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Ceramic nanofiltration-based treatment of NOM-rich ion exchange brine

Dissertation

for the purpose of obtaining the degree of doctor

at Delft University of Technology

by the authority of the Rector Magnificus, Prof.dr.ir. T.H.J.J. van der Hagen

chair of the Board for Doctorates

to be defended publicly on

Wednesday 19th May 2021 at 12:30 o' clock

by

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Content

Propositions accompanying the dissertation

Ceramic nanofiltration-based treatment of NOM-rich ion exchange brine

Irene Caltran

1. During treatment of spent anion exchange brines, rejection of natural organic matter by commercial TiO_2 ceramic nanofiltration is determined by steric hindrance rather than charge effects (*this proposition pertains to this dissertation*).

2. Currently available commercial ceramic nanofiltration membranes for water treatment only separate sulfate from chloride ions when the ionic strength of the solution is low (*this proposition pertains to this dissertation*).

3. In an hybrid system for treatment of spent anion exchange brines, consisting of ceramic nanofiltration and precipitation, nanofiltration should precede precipitation of sulfate to maximise the recovery of humic substances (*this proposition pertains to this dissertation*).

4. One-step ceramic nanofiltration treatment for natural organic matter and sulfate removal from spent anion exchange brines requires membranes with a pore size of 0.4 nm radius (or 300 Da) (*this proposition pertains to this dissertation*).

5. To customize ceramic nanofiltration by pore size reduction, one should use commercial membranes that are defect-free, and have a narrow pore size distribution.

6. The characterisation method of organic matter, and its fractions, in water should be adequately chosen dependent on the specific research purpose.

7. Management of waste streams from water treament should not only focus on “zero liquid discharge”, but also on recovery of valuable resources.

8. Concentrated humic substances, recovered from water treatment, should be considered as an alternative to industrial antiscalants (*Haidari et al., 2019*).

9. International Environmental and Water Resources Engineering students should gain sufficient tools during their studies to be able to work effectively in their country of origin.

10. Research institutions should put extra effort in actively encourage paternity leave among employees.

These propositions are regarded as opposable and defendable, and have been approved as such by the promotors Prof.dr.ir. L.C. Rietveld and Dr.ir. S.G.J. Heijman.

Stellingen behorend bij proefschrift

Ceramic nanofiltration-based treatment of NOM-rich ion exchange brine

Irene Caltran

1. Tijdens de behandeling van de gebruikte anionwisselaar brijnen met commerciële TiO_2 keramische nanofiltratie, wordt afstoting van natuurlijk organisch materiaal bepaald door sterische hindering in plaats van ladingseffecten (*deze stelling heeft betrekking op dit proefschrift*).

2. Beschikbare commerciële keramische nanofiltratiemembranen voor waterbehandeling scheiden sulfaat af van chloride indien de ionsterkte van de oplossing laag is (*deze stelling heeft betrekking op dit proefschrift*).

3. In een hybride systeem voor de behandeling van de gebruikte anionwisselaar brijnen bestaande uit keramische nanofiltratie en precipitatie, moet nanofiltratie voorafgaan aan precipitatie van sulfaat om het winnen van humusstoffen te maximaliseren (*deze stelling heeft betrekking op dit proefschrift*).

4. Eenstaps keramische nanofiltratiebehandeling voor natuurlijke organische stof en sulfaatverwijdering uit gebruikte anionwisselaar brijnen vereist membranen met poriestraal van 0,4 nm (of 300 Da) (*deze stelling heeft betrekking op dit proefschrift*).

5. Om keramische nanofiltratie te modificeren door verkleining van de poriegrootte, moet men commerciële membranen gebruiken die geen defecten vertonen en een smalle poriegrootteverdeling hebben.

6. De karakterisatiemethode van natuurlijke organische stof en zijn fracties in water dient adequaat te worden gekozen afhankelijk van het specifieke onderzoeksdoel.

7. Het beheer van afvalstromen uit waterbehandeling moet niet alleen gericht zijn op “zero liquid discharge”, maar ook op het terugwinnen van waardevolle hulpbronnen.

8. Geconcentreerde humusstoffen, teruggewonnen uit waterbehandeling, moeten worden beschouwd als een alternatief voor industriële antiscalants (*Haidari et al., 2019*).

9. Internationale studenten van Environmental Engineering en Water Management moeten tijdens hun studie voldoende tools verwerven om effectief te kunnen werken in hun land van herkomst.

10. Onderzoeksinstellingen moeten vaderschapsverlof onder werknemers actiever stimuleren.

Deze stellingen worden opponeerbaar en verdedigbaar geacht zijn zodanig goedgekeurd door de promotors Prof.dr.ir. L.C. Rietveld and Dr.ir. S.G.J. Heijman.

Chapter 1

Introduction

1 Introduction

1.1 Ion exchange as NOM removal treatment from drinking water sources

Natural organic matter (NOM) is a complex mixture of organic molecules and is always present in natural drinking water sources. NOM is related to several problems in drinking water consumption and distribution, such as color and odor, disinfection byproducts (DBPs) formation and biological instability (Jacangelo et al., 1995). Moreover, NOM has been found to decrease efficiency of drinking water treatment steps, such as activated carbon and membrane filtration, and increases the consumption of chemicals (Jacangelo et al., 1995; De Ridder et al., 2011). Therefore, NOM removal at the beginning of a drinking treatment train improves many downstream processes (Matilainen and Sillanpää, 2010).

Conventionally, NOM is removed by coagulation using aluminum- and iron-based chemicals. The primary aim of coagulation is the removal of turbidity, color and pathogens. When coagulation is optimized for turbidity, it is referred as baseline coagulation. When coagulant dose, pH changes, addition of chemical and alternative coagulants ensure more efficient NOM removal, coagulation is defined as enhanced coagulation (Matilainen et al., 2010).

Further, activated carbon has been used to remove NOM when there is a need to meet local legislation standards for DBPs concentration, or to improve taste and odor in drinking water (Jacangelo et al., 1995; Uyak et al., 2007). However, NOM removal by granular activated carbon (GAC) is limited to the first few months of the running of the filter. After these months, the remaining removal is supposed to be attributed to biological breakdown in the filter (Van der Aa et al., 2011). Therefore, most drinking water companies mainly use activated carbon to remove micropollutants.

Ion Exchange (IEX) with anion resin can remove NOM mainly by electrostatic interactions (Cornelissen et al., 2008). Anion IEX resin has chloride anions on its surface and in contact with NOM-rich water, some chloride ions on the resin surface are released and substituted by negatively charged NOM. Together with NOM, anions are also removed from the water, depending on their affinity to the specific IEX resin. The IEX resin is periodically regenerated with an electrolyte solution, usually sodium chloride, to, partially, restore the chloride ions on the resin. The conventional configuration of anion IEX is a fixed resin bed. However, the use of fixed bed at the beginning of the treatment train would lead to fouling or clogging of the IEX reactor within a short time (Galjaard and Koreman, 2015), due to the solids being retained in the resin bed. More recent configurations use non-fixed bed ion exchange configurations (Verdickt et al., 2012). A crucial problem of IEX for upstream NOM removal is related to waste management of the regenerant electrolyte. The regenerant solution is reused several times before disposal, which increases the concentrations of

NOM and anions, like sulfate (Verdickt et al., 2012; Verdickt and Schoutteten, 2018; Vaudevire et al., 2019). The spent IEX brine, rich of NOM, sodium, chloride and other anions, is polluting and expensive to dispose, and hampers the full-scale applications of IEX for upstream NOM removal (Verdickt, 2012).

1.2 Membrane based treatment of spent IEX brines

Research on NOM-rich brine treatment, including spent IEX brines, has been focused on technologies that use polymeric membranes. Pressure driven tight nanofiltration membranes, with pore sizes in the range of 200 to 400 Da, have been used with the aim to recover a permeate of reusable IEX regeneration salt solution, typically sodium chloride, by removing NOM and other anions from the spent IEX brine. In some cases, the salt concentration in the recovered regenerant needs to be increased before reuse. Therefore, other techniques have also been considered, such as membrane distillation (Jirícek et al., 2015) and dynamic vapour decompression (Vaudevire and Koreman, 2013). Further, concentrated NOM has been suggested for use in agriculture and food industry (Schippers et al, 2005; Vaudevire and Koreman, 2013). An important drawback of the technologies that use polymeric membranes is that their performances can decrease due to NOM fouling (Hong and Elimelech, 1997; Gryta et al., 2001).

Therefore, this thesis is focused on ceramic nanofiltration membranes for spent brine treatment, because of their potential advantages over polymeric membranes, such as higher fluxes and lower fouling characteristics (Hofs et al., 2011; AMTA, 2018). A further difference between the polymeric membranes used in previous studies and currently available commercial ceramic membranes is the pore size. Ceramic membranes are looser, with pore sizes above 450 Da (Puhlfürß et al., 2000). This can be favorable when a high passage of sodium chloride in the permeate is desired for IEX regeneration purposes, but it might pose a problem if some small NOM fractions and other ions are not rejected and accumulate in the recovered sodium chloride regenerant. In particular, sulfate has a high affinity to the anion IEX resin and might be present at high concentrations in the spent IEX brine. Sulfate removal treatment from the spent IEX brine, such as chemical precipitation, might then be required.

A scheme of the proposed ceramic nanofiltration treatment for spent IEX brines is shown in Figure 1.

