance and Cleaning

2.1.1 Membranes and filtration set-up

Ceramic tight UF and ceramic NF membranes were used during filtration in this research. Both types of membranes were made of TiO_2 and had a multi-channel configuration. Both ceramic tight UF and ceramic NF experiments were carried out with a cross-flow filtration system (Figure 2 and 3). The filtration was conducted using a pneumatic diaphragm pump (Hydra-cell) with a pulsation dampener.
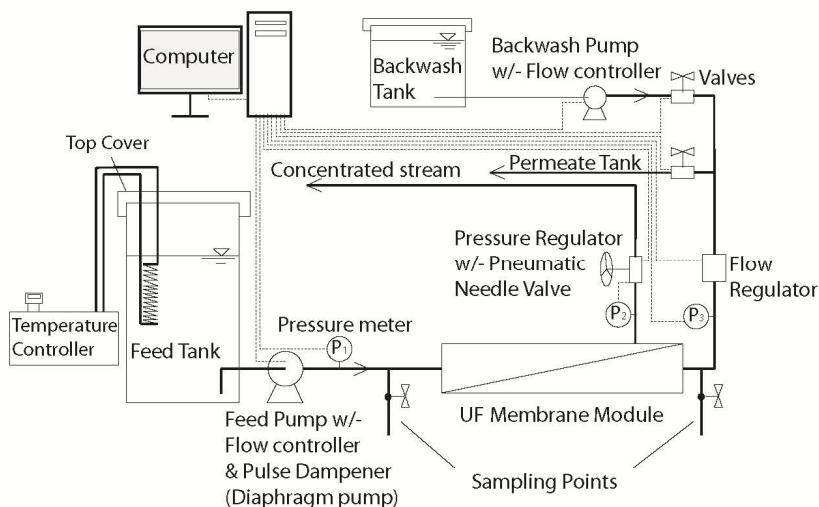

Figure 2: Schematic representation of the cross-flow ceramic tight UF filtration system.

The ceramic tight UF membrane (TAMI Industry, France) had a MWCO of 3 kDa or mean pore size of 3.06 nm (Shang et al., 2014b), 2 mm diameter channels, and an effective filtration area of 0.013 m^2. The ceramic NF membranes (Inopor, Germany) had a MWCO of 450 Da or mean pore size of 0.9 nm with 3.5 mm diameter channels, an open porosity of 30-40%, and an effective filtration area of 0.25 m^2. There were four ceramic NF membranes installed in tandem, which provided a total filtration area of 1 m^2.

The experiments using ceramic tight UF and ceramic NF membranes were conducted at different locations and with slightly different setup configurations. The filtration experiments using the ceramic tight UF membrane were carried out in the Waterlab at TU Delft. A feed tank containing 50 L was installed. Both the permeate and the concentrate were fed back into the feed tank, except the sampling volume, which was

a negligible amount (<0.1%). The chemical oxygen demand (COD) of the feed water remained constant over the duration of the experiments. Water temperature was controlled at 20±1 °C using a temperature controller (Figure 2). The single pass water recovery of the ceramic tight UF filtration systems was < 1%.

The filtration experiments using the ceramic NF were conducted at Harnaschpolder STP in Den Hoorn, the Netherlands, due to the large filtration area of the ceramic NF membranes (1 m^2). The permeate- and concentrate streams were directly discharged to the influent stream of the STP. The NF filtration system used a recirculation pump to reach a water recovery of 50% (Figure 3).
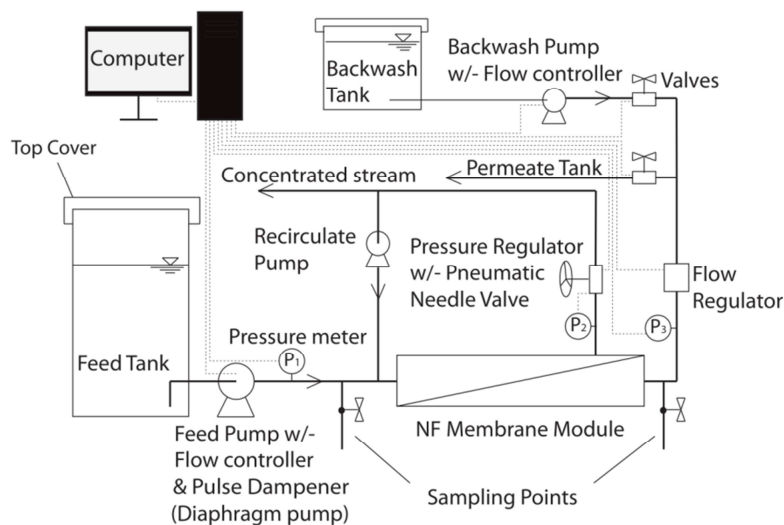

Figure 3: Schematic representation of the cross-flow ceramic NF filtration system.

2.1.2 Raw Sewage

Sewage, which was fed to the ceramic tight UF membrane, was collected on a daily basis, after the influent screening (6 mm) at the Harnaschpolder STP. The collected sewage (50L) was transported to the Waterlab at TU Delft and pre-filtrated with a fine sieve of 1 mm mesh width, before it was fed to the membranes. Key physicochemical properties of the pre-sieved sewage are summarised in Table 1 and 2.

The feed water to ceramic NF system was directly pumped from the well after the influent screening (6mm) at the Harnaschpolder STP. Prior to feeding to the ceramic NF membranes, the sewage flew through a 0.5 mm sieve to remove granulates that may clog the membrane channels. Daily, 24-hour mixed samples were collected by an automatic sampling machine for characterization.

Table 1: Key physicochemical properties of 1 mm-sieved sewage during experiments B and D (see section 2.1.3) using the ceramic tight UF system.

Parameter	Experiment B, Figure 5		Experiment D, Figure 7				
	Day 1	Day 2	Day 1	Day 2	Day 3	Day 4	Day 5
Total COD ($mg·L^{-1}$)	632	348	383	863	444	670	527
Dissolved COD ($mg·L^{-1}$)	254	157	153	294	127	265	129
DOC ($mg·L^{-1}$) [*]	20	12	12	22	17	19	6.0
Conductivity ($mS·cm^{-1}$)	1655	924	790	1305	1321	1273	831
pH (-)	7.4	7.4	7.8	7.1	7.5	7.3	7.3
NH_4^+ ($mg·L^{-1}$) [*]	28	38	42	57	61	62	13
PO_4^{3+}-P ($mg·L^{-1}$) [*]	8.5	3.7	5.3	8.1	8.3	8.9	4.7
Mg^{2+} ($mg·L^{-1}$) [*]	21	10	8.4	15	16	14	9.2

[*] *Concentration of dissolved fraction.*

Table 2: Key physicochemical properties of 1 mm-sieved sewage during experiments A and C (see section 2.1.3) using the ceramic NF system. Data measured by external laboratory of WWTP Harnaschpolder.

Parameter	Experiment A, Figure 4				Experiment C, Figure 6			
	Day 1	Day 2	Day 3	Day 4	Day 1	Day 2	Day 3	Day 4
Total COD ($mg·L^{-1}$)	700	590	610	590	420	420	480	430
TSS ($mg·L^{-1}$)	270	270	280	280	210	200	230	250
Total-N ($mg·L^{-1}$)	66	62.9	63.3	61.7	39	34	46	48
N-Kjehldahl ($mg·L^{-1}$)	66	62.9	63.3	61.7	39	34	46	48
Total-P ($mg·L^{-1}$)	9.4	8.9	8.8	8.8	5.1	5	6.5	6.5

2.1.3 Experimental Protocol

The filtration experiments were carried out at a cross-flow velocity of 1 $m·s^{-1}$. Three different cleaning methods were examined: (i) filtration with only hydraulic backwash, (ii) filtration with only chemical cleaning, and (iii) filtration with forward flush cleaning. The experiment testing different cleaning methods were performed with a constant feed pressure of 8 bar. Experiments were performed with 3 kDa

ceramic tight UF and/or 450 Da ceramic NF membranes. Chemical cleaning was performed with both membrane types, whereas hydraulic backwash and forward flush were performed with ceramic tight UF and ceramic NF, respectively. Both hydraulic backwash and forward flush were determined to be ineffective, therefore the experiments were not repeated for the other type of membrane. Table 3 gives an overview of the performed experiments: cleaning method used, membranes type used, cleaning interval, and overall filtration time.

The effect of hydraulic backwash cleaning was tested using the 3 kDa ceramic tight UF (Table 3, experiment B). The hydraulic backwash was carried out using permeate water at a flux of 70 L/(m²·h) for 3 minutes every hour with a total experimental duration of 21 hours. Then, forward flush cleaning was assessed using the 450 Da ceramic NF membrane (Table 3, experiment C). In this experiment, continuous filtration for 96 hours (3 days) was conducted with a release of the feed pressure for 5 min after every 24 hours of filtration. After the 96 hours of filtration the membrane was chemically cleaned twice. Next, the effect of chemical cleaning on both ceramic tight UF and NF membranes was examined, while different cleaning intervals were used (Table 3, experiment A and D). During experiment D the 3 kDa ceramic tight UF membrane and a 22 hour cleaning interval were used, whereas during experiment A, the 450 ceramic NF membrane was chemical cleaned once at the end of the experiment after 115 hours. Chemical cleaning was carried out with a hypochlorite (0.1%, 15 min backwash and 45 min soaking) followed by a hydrochloric acid solution (0.1 mol·L⁻¹, 15 min backwash).

The relative production downtime (RPD) (min/h) was calculated using the following equation:

$$RPD = \frac{t_{cleaning}}{t_{filtration} + t_{cleaning}}$$ (Equation 1)

where $t_{cleaning}$ is the duration of the cleaning and $t_{filtration}$ is the filtration time between cleaning two cleaning intervals (Table 3).

Membrane filtration performance was measured at a temperature-corrected permeability to 20 °C using the following equation:

$$L_{20°C} = \frac{J \cdot e^{-0.0239 \cdot (T-20)}}{\Delta P}$$ (Equation 2)

where $L_{20°C}$ is the permeability at 20 °C (L/(m²·h·bar), T is temperature of water (°C), J is membrane flux (L/(m²·h)), e^x is exponential function, and ΔP is transmembrane pressure (bar).

Table 3: Specifications of performed filtration experiments with different cleaning methods.

Experiment	Cleaning method	Ceramic membrane type	Constant pressure (bar)	Cleaning interval (h)	Cleaning time (min)	Total filtration time (h)	RPD (min/h)
A, Figure 4	No cleaning	NF	No	115	-	-	-
B, Figure 5	Hydraulic backwash	Tight UF	8	1	3	21	3
C, Figure 6	Forward flush	NF	8	24	5	96	0.2
D, Figure 7	Chemical cleaning	Tight UF	8	22	1	120	2.6

2.2 Rejection of organic matter and ions

The morphology and elemental composition of the cake layer that formed on the membrane surface of ceramic tight UF was examined by removing and collecting the cake layer with forward flush after 21 hours of ceramic tight UF (3 kDa). The cake layer was analysed using a scanning electron microscopes coupled with an energy dispersive X-ray (SEM-EDX) analyser (Ametek EDAXTSL). The samples were scanned at 10 kV accelerating voltage and 500× magnification. The scan area was approximately 0.6×0.6 mm and three random areas were measured on each sample. The composition of the cake layer was measured as described in the next paragraph.

The concentrations of organic matter and ions (nitrate, ortho-phosphate, sulphate, magnesium, and calcium) in the feed and permeate water from the ceramic tight UF membranes was measured to calculate the rejection percentages. This experiment was repeated 3 times using a ceramic NF membrane under similar conditions. During the first repetition using a ceramic NF membrane, the same parameters were measured. However, during the second and third repetition different parameters were measured, DOC and/or total phosphate were added and fewer ions were measured (no sulphate, magnesium and calcium).

Chemical oxygen demand COD was measured by COD test cells (Spectroquant). Water samples were filtered by 0.45 μm glass fibre syringe filters (Whatman) for the measurements of dissolved COD, dissolved organic carbon (DOC), and ions. The DOC was measured by a total organic carbon (TOC) analyser (TOC- VCPH, Shimadzu Instruments). Ions, including NH_4^+, PO_4^{3-}, Ca^{2+} and Mg^{2+}, were measured by ion

chromatography (Metrohm Instrument). The pH and conductivity were measured using a multi-meter (WTW inoLab 720).

2.3 Biofouling potential in the RO membrane

The MFS (Vrouwenvelder et al., 2006) containing an RO membrane sheet (Filmtec BW30LE) was used to simulate the biofouling potential in spiral wound RO membrane systems .The MFS is proven to be able to mimic polymeric membrane conditions and to measure biofouling in the feed spacer of RO-membranes (Duiven et al., 2010; Hijnen et al., 2009; Huang et al., 2013; Vrouwenvelder et al., 2010, 2007). However, since no permeate is produced with the MFS, particulate fouling, organic fouling, inorganic fouling (i.e. scaling) cannot be simulated with the MFS. The membrane element contained one RO spacer sheet with a thickness of 0.78 mm and a mesh size of 3×3 mm. The external dimensions of the MFS unit are 0.7×0.3×0.04 m and the effective membrane length and width are 0.20×0.04 m. The unit was covered to prevent daylight from affecting the biological growth. Permeate water of the ceramic NF experiment was used as feed water for the MFS. The feed water flow of the MFS was 16 L·h^{-1}, and the cross flow velocity in the feed spacer was 0.14 m·s^{-1}. The installation was set up in such a way that no air could come in the system, so oxygen was prevented from entering. The oxygen concentration, flow velocity and transmembrane pressure were continuously monitored during the experiment, which was carried out two times; one run was 7 days and the other run was 14 days. The results were compared with MFS results from Vrouwenvelder et al. (2006).

3. Results & Discussion

3.1 Performance and cleaning

Experiments were performed using a ceramic NF membrane; the results are presented in Figure 4. The permeability reduced 58% from 4.1 to 1.7 L/(m^2·h·bar) in four days, with an average reduction rate of 0.02 L/(m²·h·bar) per hour without cleaning the membrane. Sayed et al. (2007) studied direct sewage filtration with polymeric NF membranes. They observed a permeability reduction rate of 0.7 L/(m²·h·bar) per hour. Under similar filtration flux of 15-20 L/(m²·h), the ceramic NF filtration exhibited a significant lower fouling rate compared to the polymeric NF system.

During the experiment the pump pressure was maximum 8.5 bar; this was reached after about 10 hours, causing the flux to drop. The flux started at a constant value of 20 L/(m²·h) and after 10 hours slowly dropped to 15 L/(m²·h) at the end of the experiment (at 115 hours).

Hydraulic backwash is the most common used method in practice to remove the cake layer in MF and UF membranes (Pandey et al., 2012). Depending on the feed water quality, hydraulic backwashing is performed from every 15 minutes to once a day. In this study, 1 mm pre-filtered sewage was used as feed water. An hourly hydraulic backwash was applied on ceramic tight UF (3 kDa) at constant pressure. Figure 5 shows that the permeability of the ceramic tight UF membrane with and without hourly hydraulic backwash is comparable during a period of 21 hours. Thus, the hydraulic backwash was not effective in recovering the membrane permeability.
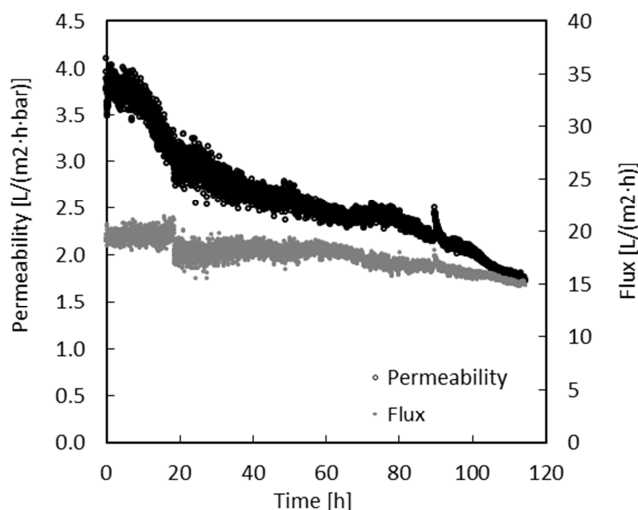
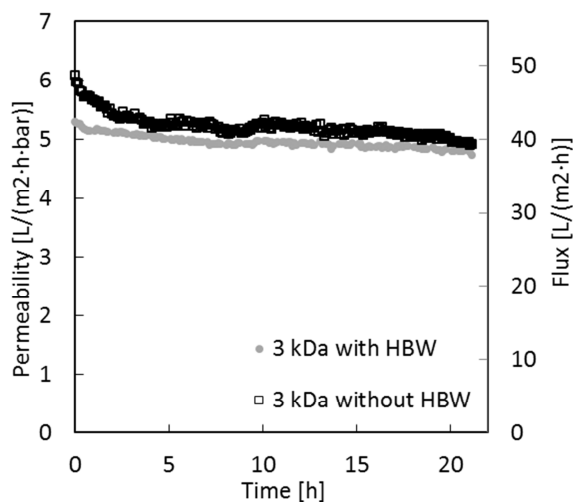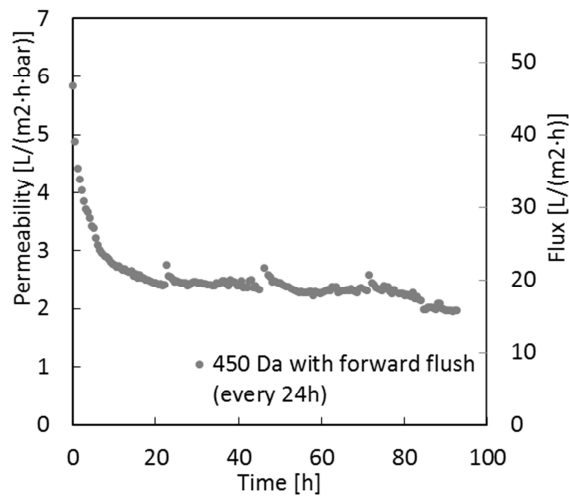*Figure 4: Temperature corrected permeability and flux over time of ceramic NF filtration (450 Da) membrane during the sewage filtration. No membrane cleaning was conducted within the 120 hours of filtration.*

The performance of the ceramic tight UF membrane was still adequate after 21 hours of filtration without cleaning. Therefore, filtration without hydraulic backwash is recommended to obtain a higher water recovery, because no permeate is used for backwashing.

The effects of daily forward flushing on the permeability of the 450 Da ceramic NF membrane was studied over a four days period at constant pressure. Figure 6 shows that the permeability decreased from 5.9 to 2.5 L/(m²·h·bar) within the first 24 hours and maintained above 2 L/(m²·h·bar), during the rest of the filtration period. The daily forward flush recovered the permeability with 22±2 %. Thus, using forward flush to remove part of the loose cake layer formed on the membrane surface did not significantly enhance the permeability of the membrane. After a continuous operation of four days, chemical cleaning was executed twice with hypochlorite (0.1%) and

hydrochloric acid (0.1 mol·L^{-1}). The permeability after these chemical cleanings was measured to be 5.7 L/(m²·h·bar), resulting in a membrane recovery of 97%.

Figure 7 shows a reduction of 16% in permeability of the 3 kDa ceramic tight UF membrane within 24 hours (from 5.8 to 4.8 L/(m²·h·bar)) and a recovery of 93±3% due to chemical cleaning. The relative production downtime during this chemical cleaning experiment was 2.6 min/h. This value can be compared with 3 and 0.2 min/h of the hydraulic backwash and the forward flush experiments respectively (Table 3).

Figure 5: Temperature corrected permeability and flux over time of ceramic tight UF filtration (3 kDa) membrane during the pre-filtered sewage filtration at constant pressure of 8 bar, operated with (dots) and without (squares) hourly hydraulic backwash (HBW).

Figure 6: Temperature corrected permeability and flux over time of ceramic NF filtration (450 Da) membrane during the pre-filtered sewage filtration at constant pressure of 8 bar, cleaned with forward flush per every 24 hours.
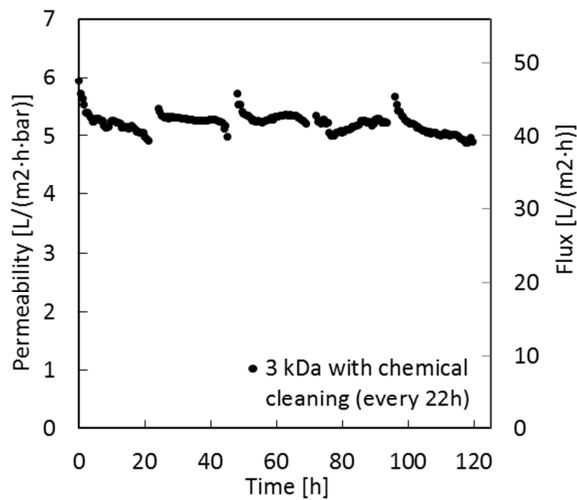

Figure 7: Temperature corrected permeability and flux over time of ceramic tight UF filtration (3 kDa) membrane during the sewage filtration at constant pressure of 8 bar, cleaned with chemical cleaning per every 22 hours.