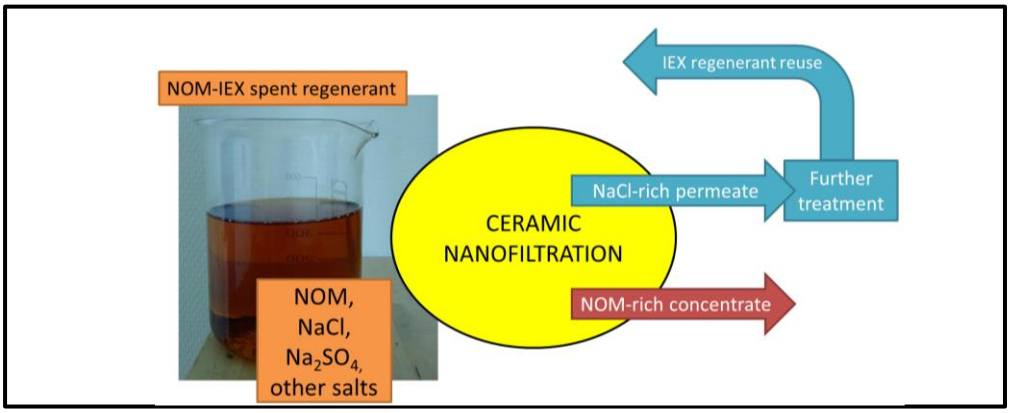

Figure 1, Ceramic nanofiltration for spent IEX brine treatment and recovery of IEX regenerant and NOM

1.3 Research questions

NOM is related to problems during drinking water treatment, distribution and consumption. Reaching low NOM concentrations is not always possible with conventional treatment. Therefore, alternative NOM removal by IEX in surface water treatment applications have been considered. However, waste management of spent IEX brine was identified as a main drawback of using IEX for NOM removal. Recovering NOM and reusing sodium chloride solution could reduce the waste volume. Treatment of spent IEX brine with commercially available ceramic nanofiltration and chemical precipitation poses issues related to

- *the behavior of ceramic membranes in high salinity applications*. Previous research showed the potential of commercial ceramic nanofiltration for the removal of NOM and multivalent ions (Kramer et al., 2015). However, spent IEX brine has a high ionic strength, that can impact the membrane rejection of charged constituents (Bargeman et al., 2015); and
- *the interaction of high concentrations of NOM with chemicals in precipitation processes*. Previous studies identified the potential of sulfate removal from brines by chemical precipitation (Almasri et al., 2015; Dou et al., 2017; Franzsen et al., 2018; Tian et al., 2019; Jin et al., 2020). However, the concentrations of NOM were low compared to spent brines of IEX for NOM removal.

Understanding these mechanisms could be a step towards the feasibility of the application of IEX for NOM removal and the disposal and reuse of spent IEX brines.

To achieve these main objectives, the following research questions were identified:

1. How does IEX for NOM removal impact surface water treatment?

2. What is the effect of ionic strength on NOM removal by ceramic nanofiltration?
3. What is the effect of ionic strength on sulfate removal by ceramic nanofiltration?
4. What is the effect of NOM on sulfate removal by calcium sulfate, ettringite and barite precipitation?

The answers to research questions 2, 3, and 4 will give new practical insights on the performance of treatment for NOM- and sulfate-rich IEX brines using integrated ceramic nanofiltration and chemical precipitation of sulfate.

1.4 Outline of the thesis

The outline of the thesis is shown in Figure 2.

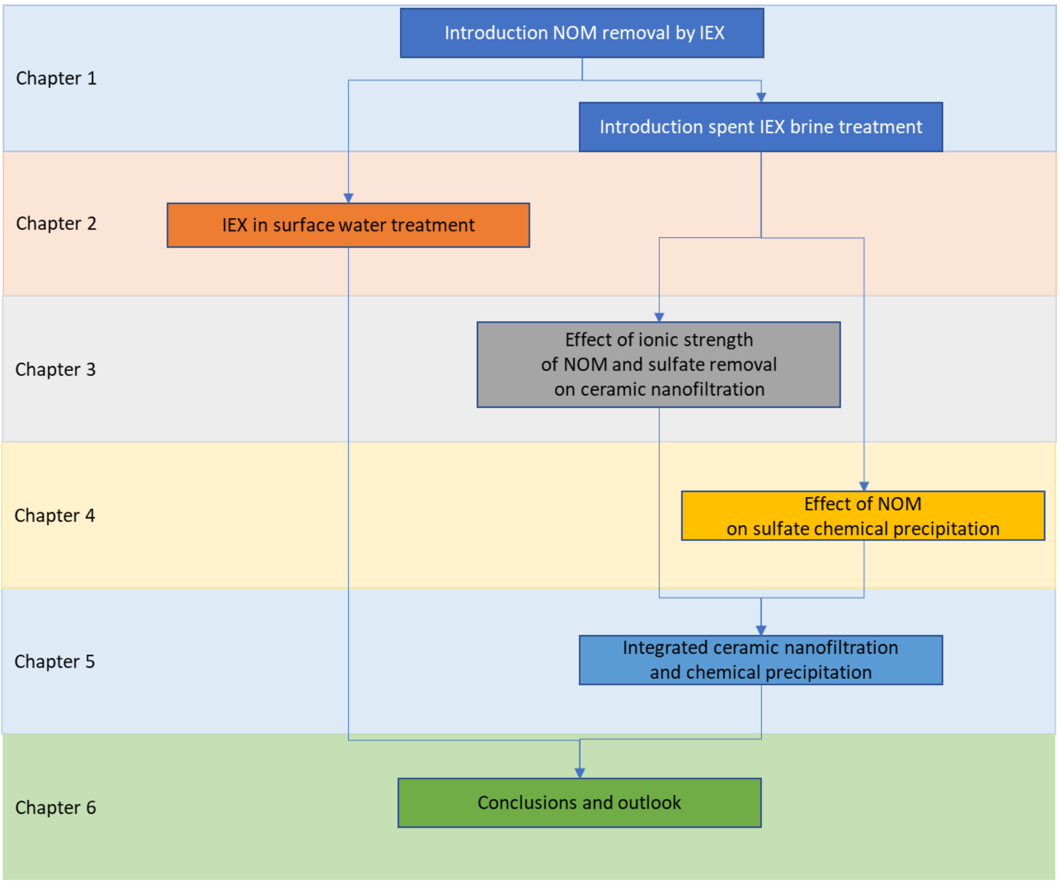

Figure 2, Outline of the thesis

In Chapter 2 the performance of IEX for NOM removal from surface water was explored by means of a case study. Chapter 3 describes the effect of ionic strength on NOM and sulfate removal by loose ceramic nanofiltration through laboratory scale experiments. The laboratory studies on the effect of NOM on chemical precipitation of sulfate are reported in Chapter 4. Integrated ceramic nanofiltration and chemical precipitation of sulfate were then tested on spent IEX brines, as described in Chapter 5. Finally, conclusions and outlooks for applications and future research can be found in Chapter 6.

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Chapter 2

Impact of removal of natural organic matter from surface water by ion exchange: a case study of pilots in Belgium, United Kingdom and the Netherlands

This chapter is based on

Caltran, I., Heijman, S., Shorney-Darby, H. L., & Rietveld, L. C. (2020). Impact of removal of natural organic matter from surface water by ion exchange: a case study of pilots in Belgium, United Kingdom and the Netherlands. *Separation and Purification Technology*, *247*.

Impact of removal of natural organic matter from surface water by ion exchange: a case study of pilots in Belgium, United Kingdom and the Netherlands

Abstract

Natural organic matter (NOM) fractions cause problems in drinking water treatment and supply. In the North Sea region, anionic ion exchange (IEX) in non-fixed bed configurations has been considered for NOM removal in drinking water treatment plants. This paper discusses several experiences of the impact of anion IEX on NOM removal and on NOM-related problems in water treatment locations of the North Sea region, considering the specific situation of the sites. The investigated parameters include the effect of anionic IEX on the removal of total NOM and specific NOM fractions, the amount of chemicals used for coagulation, the development of trans membrane pressure in microfiltration, the formation of assimilable organic carbon and the energy consumption during advanced oxidation, the removal of organics by activated carbon, and the formation of disinfection by-products. The pilot experiences at three treatment locations in Belgium, United Kingdom and the Netherlands show that anionic IEX (1) removed typically 40 to 60 percent of total NOM; (2) targeted mostly humic NOM fractions, and was not effective to remove biopolymers (3) contributed to lower coagulant doses and energy consumption in UV/advanced oxidation; (4) had limited influence on limiting the fouling of microfiltration membranes; (5) lowered the formation of disinfection by-products; and (6) it can improve biological stability.

1 Introduction

Natural organic matter (NOM) is a complex mixture of organic molecules. NOM is always present in surface water, and is responsible for several problems in drinking water treatment and supply. Some of these problems are related to drinking water consumption and distribution, e.g., colour, odour, formation of disinfection byproducts (DBPs) and biological instability of the water [1]. In addition, NOM reduces the efficiency of water treatment. For instance, activated carbon might be used to decrease NOM concentrations [1, 2, 3, 4], but this reduces the sorption sites available for the removal of other pollutants [5]. Also, NOM removal by granular activated carbon (GAC) is limited to the first few months of the running of the filter. After these months, the remaining removal is supposed to be attributed to biological breakdown in the filter [6]. Moreover, NOM increases the demand for coagulants and disinfectants, and it fouls membranes [1]. Therefore, drinking water utilities remove NOM to address different problems, depending on the specific situation on the site.

In the North Sea Region, a survey including 10 drinking water utilities in the Netherlands, Belgium, United Kingdom and Sweden showed that coagulation, the conventional NOM removal technique, was applied in all surveyed drinking water treatment plants for NOM removal (owned data). However, several companies were in the process of investigation and implementation of complementary technologies for improving NOM removal. In particular, anion ion exchange (IEX) pre-treatment was considered in this region as a part of a multi-barrier approach to NOM in drinking water treatment.

The conventional configuration of anion IEX is a fixed resin bed. Therefore, IEX is typically used in the late stage of the treatment process [7], after the suspended solids have been removed by pre-treatment. The use of fixed bed at the beginning of the treatment train, e.g., during direct treatment of surface water, would lead to fouling or clogging of the IEX reactor within a short time [8], due to the solids being retained in the resin bed. More recent configurations use non-fixed bed ion exchange configurations [7].