3.2 Rejection of organic matter and ions

The cake layer formed on the ceramic tight UF membrane was examined after 22 hours of filtration. It was clearly visible that the cake layer consisted of thin compressed grains (Figure 8). This morphology was probably caused by the high operational pressure of 8 bar. Table 4 shows the elemental composition of the cake layer; the cake layer consisted for the major part (98% of the total mass weight) of organic material (elements C, O, and P) and for a minor part of 2% of inorganic elements (Na, Al, Si, S, and Cl). This indicates that no scaling by salts occurred.
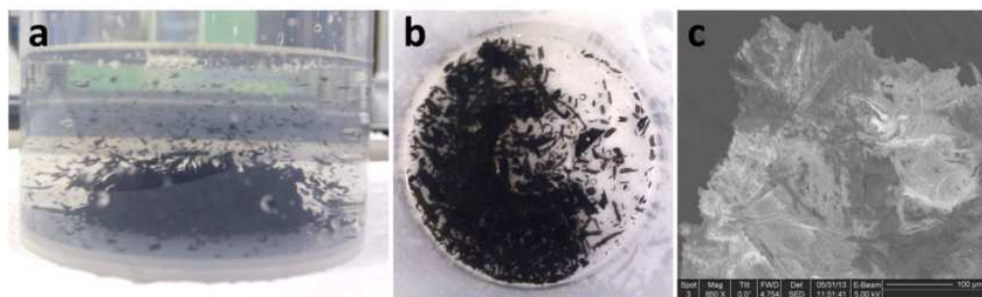
Figure 8: Morphology of the cake layer formed on the ceramic tight UF membrane (3 kDa) after 22 hours of filtration of sewage; visual observations (a&b) and microscopy image (c).

Table 4: Elemental composition of the cake layer on the 3 kDa ceramic membrane after 22 hours of filtration of municipal sewage.

Element	Weight percentage (%)
C	54.5 ± 0.7
O	43.3 ± 1.3
Na	0.4 ± 0.1
Al	0.6 ± 0.02
Si	0.4 ± 0.1
P	0.3 ± 0.2
S	0.3 ± 0.4
Cl	0.2 ± 0.3

Furthermore, the rejection of organic matter and ions by the ceramic 450 Da ceramic NF (repeated 3 times) and 3 kDa ceramic tight UF membranes was measured. Table 5

presents that both membranes rejected about 81% of total COD in all cases. However, the tighter 450 Da membrane seems to withhold a higher percentage of dissolved COD due to the greater steric exclusion of organic molecules in the 450 Dalton pores.

The ortho-phosphate rejection percentages varied for three experiments using the 450 Da ceramic NF membranes, even though the experimental conditions were similar. During the first 450 Da ceramic NF experiment, a 97% rejection of phosphate was measured, while only 14 and 9% rejection was measured during the second and third experiments respectively. During the first 450 Da ceramic NF experiment a new membrane was used, while the other experiments used older membranes. This indicates that the high rejection of phosphate decreased with the fouling of the membrane.

The rejection of ions (i.e. calcium, magnesium, and ammonium) was low, below 10% (Table 5). These ions arrive at the same concentration in the permeate and should therefore be removed during RO treatment. The rejection percentages varied between the different datasets, which can be explained by the variation in concentrations in the feed water. The water quality of sewage varies during the day.

Table 5: Rejection of compounds in sewage by the 3 kDa ceramic tight UF membrane and repeated 3 times with the 450 Da ceramic membrane (average ± standard deviation from at least duplicate measurements).

Parameter	Rejection	(%)		
	3 kDa	450 Da (1)	450 Da (2)	450 Da (3)
Total COD	81 ± 4	81 ± 2	80 ± 3	81 ± 3
Dissolved COD	42 ± 17	49 ± 5	55 ± 15	45 ± 8
DOC	-	-	49 ± 11	-
Conductivity	7.6 ± 1	0.9 ± 4	-	4.6 ± 5
NH_4^+	11 ± 3	8.2 ± 0.3	6 ± 2	6.5 ± 5
Total P	-	-	37 ± 1	40 ± 4
PO_4^{3-}-P	17 ± 7	97 ± 4	14 ± 5	9.3 ± 7
SO_4^{2-}	22 ± 9	28 ± 33	-	-
Mg^{2+}	0.4 ± 2	2.0 ± 0.1	-	-
Ca^{2+}	11 ± 8	1.1 ± 1	-	-

3.3 Fouling potential in the RO membrane

Ceramic NF is proposed as pretreatment for RO, according to the ceramic filtration concept (Figure 1). Permeate of the ceramic NF membrane was used for investigating the fouling potential in RO membranes using MFS tests. The results of the MFS tests showed a gradual, small pressure increase over time for both experiments (Figure 9), with a slope of 0.07-0.08 mbar/h. This pressure drop slope was comparable with MFS results fed with Dutch drinking water , 0.09 mbar/h (Vrouwenvelder et al. 2006), under similar operational conditions.. Drinking water has a low nutrient concentration and therefore the fouling potential of RO fed with drinking water is low (Pandey et al., 2012; Vrouwenvelder et al., 2006).

Biological growth causes resistance in the RO membrane feed spacer leading, to a higher pressure drop over the membrane (Flemming, 1997; Vrouwenvelder et al., 2006). The low increase in pressure drop indicates that the biological growth was minimal in the RO membrane during the experimental period. The absence of severe biofouling was probably because of the low oxygen concentrations (<0.01 mg/L) in the ceramic NF permeate. The MFS experiments showed that the biofouling potential of ceramic NF permeate in an RO was low and run times of at least 14 days without chemical cleaning could be expected.
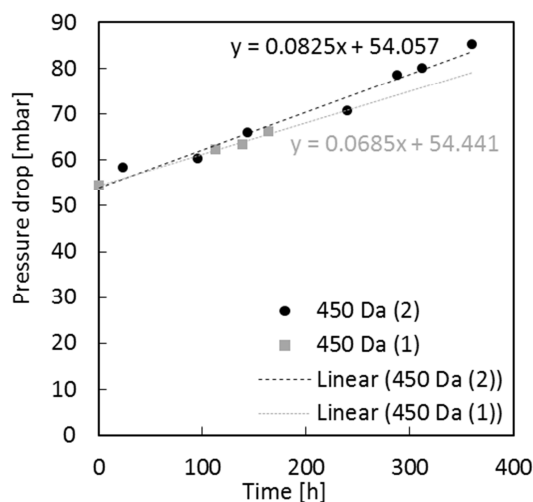

Figure 9: Pressure drop in the membrane fouling simulator (MFS) with RO membrane over time with effluent water from 450 Da ceramic NF used as feed water. Experiment was repeated two times for 7 days (450 Da (1)) and 15 days (450 Da (2)).

Conclusions

In this chapter, the use of ceramic tight UF and ceramic NF filtration for direct treatment of municipal sewage has been studied. From the results of this study, the following conclusions were drawn.

Ceramic NF (450 Da) membranes were suitable for treating raw municipal sewage. Regular chemical cleaning (with hypochlorite (0.1%) and hydrochloric acid (0.1 mol·L^{-1})) between every 1 and 4 days could maintain the high performance of the ceramic membranes with at least 93% permeability recovery of the membrane. Hydraulic backwashing and forward flush removed part of the cake layer, but this did not restore the permeability of the membrane.

The organic matter rejection for both tested ceramic tight UF and ceramic NF membranes was high (81% COD rejection). This led to a high organic load in the concentrate stream, which is potentially beneficial for further anaerobic digestion.

The permeate water of the ceramic NF had a low fouling potential for RO treatment. The biofouling potential of the permeate water, measured using the Membrane Fouling Simulator (MFS), was comparable with Dutch drinking water.

Acknowledgements

Chapter 3

QUANTIFYING DEFECTS IN CERAMIC TIGHT ULTRA- AND NANOFILTRATION AND INVESTIGATING THEIR ROBUSTNESS

'Every step that you take could be your biggest mistake. It could bend or it could break: that's the risk that you take.'

What If by Coldplay

QUANTIFYING DEFECTS IN CERAMIC TIGHT ULTRA- AND NANOFILTRATION AND INVESTIGATING THEIR ROBUSTNESS

Abstract

One of the perceived benefits of ceramic membranes is their robustness, which makes them suitable for treating high organic load waste streams. In particular, ceramic tight ultrafiltration (tUF) and nanofiltration (NF) form an important barrier against small colloids and organic molecules. In order to achieve this barrier, the quality of the membranes should be uncompromised.

An extension on a commonly used size exclusion method was developed in order to quantify defects in membranes and calculate the MWCO accurately excluding the defects. This approach gives a better representation of the membrane quality than the original method. The quality of a broad range of commercial ceramic membranes was investigated by determining the (i) hydraulic permeability, (ii) molecular weight cut-off, and (iii) quantitative defects. Several membranes - both tubular and disc membranes, selected from various suppliers - were tested to investigate their variability. Furthermore, the robustness of tubular NF membranes was studied by monitoring the effect of long-term exposure to sodium hypochlorite, which is commonly used to mitigate organic fouling.

The results showed that batches of both tubular and disc membranes of different pore size and suppliers included membranes with defects. Furthermore, the long-term treatment of tubular ceramic membranes with sodium hypochlorite negatively affected, beyond expectation, the quality of the membranes. The separation layer in these membranes was not notably compromised by sodium hypochlorite exposure, but the end seal layer was damaged.

1. Introduction

Due to their robustness, ceramic membranes have become more popular in water treatment applications over the last decade. These membranes are not only perceived to be resistant to high pressure, temperature, and concentrations of chemicals but also to have a homogeneous distribution of narrow pores and a long lifetime (Guerra and Pellegrino, 2013; Lee et al., 2015; Van Gestel et al., 2003; Weber et al., 2003).

Ceramic membranes have proven to be effective for drinking water treatment (Lee et al., 2015). In literature, studies can also be found on the treatment of water streams with a high organic load originating from various industries, such as the treatment of textile industry waste streams, both on the laboratory (Van Der Bruggen et al., 2003; Weber et al., 2003; Zebić Avdičević et al., 2017) and pilot scale (Voigt et al., 2001). In addition, the pulp and paper industry has interest in the use of ceramic membranes since its wastewater is one of the major sources of industrial water pollution. The main goal is to recover residual lignin, organic matter and water (Busse et al., 2016; Dafinov et al., 2005; Ebrahimi et al., 2015a; Mustafa et al., 2016). Furthermore, much research is conducted in the oil and gas industry (Abbasi et al., 2010; Ebrahimi et al., 2015b; Hua et al., 2007; Loganathan et al., 2015; Mustafa et al., 2016; Thibault et al., 2017) as well as in the vegetable oil industry (Hua et al., 2007; Mustafa et al., 2016). Lastly, ceramic membranes are forthcoming for sewage treatment (Kramer et al., 2015; Shang et al., 2014a) or its effluent (Garcia-Ivars et al., 2017) and for seawater desalination, specifically as pretreatment for reverse osmosis (Cui et al., 2013; Goh and Ismail, 2018; Xu et al., 2013, 2010).

A major advantage of using ultrafiltration (UF) or nanofiltration (NF) for the treatment of high organic load waste streams is that UF/NF forms a barrier against small colloids and organic molecules, which are abundantly present in those waste streams. Therefore, the quality of ceramic membranes is of utmost importance and should be monitored accurately and regularly.

Several quality tests were reported, which can be divided into direct and indirect quality methods; methods that will analyse the membrane itself and methods that will monitor the water quality of the permeate water, respectively (Guo et al., 2010). The most commonly used direct methods for microfiltration membranes are a pressure decay test (PDT) and a diffusive airflow (DAF) test, which are simple and reliable but must be monitored off-line. Indirect methods include particle counting, turbidity monitoring, and size exclusion methods can be performed online (Huang et al., 2010).

For analysing the quality of ceramic UF or NF membranes, size exclusion and permporometry methods are most commonly used (Blumenschein et al., 2016; Shirley et al., 2014; Van Der Bruggen and Vandecasteele, 2002). The disadvantage to permporometry is the requirement of specific equipment (Blumenschein et al., 2016; Hofs et al., 2011; Zeidler et al., 2014). When using size exclusion methods, the molecular weight cut-off (MWCO) is determined using a multiple monodisperse molecules of different sizes, e.g. polyethylene glycol (PEG) molecules (Causseranda et al., 2002). By using a mixture of PEG molecules only a single filtration experiment is needed to calculate the MWCO which can only be successfully achieved when using high accuracy in detection, e.g. with High Performance Liquid Chromatography (HPLC). However, the size exclusion method has its limits. When a MWCO higher than

the MWCO according to the specifications of the supplier (from now on referred to as the *purchased cut-off*) is measured, the distinction between enlarged pore sizes (larger than the purchase cut-off) and potential cracks or gaps in the membrane cannot be made. The cracks and gaps, defined as defects on the membrane surface, cause short circuiting of the feed water to the permeate; when these defects occur, the quality of the membranes is compromised. This existing method will average the overall pore size with the defects in the membranes, which will not give a good representation of the overall pore size of the membrane. Therefore, a new method is required to quantify the defects in the membrane to be able to determine whether the membrane is compromised which will be presented in this chapter.

Other encounter of the exclusion method is the effect of pore-plugging by large PEG molecules. When pore-plugging occurs, large sized PEG molecules block the (enlarged) pores or the gaps and cracks, resulting in a lower calculated MWCO than the actual MWCO. This can be prevented by keeping the range of the PEG molecules as small as possible. Therefore, we set guidelines in this chapter to prevent pore-plugging to occur.

Thibault et al. found that when using ceramic membranes during the recovery and recycling of oil sands produced water, linear defects on the filtration layer occurred (Thibault et al., 2017). The study noted these linear defects were likely induced by solvent evaporation during the fabrication of the selective layer using the sol-gel method (Thibault et al., 2017; Uchiyama, 2015). Furthermore, Buekenhoudt reviewed stability of porous ceramic membranes especially the corrosion and thermal instabilities (Buekenhoudt, 2008). They found that microporous TiO_2 membranes sintered at 450 °C showed no significant membrane degradation during dynamic corrosion tests using cross-flow filtration (Buekenhoudt, 2008; Van Gestel et al., 2003). However, only the chemicals used for the dynamic corrosion tests were limited to HNO_3 (pH 2-3) and NaOH (pH 11-13). Other studies on the quality and robustness of ceramic tight ultrafiltration (tUF) and NF membranes are limited, according to the authors' knowledge.

Sodium hypochlorite is widely used for chemical cleaning in order to remove organic and inorganic fouling from membranes (Cui et al., 2013; Kramer et al., 2015; Lee et al., 2015; Xu et al., 2013; Zebić Avdičević et al., 2017). However, there are few long-term studies on the effect of this chemical treatment in literature. Almecija et al. showed that long-term treatment with a caustic surfactant solution at a temperature of 60ºC damaged ceramic MF membranes made of ZrO_2-TiO_2 (Almecija et al., 2009). Conversely, van Gestel et al. reported a long-term chemical resistance of ceramic NF membranes between pH 1.5 and 13 using HNO_3 for acidification and NaOH for alkalisation with an exposure time of six weeks (Van Gestel et al., 2003). Studies on the long-term effect of hypochlorite have not yet been reported in literature.

Thus, the main purpose of this research was (i) to develop a suitable method to quantitatively analyse the defects in ceramic membranes in order to investigate the quality and (ii) to investigate the long-term robustness of commercially manufactured ceramic tUF and NF membranes. This information is essential to outline the potential of these membranes for the treatment of high organic load waste streams.

Firstly, the quality of the membranes was determined by investigating the (i) hydraulic permeability, (ii) MWCO of the membranes, and (iii) quantitative defects. Sixty membranes, both tubular and disc membranes, with different MWCOs from various suppliers were investigated.

Secondly, the robustness of the membranes over long-term testing was studied by exposing tubular NF membranes to 100 hours of sodium hypochlorite cleanings, which is the equivalent of one year of operation with regular chemical cleaning. Furthermore, the pore size distribution and defects were measured by determining the MWCO of the membranes before and after each experiment.

2. Materials and Methods

2.1 Membranes
A total of sixty ceramic tUF and NF membranes, both tubular and disc membranes from various suppliers, with a purchased cut-off ranging from 450 Da to 3000 Da were tested (Table 1). The following definitions were used based on the MWCO of the membranes: ceramic membranes with a MWCO between 500 Da and 3000 Da were defined as tUF membranes, and those with a MWCO smaller than 500 Da as NF membranes (Buekenhoudt et al., 2013; Kramer et al., 2015; Shang et al., 2014a). The tubular membranes had a silica glass seal of 13 mm on the edges of the membranes to prevent feed water from entering the permeate side (Figure 1). The glass seal was not present for disc membranes because the feed and permeate were separated by an O-ring. The disc membranes were housed in the Spirlab INSIDE DISRAM™ (TAMI) disc holder with a diameter of 90 mm.

2.2 Hydraulic permeability
The hydraulic permeability of the ceramic tUF and NF membranes was determined by filtration in cross-flow mode using demineralised water at room temperature with a duration of 1 h. During these tests, the flow was measured continuously and the trans-membrane pressure (TMP) was kept constant at 4 bar. As recommended by the suppliers, the cross-flow velocity was between 1.0 – 1.2 m/s for tubular and 6.0 – 7.0 m/s for disc membranes. Both cross-flow velocities correspond to turbulent flow conditions which minimises the effect of concentration polarisation. Within 10 minutes, the hydraulic permeability became constant, and the reported values are the

average of these constant values. In order to correct for the temperature, the following equation was used to calculate the permeability:

$$L_{20°C} = \frac{J \cdot e^{-0.0239 \cdot (T - 20)}}{\Delta P}$$
(Equation. 1)

where, $L_{20°C}$ is the temperature-corrected permeability at 20 °C (L·(m²·h·bar)⁻¹), T is temperature of water (°C), J is membrane flux (L·(m²·h·bar)⁻¹), and ΔP is transmembrane pressure (bar). All permeability values were temperature-corrected to 20 °C (Mulder, 1996).

Table 1: Overview of tested ceramic tUF and NF membranes.

Membrane specification	Purchased cut-off				
	450 Da	450 Da	1000 Da	2000 Da	3000 Da
Geometry	Tubular	Disc	Disc	Disc	Disc
Length or diameter	100 mm	85 mm	85 mm	85 mm	85 mm
Filtration area	0.163 dm²	0.563 dm²	0.563 dm²	0.563 dm²	0.563 dm²
Pore size	0.9 nm	0.9 nm	1 nm	3 nm	5 nm
Porosity	30-40%	30-40%	30-40%	30-55%	30-55%
Glass seal layer	Yes	No	No	No	No
Filtration layer	TiO2	TiO2	TiO2	ZrO2	TiO2
Total membranes tested	29, 3 batches	14, 1 batch	10, 1 batch	3, 1 batch	4, 1 batch

2.3 MWCO analysis

2.3.1 MWCO calculation

The MWCO and hydraulic permeability of pristine ceramic tUF and NF membranes were measured to determine the quality of the membranes. Tam & Tremblay (1991) described that with a five component mixture of PEGs, the MWCO of membranes can accurately be determined. This method is widely used for the determination of the pore size distribution of membranes (Blumenschein et al., 2016; Shirley et al., 2014; Van Der Bruggen and Vandecasteele, 2002).

The MWCO was investigated by filtering a mixture of five different PEGs (0.2 to 6 kDa) (Sigma-Aldrich) each in a concentration of 6 mg·L⁻¹. Similar settings were used as

described for the hydraulic permeability. The range of the PEGs, $PEG_{n=1}$ to $PEG_{n=5}$, was selected based on the purchased cut-off of the membranes (Equations 2 and 3,

Table 2). It's imperative to keep the PEG range as small as possible to prevent pore plugging by large PEG molecules.

$$PEG_{n=1} \leq \frac{1}{2} \cdot MWCO_{membrane} \qquad \text{(Equation 2)}$$

$$PEG_{n=5} \geq 2 \cdot MWCO_{membrane} \qquad \text{(Equation 3)}$$

Table 2: Content of the PEG mixture used during MWCO analysis for each purchased cut-off.