Based on the information that a water utility wants to know, several analytical methods can be used to quantify and/or characterize the NOM on the treatment site and along the treatment. Water companies often use carbon analytical measurements to quantify NOM. Carbon detectors can measure total organic carbon (TOC), particulate organic carbon (POC) and dissolved organic carbon (DOC). In addition, specific ultraviolet absorbance (SUVA, L/(mg*m)) gives an indication about the hydrophobicity of the NOM, where SUVA is the UV absorbance of water at 254 nm (UV_{254}, 1/m) normalized by the DOC concentration (mg/L). NOM in water with a high SUVA (>4 L/(mg*m)) is mostly more hydrophobic and aromatic than in water with low SUVA (<3 L/(mg*m)) [9, 10]. Hydrophilic NOM is known as a major component of easily biodegradable NOM [11], while humic substances (HS), that are generally considered hydrophobic, are more biologically persistent [12]. NOM is composed of fractions with various sizes. Therefore, size exclusion chromatography (SEC), combined with organic compounds detection techniques, is used as another method to characterise organics. In the fractionation method of Huber et al. [13], after SEC (using liquid chromatography – LC), samples are analysed with a UV_{254} detector (UVD); then, carbon concentrations are measured with organic carbon detection (OCD); after UVD, a side stream is analysed by organic-bound nitrogen detection (OND). The hydrophobic and cation-exchange characteristics of the SEC column give indications about the charge and hydrophobicity of the NOM fractions [13]. The LC-OCD-OND fractions are subdivided into hydrophobic organic carbon (HOC), biopolymers (BP), HS, building blocks (BB), low molecular weight acids (LMWa), and low molecular weight neutrals (LMWn). These fractions together are the chromatographic fractionation of organic carbon (CDOC). BP are mostly polysaccharides and nitrogen-containing components (e.g., protein and amino sugars); they are hydrophilic and uncharged [13]. HS are fulvic and humic acids, and their breakdown products are referred as BB [13]. LMWa includes small humics and acids, and are negatively charged [13]. Finally, LMWn consists of alcohols, aldehydes, ketones, amino acids, sugars and biogenic NOM; they are hydrophilic or amphiphilic and have low charge [13]. The fractions have different sizes: BP are larger than 10,000 Daltons [13], HS are mostly 1000-800 Daltons, BB are 500-300 Daltons, and both LMWa and LMWn are smaller than 350 Daltons [14]. They also have a different response to UV_{254}: HS respond to the detector, and BB have variable response and BP and LMNn have typically no or very little response [13].

Fractionation techniques cannot give information about the possible biological transformation of NOM. Moreover, the NOM concentrations involved in the biological processes are typically very low, which makes the detection difficult. As a result, specific methods are used to measure biodegradable NOM and evaluate the biostability of drinking water. One of them is the determination of assimilable organic carbon (AOC), based on bacteria biomass growth [15].

In a specific site, variations of NOM concentrations and characteristics in the source of a specific site may change over time. Evans et al. [16], e.g., analysed NOM data from 22 lakes or streams of the Acid Waters Monitoring Network (AWMN) in the United Kingdom, and observed that the DOC concentration at the majority of the sites was increasing with 0.06 to 0.51 mg/L per year, during the five years of monitoring. NOM concentrations and/or composition can also vary with the seasons. The variation of NOM concentration and character is due to either autochthonous (e.g., linked to the presence of algae) or allochthonous variations (e.g., changing origins of water sources, and NOM in runoff from the surrounding area) [17]. In addition, NOM charge can change, as shown, for instance, by Sharp et al. [18], who reported that the charge density of fulvic acids fluctuated during a period of almost three years in an observed water source. Seasonal changes in SUVA and NOM fractionation and the effect on, e.g., coagulation have also been studied by Jarvis et al. [19], for a moorland catchment in Yorkshire. The greatest seasonal fraction change was an increase in fulvic acids by 20 percent in the winter, which was compensated by a decrease of humic acids; in winter, the SUVA was lower (NOM became less hydrophobic), and thus the required coagulant dose was higher [19].

This paper presents an overview of the performance of anion IEX for NOM removal as a pre-treatment step of surface water used in drinking water production in the North Sea region. While the mechanisms for NOM removal by anion IEX are described in detail by, e.g., Cornelissen et al. [20], the focus of this paper is on local experiences for NOM removal with IEX. As NOM characteristics and removal are linked to the specific situation of the water treatment site, the case study fully describes each treatment plant. We studied the impact of anion IEX on NOM removal for different water companies that recently implemented anion IEX in their treatment plants, or are considering to implement anion IEX at full scale (i.e., Blankaart in Belgium, Plymouth in the United Kingdom, and Andijk in the Netherlands). Firstly, we described the main characteristics of the raw water sources and existing treatment plants and the way IEX was or will be incorporated into the treatment process. Then, we discussed reviewed publications, conference papers, reports, and unpublished data from various studies the water companies conducted at bench and pilot scale. We used these experiences to gain information on the NOM fractions that were removed by anion IEX pre-treatment and the effect on several NOM-related problems, i.e., coagulant consumption, membrane fouling, AOC formation during advanced oxidation, limitation of efficiency of UV-based oxidation and activated carbon, and formation of DBPs.

2 Materials and methods

2.1 Detection of NOM and NOM-related parameters in IEX pilot studies

2.1.1 Blankaart

At the pilot site Blankaart, Belgium, UV_{254} absorption was measured on site using a spectrometer (Thermo Scientific, Evolution 160); the samples were filtered using a 0.45 µm filter prior to measurement. TOC samples were measured at the laboratory of De Watergroep, Belgium, with an Analytik Jena Multi N/C 3100 analyser; here there was no filtration prior to measurement. The samples were acidified with 6 M HCl; afterwards, the inorganic carbon was stripped with pure oxygen; then, 0.5 mL of the sample was burned at 720°C using a Pt catalyst to oxidize all organic carbon to CO_2. The amount of formed CO_2 was measured with a non-dispersive infrared detector. The SUVA was calculated using TOC instead of DOC, thus the SUVA values reported for this case study are lower than the real SUVA values, considering that TOC is always higher than DOC. However, according to Edzwald and Van Benschoten [10], undissolved organic carbon concentrations are typically much lower than TOC concentrations. In the work of Wetzel [21], for instance, the average DOC: undissolved organic carbon ratio from many surface water bodies was 6:1 for rivers and 10:1

for lakes. In this case, the SUVA calculated with DOC would be in the range of only 10 to 16 percent higher than the SUVA calculated with TOC.

2.1.2 Plymouth and Andijk

At the pilot sites of Plymouth, United Kingdom, and Andijk, the Netherlands, NOM related parameters, including DOC, UV_{254}, and the concentrations of HOC, BP, HS, BB, LMWa and LMWn, were measured by Het Water Laboratorium (the Netherlands), using LC-OCD analyses (as described in Huber et al. [13]. At Andijk, AOC analyses were performed according to the procedure of Van der Kooij [22]. At Plymouth, DBP formation potentials were measured at the laboratory of South West Water, United Kingdom, according to the procedure described by Metcalfe et al. [23].

2.2 Non-fixed bed IEX for NOM removal in the North Sea region

Non-fixed bed IEX techniques include the use of small size magnetic resin systems (MIEX®), IEX in fluidized bed (FIX), and suspended IEX (SIX®) [8].

MIEX® (now commercialized by Ixom Water care, and previously by Orica Watercare) uses a mixed bed of magnetic resin. The magnetic resin is smaller than conventional resins, i.e., 0.1 to 0.2 mm instead of, e.g., 0.4 to 2 mm; therefore, due to the larger specific surface area the kinetics is rapid [24], and less contact time is required in the contactor [25]. The resin is strong base, and it has a magnetic core of iron oxides [25]. After removing NOM, the magnetic resin agglomerates, and the formed larger particles settle rapidly [26]. High resin concentrations enhance the agglomeration of resin and can reduce the resin loss [27]. MIEX® is available in different configurations, including mixing contactors and a settling vessel resin separator in series, and FIX.

FIX can use small bead MIEX® resin because of its rapid settling, but also larger, conventional resins can be used in this configuration. Raw water flows upward in a reactor containing a resin bed. The controlled velocity of the raw water fluidizes the resin bed, and at the same time it should avoid that the resin is washed out of the reactor. The sedimentation rate of the resin depends on the resin characteristics and on the water temperature [28]. The upflow velocity should be high enough to fluidize the resin bed and to prevent solids present in the raw water from getting trapped in the resin bed [28]. At the same time, the upflow velocity should be low enough to guarantee sufficient contact time between water and resin and to limit the required height of the reactor.

In SIX®, the resin is dosed into the raw water and flows through five mixed contactors. A conventional strong base resin is used in the system, and it is selected according to the characteristics of the water source to be treated [8]. The resin concentration is in the range of 4 to 20 mL/L, and the typical contact time is between 10 and 30 min [8]. The resin in the contactors has the same contact and retention time as the water. Afterwards, the resin is separated from the water by a lamella settler and then regenerated and reused.

MIEX® and FIX, on the one hand, use long resin retention times for the resin, until it has a high NOM loading, with the aim to make efficient use of the exchange capacity of the resin and reduce the use of regeneration salt [8]. On the other hand, SIX® is a single-pass process with a shorter resin retention time and regeneration at low NOM loadings; the aim is to reduce bacteria growth on the resin, which can occur when the raw water contains high concentrations of growth promoting nutrients, such as phosphate [8].

2.3 Introduction of non-fixed bed IEX in drinking water treatment plants in the North Sea region

2.3.1 Blankaart

De Watergroep has planned to introduce IEX pre-treatment, amongst others, in the full-scale water works at Blankaart. IEX is being considered as a pre-treatment to the existing enhanced coagulation (Figure 1a). The new post-treatment will include advanced oxidation with hydrogen peroxide and ozone, dual stage GAC, and UV/NaOCl disinfection. Membrane filtration has also been considered for further modifications to the treatment process. The current pre-treatment consists of pre-filtration, biological ammonia oxidation, enhanced coagulation, settling and filtration; the current post-treatment consists of GAC filtration and disinfection with NaOCl (Figure 1b).