Purchased cut-off	PEG mixture
450 Da	200, 300, 400, 600, 1000 Da
1000 Da	600, 1000, 1500, 2000, 3000 Da
2000 Da	1000, 1500, 3000, 4000, 6000 Da
3000 Da	1000, 1500, 3000, 4000, 6000 Da

The feed and permeate samples were analysed using HPLC (Shimadzu) equipped with size exclusion chromatography columns (SEC, 5 µm 30 Å PSS SUPREMA) and a RID-20A refractive index detector. Ultrapure water was used as carrier liquid in the HPLC at a flow rate of 1 mL·min^{-1}. The molecular weight distribution curves of the dissolved PEG molecules in the feed and permeate, derived from the HPLC analyses, were transformed into retention curves by calculating the rejection percentage of a PEG with a certain molecular weight (R_i) using Equation 4.

$$R_i(\%) = \left(\frac{c_{i,feed} - c_{i,permeate}}{c_{i,feed}} \right) \cdot 100\% \qquad \text{(Equation 4)}$$

where, $c_{i,\ feed}$ and $c_{i,\ permeate}$ are the PEG concentration in the feed and the permeate samples. Afterwards, the experimental retention curves were described by a log-normal model as function of MW and MWCO using Equation 5 (Shang et al., 2017; Shirley et al., 2014; Van Der Bruggen and Vandecasteele, 2002). Equation 5 was used to model retention curve (see Figure 2) to be able to calculate the MWCO.

$$\sigma(MW_s) = \int_0^{MW_s} \frac{1}{s_{MW}\sqrt{2\pi}} \cdot \frac{1}{MW} \cdot exp\left[-\frac{(\ln(MW) - \ln(MWCO) + 0.56 \cdot s_{MW})^2}{2 \cdot s_{MW}^2} \right] \cdot dMW \quad \text{(Eq. 5)}$$

where, $\sigma(MW_s)$ is the reflection coefficient for a PEG with a molecular weight MW_s, s_{MW} is the standard deviation of the molecular weight distribution.

It is assumed that the separation of the PEG molecules is only based on size exclusion with negligible solute diffusion. Therefore, the molecular size of the PEG solutes (d_s in

nm) is correlated to their molecular weight (*MW* in Da) as shown in Equation 6 (Shang et al., 2017; Shirley et al., 2014).

$$d_s = 0.065 \cdot MW^{0.438} \hspace{4cm} \text{(Equation 6)}$$

The MWCO was estimated at 90% of the retention curve (Mulder, 1996; Van Der Bruggen and Vandecasteele, 2002). Figure 2 shows an example of a retention curve derived from the HPLC data.

2.3.2 Corrected MWCO calculation

The MWCO calculation described in the previous section is commonly used for membrane research. However, it is not applicable for membranes with defects. Defects are (small) gaps or cracks in the membrane with a size larger than the largest PEG molecule used in the test, as illustrated in Figure 3. Defects can occur in the filtration layer and/or the glass seal layer on the edge of the membrane (Figure 1). Figure 2 shows the PEG-retention curve of a membrane with defects. The retention curve does not reach 100%, meaning that not all of the largest PEG-molecules are rejected by the membrane. Due to defects, PEG molecules with a MW larger than the pore size of the membrane will be able to pass the membrane (Figures 2 and 3). Therefore, we developed an extension to the MWCO calculation in order to correct for the defects. In this calculation, it is defined that the defects are the percentage of the largest PEG molecule passing through the membrane, which is also the percentage of feed water leaked to the permeate via the defects. Thus, the percentage of defects can be calculated with Equation 7.

$$defects(\%) = \left(1 - R_{PEG,n=5}\right) \cdot 100\% \hspace{3cm} \text{(Equation 7)}$$

where $R_{PEG, n=5}$ is the rejection rate of the largest PEG molecule by the membrane. For example, it can be concluded from Figure 2 that 30% of the PEGs passed the defect(s) in the membrane. By correcting the rejection curve to 100%, an estimation of the rejection of the filtration layer is given (Figure 2). Thus, the defects are excluded to be able to calculate the overall MWCO of the filtration layer without the defects, while also quantifying defects. Figure 3 illustrates the derivation of the rejection percentage from Equation 4 to Equation 8 for the mass balance, where the rejection rate is corrected for defects ($R_{i, d}$). Equation 8 is found below.

$$R_{i,d}(\%) = \left(\frac{c_{i,feed} - \left(c_{i,permeate} + c_{i,feed} \cdot (1 - R_{PEG,n=5})\right)}{c_{i,feed}}\right) \cdot 100\% \hspace{1cm} \text{(Equation 8)}$$

where, $c_{i, feed}$ and $c_{i, permeate}$ are the PEG concentrations in the feed and the permeate samples, respectively, and $R_{PEG, n=5}$ is the removal rate of the largest PEG molecules, permeating through the defects. 1- $R_{PEG, n=5}$ represents the ratio of the largest PEG molecules flowing through the defects (Figure 3). This equation can be simplified to Equation 9.

$$R_{i,d}(\%) = \left(\frac{c_{i,feed} \cdot R_{PEG,n=5} - c_{i,permeate}}{c_{i,feed}}\right) \cdot 100\% \qquad \text{(Equation 9)}$$

The corrected rejection percentage of a PEG with a certain molecular weight ($R_{i, corrected}$) used for membranes with defects was calculated using Equation 10.

$$R_{i,corrected}(\%) = \left(\frac{R_{i,d}}{R_{PEG,n=5}}\right) \cdot 100\% \qquad \text{(Equation 10)}$$

It must be noted that the corrected MWCO only corrects for defects larger than the largest PEG used for the analysis, $PEG_{n=5}$ (Equations 7, 8 and 10). Due to this assumption, smaller sized defects were not accounted for in this calculation. These smaller sized defects would range between the pore size and the largest PEG used for the analysis.
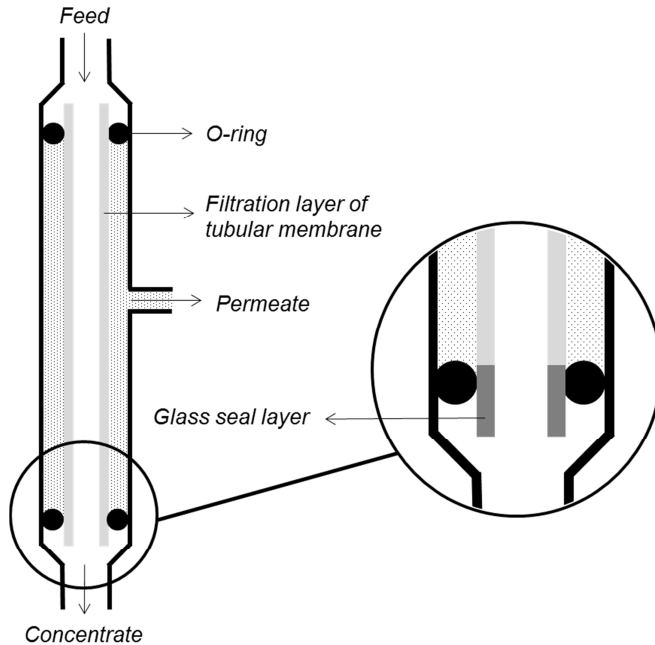
Figure 1: Illustration of the tubular membranes in the membrane module during filtration. The detailed illustration shows the glass seal layer at the edges of the tubular membrane. These glass seal layers prevent the feed from short-circuiting to the permeate side via the support layer of the membrane.

2.3.3 Chemical cleaning
The effect of long-term chemical cleaning with sodium hypochlorite on the tubular ceramic NF membranes was investigated because it is known as the most effective cleaning agent for (organically) fouled ceramic membranes (Cui et al., 2013; Kramer et

al., 2015; Lee et al., 2015; Zebić Avdičević et al., 2017). The permeability and MWCO were tested after 100 hours of chemical cleaning with 1% sodium hypochlorite to simulate the cleaning intensity of one year of operation, assuming five days of continuous filtration followed by 1.33 hours of chemical cleaning with 1% sodium hypochlorite for 365 days (Kramer et al., 2015). These concentrations were within the specifications of the supplier. In addition, a more intense chemical cleaning was tested, using 2% sodium hydroxide at 97^{0}C for 30 minutes.

2.3.4 Applying epoxy glue on the edges of the tubular membranes

After chemical cleaning, the edges of the tubular membranes were sealed again with a two-component epoxy glue, Araldite 2020. Figure 1 illustrates the glass seal layer at the edges of the tubular membranes. The resulting glued layer was microscopically examined to ensure that the edges were properly sealed.
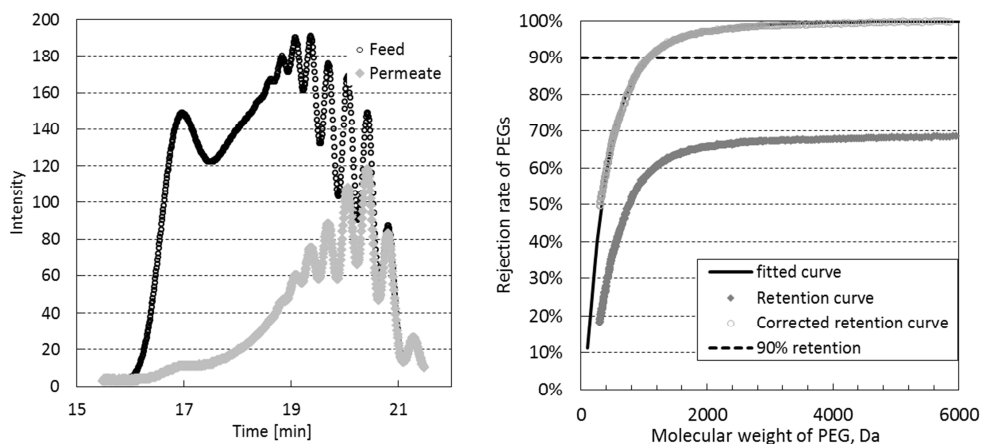
Figure 2 (a-b): (a) Output of the HPLC: the intensity versus time for a feed and permeate sample of a membrane with a purchase cut-off of 450 Da. The difference between feed and permeate was large indicating a high retention of PEG's; no defects were measured in this membrane. The retention was calculated using Equation 4 or 9. (b)The original and corrected retention curve of a pristine disc membrane with a purchased cut-off of 1 kDa, calculated with HPLC data and Equation 4 or 9. The fitted curve was derived from Equation 5 and 6. It was not possible to determine the MWCO from the original graph because the retention curve never reaches 90% retention due to the defects in this membrane. Using the MWCO calculation with correction for defects (corrected graph) makes it possible to calculate the MWCO of this membrane with defects.
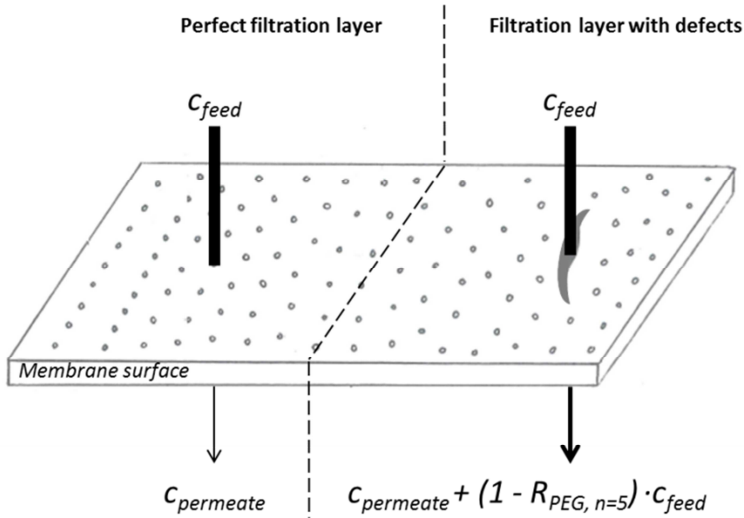
Figure 3: Illustration of the concentration of PEGs passing the membrane surface based on the mass balance for membranes without (left side) and with (right side) defects. When defects occur in the membrane, a greater amount of PEG compounds can pass the membrane to the permeate side. This should be taken into account when calculating the MWCO of the membrane filtration layer.

3. Results and Discussion

3.1 Quality of pristine ceramic tUF and NF membranes

An extension on the commonly used size exclusion method described by Tam & Tremblay (1991) was developed to be able to quantify defects in membranes and accurately calculate the MWCO excluding the defects. In this section, the MWCO values of the extended method (*corrected MWCO*) and the original MWCO method (*uncorrected MWCO*) were compared. The uncorrected MWCO calculation gives an average of the overall pore size of the membrane, including the potential defects. Whereas, the corrected MWCO calculation gives a represents the overall pore size by excluding the defects in the calculation for the MWCO while also quantifying the defects present in the membrane. Thus, the corrected MWCO together with the defects gives a better representation of the quality of the membrane. This method is described in the Materials & Methods.

In this section, the quality of sixty pristine ceramic tUF and NF membranes was analysed by measuring the MWCO, hydraulic permeability, and defects. The results of three batches of pristine ceramic NF membranes with a purchased cut-off of 450 Da were compared (Figure 4). The defects were shown in the graph with the both the

MWCO and the permeability data, to be able to compare. First, there is a notable variation in the (i) uncorrected and corrected MWCO, (ii) hydraulic permeability, and (iii) percentage of defects measured in the pristine membranes, even within one batch. This indicates that the production process is not consistent for these tested batches.

Second, the graphs in Figure 4 show that a higher percentage of defects in the membranes led, as expected, to a higher uncorrected MWCO. There was a clear relation between the uncorrected MWCO and defects: this is visible in Figure 5a. A higher percentage of defects also led to a higher corrected MWCO, even though the defects are excluded in this calculation. This means that defects occurred in the range between 450 and 1000 Da, and defects in this range were not excluded from the MWCO calculation as explained in the Materials & Methods.

Third, the hydraulic permeability varied between 5 and 37 L·(m²·h·bar)⁻¹ (Figure 4 b, d, f). This could also be explained by the occurrence of defects on the membrane surface; the feed solution can pass the membrane surface more easily through the defects, leading to a higher permeability. However, the results in Figure 5c show no clear relation between the permeability and the percentage of defects for the twenty-nine tubular 450 Da membranes tested. Moreover, there was also no direct link between the uncorrected MWCO and the permeability (Figure 5b). Another explanation for the increase in permeability is the variation in thickness of the filtration layer. Figure 10 shows an electron microscopy photo with variations of 1.4 to 2.4 µm of filtration layer thickness on the ceramic membranes with a purchased cut-off of 3 kDa. According to the Carman-Kozeny relation, the thickness of the filtration layer exhibits an inverse linear relationship with the permeability (Mulder, 1996). So, a thinner filtration layer thickness leads to a higher permeability. This indicates variation in the filtration layer thickness of the analysed pristine membranes.

Next, membranes with a different geometry, disc membranes, were compared to the tubular ceramic NF membranes. First, disc membranes with a purchased cut-off of 450 Da were tested (Figure 6). The results were better than the tubular ceramic NF membranes; 13 out of 14 disc membranes contained less than 2% defects, whereas one membrane had 6% defects (Figure 6).

In addition, disc membranes with a purchased cut-off of 1 kDa were tested, with defects ranging from 4 to 18%. The corrected MWCO ranged from 1.1 to 1.4 kDa, with permeabilities between 77 and 210 L·(m²·h·bar)⁻¹ (Figure 7). The three disc membranes with a purchased cut-off of 2 kDa showed no defects. However, the corrected MWCO ranged between 3 and 4 kDa, which indicates that the pores of these membranes were considerably larger than the purchased cut-off. The hydraulic permeability was about 150 L·(m²·h·bar)⁻¹ for all tested membranes (Figure 8). The