2.3.2 Plymouth

South West Water has been introducing anion IEX in the new full-scale water works of Plymouth. IEX will be used as pre-treatment before in-line coagulation and ceramic microfiltration. The post-treatment will consist of GAC, UV and chlorination and stabilisation (Figure 2a). The current pre-treatment includes coagulation and flocculation before rapid sand filtration; the post-treatment is chlorine disinfection and final conditioning for plumbosolvency (Figure 2b).

2.3.3 Andijk

PWNT has built a new treatment plant at Andijk, the Netherlands. This new plant, that uses anion IEX as pre-treatment before ceramic microfiltration, is operated in parallel to an older conventional plant. The post-treatment of the new plant is advanced oxidation with UV/H_2O_2, GAC filtration, and final disinfection with chlorine dioxide (Figure 3a). The current conventional pre-treatment uses iron-based coagulation in the water reservoirs of the IJssel Lake, and includes also softening in the reservoirs, sedimentation and double layer filtration; the post-treatment is primary UV/H_2O_2 advanced oxidation and disinfection, GAC filtration, and final ClO_2 disinfection (Figure 3b).

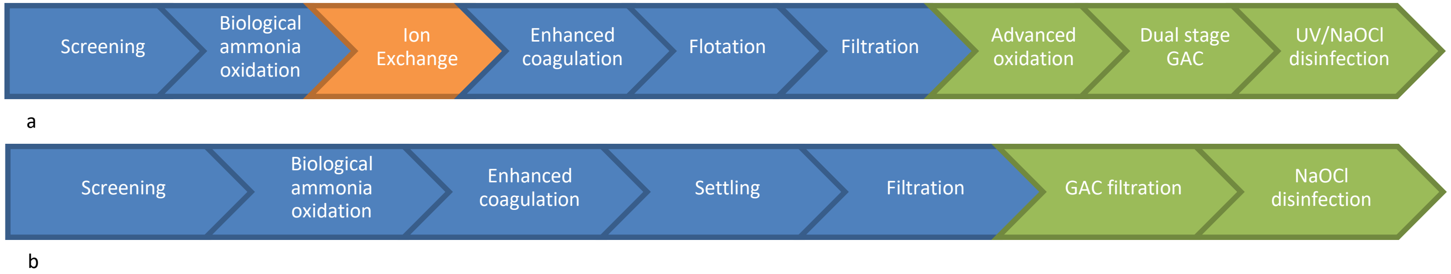

Figure 1, Planned upgrading of treatment plant with ion exchange in Blankaart (a), and current treatment plant in Blankaart (b)

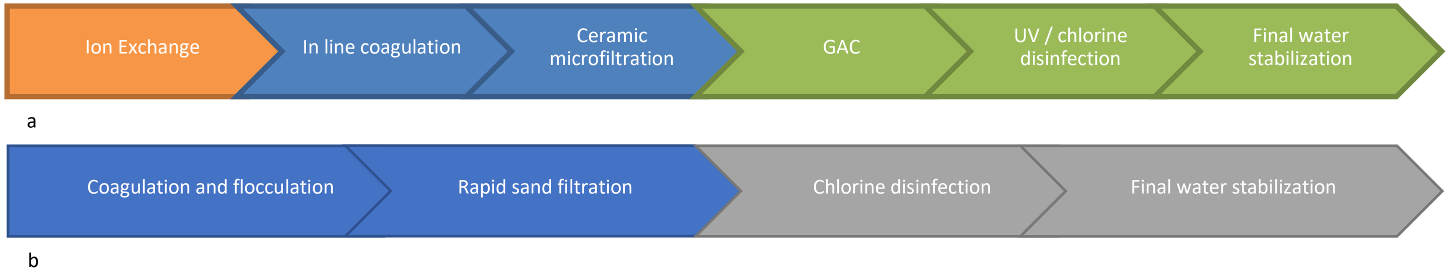

Figure 2, Upscaled treatment plant with ion exchange in Plymouth (a), and current conventional treatment plant in Plymouth (b)

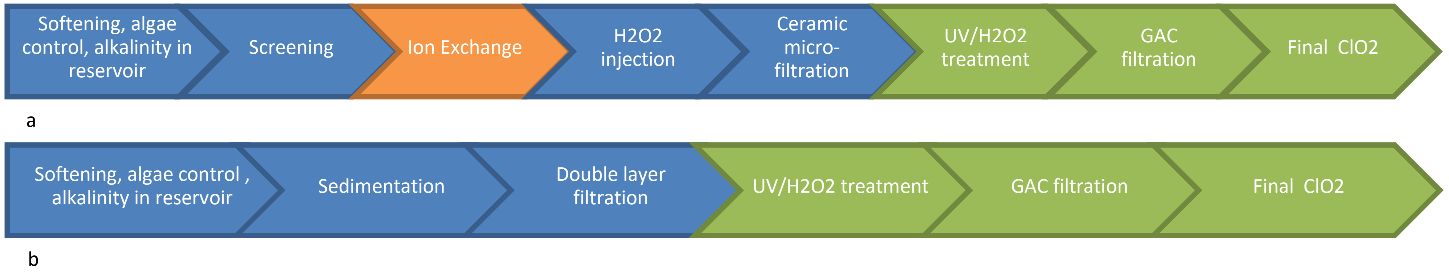

Figure 3, New treatment plant with ion exchange in Andijk (a), and current conventional treatment plant in Andijk (b)

2.4 Pilots for IEX with non-fixed bed

Three different IEX systems were studied at Blankaart, Plymouth and Andijk, and these were MIEX®, FIX and SIX® (Table 1). In Table 1 gives an overview of the different design characteristics of the pilot plants. Table 2 shows the characteristics of the resins used in the pilot studies.

Table 1, IEX technologies and resins in the studied cases

Pilot	Resin	Contact time [s]	Retention time resin [min]	Resin concentration in non-fixed filter bed [mL/L]	Effective resin concentration ^ [mL/L]	Flow rate pilot [m³/h]	Upward velocity pilot [m/h]
MIEX® (Blankaart)	Magnetic resin	Unknown	Unknown	unknown	1	1.25	20
FIX (Blankaart)	Purolite A860S	37-120	925-3000	150-700*	not applicable	0.05 – 0.2	6– 25
	Lewatit VPOC 1017						
	Magnetic resin						
	Purolite PPA860S	108 – 125	840-960	250-500**	2	50-58	17-20
SIX®	Lewatit S5128 (Plymouth)	1800	30	18	18	6.25	-
	Lewatit VPOC 1017 (Andijk)	1500-1800	25-30	13-15	13-15	60	-

^ Amount of regenerated resin per liter of treated water. * Estimated value calculated from the height of the fluidized bed (in the range of 0.25 to 0.38 m), and range of expansion of the fluidized bed (40 to 500 percent) of resins with upward velocity between 12.5 and 25 m/h at water temperatures between 4 and 20°C (shown by Verdickt et al. [7]). ** Estimated value calculated from the height of the fluidized bed (0.6 m), and range of expansion of the fluidized bed (200 to 300 percent) of resins with upward velocity between 15 and 20 m/h at 4 °C in previous experiments (shown by Verdickt et al. [7]), and the expansion of the fluidized bed at 12 m/h at 20°C (100 percent), from the product information sheet of the resin [30].

Table 2, Resin used in the pilot studies

Resin	Characteristics
Miex® resin	Type I, Macroporous, bead size 0.15-0.18 mm, exchange capacity 0.52 meq/ml, acryl*
Purolite A860S	Type I, Macroporous, mean bead size 0.43-1.20 mm, exchange capacity 0.8 meq/ml, acryl**
Purolite PPA860S	Type I, Macroporous, mean bead size 0.63-0.85 mm, exchange capacity 0.8 meq/ml, acryl**
Lewatit S5128	Type I, Gel structure, effective bead size 0.50-0.75 mm, exchange capacity 1.25 meq/ml, acryl***
Lewatit VPOC 1017	Type I, Gel structure, effective bead size 0.50-0.60 mm, exchange capacity 1.25 meq/ml, acryl***

* From Verdickt et al. [7]; **from product information Purolite [30, 31]; ***from product information Lewatit [32, 33].

A cost-analysis of the introduction of anion IEX pre-treatment in a water treatment plant is not the scope of this paper, because the optimisation of the system depends on many limiting factors, e.g., contact time between water and resin, contact surface of the resin, pH, the character of NOM fractions, and the concentration of uncharged, refractory NOM. Nevertheless, in Andijk and in Plymouth cost considerations were made in preliminary studies, that compared the existing or conventional treatment to a treatment that includes anion IEX and microfiltration. For Andijk, less energy consumption and waste volumes were predicted in the new treatment, with similar construction costs [29]. For Plymouth, it was considered that the new treatment requires a smaller footprint, and the expected operational costs were similar, as the result of a combination of reduced coagulant dose, increased energy consumption due to microfiltration, and higher chemical and disposal costs for IEX [23].

When comparing the non-fixed anionic IEX systems, Table 1 shows that suspended reactors work with lower resin concentrations and a higher contact time than fluidized reactors. Therefore, SIX® requires reactors with a larger volume, in the range of 10 to 20 times higher, and thus a larger footprint.

2.4.1 FIX with MIEX® and conventional resins at Blankaart

A MIEX® pilot in FIX configuration was operated at Blankaart from June 2008 to July 2009. At Blankaart, the pH in the water source was mostly in the range between 8 and 9. The pilot consisted of an upflow mixed reactor followed by a lamella separator [7]. A small flow of resin was continuously removed from the contactor and replaced by freshly regenerated resin. Regeneration was performed batch wise [7]. The pilot had a capacity of 1.25 m^3/h, with an upflow velocity of 20 m/h. The dose of MIEX® resin is given as an effective resin dose, which is the amount of regenerated resin per liter of treated water, and it was 1.0 mL/L [7].