highest percentage of defects were measured in disc membranes with a purchased cut-off of 3 kDa, where defects ranged between 10 and 61% and permeability ranged from 23 to 82 L·(m²·h·bar)⁻¹ (Figure 9).
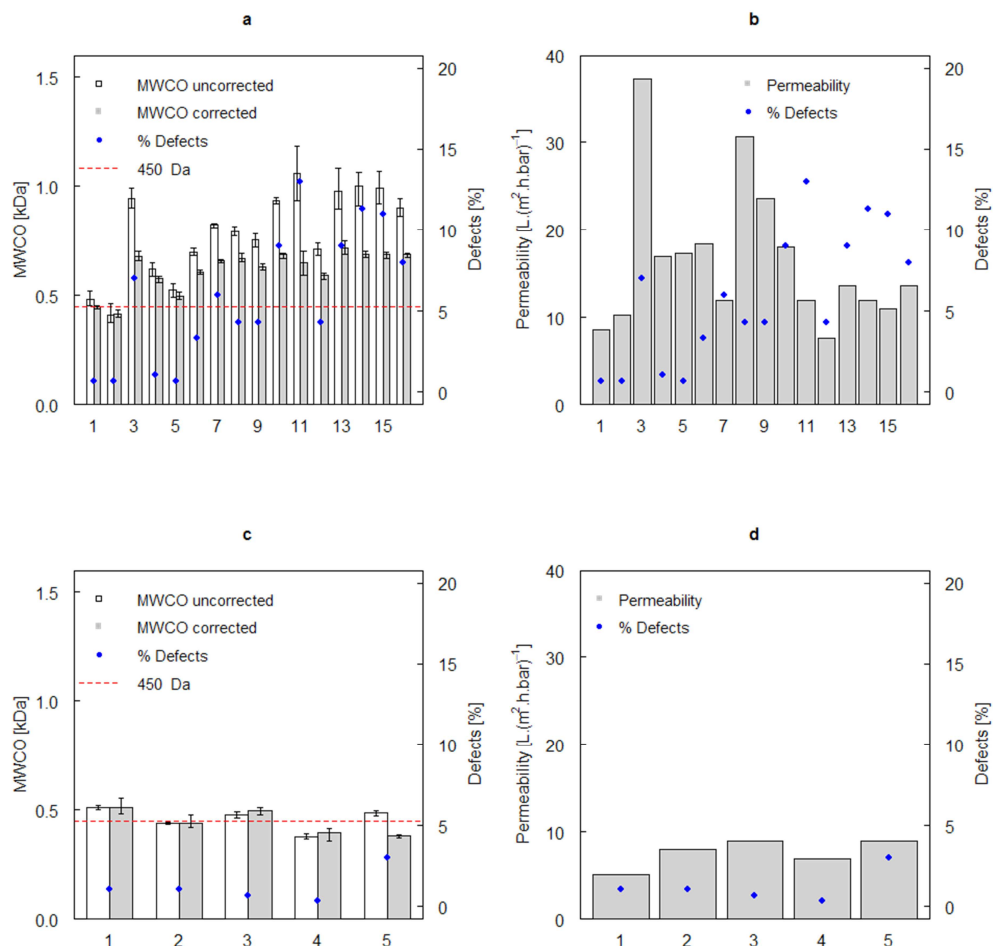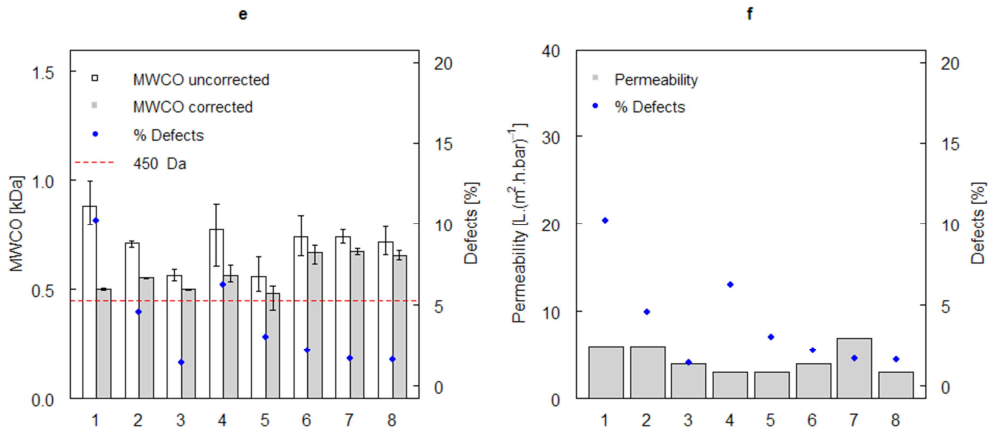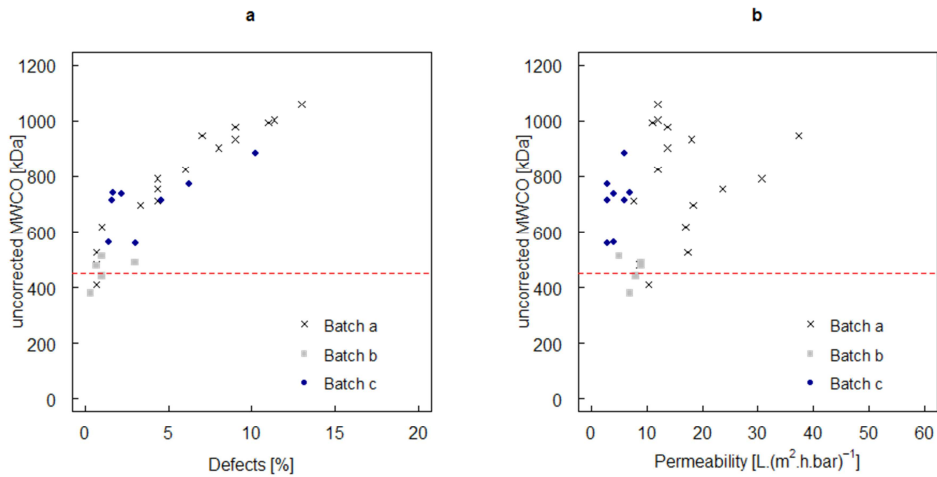
Figure 4 (a-f): MWCO in kDa (left) and hydraulic permeability in L·(m²·h·bar)⁻¹ (right) of pristine ceramic NF membranes. MWCO of tubular membranes with a purchased cut-off of 450 Da (dashed line) was calculated without (white bars) and with correction for defects (grey bars). The percentages of defects in the membrane are shown (dots). The error bars represent the standard deviation of triplicate measurements. Three different batches are shown consisting of 16, 5, and 8 membranes, respectively.
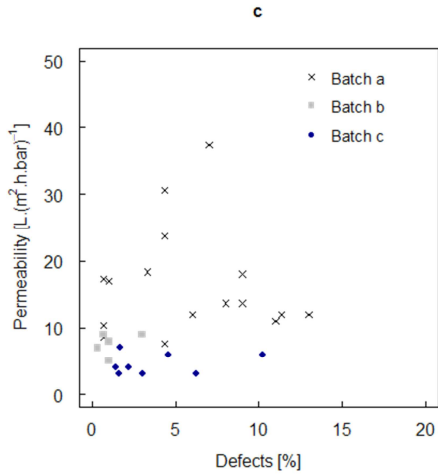
Figure 5 (a-c): Uncorrected MWCO in kDa versus (a) the permeability in L·(m2·h·bar)-1 and (b) percentage of defects. (c) Permeability versus the percentage of defects. The graphs show data of tubular membranes with a purchased cut-off of 450 Da (dashed line). Three batches are shown consisting of 16, 5, and 8 membranes.
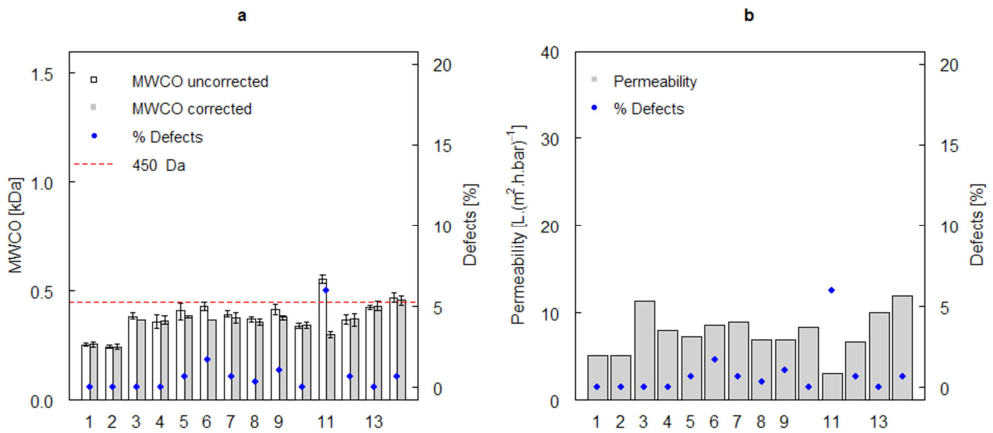
Figure 6 (a-b): MWCO in kDa (a) and hydraulic permeability in L·(m2·h·bar)-1 (b) of pristine ceramic NF membranes. MWCO of disc membranes with a purchased cut-off of 450 Da (dashed line) was calculated without (white bars) and with correction for defects (grey bars). The percentages of defects in the membrane are shown (dots). The error bars represent the standard deviation of triplicate measurements. One batch is shown.
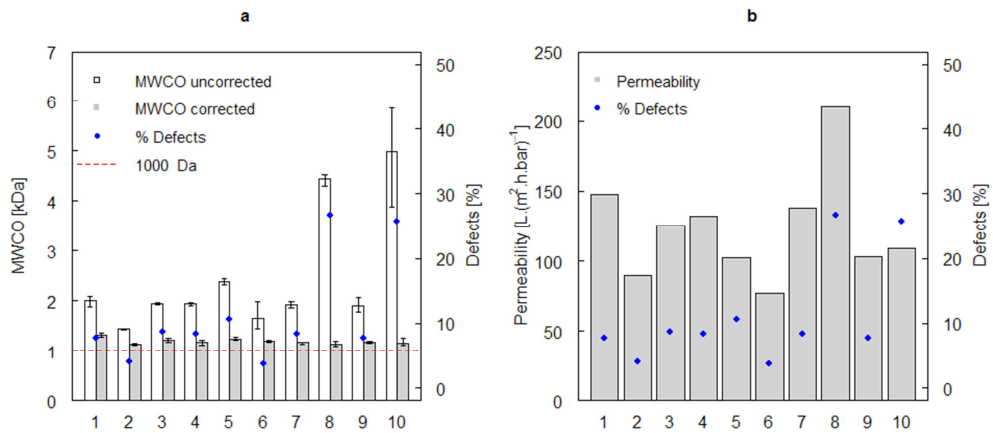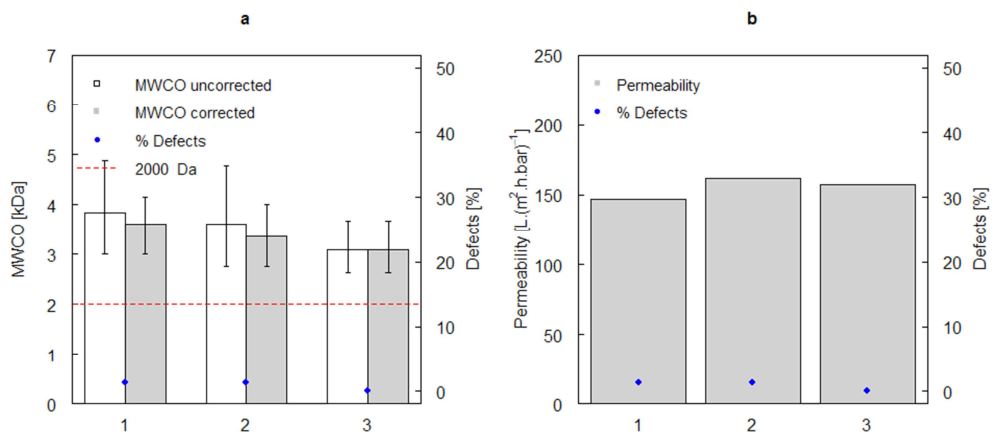
Figure 7 (a-b): MWCO in kDa (a) and hydraulic permeability in L·(m²·h·bar)⁻¹ (b) of pristine ceramic tUF membranes. MWCO of disc membranes with a purchased cut-off of 1 kDa (dashed line) was calculated without (white bars) and with correction for defects (grey bars). The percentages of defects in the membrane are shown (dots). The error bars represent the standard deviation of triplicate measurements. One batch is shown.
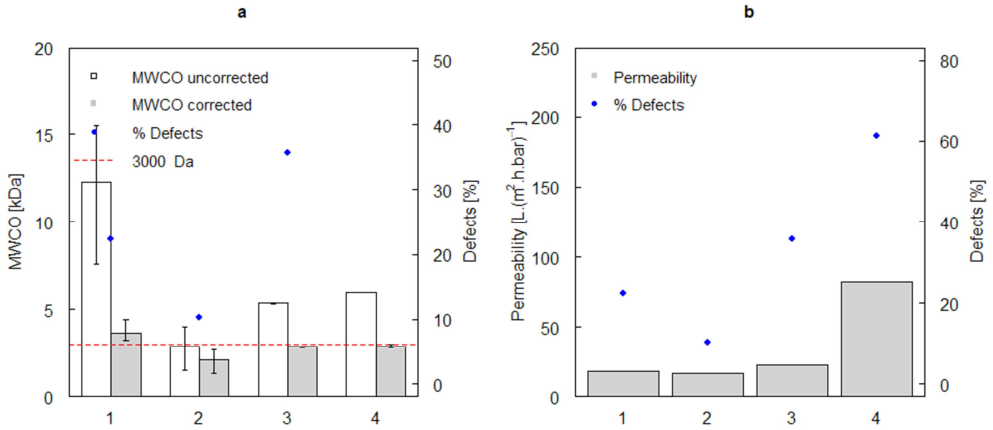

Figure 8 (a-b): MWCO in kDa (a) and hydraulic permeability in L·(m²·h·bar)⁻¹ (b) of pristine ceramic tUF membranes. MWCO of disc membranes with a purchased cut-off of 2 kDa (dashed line) was calculated without (white bars) and with correction for defects (grey bars). The percentages of defects in the membrane are shown (dots). The error bars represent the standard deviation of triplicate measurements. One batch is shown.

Figure 9 (a-b): MWCO in kDa (a) and hydraulic permeability in L·(m²·h·bar)⁻¹ (b) of pristine ceramic tUF membranes. MWCO of disc membranes with a purchased cut-off of 3 kDa (dashed line) was calculated without (white bars) and with correction for defects (grey bars). The percentages of defects in the membrane are shown (dots). The error bars represent the standard deviation of triplicate measurements. One batch is shown.
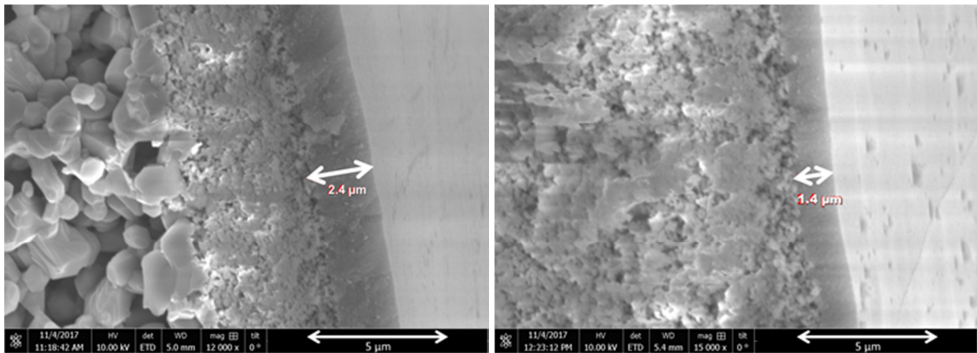
Figure 10 (a-b): Scanning electron microscope (SEM) picture of the filtration surface of two different ceramic tUF membrane with a purchased cut-off of 3 kDa. The thickness of the layer varies from 1.4 to 2.4 µm.

3.2 Robustness of ceramic NF membranes

The robustness of the ceramic membranes was investigated by exposing the membranes to sodium hypochlorite for the equivalent of one year of chemical cleaning. Results showed that long-term treatment with sodium hypochlorite caused a considerable increase of the MWCO and hydraulic permeability (Figure 11). In this

section the corrected MWCO method was used to calculate the corrected MWCO and the defects, since these represent the membrane condition the best. The four pristine ceramic NF membranes used for this experiment had a corrected MWCO between 482 and 566 Da, defects lower than 7%, and a hydraulic permeability ranging between 3.2 and 5.7 L·(m²·h·bar)$^{-1}$. After 100 h of sodium hypochlorite treatment, the percentages of defects in all of the membranes increased up to 16%. Moreover, the corrected MWCO increased to 769-799 Da. Thus, this increase in MWCO was caused by the occurrence of additional defects, in the range of the pore size of the membrane (Figures 11a). Furthermore, the increase in hydraulic permeability to 32 – 41 L·(m²·h·bar)$^{-1}$ is explained by the occurrence of additional defects (Figures 11b).

After chemical treatment, one of the ceramic NF membranes had a visible crack in the glass seal layer on one edge of the membrane, see Figure 12a. After repair with epoxy glue, the MWCO and the permeability of the membrane decreased to their original value (Figure 11). This suggests that the additional defects, caused by sodium hypochlorite exposure, only occurred in the glass seal edges of this membrane. This hypothesis was tested by repeating the experiment for all membranes; similar effects were revealed for all membranes (Figure 11).

It should be noted that after repair, no defects were measured in the membranes, while the pristine membranes contained 2 to 7% defects. Thus, the repair removed not only the additional defects due to the chemical treatment but also the initial defects. This suggests that the initial defects in the pristine membranes were also located in the glass seal layer, which explains the decrease of the corrected MWCO after repair compared to the pristine membranes. It should be noted that this conclusion does not apply for all pristine membranes; we cannot state that defects in pristine membranes e.g. the membranes analysed in section 3.1 only occur on the glass seal layer.

 These results thus suggest that the sodium hypochlorite damaged the silica glass seal layer on the edge of the membranes, which is also shown on the scanning electron microscope (SEM) image of the glass seal layer (Figure 12b). Not only is the crack on the edge of the membrane visible in this picture but also the cracks in the entire silica glass seal layer.

Finally, the effect of more severe chemical cleaning with sodium hydroxide was investigated using 2% sodium hydroxide for 30 minutes at a temperature of 97^{0}C and a pH of 13.69. Figure 13 shows that the hydraulic permeability and corrected MWCO increased after this chemical cleaning, and the epoxy glue at the edges of the membrane restored the values to the initial value. Thus, the higher concentration of sodium hydroxide also damaged the glass seal layer at the edges of the membranes, in a similar manner as the regular concentration of sodium hypochlorite, without affecting the separation layer. Van Gestel et al. performed similar long-term exposure

experiments using NaOH for six weeks at a pH of 13 at 25° C and did not detect damage on the membranes (Van Gestel et al., 2003). This indicates that a pH of 13 at 25° C lies within the boundaries of chemical resistance of the ceramic NF membrane.
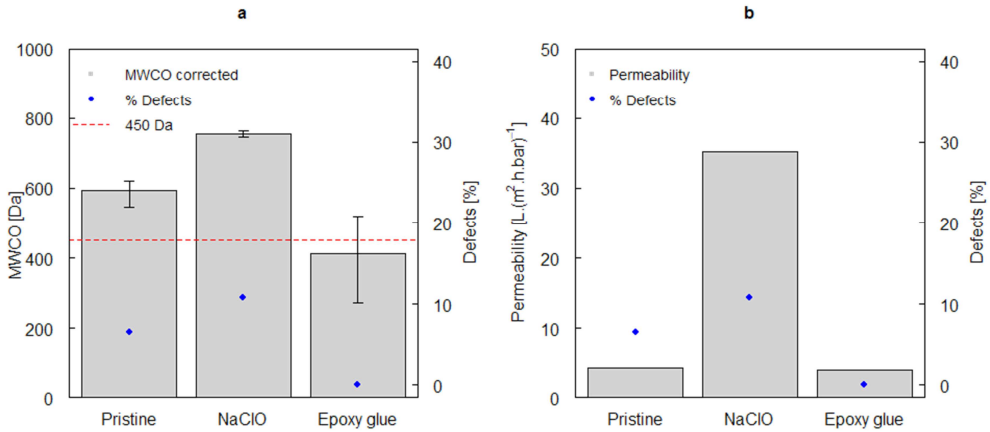

Figure 11 (a-b): MWCO in kDa (a), permeability in L·(m²·h·bar)⁻¹ (b) and percentages of defects in tubular ceramic NF membranes with a purchased cut-off of 450 Da (dashed line). The pristine membranes (Pristine) were treated with 1% sodium hypochlorite for 100 hours (NaClO), then an epoxy glue layer was applied at the edges to cover the glass seal layer of the membranes (Epoxy glue). This experiment was executed four times, the data was averaged and the error bars represent the standard deviation of the different measurements.
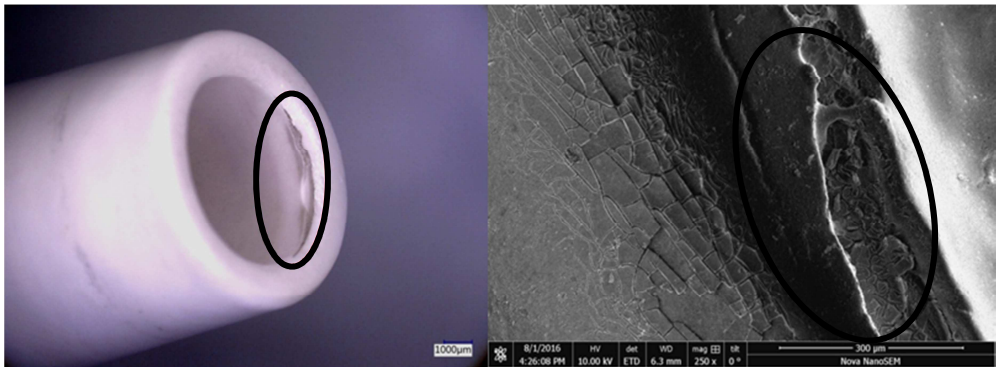

Figure 12 (a-b): Ceramic NF membrane with a purchased cut-off of 450 Da after 100 h of chemical cleaning with 1% sodium hypochlorite shown with a digital microscope (a) and a scanning electron microscope (SEM)(b). A large crack is visible on the edge of the membrane (circle) as well as small cracks throughout the silica glass seal layer.
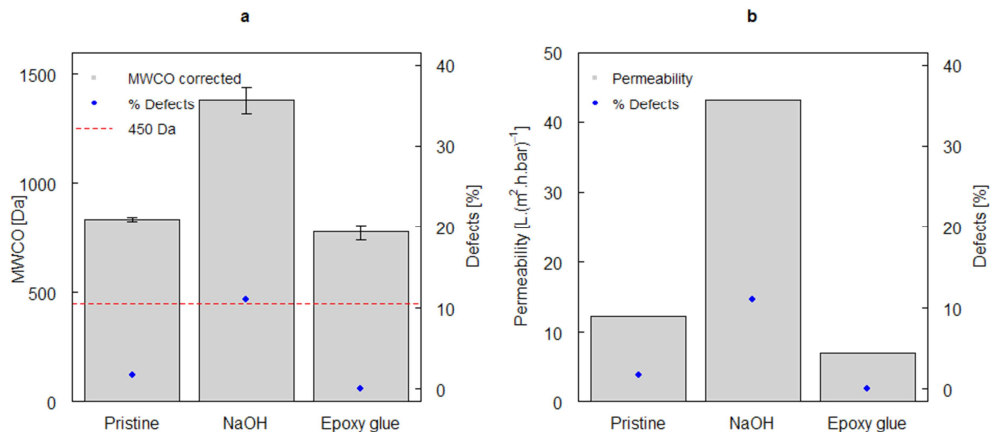
Figure 13 (a-b): MWCO and permeability of tubular ceramic NF membranes with a purchased cut-off of 450 Da (dashed line) when pristine (Before), treated with 2% sodium hydroxide (NaOH) for 30 min at 97⁰C, and with end layer restored using epoxy glue (Glue). The error bars represent the standard deviation of triplicate measurements.

Conclusions

For the treatment of high organic load waste streams, it is important that the quality of ceramic tUF and NF are intact, for both pristine membranes and those after frequent chemical cleaning. An extension to the existing MWCO method was developed to quantify defects on ceramic membranes. The quality and the robustness of a broad range of pristine ceramic tUF and NF membranes was investigated using this extension. The following conclusions can be drawn:

- Defects in membranes can be quantified using an extension to the commonly used MWCO method.
- Defects are frequently detected in the studied commercial ceramic membranes.
- The MWCO, both uncorrected and corrected, of pristine membranes varied often from the purchase cut-off, even within membranes from the same batch. This was tested with membranes of different pore sizes and geometries from various suppliers.
- The hydraulic permeability of pristine membranes varied notably for pristine membranes with a similar purchased cut-off.

- Long-term treatment with chemicals, especially sodium hypochlorite, damaged the tubular ceramic membranes, although this chemical is widely used to clean ceramic membranes. However, the chemicals only affected the glass seal layer on the edges of the membranes. Similar results were found using high concentrations of NaOH.
- Re-sealing of the edges of the membranes recovered the original properties of the tubular membranes. Moreover, the defects present in the pristine membranes were removed as well.

Acknowledgments

Chapter 4

INFLUENCE OF PH, MULTIVALENT COUNTER IONS, AND MEMBRANE FOULING ON PHOSPHATE RETENTION DURING CERAMIC NANOFILTRATION

'The more you know, the more you know you don't know.'

Aristoteles

INFLUENCE OF PH, MULTIVALENT COUNTER IONS, AND MEMBRANE FOULING ON PHOSPHATE RETENTION DURING CERAMIC NANOFILTRATION

Abstract

Ceramic nanofiltration is an emerging technology for the recovery of water and nutrients (including phosphate) from municipal sewage which becomes more imperative worldwide. In order to use ceramic nanofiltration for phosphate recovery from municipal sewage, more knowledge is needed. In this chapter the influence of pH, multivalent counter ions, and membrane fouling on phosphate retention is reported. Various experiments were executed to analyse the phosphate retention and zeta potential under varying conditions. During filtration of a salt solution including phosphate, the phosphate retention increased, from 76% to 99%, with a change in pH from 5 to 9. Furthermore, magnesium ions and organic fouling had a large influence on the phosphate retention: at pH 7 the phosphate retention dropped from 92% to 42-43% due to the presence of either magnesium ions or organic fouling.

1. Introduction

The demand for water and nutrient recovery from (municipal) sewage is increasing worldwide (Cordell et al., 2009; Drangert, 2012; McCarty et al., 2011; Wielemaker et al., 2018). An upcoming economic and sustainable alternative for the conventional sewage treatment plants are sewer mining concepts, treating municipal sewage directly for on-site usage while recovering nutrients, water, and, possibly, energy (Butler and Maccormick, 1996; Kramer et al., 2015; Xie et al., 2013).

Ceramic nanofiltration (NF) is for several reasons an interesting technology to explore for this application. First, most components in the water can potentially be recovered, since it is based on physico-chemical separation in contrast to biological treatment. Second, membrane technology has flexibility in configuration, pore size, and membrane material which enables to tailor the treatment to achieve the highest recovery of a specific element or compound; NF has the ability to separate inorganic ions with smaller sizes and hydraulic radii than the pore size due to electrostatic repulsion in certain pH ranges (Kotrappanavar et al., 2011; Nyström et al., 1995; Schaep and Vandecasteele, 2001; Tansel et al., 2006); various membrane materials have a different membrane surface charge with varying ion repulsion. Third, based on the high potential for retention of multivalent ions, this technology could support e.g.

struvite production from sewage; when the concentrate stream of the NF is treated in an anaerobic digester, the digestate supernatant could afterwards be used for the production of struvite (Doyle and Parsons, 2002; Münch and Barr, 2001; Shu et al., 2006; Verstraete et al., 2009). Fourth, ceramic membranes are susceptible to less irreversible fouling than polymeric membranes (Lee et al., 2013; Zhao et al., 2018) which makes this technology more suitable for treatment of municipal sewage.

In this chapter ceramic NF membranes with a titanium oxide membrane layer were selected. Previous research showed that phosphate retention varies, using real municipal sewage in a bench scale sized filtration set-up with ceramic NF membranes of the same type (Kramer et al., 2015). However, no conclusive study was performed to determine the cause of this variation in phosphate retention. The negative charge in the pH 7-9 range (Cui et al., 2013; Puhlfürß et al., 2000) suggests that ceramic NF membranes could reject phosphate ions due to electrostatic repulsion. Moreover, Shang et al. (2014b) found that ceramic ultrafiltration (UF) membranes, made of similar material but with a larger pore size, had a high phosphate retention of 87% at pH 8.5 in clean water.

Literature describes that the pH and the presence of other compounds in the water can have an influence on ion retention, both in ceramic NF (Puhlfürß et al., 2000; Tsuru et al., 2002) and ceramic UF membranes (Chevereau et al., 2010). These compounds have mainly an effect on the electrostatic interactions around the membrane surface. For instance, multivalent counter ions can cause suppression of the diffuse double layer (Afonso et al., 2001; Déon et al., 2011; Hunter, 1981) or can adsorb to the membrane surface which changes the surface charge of the membrane and thus the ion retention (Dutournié et al., 2017). Thus, multivalent counter ions might also have influence on the phosphate retention during ceramic NF. In order to get insight in the electrostatic interactions on the membrane surface, streaming potential measurements are often executed to determine the membrane charge.

Another important influencing factor on the phosphate retention might be fouling on the ceramic NF membrane surface when treating municipal sewage. In literature, the influence of a fouling layer on polymeric NF membranes on ions' retention can be found (Déon et al., 2011; García-Martín et al., 2014; Hoek and Elimelech, 2003; Kilduff et al., 2004; Verliefde et al., 2008; Wang et al., 2014). Zhao et al. (2018) describes a similar effect for retention of several pharmaceuticals during ceramic NF using model sewage. This suggest that a fouling layer potentially affects the phosphate retention in ceramic NF membranes when treating municipal sewage.

Both the phosphate retention in clean water and the effects of multivalent counter ions and a fouling layer on the membrane surface, especially relevant when using municipal sewage, has not been reported in literature yet. Therefore, the objective of this chapter is to determine the retention (or passage) of phosphate by ceramic NF

membranes in the presence of multivalent counter ions and a fouling layer on the membrane surface. In order to be able to design a strategy for phosphate recovery from municipal sewage using ceramic NF.

2. Materials & Methods

2.1 Ceramic NF membranes

Filtration experiments were performed using ceramic NF membranes with a filtration layer of titanium oxide, indicated MWCO of 450 Da, indicated mean pore size of 0.9 nm, and open porosity of 30-40%. The accurate MWCO was measured before and after each experiment to monitor their quality, using the method described below. For the phosphate retention experiments, a single-channel, tubular configuration was used with a length of 100 mm and an effective filtration area of 0.163 dm^2 (Inopor GmbH, Germany).

Moreover, ceramic NF membranes with a disc configuration were used for the streaming potential experiments. The disc membranes had the same specifications as the tubular membranes describe above, a diameter of 85 mm, and a specific membrane area of 0.563 dm^2. The disc membranes were placed in the Spirlab INSIDE DISRAM™ (TAMI) disc holder with a diameter of 90 mm.

2.2 Filtration experiments

Ceramic NF experiments were carried out with a cross-flow filtration system using a pneumatic diaphragm pump (Hydra-cell) with a pulsation dampener. The single pass water recovery of the ceramic NF system was < 1%. In addition, the feed water was recirculated; both the permeate and the concentrate were fed back into the feed tank, except for the sampling volume, which was a negligible amount (<0.1%). The feed water composition remained constant over the duration of the experiment: this was monitored by analysing samples throughout the experiment. In order to ensure that the feed water remained constant over the duration of the experiment, feed water samples were analysed regularly. The experiments were executed at room temperature with a trans-membrane pressure (TMP) of 4.5-5.5 bar, and flux of 50-60 $L \cdot (m^2 \cdot h)^{-1}$, unless otherwise specified. The cross-flow velocity was 1.0-1.2 $m \cdot s^{-1}$ resulting in a turbulent flow with a Reynold number of 4200, as recommended by the suppliers. The following equation (Eq. 1) was used to calculate the temperature-corrected permeability:

$$L_{20°C} = \frac{J \cdot e^{-0.0239 \cdot (T-20)}}{\Delta P}$$

(Equation 1)

where, $L_{20 °C}$ is the temperature-corrected permeability at 20 °C ($L \cdot (m^2 \cdot h \cdot bar)^{-1}$), T is temperature of water (°C), J is membrane flux ($L \cdot (m^2 \cdot h)^{-1}$), and ΔP is trans-membrane

pressure (bar). All permeability values were temperature-corrected to 20 °C (Mulder, 1996).

2.2.3 Hydraulic permeability
A demineralised water filtration test was performed before each filtration experiment to determine the initial hydraulic permeability. These hydraulic permeability tests were executed under similar conditions as the filtration tests with a duration of 1 hour.

2.2.3 Filtration with salt solution
Phosphate retention tests were performed according to the filtration conditions mentioned earlier. The feed solution contained 1 mM NaCl salt, which served as a background to reduce the effect of pH adjustment on the salinity, and it was comparable with the concentration in municipal sewage (Kramer et al., 2015; Ozgun et al., 2015). Multivalent anions and cations were added to the salt solution to test their effect in a concentration of 0.3 mM H_2NaPO_4, and/or 0.3 mM $MgCl_2$ (Table 1). These concentrations were chosen in the range of municipal sewage.

The retention tests were executed in the pH range 5 to 9, while the pH was adjusted using NaOH or HCl. In order to maintain a pH of 9 in the feed tank, a nitrogen blanket was created over the feed tank using nitrogen gas. Then, feed, concentrate and permeate samples were taken for analysing the phosphate retention. These samples were taken 60 min after the pH adjustment to ensure stabilisation of the system.

Table 1: Overview of the phosphate retention and streaming potential experiments performed.

Experiment	Present during experiment				Measured	
	NaCl	H_2NaPO_4	$MgCl_2$	Fouling layer	P retention	Streaming potential
1	1 mM					X
2	1 mM			0.8 g·L^{-1}		X
3	1 mM	0.3 mM			X	X
4	1 mM	0.3 mM		0.8 g·L^{-1}	X	X
5	1 mM	0.3 mM	0.3 mM		X	X
6	1 mM	0.3 mM	0.3 mM	0.8 g·L^{-1}	X	

2.2.4 Filtration with model sewage

Fouling tests were performed using sodium alginate as model compound for sewage (Katsoufidou et al., 2007; Ye et al., 2005). The feed water composition consisted of 0.8 g·L^{-1} sodium alginate (Sigma-Aldrich), 1 mM NaCl (Sigma-Aldrich) as background salt concentration, 1 mM NaHCO$_3$ (Sigma-Aldrich) as buffer, and 3 mM CaCl$_2$ (Sigma-Aldrich) adjusted to pH of 7. Sodium alginate is known to form a gel in the presence of calcium ions and to aggregate according to the "egg-box" model which promotes cake layer development during filtration (Alazmi, Radhi, 2010; Katsoufidou et al., 2007; van den Brink et al., 2009; Zhao et al., 2015). With the concentrated model sewage a pre-sieved municipal sewage experiment of 5 days could be simulated in two hours with the same membrane type (Kramer et al., 2015).

As preparation for the streaming potential experiments of membranes with a fouling layer, the disc membranes were filtered with model sewage. During filtration the TMP was kept constant at 4 bar at a turbulent flow with a cross-flow velocity of 6.0-7.0 m·s^{-1}, as recommended by the supplier. Followed by a forward flush to maintain merely the irreversible fouling on the membrane.

2.2.4 Retention tests

During filtration samples were taken to monitor the retention of the ions. The retention of ions R_i was calculated using Equation 2.

$$R_i = \left(1 - \frac{c_{i,p}}{c_{i,f}} \right) \cdot 100\% \qquad\qquad \text{(Equation 2)}$$

where, $c_{p,i}$ is the ion concentration in the permeate and $c_{i,f}$ the ion concentration in the feed water.

2.3 Analytical methods

2.3.1 Ion chromatography

The ion composition of the concentrate and permeate water were analysed using a ProfIC 15–AnCat ion chromatograph (Metrohm 881 anion (suppressed) and 883 cation system, Metrohm, Switzerland). Prior to these analyses the aqueous samples were filtered through 0.45 μm filters (Whatman, Germany). An A Supp 150/4.0 anion column was used with 3.2 mM Na$_2$CO$_3$ and 1 mM NaHCO$_3$ eluent for anions. For the cations a C5 cation column with 3 mM HNO$_3$ eluent was used. The regeneration solution, used for the suppressor, was 50 mM H$_2$SO$_4$.

2.3.2 Streaming potential experiments

In order to determine the membrane surface charge, the zeta potential was calculated by measuring the streaming potential. Disc membranes were used for this experiment because the streaming potential can only be determined on a flat membrane surface.

The streaming potential of the ceramic NF membrane was determined using a SurPASS electro kinetic analyser (Anton Paar GmbH, Austria). The zeta potential was determined with the Helmholtz-Smoluchowski equation. Several solutions with various ionic compositions were analysed, all with an total ionic strength of 10 mM; 0.3 mM of the different ions – NaH_2PO_4, $MgCl_2$ and $NaSO_4$ – were present in a NaCl salt solution. KCl solution is most commonly used for streaming potential measurements. Puhlfürß et al. found that using NaCl solution for streaming potential measurements is comparable with using KCl solution, when using similar ceramic NF membranes (Zeidler et al., 2014). Since NaCl is present in municipal sewage this was used during the measurements.

2.3.3 MWCO analysis

The MWCO of ceramic NF membranes was regularly measured to monitor the quality of the membranes, using the method described by Tam & Tremblay (1991), also used in other studies (Blumenschein et al., 2016; Causseranda et al., 2002; Shirley et al., 2014; Van Der Bruggen and Vandecasteele, 2002).

First, a mixture of five different polyethylene glycol (PEG) molecules (200, 300, 400, 600, and 1000 Da) (Sigma-Aldrich), each in a concentration of 6 mg·L^{-1}, was filtered using a clean ceramic NF membrane. The same settings were used during filtration as described for the hydraulic permeability.

Then, the feed and permeate samples were analysed using HPLC (Shimadzu) equipped with size exclusion chromatography columns (SEC, 5 µm 30 Å PSS SUPREMA) and a RID-20A refractive index detector. The carrier liquid in the HPLC was ultrapure water at a flow rate of 1 mL·min^{-1}. From the HPLC analyses, the molecular weight distribution curves of the dissolved PEG molecules in the feed and permeate were derived. These were converted into retention curves by calculating the rejection percentage of a PEG with a certain molecular weight (R_i) using Equation 3:

$$R_i(\%) = \left(\frac{c_{i,feed} - c_{i,permeate}}{c_{i,feed}} \right) \cdot 100\% \qquad \text{(Equation 3)}$$

where, $c_{i,\,feed}$ is the PEG concentration in the feed samples and $c_{i,\,permeate}$ in the permeate samples.

Afterwards, the experimental retention curves were described by a log-normal model as function of molecular weight (MW) and MWCO using Equation 4 (Shang et al., 2017; Shirley et al., 2014; Van Der Bruggen and Vandecasteele, 2002). Equation 4 was used to model retention curve to be able to calculate the MWCO.

$$\sigma(MW_s) = \int_0^{MW_s} \frac{1}{s_{MW}\sqrt{2\pi}} \cdot \frac{1}{MW} \cdot exp\left[-\frac{(\ln(MW) - \ln(MWCO) + 0.56 \cdot s_{MW})^2}{2 \cdot s_{MW}^2} \right] \cdot dMW \quad \text{(Eq. 4)}$$

where, $\sigma(MW_s)$ is the reflection coefficient for a PEG with a molecular weight MW_s, s_{MW} is the standard deviation of the molecular weight distribution.

In this method, the separation of the PEG molecules is assumed to be only based on size exclusion with negligible solute diffusion. Therefore, the molecular size of the PEG solutes (d_s in nm) is correlated to their molecular weight (MW in Da) as shown in Equation 5 (Shang et al., 2017; Shirley et al., 2014).

$$d_s = 0.065 \cdot MW^{0.438} \qquad\qquad\qquad\qquad \text{(Equation 5)}$$

Finally, the MWCO was estimated at 90% of the retention curve (Mulder, 1996; Van Der Bruggen and Vandecasteele, 2002).

3. Results & Discussion

3.1 Determination of MWCO
Previous research has shown that the quality of these membranes can vary within one batch (Kramer et al., 2019). Therefore, the quality of the three ceramic NF membranes, used in this study, was determined before and after each experiment by calculating the MWCO. The initial MWCO was measured to be 500, 503, and 549 Da, respectively, and remained stable throughout the experiments. The streaming potential experiments were performed with two disc membranes with a measured MWCO of 495 and 538 Da.

3.2 Influence of pH on retention of phosphate by clean membranes
The phosphate retention during ceramic NF with clean membranes was measured in a salt solution at pH varying from 5 to 9. The phosphate retention increased with the pH from 76% to 99%, respectively (Figure 1). The phosphate was not rejected due to size exclusion, since the pore size of the ceramic NF membranes is around 0.9 nm (according to the supplier) and the hydraulic radii of phosphate, in the forms $H_2PO_4^-$ and HPO_4^{2-}, are 0.302 and 0.327 nm, respectively (Kiriukhin and Collins, 2002; Tansel et al., 2006). Thus, electrostatic repulsion, probably, played a decisive role in retention.

With an increasing pH, from 5 to 9, phosphate shifts from a monovalent ($H_2PO_4^-$) to a divalent (HPO_4^{2-}) form. The divalent form has a lower diffusion coefficient ($7.34 \cdot 10^{10}$ $m \cdot s^{-2}$) than the monovalent form ($8.46 \cdot 10^{10}$ $m \cdot s^{-2}$)(Krom and Berner, 1980), which possibly enhanced the retention at higher pH.
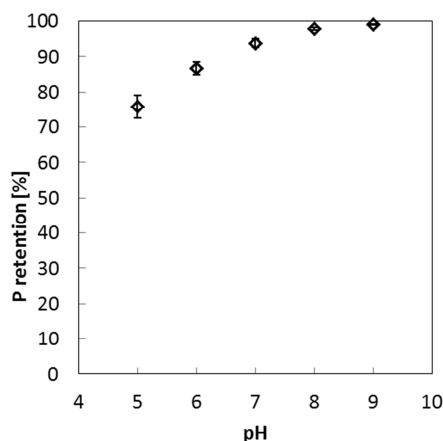
Figure 1: Retention curve of phosphate for a pH range of 5 to 9 during ceramic NF in 0.01 M salt solution.

To confirm the role of electrostatic repulsion, the membrane surface charge was determined by measuring the streaming potential from which the zeta potential can be calculated (Figure 2). The results show that the zeta potential of the membranes was negative, -8 to -22 mV for pH 4 to 9, respectively. Upon addition of phosphate to the solution the negative membrane charge increased to -28 to -39 mV, respectively, in the same pH range (Figure 2). This probably caused the increase in phosphate retention at high pH (Figure 1). Apparently, phosphate adsorbed on the membrane surface, resulting in a more negatively charged membrane which is referred to as specific adsorption. This was also observed by Shang et al. (2014b, 2014a) when using ceramic UF membranes of similar material.

Puhlfürß et al. (2000) also determined the zeta potential of similar ceramic NF membranes, but in a broader pH range, from 2.5 to 10.5. They found the iso-electrical point to be at pH 3.3. At pH 4 the zeta potential was comparable to the results in Figure 2, albeit with increasing pH the zeta potential decreased faster, to -33 mV instead of -22 mV at pH 9. However, Puhlfürß et al. (2000) used a lower concentration of NaCl solution, which probably caused a higher negative membrane charge. This effect on the membrane charge was also observed by Afonso et al. and Deon et al. (Afonso et al., 2001; Déon et al., 2011).
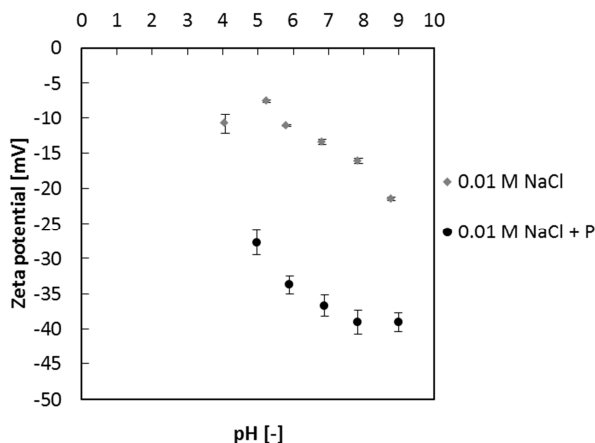
Figure 2: Zeta potential of ceramic NF membrane at a pH range of 4 to 9 using a solution of 0.01 M NaCl (diamonds) or 0.01 M NaCl with phosphate (dots).

3.3 Influence of multivalent counter ions on retention of phosphate by clean membranes

Co-existent ions could have an (negative) effect on the phosphate retention, in particular, multivalent cations that are present in sewage. Therefore, first, the phosphate retention was analysed in the presence of $MgCl_2$ (0.3 mM), added to the salt solution that included phosphate. $MgCl_2$ addition caused a drop in phosphate retention in the range of 42% to 44% for a change in pH from 5 to 9 (Figure 3). Moreover, the zeta potential showed a lower negative charge in the presence of $MgCl_2$, from -12 to -27 mV in the pH range from 4 to 9, respectively, compared to the membrane charge measured in the solution with only NaCl and phosphate (Figure 4).

This was also observed by Tsuru et al. (2002): they described that divalent counter ions, e.g. calcium and magnesium, reduced the active pore size of ceramic NF membranes with a titanium oxide filtration layer. Furthermore, Chevereau et al. (2010) observed that magnesium ions have the ability to adsorb to negatively charged ceramic UF membranes. When this happens the membrane charge can even switch from negative to positive due to the charge of the magnesium ion. Another phenomenon described in literature is that divalent ions, such as magnesium, can suppress the diffuse double layer on the membrane surfaces (Hunter, 1981; Tsuru et al., 2008; Wang et al., 2014). The distinction between the two described phenomena could not be made with the zeta potential calculations because streaming potential is measured in the diffuse double layer, so both adsorption and diffuse double layer suppression were determined.
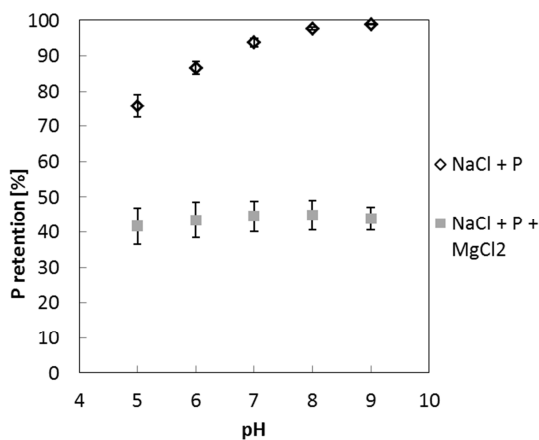
Figure 3: Retention curve of phosphate for a pH range of 5 to 9 during ceramic NF. The effect of MgCl₂ on phosphate retention was determined.
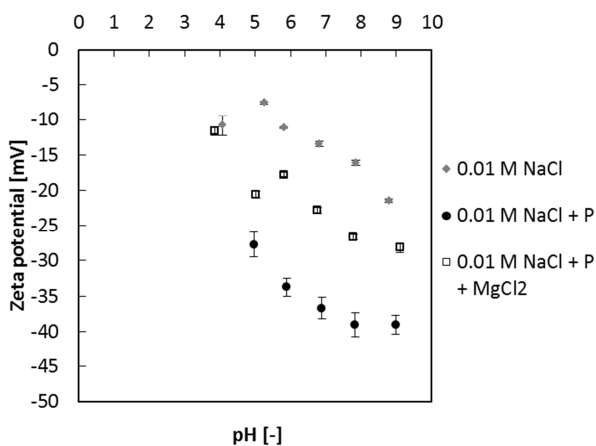

Figure 4: Zeta potential of ceramic NF membrane at a pH range of 4 to 9 using a solution of 0.01 M NaCl (diamonds), NaCl with phosphate (dots), and NaCl with phosphate and MgCl₂ (squares).