Jar experiments were also performed to test the effect of MIEX® resin IEX on subsequent coagulant doses. Raw water was contacted with MIEX® resin, subtracted from the contactor, for 20 min at a concentration of 25 mL resin/L. The pH of the raw water before the MIEX® treatment was adjusted to a value between 7.6 and 7.8, while the pH after the MIEX® treatment is unknown. Subsequently, coagulation tests were performed on the supernatant with coagulant doses of 0 to 20 mg Fe/L. The results with respect to NOM and turbidity removal were compared with the results obtained by coagulating the raw water directly with ferric after pH conditioning with 80 mg/L H_2SO_4 [7]. The pH conditioning was applied if needed to reach the optimal pH of 6, depending on the water quality of the moment. The dosage of coagulant varied from 0 to 20 mg/L as Fe [7].

At Blankaart, FIX was tested again between 2008 and 2010, this time in a column with various strong base resins, i.e., MIEX® resin, Purolite A860S, and Lewatit VPOC 1071 [7]. The last two resins have bead sizes between 0.4 and 1.2 mm, respectively. The column had a diameter of 0.1 m and the resin volume in the column was 2 L. The pilot had a capacity of 50 to 200 L/h (0.05 to 0.2 m^3/h), resulting in upflow velocities of 7.5 to 25 m/h and contact times of 37 to 120 s [7]. The resin was regenerated in situ with a 10 percent NaCl solution every 1,500 bed volumes of treated water resulting in a resin residence time of 925 to 3000 min between regenerations [7]. The approximate resin concentration in the fluidized bed was in the range of 150 to 700 mL/L (according to our calculation in Table 1).

Based on the results of the small scale pilot tests, a larger FIX pilot, with a capacity of 50 to 58 m^3/h, was built and operated from 2016 to 2018. The effluent of the pilot was treated further by means of enhanced coagulation (using $FeCl_3$ and H_2SO_4) and flotation [34]. In this case, Purolite PPA860S was used, with contact times in the range of 108 to 125 s. The fluidized bed had a height of about 0.6 m, and periodically, a resin volume of 25-50 L was removed to be regenerated batch wise [34]. The approximate resin concentration in the fluidized bed, according to our calculation in Table 1, ranged from 250 and 500 mL/L, and the effective resin concentration was 2 mL/L.

2.4.2 SIX® at Andijk and Plymouth

At Andijk, the pH of the water source was mostly 7.8 - 8. There, a SIX® pilot was installed with a capacity of about 100 m^3/h and Lewatit VPOC 1017 resin (strong base, effective bead size of 0.5 to 0.6 mm) was selected after bench-scale kinetics tests for further application. The selection took various characteristics into account, such as mechanical strength, sedimentation properties, and regeneration salt consumption [8]. The resin concentration in Andijk was 13 to 15 mL/L, with 25 to 30 min contact time [8]. At Plymouth, with the water sources used had a pH mostly in the range of 6.6 and 8. There, SIX® was tested with a pilot with a capacity of 6.25 m^3/h, with pre-rinsed Lewatit S5128 resin, using a concentration of 18 mL/L and an average contact time of 30 min [23]. Both at Plymouth and Andijk, SIX® has been tested in combination with conventional and in-line coagulation to study their impact on fouling of microfiltration membranes (ceramic microfilter, Metawater, Japan). At Plymouth, the effect of SIX® on DBPs' formation has also been studied. At Andijk, the effect of pre-treatment with SIX® in combination with microfiltration membranes (Metawater, Japan) on UV/H_2O_2, activated carbon filters (Norit 0,8S or Chemiviron TL 830) and AOC formation has been compared to that of conventional, full-scale treatment. The H_2O_2 dosage was 6 mg/L in full-scale and pilot-scale and the UV dose was 600 mJ/cm^2 in full-scale and above 600 mJ/cm^2 in pilot-scale; for the activated carbon filters, the empty bed contact time was 25 min and the hydraulic loading rate was 9 to 13 m/h in full-scale and 10 m/h in pilot-scale. The regeneration frequency was 2 years in full-scale, and the pilot has been tested less than 2 years. Therefore, the average reactivation time of the carbon in both full- and pilot-scale during the test was 1 year.

3 Experiences of NOM removal and impact of anion IEX pre-treatment

3.1 NOM in water sources and NOM removal by conventional treatment in the North Sea region

In the surface water source at Blankaart, the average TOC was about 12 mg/L with a seasonal TOC fluctuation between 9 and 16 mg/L. The high TOC peaks were in summer and early autumn and can be attributed to algae blooms. Also the SUVA, calculated using TOC instead of DOC, fluctuated seasonally with low values in summer and early autumn, typically between 1.5 and 2.6 L/(mg*m) (Figure 4), or between 1.6 and 3 L/(mg*m), if correcting the value for DOC using a typical DOC: undissolved organic carbon ratio between 6:1 and 10:1, as explained in section 2.1.1. However, at Blankaart has been observed that, when algae blooms occurred in summer and early autumn, the DOC: undissolved organic carbon ratio could be in the range of 1:1, as microsieves of 30 µm could remove up to 50 percent of the TOC. In this case, the SUVA corrected for DOC would be considerably higher.

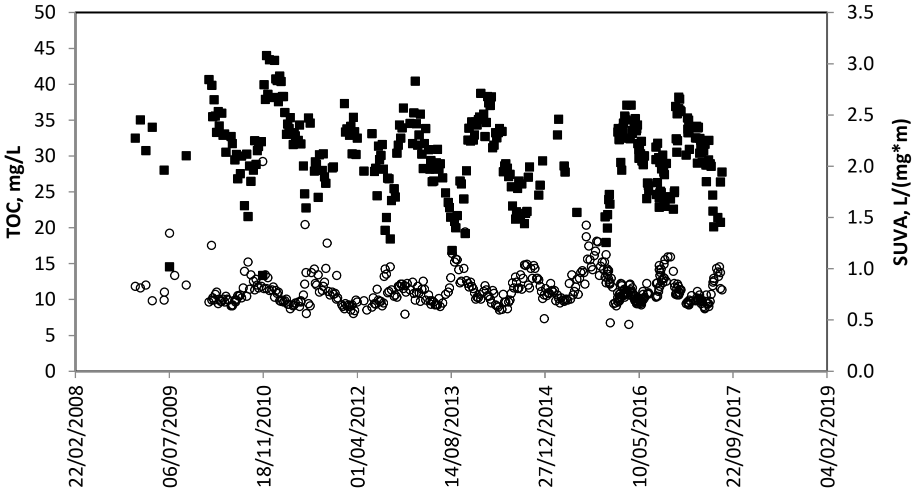

Figure 4, Seasonal variations of NOM at Blankaart source water. SUVA is calculated using TOC instead of DOC. Squares represent the calculated SUVA, dots represent the measured TOC

The current pre-treatment removed, on average, 60 percent of the TOC. The current post treatment, consisting of GAC filtration and disinfection NaOCl, removed an additional 25 percent of the remaining TOC, with an overall removal of 70 percent. Next to high NOM concentrations and seasonal NOM variations, the main challenges of the current treatment process are the negative influence of algae blooms in the settling and filtration steps, and the presence of micropollutants.

Also, the water source has a high alkalinity, resulting in a high chemical demand for the enhanced coagulation.

The water works in the Plymouth area use three surface water sources: Burrator reservoir, river Tavy and river Tamar. Burrator had a low DOC concentration (i.e., as low as 1 mg/L); however, the concentration could increase to 5 mg/L in autumn. The Tavy and Tamar rivers had low DOC concentrations in periods without rainfall (i.e., 1.5 and 2 mg/L, respectively), but when it rained the DOC concentration could increase rapidly to 10 mg/L. The typical SUVA was 4 to 5 L/(mg*m), which indicates that NOM was mostly hydrophobic of character. The existing water plants removed most of the NOM by coagulation, with a typical DOC removal of 60 to 80 percent; in days without rainfall, DOC removal was about 50 percent. Further optimization of the coagulation process is difficult because of large variations in NOM concentration, which are due to the seasons and rainfalls. In addition, NOM concentrations have gradually increased over time in some water sources (Figure 5).

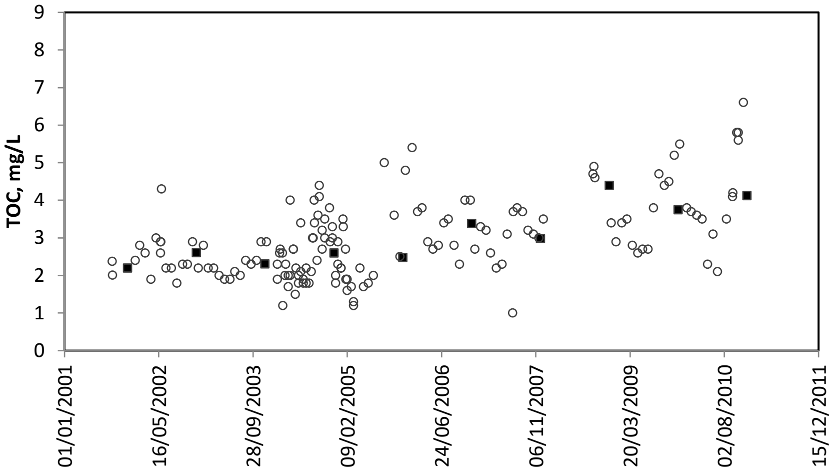

Figure 5, TOC of a South West Water upland reservoir over 10 years (2001-2010). Squares represent the calculated yearly average TOC, dots represent the measured TOC

The water source at Andijk is the IJssel Lake, an 110,000 ha freshwater basin fed by the river IJssel (90 percent) and by polders and other lakes (10 percent). Between 2012 and 2019, the DOC varied seasonally between about 4 and 8 mg/L (Figure 6). The average SUVA was 2.5 L/(mg*m). The IJssel Lake is shallow, it has a long residence time, and it is rich in nutrients. Therefore, the biological composition of the water had a high seasonal variation and a high concentration of algal NOM in summer. The lowest BP concentration has been observed in spring, before algae typically bloom [35]. Due to algae blooming, higher doses of iron-based coagulant for enhanced coagulation are used during summer. The TOC removal of the conventional treatment plant was more than 70 percent, on average. GAC filtration can also contribute to NOM removal, but NOM removal was not the reason for GAC contacting at Andijk.