3.4 Influence of fouling layer on retention of phosphate

Subsequently, model sewage was used to examine the effect of a fouling layer on the phosphate retention. Phosphate was added during filtration of model sewage to analyse the effect on the permeability and the phosphate retention. In order to also examine the influence of the thickness of the fouling layer, phosphate was added after 60, 75, and 120 min of filtration. Then, when the system stabilised, the phosphate retention was determined (see grey crosses in Figure 5a-c).
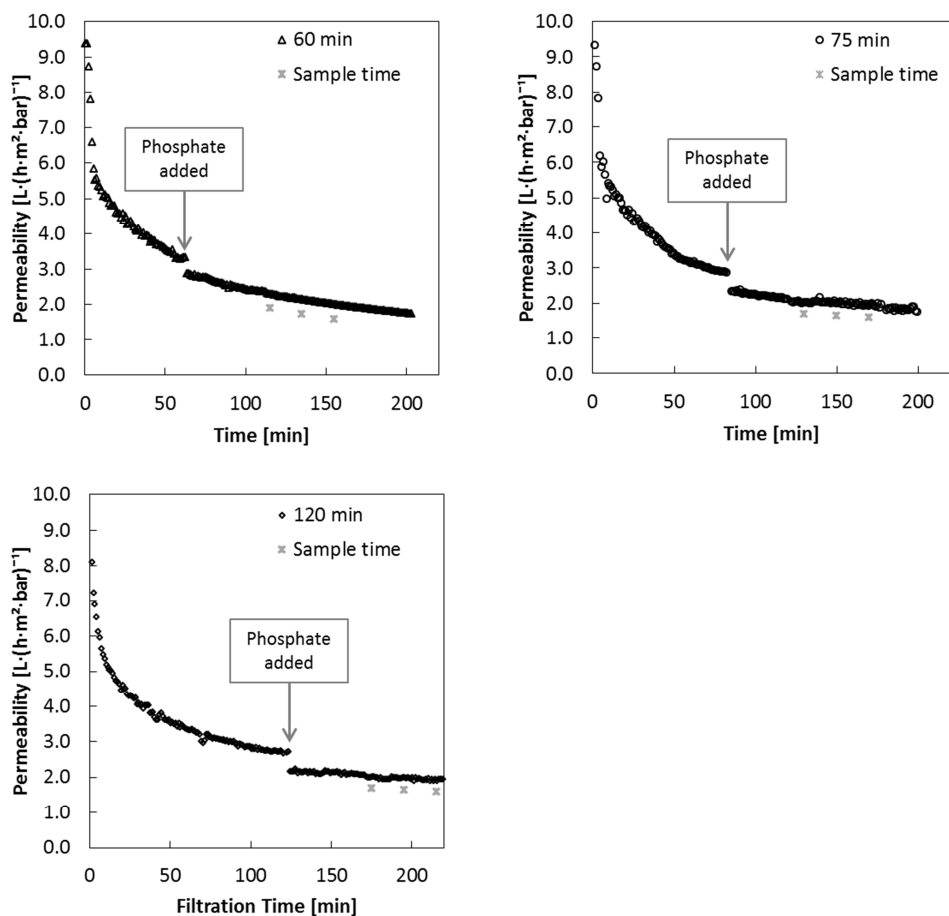
Figure 5a-c: Fouling experiments of ceramic NF using model sewage at pH of 7. (a-c) Permeability in time. Phosphate was added to the feed solution after 60, 75, and 120 min filtration. Three samples were taken (grey crosses).

An additional, clear, drop in permeability was visible due to the addition of phosphate (Figure 5a-c). This might have been caused by the cake-enhanced concentration polarisation (Hoek and Elimelech, 2003; Wang et al., 2014; Zhao et al., 2018). Another explanation of the drop could be the compaction of the cake layer in the presence of phosphate which made the cake layer less penetrable, resulting in a lower permeability (Visvanathan et al., 1998). The permeability drop was 0.85 L·(m²·h·bar)⁻¹ after 60 min of filtration, 0.82 L·(m²·h·bar)⁻¹ after 75 min of filtration, and 0.85 L·(m²·h·bar)⁻¹ after 120 min of filtration, respectively.

The phosphate retention stabilised at 43-44% in the presence of a cake layer. Thus, the fouling layer on the membrane surface had a large impact on the phosphate retention (Figure 6), when compared to clean membranes without fouling layer which had a phosphate retention of 94% (Figure 1). This could be explained by the occurrence of cake-enhanced concentration polarisation: when the concentration of phosphate is higher on the membrane surface due to cake-enhanced concentration polarisation, the concentration of phosphate was higher in the permeate which caused a lower phosphate retention.

It should be noted that the flux was lower when the phosphate retention was measured in the presence of a cake layer than with a clean membrane. A known phenomena in membrane filtration is the dilution effect: at higher permeate flux, a higher retention of solvents is observed due to enhance convective transport (Luo and Wan, 2013). In this case the reverse dilution effect could explain part of the lower phosphate retention measured in the presence of a cake layer, because the flux was about 5 times lower than without the presence of a cake layer. When assuming that the diffusion of phosphate is not changing due to the fouling layer, it can be calculated that the rejection of the pristine membrane of 94% (pH=7) is decreasing to about 75% when the flux decreases 5 times (5 times higher permeate concentration). So, the lower flux cannot fully explain the measured decrease of the phosphate rejection.
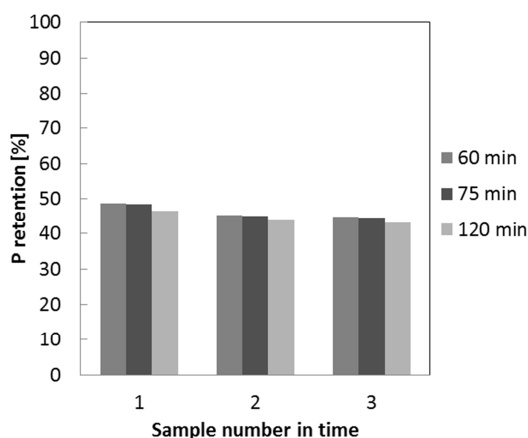

Figure 6: Retention curve of phosphate during ceramic NF with model sewage. Phosphate was added after 60, 75, and 120 minutes of filtration (dark grey, black, and light grey, respectively). When the system stabilised three samples were taken (grey crosses in Figure 5a-c).

The results of the zeta potential analysis of ceramic NF membranes with and without a fouling layer are presented in Figure 7. When compared to the clean membranes in a NaCl solution, the membranes with fouling layer were more negatively charged. This can be explained by the negative charge of sodium alginate present in the model sewage (Simon et al., 2013; Zhao et al., 2018). However, when phosphate was present in the solution, the membranes without fouling layer were more negatively charged (-37 mV at pH 7) than in the presence of the fouling layer (-31 mV at pH 7)(Figure 7). This could indicate that the fouling layer reduced the effect of the phosphate adsorption on the membrane layer which lead to a lower phosphate retention. Thus, three phenomena caused the reduction of the phosphate retention: (i) cake-enhanced concentration polarisation, (ii) the reverse dilution effect, and (iii) the lower zeta potential on the membranes.
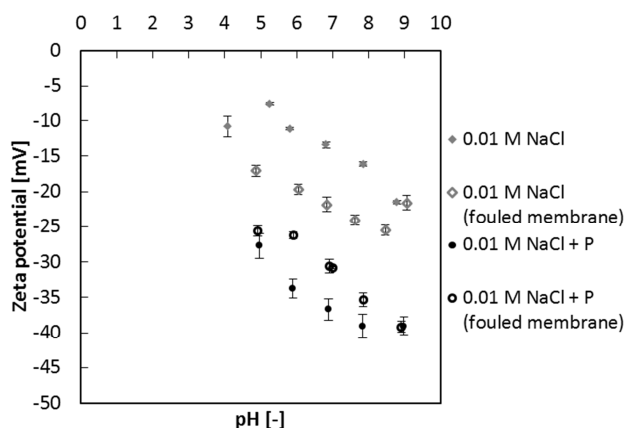
Figure 7: Zeta potential of ceramic NF membrane at a pH range of 4 to 9 using a solution of 0.01 M NaCl (diamonds) and NaCl with phosphate (dots) for membranes with and without a fouling layer. The fouled membranes were prepared by filtering model sewage for over 2 hours.

Conclusions

In this chapter the phosphate retention during ceramic NF was reported for phosphate reclamation purposes from municipal sewage. The phosphate retention during ceramic NF in a (monovalent) salt solution was 76 to 99% for a pH from 5 to 9, respectively, probably due to electrostatic repulsion. Specific adsorption of phosphate onto the membrane surface increased the membrane charge and thus the electrostatic repulsion. However, this effect was negatively influenced by multivalent counter ions such as magnesium, resulting in a drop in phosphate retention to only 42 to 44% for a change in pH from 5 to 9, respectively. The phosphate retention was lower due to a lower zeta potential which was caused either by adsorption of magnesium ions on the

membrane surface and/or suppression of the diffuse double layer due to presence of magnesium ions.

The fouling on ceramic NF membranes also reduced the phosphate retention (43-44%). Even though the model foulant sodium alginate is negatively charged, the zeta potential on the membrane surface decreased in the presence of the fouling layer compared to a clean membrane. Moreover, occurrence of cake-enhanced concentration polarisation and the reverse dilution effect also contributed to the reduced phosphate retention in the presence of a cake layer.

Acknowledgements

Chapter 5

FOULING CONTROL IN CERAMIC NANOFILTRATION MEMBRANES USING MUNIPAL SEWAGE

'Insane in the membrane.'
Song by Cypress Hill

This chapter is based on:

FOULING CONTROL IN CERAMIC NANOFILTRATION MEMBRANES USING MUNIPAL SEWAGE

Abstract

Knowledge on fouling control methods for ceramic nanofiltration membranes using municipal sewage is limited. The most commonly used method, chemical cleaning, especially when using sodium hypochlorite for removal of organic fouling, negatively impacts (i) the glass seal layer of tubular ceramic nanofiltration membranes and (ii) the environment, and should be limited as much as possible. In this research, first, the well-known fouling control methods polymeric for micro- and ultrafiltration membranes, hydraulic backwash and forward flush, were studied on ceramic nanofiltration membranes. Second, a precoat method was combined with a chemical reaction to aid the detachment of the formed cake layer. In this method, a precoat layer is filtered atop of the membrane surface before the start of filtration. The precoat layer then acts as a barrier between the foulants and the membrane surface. After filtration, the precoat layer reacts with the cleaning reagent underneath the fouling layer to enable fast removal of fouling. Results showed that hydraulic backwash was not effective to be used for this type of membranes. Forward flush was able to maintain a higher flux but the relative production downtime was high. Reaction based precoat was most effective in maintaining a high flux and resulted in the highest net water production. Two reaction based precoat methods were tested of which the reaction of calcium carbonate with citric acid was more effective than a Fenton reaction.

1. Introduction

Worldwide water scarcity creates a need for different water sources such as municipal sewage (Bixio et al., 2005; Raffin et al., 2013; Rietveld et al., 2011). Since two decades, the interest for ceramic nanofiltration (NF) has emerged for this purpose. Several characteristics make ceramic membranes suitable: its resistance to high temperatures, pressures, and concentrations of chemicals (Guerra and Pellegrino, 2013; Lee et al., 2015; Van Gestel et al., 2003; Weber et al., 2003). Furthermore, ceramic NF membranes are less susceptible to organic fouling than polymeric NF (Lee et al., 2013; Zhao et al., 2018).

One of the largest challenges of using membranes for treatment of municipal sewage is controlling fouling on the membrane surface in order to produce as much water as possible. The two most important performance indicators for fouling control

strategies are: (i) keeping the filtration down-time as low as possible and (ii) maintaining a high flux during filtration. Both of these aspects contribute to a higher water production.

The most common cleaning method used for ceramic membrane filtration is by chemicals (Hunter, 1981; Kramer et al., 2015; Puhlfürß et al., 2000; Weber et al., 2003; Zebić Avdičević et al., 2017). Depending on the type of fouling, sodium hypochlorite, acid solutions, and/or base solutions are the most commonly used chemicals to clean the membranes. Chemical cleaning is effective for the removal of irreversible fouling. However, when only applying chemical cleaning the permeability is, on average, low during the filtration cycle; resulting in a low water production. Moreover, from a sustainability point of view fouling control methods with a lower chemical consumption are preferred.

Previous research showed that long term use of chemical cleaning, such as sodium hypochlorite, damages the glass seal layer at the edges of tubular ceramic NF membranes (Kramer et al., 2019). Therefore, chemical treatment using sodium hypochlorite should be avoided.

In literature, research on alternative fouling control method using ceramic and polymeric NF is limitedly available. However, for polymeric ultrafiltration (UF) and microfiltration (MF). Backwash and forward flush are the most commonly used methods for polymeric UF and MF to remove hydraulic reversible fouling (Crittenden et al., 2012). Applying hydraulic backwash or forward flush has the benefit of keeping the permeability higher compared to regular filtration. The advantage of forward flush over backwash is that feed water can be used to flush the membrane without produced water loss, which results in a higher net water production. Much variation in backwash and forward flush methods can be found for polymeric UF and MF, e.g. using a combination of backwash and forward flush, cross-flushing with pressure pulsing (Kennedy et al., 1998), air-enhanced backwashing (Remize et al., 2010; Verberk, 2005). The filtration layer of polymeric NF membranes is thin and fragile which makes them not suitable for these methods. However, these methods could have potential for removal of organic fouling during ceramic NF, since these membranes are more robust.

Another fouling control method found in literature is enhanced precoat engineering (EPCE®) used for polymeric UF and MF (Galjaard et al., 2003, 2001). In this method, a suspension is dosed on the membrane (the precoat layer) to form an easily removable and permeable layer on the membrane. During filtration the fouling attaches or adsorbs onto the precoat layer instead of on the membrane. When the threshold pressure is reached, the membrane will be hydraulic backwashed. Then, during backwash the cake layer detaches easily from the membrane (Galjaard et al., 2003, 2001). Alternatively, precoating using coagulants has been used to enable UF

membranes to remove natural organic matter (Yonekawa et al., 2004). These methods have not been tested on ceramic NF so far.

Therefore, several fouling control protocols were studied to control fouling in ceramic NF, filtering high municipal sewage. First, several commonly known methods for polymeric UF membranes were tested on ceramic NF: hydraulic backwash and forward flush. Second, a reaction based precoat was tested, combined with chemical reactions to enhance the detachment of the cake layer, using both a Fenton reaction and a calcium carbonate reaction with acid, forming carbon dioxide.

The experiments were realised under lab conditions using the model compound sodium alginate to mimic fouling on the membranes. Sodium alginate is commonly used as a surrogate for extracellular polymeric substance (EPS) which is one of the largest contributors to fouling in organic loaded waste streams (Arndt et al., 2016; Daemi and Barikani, 2012; El-Mohdy, 2012; Katsoufidou et al., 2007; van den Brink et al., 2009; Van Der Bruggen et al., 2003; Ye et al., 2005).

2. Materials & Methods

2.1 Membranes
Filtration experiments were performed using ceramic NF membranes with a molecular weight cut-off (MWCO), as indicated by the manufacturer, of 450 Da, a mean pore size of 0.9 nm, and an open porosity of 30-40%. The actual MWCO was measured regularly, the results follow later in this paragraph. Two different membrane configurations were used; consisting of (i) four large membranes in a tandem, and (ii) one small membrane. First, the hydraulic backwash experiments were executed with the large membranes. However, these membranes were damaged during the tests see section 3.1, and could not be used for further studies. Therefore, the alternative membrane configuration, with smaller membranes, was used for the other experiments. The large membrane consisted of a 19 channel tube with a length of 1200 mm and an effective membrane area of 0.25 m^2. The small membrane has a single-channel, tubular configuration with a length of 100 mm and an effective filtration area of 0.163 dm^2 (Inopor GmbH, Germany).

2.2 Filtration setup
Ceramic NF experiments were performed with a cross-flow filtration system using a pneumatic diaphragm pump (Hydra-cell) with a pulsation dampener. The feed water was recirculated; both the permeate and the concentrate were fed back into the feed tank, except for the sampling volume, which was a negligible amount (<0.1%). In order to ensure that the feed water quality remained constant during the experiment, feed water samples were analysed regularly.

The experiments using small and large membrane configurations were conducted with slightly different conditions at room temperature. When using the small configuration, the single pass water recovery was < 1% and the flux was 50-60 L·(m^2·h)$^{-1}$, unless otherwise specified, and a cross-flow velocity of 1.0-1.2 m·s^{-1}. In the experiments using the configuration with the large membrane, a recirculation pump was added to the setup to reach a cross-flow velocity of 1.0-1.2 m·s^{-1}. The flux of these membranes was between 15-40 L·(m^2·h)$^{-1}$, unless otherwise specified, and the water recovery 50%. The experiments with both configurations were conducted at a transmembrane pressure (TMP) of 4.5-5.5 bar.

Temperature correction of permeability

In order to correct for the temperature, the following equation (Equation 1) was used to calculate the permeability of the membrane:

$$L_{20°C} = \frac{J \cdot e^{-0.0239 \cdot (T-20)}}{\Delta P} \qquad \text{(Equation 1)}$$

where, $L_{20°C}$ is the temperature-corrected permeability at 20 °C (L·(m^2·h·bar)$^{-1}$), T is temperature of water (°C), J is membrane flux (L·(m^2·h)$^{-1}$), and ΔP is transmembrane pressure (bar). All permeability values were temperature-corrected to 20 °C (Mulder, 1996).

Hydraulic permeability of clean membranes

A demineralised water filtration test was performed after chemical cleaning and before each filtration experiment to determine the hydraulic permeability. The hydraulic permeability indicates if the (ir)reversible fouling was removed during chemical cleaning. These hydraulic permeability tests were executed under similar conditions as the filtration tests with a duration of 1 hour.

Relative production downtime

The relative production downtime (*RPD*) (min·h^{-1}) was calculated using Equation 2.

$$RPD = \frac{t_{cleaning}}{t_{filtration} + t_{cleaning}} \left(\frac{min}{h}\right) \qquad \text{(Equation 2)}$$

where $t_{cleaning}$ is the duration of the cleaning and/or precoating and $t_{filtration}$ is the filtration time between cleaning two cleaning intervals (Table 2).

2.3 Model sewage

Fouling tests were performed using sodium alginate as model compound for sewage (Katsoufidou et al., 2007; Ye et al., 2005). The feed water composition consisted of 0.8 g·L^{-1} sodium alginate (Sigma-Aldrich), 1 mM NaCl (Sigma-Aldrich) as background salt concentration, 1 mM NaHCO$_3$ (Sigma-Aldrich) as buffer, and 3 mM CaCl$_2$ (Sigma-Aldrich) adjusted to pH of 7. Sodium alginate is known to form a gel in the presence of calcium; sodium alginate aggregates according to the so called egg-box model which

promotes cake development during filtration (Alazmi, Radhi, 2010; Katsoufidou et al., 2007; van den Brink et al., 2009; Zhao et al., 2015). The model sewage contains a higher organic load than municipal sewage: with the model sewage a pre-sieved municipal sewage experiment of five days could be simulated in two hours (Kramer et al., 2015).

2.4 Fouling control methods

2.4.1 Hydraulic backwash
The effect of hydraulic backwash was tested using the large membrane configuration. The experiment was performed at a constant flux of 30 L·(m²·h)⁻¹ using permeate water as backwash water. The hydraulic backwash was initiated when the permeability reached 10 L·(m²·h·bar)⁻¹: the hydraulic backwash pressure was 6 bar with a duration of 5 min. This process was repeated four times.

2.4.2 Forward flush
Forward flush cleaning was studied using the small membrane configuration. During forward flush the pressure on the membranes was released and feed water was used to flush away the cake layer. Moreover, the valve at the permeate side was closed to prevent flow through the membrane during forward flush. Preliminary results showed that forward flush was most effective with an interval of 20 min and a forward flush duration of 3 min; these conditions were used in this research. The influence of cross-flow was determined using four different cross-flow velocities: 0.4, 1.1, 2.2 and 4.3 m·s⁻¹ corresponding to Reynolds numbers of 2100, 4200, 6300, 12600, and 25300, respectively.