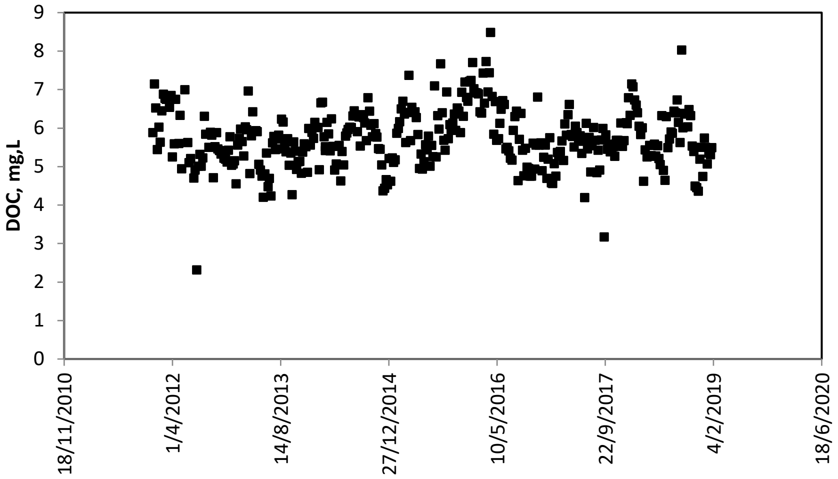

Figure 6, Measured DOC concentration in the Ijssel Lake between 2012 and 2016

3.2 NOM removal by anion IEX

Table 4 shows the NOM removal by anion IEX at the three pilots at Blankaart, i.e., MIEX® pilot (1.25 m^3/h), FIX column (0.15 m^3/h), and the large FIX pilot (50 m^3/h). The MIEX® pilot at Blankaart (effective resin dose 1 mL/L) removed between 40 and 50 percent of TOC. The decrease in UV_{254}, by 60 to 70 percent, was larger than the decrease of TOC. Thus, as aromatic structures absorb UV_{254} [10], MIEX® removed preferentially aromatic NOM fractions. When the UV_{254} was the lowest (typically in summer and early autumn), less TOC removal was observed in the MIEX pilot [7].

For the FIX column, the removal of TOC ranged from 40 to 60 percent, and the removal of UV_{254} ranged from 70 to 80 percent. The conventional resins (Purolite A860S and Lewatit VPOC 1017) required a longer contact time to achieve their maximum NOM removal, compared to the magnetic resin [7]. The magnetic resin has a smaller bead size, thus it has also a larger contact area and faster kinetics than the conventional resins [7]. After a contact time of 37 s, the maximum NOM removal by magnetic resin was already achieved: on average, 40 to 45 percent for TOC and 75 to 80 percent for UV_{254} [7]. On the other hand, when the contact time increased from 37 to 120 s, the removal of TOC by Purolite A860S increased from 40 to 55 percent, and the removal of UV_{254} increased from 60 to 75 percent [7].

The FIX pilot of 50 m^3/h (effective resin dose 2 mL/L) removed, on average, about 40 percent of TOC and 60 percent of UV_{254} (Figure 7), decreasing the SUVA. The lower average removal compared to the FIX column was attributed to seasonal algae growth [34]. Another possible cause is the difference in the regeneration procedure between the two pilots. In the smaller FIX column pilot, the spent brine was completely removed from the system; therefore, there was no spill of NOM going directly to the drinking water. In the larger FIX pilot of 50 m^3/h, to reduce the volume of the spent regenerant, the resin was rinsed with less water, and a part of the NOM removed from the resin could spill in the drinking water.

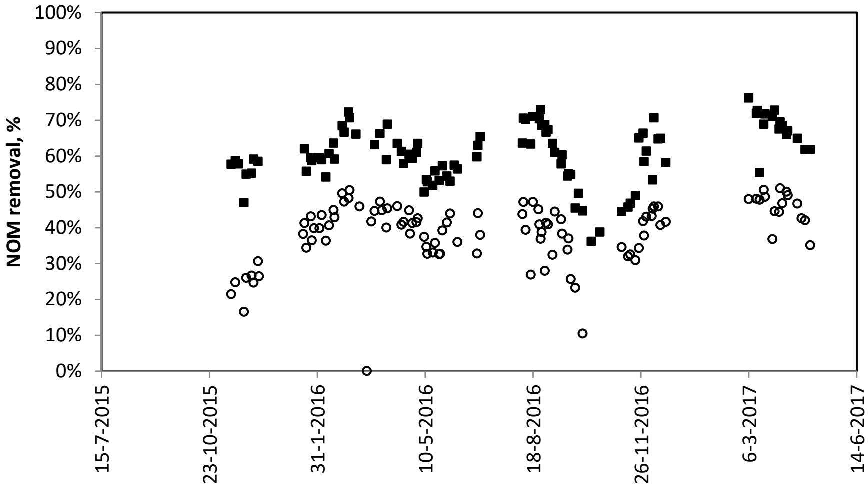

Figure 7, TOC removal and UV_{254} removal of the larger FIX pilot (50 m^3/h) in Blankaart. Squares represent the UV_{254} removal, dots represent the TOC removal

The SUVA also decreased at the SIX® pilots at Andijk and Plymouth (effective resin dose of 13 to 15 mL/L and 18 mL/L, respectively). Table 4 shows that, at these sites, the DOC removal by anionic IEX was 52 percent at Andijk [35] and 54 to 60 percent at Plymouth (Table 3 and Zheng et al. [36]). There was a high removal of the humic fractions, i.e., HS and BB. The HS and BB decreased by 80 to 85 percent at Andijk [35], while the HS decreased by 70 to 80 percent and the BB by 60 to 80 percent at Plymouth (Table 3 and Zheng et al. [36]). Although in the raw water the LMWa and LMWn concentrations were much lower than the concentrations of HS, 60 percent of the LMWn were removed by SIX® at Plymouth. For both sites there was no removal of BP [35, 36].

Table 3, NOM concentration and SUVA before and after SIX® treatment in Plymouth, 07/03/2014

	DOC, mg/L	BP, mg/L	HS, mg/L	BB, mg/L	LMWa, mg/L	LMWn, mg/L	SUVA, L/(mg*m)
Raw water	1.92	0.19	1.19	0.3	0	0.29	4.59
SIX® treated water	0.88	0.16	0.32	0.12	0	0.17	2.93

The preferential removal of hydrophobic and charged humic fractions, and the inefficacy on the uncharged hydrophilic biopolymers is in accordance with previous research [37]. This has also been confirmed in the work of Hu et al. [38]: with canal water, anion IEX removed mostly HS (88 percent), BB (74 percent) and LMWa (55 percent), while the removal of BP was ineffective. Electrostatic interactions are dominant in NOM removal by IEX, although NOM can also be partially removed by hydrophobic interactions [20]. This could explain why also LMWn were partially removed by SIX®. Not only can the character of NOM influence the efficiency of removal by IEX, but also competing ions might hinder the NOM removal capacity of the resin, as observed at Blankaart. There, the sulphate concentration in raw water was typically 100 mg/L. In the resin of the MIEX® pilot, only 11 percent of the resin capacity was used for NOM removal, while 68 percent of capacity was used to remove sulphate (the rest of the capacity was used for bicarbonate, 21 percent, and nitrate, about 4 percent) [7].

Table 4, NOM and NOM fractions removal by IEX at various locations

Installation	Technology (resin)	Water type	NOM type	Initial NOM	NOM removal	Type measurement	Reference
MIEX® pilot (Belgium)	FIX (Miex® resin)	Reservoir water from river IJzel and lowlands	TOC (mg C/L)	11	42%	-	[7]
			UV$_{254}$ (m^{-1})	25	68%	-	
FIX column Blankaart (Belgium)	FIX (Miex® resin, Purolite A860S and VPOC1071)		TOC (mg C/L)	-	40-60%	-	
			UV$_{254}$ (m^{-1})	-	70-80%	-	
FIX pilot 50m^3/h Blankaart (Belgium)	FIX (Purolite PPA860S)	Reservoir water from river IJzel and lowlands	TOC (mg C/L)	11	39%	Average value between 12-11-2015 and 2-5-2017	[34] and Figure 7
			UV$_{254}$ (m^{-1})	23	61%		
Pilot treatment plant Plymouth (United Kingdom)	SIX® (Lewatit S5128)	River	CDOC (mg C/L)	6.7	60%,	Single measurement 16-08-2014, LC-OCD	[36]
			Bio-polymers (mg C/L)	-	Almost no removal		
			Humics (mg C/L)	-	in the range of 80%		
			Building Blocks (mg C/L)	-	in the range of 80%		
			LMW neutrals (mg C/L)	-	in the range of 60%		
	SIX® (Lewatit S5128)	Burrator reservoir	DOC (mg C/L)	1.91	54%	Single measurement 07-03-2014, LC-OCD	Table 3
			SUVA (L/(mg*m))	4.59	36%		
			Bio-polymers (mg C/L)	0.19	14%		
			Humics (mg C/L)	1.19	73%		
			Building Blocks (mg C/L)	0.30	62%		
			LMW acids (mg C/L)	0	-		
			LMW neutrals (mg C/L)	0.29	41%		
Pilot plant Andijk (The Netherlands)	SIX®	IJssel Lake water stored in a reservoir for several days, is chemically softened and the pH is adjusted with CO_2	DOC (mg C/L)	5.6	52%	Average value from 01-01-2012 to 15-04-2015	[35]
			Humics and Building blocks	-	In the range of 80-85%	Single measurement 31-07-2013, LC-OCD	
			LMW acids	-	In the range of 60-70%		
			Biopolymers	-	~0%		

3.3 Effect on coagulant dose

Coagulation removes preferentially high molecular weight hydrophobic NOM (including part of HS) and BP [37]. At Plymouth, the combination of SIX® and in-line coagulation with ceramic membrane filtration, compared to conventional treatment, resulted not only in a higher NOM removal (up to 0.9 mg/L of DOC more), but also in 50 percent lower dose of coagulants [23]. At Blankaart, during the batch tests on raw water and on water treated with MIEX® resin, there was a reduction of the required coagulant dose as well, from 20 to 8 mg/L of Fe, and the same overall NOM removal efficiency was obtained [7], even if the coagulation pH of the water after the MIEX® resin treatment was not checked or adjusted to be optimal. In addition, the 50 m^3/h FIX pilot at Blankaart showed that IEX could reduce the coagulant dose from a range of 23 to 30 mg/L of Fe (full scale plant without IEX) to a range of 10 to 15 mg/L of Fe [34].

Verdickt and Schoutteten [34] observed differences between the 50 m^3/h FIX pilot at Blankaart and a FIX pilot at another drinking water treatment location at Kluizen. Firstly, due to higher sulphate concentration in the raw water, the treatment in Blankaart required higher resin doses than in Kluizen for the same NOM removal efficiency. Secondly, the NOM removal by ferric coagulation in Blankaart, at pH 6, was higher than in Kluizen. In Kluizen, the pH of the polyaluminum chloride conventional coagulation was 7.6, thus not at an optimal pH; therefore, the FIX pilot in Kluizen (with only 0.45 mL/L effective resin concentration) had more impact on reduction of the coagulant dosed. In addition, IEX had a larger contribution to the improvement of overall NOM removal at Kluizen, compared to the conventional treatment plant [34]. This experience shows that the overall NOM removal and the reduction of coagulant dose by IEX depend on the quality of the untreated water.

Verdickt and Schoutteten [34] also observed a potential disadvantage of using FIX before coagulation. During the algae blooms' season, the FIX bed of the 50 m^3/h pilot experienced algae accumulation in the top layer of the resin bed; this caused stratification of the bed and consequently, uneven regeneration of the resin. In this case, the problem was mitigated by increasing the upflow velocity and the resin dose.

3.4 Limitation of membrane fouling

At Andijk and Plymouth, SIX®, coagulation (coagulation/clarification and in-line coagulation), or a combination of these two techniques were tested to study their effect on fouling on ceramic microfiltration membranes [36, 35]. When both SIX® and coagulation were used, the membrane performance was stable: 0 to 1.2 kPa/day of trans membrane pressure (TMP) increase were observed, depending on the location and the cleaning regime (i.e., backwash frequency and chemical cleaning). SIX® and in-line coagulation lowered the TMP and its rate of increase. With SIX® pre-treatment only, fouling varied at the different locations. At Andijk, there was a very low TMP increase (0.01 KPa/day with 68 LMH and 30 min filtration time) [39], whereas the TMP increase was still high for Plymouth (about 6.5 KPa/day, 112 LMH and filtration time 54 min) [36].

This can be attributed to the different characteristics of the BP at the two locations, which showed differences in the absorption of UV 254nm. At Andijk, BP did not absorb UV, where the BP at Plymouth responded to UV [39]. A possible cause of the UV absorption of the BP at Plymouth could be the presence of aromatic structures. The fouling behaviour was also different: at Andijk, the BP could be removed easily by backwashing, and this was not the case for the BP at Plymouth [39]. When aromatic structures are present, calcium can bind to the acid functional groups of NOM and enhance membrane fouling by calcium bridging with a membrane surface or by charge screening [40, 41]. For ultrafiltration membranes it was found that backwashing with permeate water is then not effective [40].

The results at Andijk and Plymouth suggest that, depending on the characteristics of the water to be treated, coagulation may have a larger beneficial influence on ceramic microfiltration fouling than anion IEX. In particular, at Plymouth, coagulation was the key to control membrane fouling at IEX had no effect. Two possible causes were identified, namely the high level of BP removal by coagulation, and the protection of the membrane surface by coagulation micro flocs, i.e., forming a cake layer [39]. The BP, targeted by coagulation, has also been identified as main foulant of polymeric micro- and ultrafiltration membranes by others [17, 42, 43]. In some instances, humics, targeted by IEX, also might contribute to membrane fouling, depending on the type of membrane, e.g., in tighter polymeric membranes [44], or in case of sorption on the membrane [45]. However, Cornelissen et al. [46] observed that NOM removal by IEX is not always effective in reducing organic fouling on polymeric membranes, and showed that IEX can even be the cause of a flux decline due to biofouling. In the study of Cornelissen et al. [46], the fouling was attributed to the release of bacteria growing on the resin of a FIX system into the membrane system.

3.5 Effect on advanced oxidation based on UV/H_2O_2: AOC formation during oxidation and UV energy consumption

Advanced oxidation processes that are based on UV/H_2O_2 are used in drinking water treatment for disinfection and mainly for removal of organic micropollutants. At Andijk, the pilot scale pre-treatment with SIX® and ceramic microfiltration was more efficient in removing DOC than the conventional full-scale treatment. In both full-scale and pilot scale pre-treatment, the UV/H_2O_2 treatment did not change the concentration of DOC: on average, before and after this step, the average DOC remained 2.4-2.3 mg/L for the full-scale treatment and 1.8-1.7 mg/L for the pilot.

However, the average AOC concentration during advanced oxidation increased considerably, from 6.2 µg C/L to 40.7 µg C/L in the conventional full-scale treatment, and from 12.9 µg C/L to 35.1 µg C/L at the IEX/microfiltration pilot (Table 5).

Table 5, DOC and AOC before and after UV/H_2O_2 treatment, for SIX®/microfiltration pilot and for full scale treatment at Andijk. The standard deviation is indicated by "±" and number of measurements is indicated by "()".

	DOC, mg/L		AOC, µg/L	
	Feed of UV/H_2O_2	Effluent of UV/H_2O_2	Feed of UV/H_2O_2	Effluent of UV/H_2O_2
SIX®/microfiltration pilot	1.8 ± 0.2 (30)	1.7 ± 0.2 (31)	12.9 ± 6.7 (43)	35.1 ± 21.1 (26)
Full scale treatment	2.4 ± 0.2 (13)	2.3 ± 0.1 (13)	6.2 ± 2.9 (27)	40.7 ± 22 (47)

This is confirmed by literature; when NOM is not fully mineralized after (advanced) oxidation, there is a preferential shift from NOM aromatic fractions into more biodegradable and hydrophilic fractions [47]. Thus, small assimilable compounds are formed, and the AOC concentration may increase, deteriorating the biostability of the water [15].

At Andijk, due to the two different pre-treatments, i.e., conventional pre-treatment and IEX/microfiltration, the water quality of the UV/H_2O_2 feed was different for the conventional full scale treatment and for the pilot. In particular, the average BP concentration in the UV/H_2O_2 feed after IEX/microfiltration pre-treatment, 0.2 mg/L, was larger than after the conventional pre-treatment, 0.1 mg/L. As BP are typically not aromatic [13] and thus not targeted by advanced oxidation, this could explain why the average AOC increased less during the UV/H_2O_2 after IEX/microfiltration treatment.

The test at Andijk showed that both coagulation and ion exchange had a role in reducing AOC formation during advanced oxidation with UV/H_2O_2, because these treatment steps lowered the incoming NOM concentration, which is a key precursor for AOC formation. Grefte et al. [37] studied the effect of FIX in pre-treatment before oxidation with ozone, and observed that prevention of AOC formation was more important than AOC removal in subsequent treatment steps, to achieve biostable drinking water. When FIX was added to the pre-treatment, the DOC concentration before ozonation was 49 percent lower and, as a consequence, the AOC formation during ozonation was then 53 percent lower.

Martijn et al. [48] showed another benefit of using IEX before UV/H_2O_2, as IEX removes both NOM and nitrate. Dissolved NOM and nitrate interfered in advanced oxidation, by absorbing UV light and consuming hydroxyl radicals that are produced and intended for oxidation of micropollutants. As a result, compared to conventional coagulation and sand filtration, the combination of IEX and ceramic microfiltration was able to lower by 30 percent the electrical energy per order, which is the specific electrical energy consumption per m^3 of water required to reduce the micropollutant concentration by 90 percent [48].

3.6 Effect on efficiency of activated carbon

At Andijk, the NOM and AOC removal by GAC was studied after conventional full-scale and SIX®/microfiltration pilot pre-treatment, and after UV/H_2O_2. At the pilot with SIX®/microfiltration pre-treatment, DOC removal in the GAC was less efficient than at the conventional full-scale plant, while the AOC removal in the GAC was almost the same (Figure 8 and Figure 9).

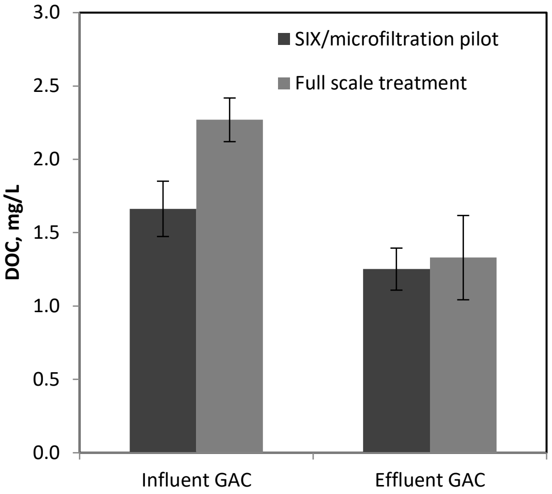

Figure 8, DOC before and after GAC. The error bars give the standard deviations. The number of measurements is 13 for the influent GAC in full scale, 12 for the effluent GAC in full scale, 31 for the inlet GAC in the SIX®/microfiltration pilot and 31 for the effluent GAC at the SIX®/microfiltration pilot