2.4.3 Reaction based precoat
Two different reactions were tested using the reaction based precoat method; a reaction to initiate a Fenton reaction and a reaction to create carbon dioxide vapour using calcium carbonate and acid. These experiments were performed using the small membrane configuration.

Reaction based precoat using a Fenton reaction
In a Fenton reaction iron works as a catalyst for hydrogen peroxide, resulting in an advanced oxidation reaction. Free radicals are formed being able to degrade organic matter (OM). Both iron forms, iron(II) and iron(III), react with hydrogen peroxide which are known as a Fenton (Equation 4&5) and a Fenton-like reaction (Equation 3&5) (Pignatello et al., 2006; Wang, 2008).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\cdot \ + H^+ \qquad \text{(Equation 3)}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\cdot \ + OH^- \qquad \text{(Equation 4)}$$

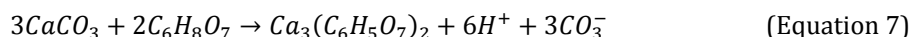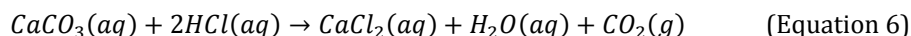$HO \cdot + OM \rightarrow OM_{oxid}$ (Equation 5)

Iron(III) chloride 41% solution (Merck) was used for the precoating suspension. Iron(III) chloride was diluted in demineralised water to the required concentration. Various concentrations were tested: 40, 420, 2100, and 4200 mg·L^{-1}. Moreover, the pH was adjusted to 5, 7, and 8 to determine the most effective pH, since it affects iron floc sizes (Bratby, 2006).

The precoating suspension was filtered on a clean ceramic NF membrane at laminar flow conditions with a cross-flow velocity of 0.4 m·s^{-1} at 5 bar with a duration of 10 min. Then, a fouling test was done using model sewage for 40 min as described before. Next, a hydrogen peroxide solution was dosed for 1, 5, or 10 min with a pH of around 2.5, since this is the optimal pH to initiate a Fenton or Fenton-like reaction (Galjaard et al., 2001). Only iron(III) was dosed, however, iron(III) converts into iron(II) in the presence of hydrogen peroxide (Equation 3). Thus, during dosage of hydrogen peroxide, both iron(II) and Iron(III) were present on the membrane surface resulting in a Fenton and a Fenton-like reaction. Finally, forward flush was executed at a cross-flow velocity of 1.1 m·s^{-1} for 5 min without pressure using feed water to remove the loosened cake layer. This procedure of precoating and hydrogen peroxide dosing was repeated three times.

The amount of iron which deposited on the membrane surface during precoating was measured and analysed using a mass balance. The iron concentration of the feed, concentrate, and permeate stream was analysed using the total iron test cell test using the NOVA 60 Spectroquant® (Merck) (Table 1).

Reaction based precoat using calcium carbonate
For the reaction based precoat using calcium carbonate two different acids were tested to initiate carbon dioxide release: hydrochloric acid (Equation 6) or citric acid (Equation 7 & 8).

$CaCO_3(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(aq) + CO_2(g)$ (Equation 6)

$3CaCO_3 + 2C_6H_8O_7 \rightarrow Ca_3(C_6H_5O_7)_2 + 6H^+ + 3CO_3^-$ (Equation 7)

$H_2CO_3(aq) \rightarrow H_2O(aq) + CO_2(g)$ (Equation 8)

A calcium carbonate suspension used for precoating was prepared from CaCO$_3$ powder (Merck). The powder was carefully mixed with water in a concentration of 100, 200, or 400 mg·L^{-1} to make a colloid suspension. To avoid dissolution of Ca^{2+} and CO$_3^{2-}$ the suspension was kept at a pH of 10, and to ensure uniformly distributed CaCO$_3$ nanoparticles, the suspension was sonicated at 40% amplitude for three hours (Kawashima et al., 2014). Then, the suspension was filtrated over the clean membranes for 10 min to create a precoat layer. After filtration with model sewage, the membrane was cleaned using citric acid or hydrochloric acid in a concentration of

400 mg·L^{-1} for a duration of 1, 5, or 15 min. This procedure of precoating and acid dosing was repeated three times.

The amount of calcium which was deposited on the membrane surface during precoating was measured and analysed using a mass balance. The calcium concentration of the feed, concentrate, and permeate stream was analysed using the calcium test cell test using the NOVA 60 Spectroquant® (Merck) (Table 1).

Table 1: Deposition of iron membrane surface during precoating derived from mass balance.

Precoating suspension, concentration iron chloride	Net Iron deposited	Precoating suspension, concentration CaCO$_3$	Net calcium deposited
40 mg·L^{-1}	0.2 mg	100 mg·L^{-1}	104 mg
420 mg·L^{-1}	97 mg	200 mg·L^{-1}	239 mg
2100 mg·L^{-1}	406 mg	400 mg·L^{-1}	801 mg
4200 mg·L^{-1}	626 mg	-	-

2.4.4 Chemical cleaning

After each experiment, the membranes were chemically cleaned to remove all fouling. The chemical cleaning was carried out by soaking the membranes in a 0.1% sodium hypochlorite solution for 1 hour.

2.5 MWCO analysis

The MWCO of the ceramic NF membranes were measured before and after each experiment to monitor the quality of the membranes. Tam & Tremblay (1991) described a method to calculate the MWCO; this method is widely used for the determination of the pore size distribution of polymeric and ceramic membranes (Blumenschein et al., 2016; Causseranda et al., 2002; Shirley et al., 2014; Van Der Bruggen and Vandecasteele, 2002).

The MWCO was investigated by filtering a mixture of five different polyethylene glycol (PEG) molecules (200, 300, 400, 600, and 1000 Da) (Sigma-Aldrich) each in a concentration of 6 mg·L^{-1}. The same settings were used during filtration as described for the hydraulic permeability.

The feed and permeate samples were analysed using HPLC (Shimadzu) equipped with size exclusion chromatography columns (SEC, 5 μm 30 Å PSS SUPREMA) and a RID-20A refractive index detector. The carrier liquid in the HPLC was ultrapure water at a flow rate of 1 mL·min^{-1}. From the HPLC analyses, the molecular weight distribution

curves of the dissolved PEG molecules in the feed and permeate were derived. These were transformed into retention curves by calculating the rejection percentage of a PEG with a certain molecular weight (R_i) using Equation 4.

$$R_i(\%) = \left(\frac{c_{i,feed} - c_{i,permeate}}{c_{i,feed}} \right) \cdot 100\% \qquad \text{(Equation 9)}$$

where, $c_{i,\,feed}$ is the PEG concentration in the feed samples and $c_{i,\,permeate}$ in the permeate samples. Afterwards, the experimental retention curves were described by a log-normal model as function of molecular weight (MW) and MWCO using Equation 5 (Shang et al., 2017; Shirley et al., 2014; Van Der Bruggen and Vandecasteele, 2002). Equation 5 was used to model retention curve to be able to calculate the MWCO.

$$\sigma(MW_s) = \int_0^{MW_s} \frac{1}{s_{MW}\sqrt{2\pi}} \cdot \frac{1}{MW} \cdot exp\left[-\frac{(\ln(MW) - \ln(MWCO) + 0.56 \cdot s_{MW})^2}{2 \cdot s_{MW}^2} \right] \cdot dMW \quad \text{(Eq. 10)}$$

where, $\sigma(MW_s)$ is the reflection coefficient for a PEG with a molecular weight MW_s, s_{MW} is the standard deviation of the molecular weight distribution.

In this method, the separation of the PEG molecules is assumed to be only based on size exclusion with negligible solute diffusion. Therefore, the molecular size of the PEG solutes (d_s in nm) is correlated to their molecular weight (MW in Da) as shown in Equation 6 (Shang et al., 2017; Shirley et al., 2014).

$$d_s = 0.065 \cdot MW^{0.438} \qquad \text{(Equation 11)}$$

Finally, the MWCO was estimated at 90% of the retention curve (Mulder, 1996; Van Der Bruggen and Vandecasteele, 2002).

3. Results & Discussion

3.1 Hydraulic backwash
First, the MWCO of the four large membranes was determined to ensure the right quality of the membranes. Then, the effect of hydraulic backwash was studied by comparing it with the permeability of the membrane and without cleaning. In the experiment without hydraulic backwash the permeability decreased from 22 to 4.5 L·(m²·h·bar)⁻¹ within two hours (Figure 1a). After hydraulic backwash was applied, an increase in permeability was shown; 43, 37, 31, and 25%, respectively, resulting in a higher permeability than without cleaning and thus postponing the chemical cleaning. However, the performed hydraulic backwash had a high relative production downtime (Table 2).

Afterwards, the effect of hydraulic backwash on the filtration layers was analysed by determining the MWCO of the membranes. The results showed that the MWCO of the membranes after the hydraulic backwash experiments was too high to measure.

Therefore it was concluded that the ceramic NF membranes were damaged during the backwash operation. After opening the membrane modules, the damage on the edges of the membranes was clearly visible; resulting in the transport of feed water to the permeate via the support layer of the membranes (Figure 1b). The experiments were repeated at lower pressures of 1 and 2 bar. However, this did not affect the permeability compared to the permeability without cleaning; apparently the cleaning back flux or hydraulic sheer force was too low to have an effect. This is in line with the finding of Chang et al. (2017) who studied hydraulic backwash parameters of polymeric membranes treating surface water. They found that the hydraulic backwash strength should be 2.1 times the filtration flow. The backwash strength was expressed as the ratio between the backwash flux to permeate flux under constant flux, or the ratio of backwash pressure to operating pressure under constant pressure. In our case, at a pressure of 1 and 2 bar, a backwash strength of 2.1 was not reached.
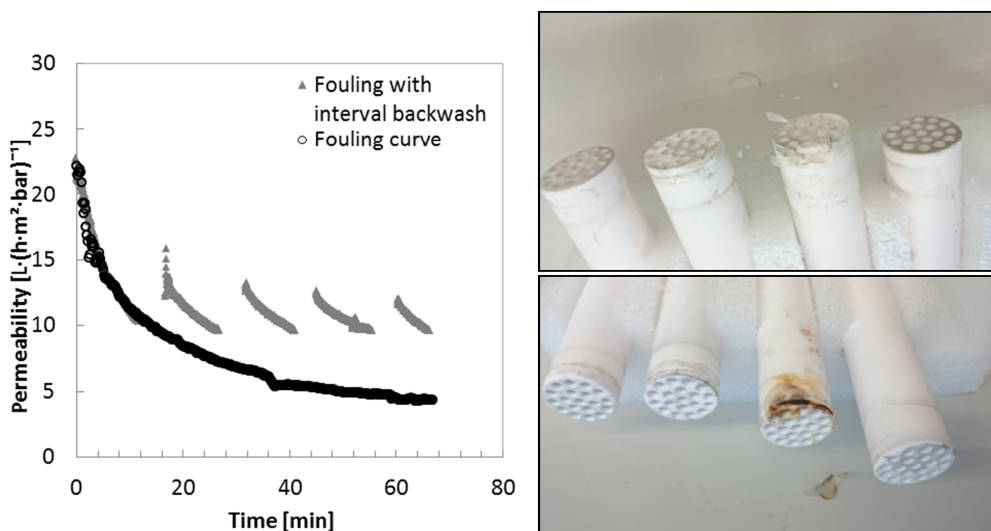
Figure 1: (a) Permeability in time of ceramic NF using model sewage with and without interval hydraulic backwash performed with the configuration with large membranes. Hydraulic backwash was applied at 6 bar pressure for 5 minutes when the permeability had reached 10 L·(m²·h·bar)⁻¹.
(b) Pictures of damage of the ceramic NF membranes after hydraulic backwash was applied. The layer on the edges of the membrane were damaged. Therefore, the feed water can flow directly to the permeate via the support layer of the membrane.

Table 2: Summary of the cleaning protocol of different fouling control methods.

Cleaning method	Membrane configuration	Cleaning interval	Cleaning time	Precoat time	Relative production downtime
Forward flush	Small	20 min	3 min	NA	7.8 min·h^{-1}
Reaction based precoat: Fenton	Small	40 min	1 min	10 min	16.1 min·h^{-1}
Reaction based precoat: CaCO$_3$	Small	40 min	1 min	10 min	16.1 min·h^{-1}

3.2 Forward flush cleaning

First, the MWCO of the small membranes, used for these experiments, were measured to be between 602 and 649 Da. The MWCO remained constant for the whole duration of this study. Next, interval forward flush cleaning was studied using feed water at 20 min intervals, since these intervals were found to be the most effective in removing reversible fouling (results not shown). Various cross-flow velocities, ranging from 0.4 to 4.3 m·s^{-1}, during forward flush were compared. At a cross-flow velocity of 0.4 m·s^{-1} the flow was laminar and at higher cross-flow velocities the flow was turbulent. The fouling experiment was performed with a cross-flow velocity of 1.1 m·s^{-1}. The results indicate that the effect of the forward flush was similar for all cross-flow velocities (Figure 2). This is in contrast with results obtained with polymeric UF, where forward flush is commonly applied, and where higher forward flush cross-flow velocities have resulted in higher fouling removals (Crittenden et al., 2012; Heijman et al., 2007; Verberk, 2005). This could be explained by the weak attachment of the fouling layer on the membranes surface of ceramic NF than polymeric NF membranes (Lee et al., 2013; Zhao et al., 2018), which makes a low cross-flow sufficient to remove organic fouling.

The decrease in permeability – meaning the accumulation of fouling – reduced with each forward flush cycle until a steady state was reached (Figure 2b). The impact of the forward flush (the hydraulic removal) thus increased with each cycle, and fouling became more reversible. This can be explained by the fact that irreversible fouling stabilises in time (Bacchin et al., 2006).
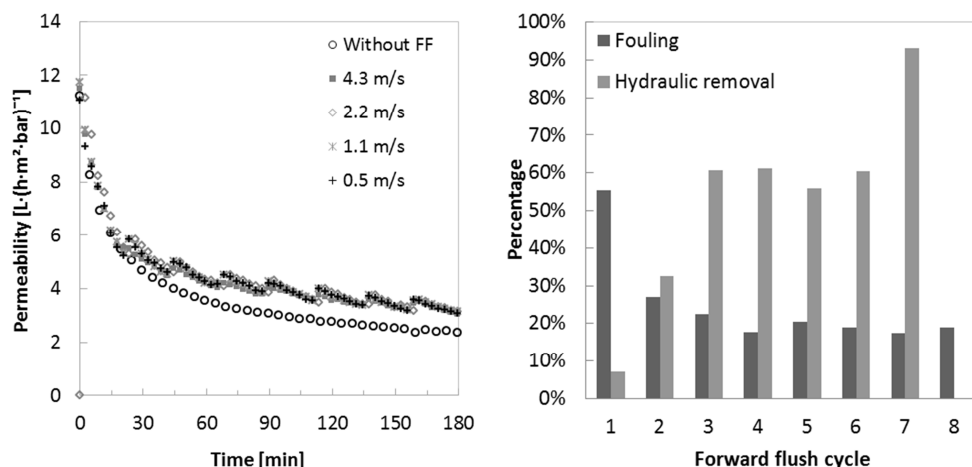
Figure 2: (a) Permeability in time of ceramic NF using model sewage with and without interval forward flush (20 min). Different cross-flow velocities during forward flush were compared, ranging from 0.5 to 4.3 m·s⁻¹. (b) Fouling and hydraulic removal per forward flush cycle. Forward flush cycles of 20 minutes were executed.

3.3 Reaction based precoat

3.3.1 Reaction based precoat using a Fenton-reaction

In order to test the effectiveness of a Fenton (like) reactions, two preliminary tests were executed. Firstly, the fouling curve of a membrane with a precoat layer was compared with a fouling curve of a clean membrane; the shape of the curve was more or less similar and both curves ended at the same value after 130 min (Figure 3a). Secondly, the effect of hydrogen peroxide dosing was tested on both the untreated and the precoated membranes. The permeability of the uncoated membrane increased with 8% after the first hydrogen peroxide cleaning, while the precoated membranes showed an increase of about 75% in permeability (Figure 3b), which is a clear indication of the occurrence of Fenton (like) reactions.

Next, several experiments were executed to optimise the Fenton reactions. Firstly, the feed suspension, used for the precoating, of iron chloride was prepared at pH 5, 7, and 8, which affects the size and strength of the iron flocs (Bratby, 2006). The deposition of the flocs on the membrane surface was influenced by the size and strength of the flocs and, thus, determines the stability of the precoat layer (Galjaard et al., 2001). The highest recovery was obtained when the reaction was realised at a pH of 7 (Figure 3c). Thus, the deposition of the flocs was most stable with a feed suspension of pH 7. Secondly, the concentration of iron chloride in the feed suspension, used for precoating, was optimised. When comparing feed concentrations of 42, 420, 2100, and

4200 mg·L⁻¹ iron chloride, the concentration of 420 and 4200 mg·L⁻¹ iron chloride performed the best (Figure 3d). When precoating with a feed concentration of 420 mg·L⁻¹ iron chloride, net 97 mg iron deposited on the membrane surface (Table 1). The rest of the suspension could be reused.
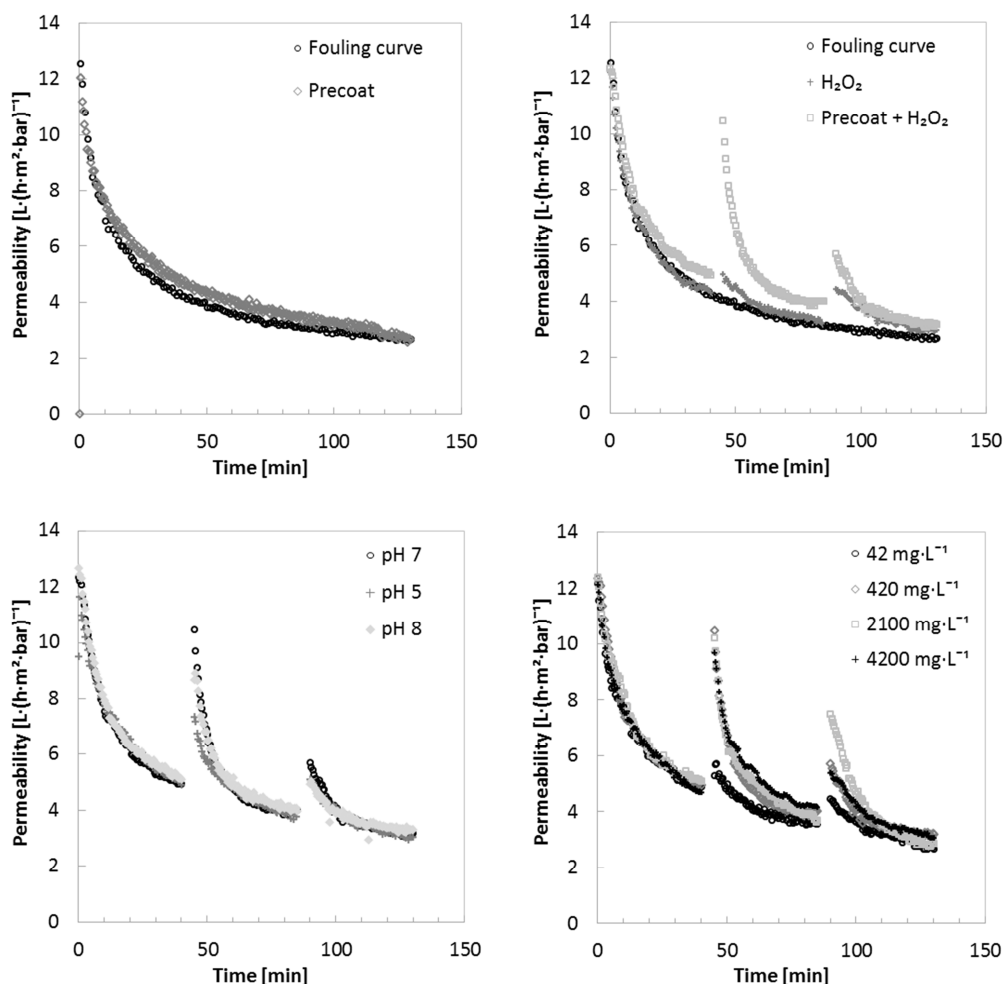

Figure 3a-d: Permeability in time of ceramic NF using model sewage using (a) untreated and iron chlorite precoated membranes. (b) Comparison of hydrogen peroxide cleaning on an untreated and precoated membrane. (c) Comparison of precoating suspensions of pH 5, 7, and 8. (d) Comparison of different precoating suspension concentrations.

After the first reaction based precoat, the method was repeated a second time including precoating and hydrogen peroxide treatment. Since not all fouling was

removed, probably the precoat was not deposited on the membrane surface itself, but on the fouling layer on the membrane surface. The results therefore showed that the second cleaning was less effective than the first cleaning (Figure 3b-d). The increase in irreversible fouling was probably caused by the fact that the precoat layer was not evenly distributed on the membrane surface due to the presence of fouling on the membrane surface. Galjaard et al. (2001) also saw an increase in irreversible fouling after the first cycle because the membrane surface was not entirely covered with the dosed precoat material. Causing the non-protected layer to foul and not being restored after backwash.

3.3.2 Reaction based precoat using calcium carbonate

The effectiveness of a calcium carbonate reaction with acid was studied with a series of preliminary tests. Firstly, the fouling curves of an untreated and a precoated membrane were compared; the permeability drop of the precoated membrane in comparison with the un-coated membrane was slower but after 130 min the curves were at the same permeability value (Figure 4a). Secondly, the effect of an acid cleaning, using either citric acid or HCl, on the permeability of an untreated fouled membrane was studied. The citric acid cleaning of the untreated membrane resulted in a permeability increase of 27%, whereas HCl was less effective with 11% permeability increase (Figure 4b). Thirdly, the fouled precoated membranes were cleaned with HCl, causing an increase of 12% in permeability (Figure 4c). However, the effect was much greater when cleaning the fouled precoated membranes with citric acid: 76% permeability increase. This is probably due to the fact that citric acid is a weak acid whereas HCl is an strong acid. When all H^+ from HCl would react with calcium carbonate, the pH increases. This will not happen in the presence of citric acid: the acid molecule will still be able to react with calcium carbonate and the pH will remain low which keeps the reaction going.

Then, the concentration of calcium carbonate in the feed suspension, used for precoating, was optimised. When comparing a feed concentration of 100, 200, and 400 mg·L^{-1} calcium carbonate, the concentration of 200 and 400 mg·L^{-1} calcium carbonate showed the highest permeability recovery after cleaning (Figure 4d). This relates to a deposition of 239 and 801 mg calcium carbonate on the membrane surface during precoating (Table 1).

Again, the second cleaning of the reaction based precoat was less effective in permeability increase than the first one (Figure 4c-d). Probably, a calcium carbonate deposition was less stable during the second interval, since not all fouling was removed during the first interval, similar results were observed by the reaction based precoat using the Fenton reaction (Figure 3a-d).
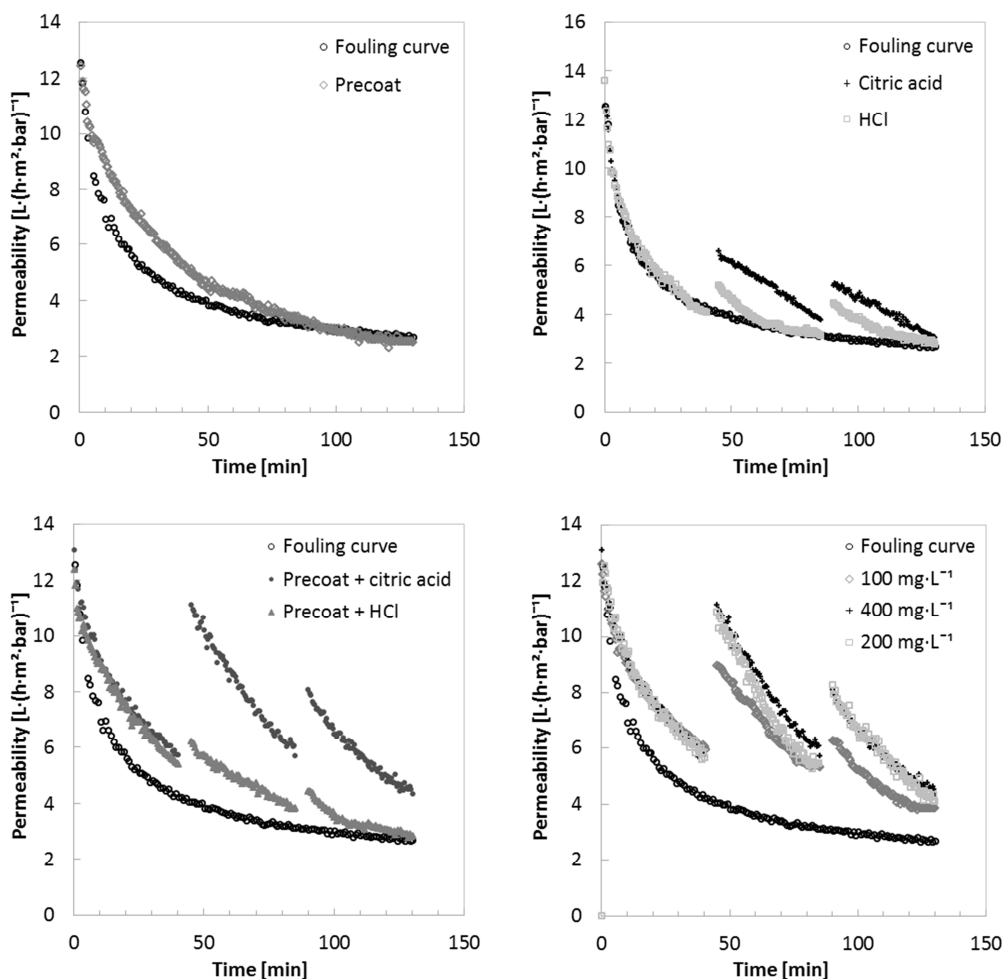
Figure 4: Permeability in time of ceramic NF using model sewage using (a) untreated and calcium carbonate precoated membranes. (b) Comparison of hydrochloric acid and citric acid on an untreated membrane. (c) Comparison of hydrochloric acid and citric acid on an precoated membrane. (d) Comparison of different precoating suspension concentrations.

3.4 Net water production

To compare the various fouling control methods, the net water production was calculated for all experiments and compared to a situation without fouling control with a duration of 130 min including downtime. For none of the fouling control methods permeate water was used. The water production of membranes cleaned with forward flush and reaction based precoat, using the Fenton reactions, were more or less similar to the curve without the use of a fouling control method, resulting in a net

water production of 51 L·m^{-2} for a duration of 130 min (Figure 5). Reaction based precoat using calcium carbonate produced the most net water with 80 L·m^{-2} (58% more than without cleaning), even though this method requires a high relative production downtime of 16.1 min·h^{-1} (Table 2). Moreover, calcium carbonate and citric acid are biodegradable compounds and thus environmentally suitable for postponing chemical cleaning of ceramic NF membranes.
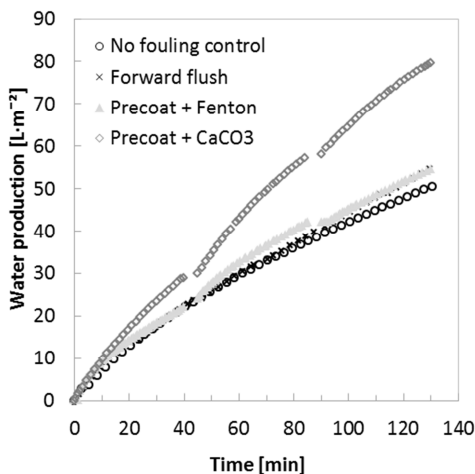
Figure 5: Net water production in litre per membrane area during ceramic NF. Different fouling control methods compared with no fouling control (○): interval forward flush (x), reaction based precoat with Fenton reaction (Δ) and CaCO₃ reaction (◊).

Conclusions

Various fouling control methods of ceramic NF were studied, resulting in the following conclusions:

- Hydraulic backwash was not an appropriate cleaning method for ceramic NF since the glass seal layer at the edges of the membranes was damaged due the hydraulic sheer force. At lower pressure hydraulic backwash the fouling was not removed.
- Interval forward flush increased the flux of the ceramic NF. However, the water production was not higher than during fouling without forward flush, due to the high relative production downtime of 7.8 min·h^{-1}.
- During forward flush the cross-flow velocity had no effect on the efficiency.

- Reaction based precoat was tested with two different reactions. The calcium carbonate reaction was more effective in fouling removal than the Fenton based reactions.
- The net water production of using reaction based precoat with calcium carbonate was the highest of all fouling control methods.

Acknowledgements

Chapter 6

CONCLUSIONS & OUTLOOK

'The important thing is not to stop questioning. Curiosity has its own reason for existence.'

Albert Einstein

CONCLUSIONS & OUTLOOK

Conclusions

In this thesis the potential of the application of ceramic nanofiltration (NF) for municipal sewage was studied. First, the effectiveness of treating raw sewage using ceramic NF, including the possibility of ceramic NF as pretreatment for RO, was studied. Afterwards, the quality and robustness of the ceramic NF membranes was analysed to determine the suitability of these membranes for this application. Then, the phosphate retention for ceramic NF was studied, and the interference of various compounds present in sewage, to determine the best strategy for phosphate recovery from sewage. Finally, various, alternative fouling control methods were studied to find the most effective and sustainable filtration protocol.

Overall, it can be concluded that indeed ceramic NF has potential for direct treatment of municipal sewage, as pretreatment for RO, in terms of water production and organic matter removal. However, the quality of the ceramic NF membranes was not yet sufficient to use them for this purpose on a large scale. The quality of the pristine membranes varied within one batch, and the robustness of the membranes was less than expected; i.e. long-term chemical cleaning damaged the glass seal edge of the membranes.

In the following the specific conclusions of the thesis are high-lighted.

Feasibility of sewer mining concept
Chapter 2 describes preliminary pilot scale experiments with ceramic NF and it was concluded that ceramic NF has a potential for treating raw municipal sewage. Filtration could run effectively up to 5 days without cleaning required. While, chemical cleaning could maintain the performance of the ceramic membranes high with at least 93% permeability recovery. The chemical cleaning protocol consisted of sodium hypochlorite (0.1% for 45 min) and hydrochloric acid (0.1 mol·L^{-1} for 15 min) treatment. This gave a low relative production downtime of 0.6 min·h^{-1}.

The organic matter rejection by ceramic NF membranes was high (81% COD rejection) which led to a concentrate stream with a high organic load. The permeate water of the ceramic NF had a low fouling potential for RO treatment which was analysed using the Membrane Fouling Simulator. The fouling potential of the permeate was as low as the potential of Dutch drinking water. Thus, ceramic NF was regarded as an suitable pretreatment for RO.

During the experiments the phosphate retention by the ceramic NF varied.

Quality and robustness of ceramic NF membranes

When treating municipal sewage, ceramic NF membranes should form an important barrier against small colloids and organic molecules which are abundantly present in sewage. Therefore, regularly and accurately monitoring of the quality of ceramic NF membranes is of utmost importance to ensure the integrity. In order to analyse the quality of the membranes properly, an extension to the existing MWCO method was developed to be able to quantify the defects in the membranes. In the studied commercial ceramic membranes these defects were frequently detected: membranes of different pore sizes and geometries from various suppliers were tested. The MWCO, both uncorrected and corrected, of pristine membranes diverted often from the purchase cut-off specifications. Moreover, large variations of quality of membranes within one batch were measured (Chapter 3).

Long-term treatment with chemicals to mimic one year of operation, especially sodium hypochlorite, which is widely used to clean organic fouling from ceramic membranes, damaged the tubular ceramic NF membranes. . However, it was found that specifically the glass seal at the edges of the membranes was damaged. Re-sealing of the edges of the membranes recovered the original properties of the tubular membranes (Chapter 3).

Phosphate retention of ceramic NF membranes

The phosphate retention during ceramic NF was studied for potential phosphate recovery purposes. The phosphate retention was high in a monovalent salt solution due to electrostatic repulsion on the membrane surface: 76% to 99%, respectively, with an increasing pH from 5 to 9. Zeta potential measurements showed that the membrane charge increased in the presence of phosphate. This can be explained by specific adsorption of phosphate onto the membrane surface which caused an increase in the surface charge. However, multivalent counter ions influenced this effect, resulting in a drop in phosphate retention. In the presence of magnesium ions, the phosphate retention was only 42% to 44% for pH 5 to 9, respectively. Magnesium ions adsorbed onto the membrane surface and/or magnesium ions suppressed the diffuse double layer on the membrane surface which led to a lower negative charge and thus a lower phosphate retention (Chapter 4).

Moreover, an organic fouling layer (model sewage) on the membrane surface also caused the phosphate retention to drop to 43%. This was probably due to the lower zeta potential and thus a lower phosphate retention (Chapter 4).

Fouling control during ceramic NF

The most commonly used method for fouling control in ceramic NF is chemical cleaning, specifically sodium hypochlorite, for removal of organic fouling. Chemical cleaning impacts the environment and should be limited as much as possible. Even

though hydraulic backwash seemed a promising method to maintain a high flux during filtration, the glass seal layer at the edges of the membranes was damage due the hydraulic sheer force. Low pressure hydraulic backwash was not effective in removing the fouling layer on the membrane surface (Chapter 5).

Forward flush increased the flux during ceramic NF using model sewage. However, due to the high relative production downtime of forward flush the net water production was similar to the net water production without fouling control. Different crossflow velocities were studied in laminar and turbulent flow: the crossflow velocity did not have an effect on the performance of the forward flush (Chapter 5).

Finally, reaction based precoat was studied for two different reactions: calcium carbonate with acid resulting in carbon dioxide bubbles, and Fenton(-like) reaction. The reaction based precoat using calcium carbonate resulted in the highest net water production of all fouling control methods tested (Chapter 5).

Outlook

Improvements to production quality and robustness of the ceramic NF membranes
In order to make the sewer mining concept feasible, the robustness of the ceramic NF membranes should be improved. Specifically, the quality of the glass seal layer at the edges of the tubular membranes needs to be improved. A stronger seal layer at the edges of the membranes will enable chemical cleaning for removal of fouling from the membrane surface without creating defects. Also, the hydraulic backwash during ceramic NF would be made possible with a stronger seal layer at the edges of the tubular membranes.

Moreover, the stability of the production process of the ceramic NF membranes should be improved, since the quality of the membranes (in terms of MWCO) differs within one batch. This was probably caused by the application of the filtration layer on the support layers using the sol-gel method (Puhlfürß et al., 2000), which is a delicate process, sensitive to external conditions and thus resulting in variation in the quality of the membranes.

Further research
Apart from the robustness and quality of the membranes, this thesis shows that phosphate recovery from municipal sewage is not constant, using ceramic NF. The phosphate retention in clean water is high: 76% or higher. However, retention of phosphate strongly depends on pH and the presence of multivalent ions and a fouling layer (Chapter 4). This resulted in a varying phosphate retention during ceramic NF using raw municipal sewage (Chapter 2) and a presence of phosphate in both

permeate and concentrate streams of the ceramic NF. However, to maximise recovery of phosphate, it is preferred to have the highest possible concentration in either the concentrate or the permeate. In case of a high phosphate retention by the ceramic NF membrane, the phosphate could be recovered from the sidestream of the anaerobic digester by using struvite crystallisation (Münch and Barr, 2001; Schulze-Rettmer, 1991). When this last scenario is preferred, ceramic NF membranes should be developed that are able to reject phosphate under all conditions.

For efficient separation of ions, tight ceramic NF membranes are required with a MWCO smaller than 400 Da. The most commonly applied method for a filtration layer onto ceramic NF membranes is the sol-gel method, but this method has its limitations: when producing a MWCO smaller than 450 Da the permeability of the membranes become very low, e.g. 0.5-1.5 $L·m^{-2}·h^{-1}·bar$ for 200 Da ceramic membranes (Tsuru et al., 2008). As an alternative, Shang et al. (2017) demonstrated the synthesis of tight ceramic NF by using atmospheric pressure atomic layer disposition (APALD). In this method, titanium dioxide is coated on commercially available ceramic NF membranes of 450 Da in one to three cycles of APALD. The average size of the active pores was effectively narrowed from 0.7 nm to 0.5 nm (or 450 to 300 Da), maintaining the permeability or the membrane relatively high.

Currently, these APALD coated ceramic NF membranes are also investigated for advanced water treatment, in the context of the European Interreg project DOC2C's, for the rejection of natural organic matter and sulphate from anion exchange brines *.

Other, ongoing, research focusses on oil/water emulsion separation using ceramic membranes. There is urgent need for this separation due to the growth of oil and gas, petrochemical, food, textile, leather and metal finishing industries which produce vast amounts of oily wastewater. When surface properties of the ceramic membranes are improved with chemical vapour deposition or APALD for this purpose. The surface charge of the membranes will be made strongly negative by coating with silicium carbide. The negative charge will repel negatively charged oil droplets and therefore reduce fouling *.

Cleaning of ceramic NF membranes remains important. the reaction based precoat showed to be a promising fouling control method for ceramic NF using modelled sewage. In the next step, this method should also be tested using raw municipal sewage. During these tests the influence of daily and seasonal variations of municipal sewage can then further be analysed. Chapter 4 showed that forward flush did not result in a higher net water production compared to no fouling control. However, this could be different using raw sewage, since the composition of the water is different from the model sewage. Therefore, this method should also be studied under other circumstances as well. Fujioka et al. (2018) performed fouling control tests using ozonated water and surface flushing. Such alternative, periodical flushes with e.g.

ozonated water could reduce the conventional chemical cleaning frequency and should be compared to the proposed precoat and the forward flush methods.

LITERATURE

'If I have been able to see further, it was only because I stood on the shoulders of giants.'

Isaac Newton.

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'Cuiusvis hominis est errare, nullius nisi insipientis in errore perseverare.'

'Everybody can wander, only fools persevere in their wandering.'

'Dwalen kan iedereen, maar alleen dwazen volharden in hun dwaling'.

Cicero

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CURRICULUM VITAE

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Education

2014 – 2019   PhD candidate – Delft University of Technology
'Ceramic nanofiltration as key step for reclamation of water, nutrients and energy using sewage'.

2009 – 2012   Master Water management – Delft University of Technology
Specialisation drinking water treatment.

Graduation Thesis – Delft University of Technology
Independent research 'Removal of organic micro pollutants in batch experiments mimicking riverbank filtration' supervised by prof. dr. ir. Jan-Peter van der Hoek.

Research internship – ITB Technical University of Bandung, Indonesia
Investigation of the performance of the water treatment company PDAM Bandung.

2005 – 2009   Bachelor Life Science & Technology – Delft University of Technology/University of Leiden

Research internship – LUMC Leiden University Medical Centre
Contribute to the research of human lactoferrin peptide, a protein which has anti-infective characteristics at the department of infectious diseases.

1999 – 2005   Gymnasium – St. Stanislas College Westplantsoen Delft

Experience

2018 – 2019   Education coordinator – Delft University of Technology
Responsible for the several bachelor and master courses involving water treatment and the online course for professionals 'Nanofiltration and RO for Water Treatment'.

2013 – 2014   Water technology consultant/process engineer – Witteveen+Bos
Contribute to international wastewater and water supply projects, responsible for e.g. the technological design and the water quality monitoring.

Water Supply Project Essakyir, Ghana
Prepare and execute commissioning of the new build drinking water treatment plant in Essakyir, Ghana. Training of local staff of Ghana Water Company Ltd. (GWCL) at location and in the Netherlands.

2012   Member of the accreditation committee – QANU (Quality Assurance Netherlands Universities)
Evaluate the quality of the education of the international water institute UNESCO-IHE according to the standard of the NVAO (Dutch-Flemish Accreditation Organisation).

List of Publications

Kramer, F.C., Shang, R., Heijman, S.G.J., Scherrenberg, S.M., van Lier, J.B., Rietveld, L.C., 2015. Direct water reclamation from sewage using ceramic tight ultra- and nanofiltration. Sep. Purif. Technol. 1–21. https://doi.org/10.1111/j.1747-6593.2011.00271.x.Olsson

Kramer, F.C., Shang, R., Scherrenberg, S.M., Rietveld, L.C., Heijman, S.G.J., Quantifying defects in ceramic tight ultra- and nanofiltration membranes and investigating their robustness, Sep. Purif. Technol. 219 (2019) 159–168. Doi:10.1016/j.seppur.2019.03.019

Kramer, F.C., Shang, R., Rietveld, L.C., Heijman, S.G.J., Influence of pH, multivalent counter ions, and membrane fouling on phosphate retention during ceramic nanofiltration (under review)

Kramer, F.C., Shang, R., Rietveld, L.C., Heijman, S.G.J., Fouling control in ceramic nanofiltration membranes during municipal sewage treatment (under review)

Conferences

Jul 2014   Speaker at International Conference on Inorganic Membranes (ICIM) in Brisbane, Australia.

Aug 2015   Speaker at IWA Resources Recovery conference in Gent, Belgium.

Oct 2015   Speaker during opening of the pilot hall at Delfluent Services, Harnaschpolder, Den Hoorn.

Jan 2016   Flash presentation during the 68th Vakantiecursus at Delft University of Technology.

Jul 2016   Speaker at Young Water Professionals (YWP) conference in Gent, Belgium.

Jul 2018   Speaker at International Conference on Inorganic Membranes (ICIM) in Dresden, Germany