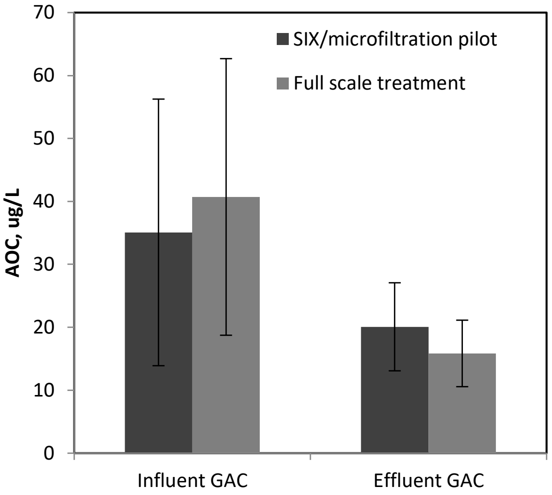

Figure 9, AOC before and after GAC. The error bars give the standard deviations. The number of measurements is 47 for the influent GAC in full scale, 55 for the effluent GAC in full scale, 26 for the inlet GAC in the SIX®/microfiltration pilot and 26 for the effluent GAC in the SIX®/microfiltration pilot

After GAC, the average DOC was 1.3 mg/L DOC for both the pilot and the full-scale treatment, and the average AOC was 20.1 µg/L for the pilot and 15.8 µg/L for the full-scale treatment. The GAC at both pilot and conventional full-scale removed mostly HS and neutrals; however the contribution of the various fractions was different (Table 6). In particular, almost 50 percent of the average removed DOC was HS for the conventional full-scale plant, and at the SIX®/microfiltration pilot the average removal was lower, about 30 percent. One explanation is linked to the older carbon used in the pilot filter, which had a lifetime of 1.5 to 2 years. However, it could also be due to a lower concentration of HS in the GAC influent after the SIX®/microfiltration pre-treatment (0.7 ± 0.1 mg/L) compared to the GAC influent after the conventional pre-treatment (1.0 ± 0.1 mg/L).

Table 6, BP, HS, BB and LMWn before and after GAC treatment, with SIX®/microfiltration pilot pre-treatment and with conventional full scale pre-treatment. The standard deviation is indicated by "±" and number of measurements is indicated by "()". The LMWa are not included because of their low concentration.

	BP µg/L		HS µg/L		BB µg/L		LMWn µg/L	
	Influent GAC	Effluent GAC	Influent GAC	Effluent GAC	Influent GAC	Effluent GAC	Influent GAC	Effluent GAC
SIX®/microfiltration pilot	177±37 (31)	143±24 (31)	669±132 (31)	538±94 (31)	358±30 (31)	302±41 (31)	370±25 (31)	240±31 (31)
Full scale treatment	124±14 (13)	88±18 (12)	989±134 (13)	551±126 (12)	559±138 (13)	443±103 (12)	468±34 (13)	223±51 (12)

Activated carbon has been used in water treatment with the aim to remove NOM, e.g., to meet local legislation standards for DBP concentration in drinking water [2], or to improve taste and odor of the drinking water [1]. However, most drinking water companies nowadays use GAC mainly to remove micropollutants. NOM can considerably reduce the efficiency of activated carbon for the removal of micropollutants, occupying available carbon surface through adsorption competition or pore blocking, as shown by, e.g., De Ridder et al. [5]. Hu et al. [38] showed that the removal of NOM by IEX, that targeted HS and BB and partially LMWa, was beneficial to limit pore blocking of GAC filters. However, IEX did not limit the adsorption competition between NOM and micropollutants in powdered activated carbon (PAC), suggesting that HS and BB were not responsible for adsorption competition into the smaller pores of PAC [38]. Hu et al. [38] also argued that low molecular weight hydrophobic NOM, which is not removed by IEX, could be responsible for adsorption competition.

3.7 Effect on DBP formation

When NOM reacts with chlorine or other disinfection chemicals, it forms DBPs. The toxicity of an organic DBP is correlated to the production of organic halogens, and depends from, e.g., applied disinfection chemical, and presence of inorganic DBPs, such as bromate, chlorite and chlorate [49]. DBP concentrations in drinking water are regulated by, e.g., European Union legislation [50]. Because

DBPs are potentially harmful for human health, the DBPs regulations from European Union from are in the process of becoming more stringent [51]. Two major groups of DBPs in drinking water after chlorination are trihalomethanes (THMs) and haloacetic acids (HAAs) [52]. THMs and HAAs are formed by various NOM fractions, and each with different potentials [53]. Hydrophobic, high molecular weight NOM is highly reactive with chlorine and is the main DBP precursor [54]. However, hydrophilic NOM can also contribute to DBP formation [54]. For example, hydrophilic NOM can form the more toxic bromated DBPs during chlorination when bromide is present [55]. The option of reducing the dose of disinfectant to lower DBP formation is limited [56]. Therefore, DBP formation should be lowered by adding an extra treatment step for NOM removal before disinfection, especially when enhanced coagulation is already in use [1].

At Plymouth, the pilot tested the role of SIX® and microfiltration on DBP/THM precursor removal and DBP/THM formation potential (DBPFP and THMFP) before disinfection. SIX® was tested both alone and in combination with in-line coagulation [23]. The performance was compared to the existing conventional water treatment plant which used coagulation as the NOM removal technology. The SIX® and in-line coagulation pre-treatment with ceramic membrane filtration led to 58 to 67 percent lower THMFP and HAAFP than conventional coagulation. When SIX® was used without in-line coagulation as membrane pre-treatment, only in one case the DBPFP was lower than in conventional treatment, i.e., when the raw concentration of DOC was high, about 6 mg/L [23]. This was to be expected, because these high DOC concentrations were typically due to HS flushed into water supplies during rainfall events, and HS were readily removed by IEX. Also, the formation of brominated DBPs was 30 to 67 percent lower for the SIX® and in-line coagulation pre-treatment with ceramic microfiltration compared to conventional coagulation [23]. In the case of high DOC concentrations, the brominated DBPFP of the SIX®-treated water was, again, lower when compared to that of conventional treatment.

4 Conclusions

Three drinking water companies in the North Sea region use or are considering to use anionic IEX on surface water in the early stage of their full scale treatment plants. In this situation, the (considered) anionic IEX systems use non-fixed bed technologies: MIEX®, FIX, and SIX®. The studies on bench and pilot scale showed that anionic IEX removed typically 40 to 60 percent of the total NOM. The NOM removed by IEX was mostly in the hydrophobic range, and, according to LC-OCD, IEX predominantly targeted HS and BB, which are negatively charged, while almost no BP were removed.

Although the benefit of IEX pre-treatment depended on the type of NOM in the feed water quality, the studies revealed the following NOM-related effects in drinking water treatment:

- IEX removed NOM fractions that partially overlap the NOM targeted by coagulation. As a consequence, IEX before coagulation resulted in lower doses of coagulants to achieve NOM removal of 50 percent or more.
- Used as pre-treatment, IEX had a limited direct influence on improving fouling of ceramic microfiltration membranes.
- IEX removes precursors of AOC, which is formed during advanced oxidation with UV/H_2O_2, diminishing the impact on biological stability of treated drinking water.
- IEX removed NOM and nitrate, which interfere in UV treatment. This resulted in lower energy consumption during UV/H_2O_2 treatment.
- IEX in pre-treatment contributed to lower subsequent DBP formation. A combination of IEX, coagulation and ceramic microfiltration was shown to outperform conventional coagulation with sand filtration. The improvement in DBP formation by NOM removal by IEX was dependent on NOM character and concentrations.

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Chapter 3

Separating NOM from salts in ion exchange brine with ceramic nanofiltration

This chapter is based on

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Separating NOM from salts in ion exchange brine with ceramic nanofiltration

Abstract

In drinking water treatment, natural organic matter (NOM) is effectively removed from surface water using ion exchange (IEX). A main drawback of using IEX for NOM removal is the production of spent IEX regeneration brine, a polluting waste that is expensive to discharge. In this work, we studied ceramic nanofiltration as a treatment for the spent NOM-rich brine, with the aim to reduce the volume of this waste and to recycle salt. Compared to polymeric nanofiltration, the fouling was limited. When NOM is rejected and concentrated, a clean permeate with the regeneration salt (NaCl) could be produced and reused in the IEX regeneration process. Bench scale studies revealed that NOM could be effectively separated from the NaCl solution by steric effects. However, the separation of NaCl from other salts present in the brine, such as Na_2SO_4, was not sufficient for reuse purposes. The low sulphate rejection was mainly due to the low zeta potential of the membrane at the high ionic strength of the brine. The permeate of the ceramic nanofiltration should be treated further to obtain a sodium chloride quality that can be recycled as a regenerant solution for ion exchange. Further treatment steps will benefit from the removal of NOM from the brine.

1 Introduction

Natural organic matter (NOM) is one of the rising problems for drinking water treatment from surface waters, and its removal at the beginning of a treatment train improves many downstream processes (Matilainen and Sillanpää, 2010). Ion Exchange (IEX) can remove negatively charged NOM, including NOM fractions that are not targeted by conventional coagulation (Grefte et al., 2011). There are two main problems related to the use of IEX for NOM removal upstream the surface water treatment system: (1) the conventional fixed IEX bed configuration is not suitable for application at the beginning of the treatment, and (2) regeneration of IEX resin produces a polluting waste stream, that can be difficult to manage and expensive to discharge.

The first problem is mainly linked to clogging by suspended solids; however, it can be solved by avoiding packed beds columns (Verdickt et al., 2012; Galjaard and Koreman, 2015). This was first achieved with the introduction of the magnetic ion exchange process (MIEX) over twenty years ago (Morran et al., 1996). Afterwards, the MIEX system is scaled up and patented (Bourke et al., 1999). More recently two new configurations have been introduced: the suspended ion exchange (SIX®) (Galjaard and Koreman, 2015) and Fluidized IEX (FIX) (Cornelissen et al., 2010; Verdickt et al., 2012). These two systems can also be used in the first stages of a surface water treatment train. A recent review by Levchuk et al. (2018) showed that IEX consistently removes NOM from drinking water sources, and that the unremoved NOM, generally between 10 and 40 percent, is uncharged. Although the concentrations may differ, all configurations produce high saline waste streams which consist of sodium chloride (NaCl), sodium sulphate (Na_2SO_4), sodium nitrate, and humic and fulvic acids.

The second problem is the disposal of this waste stream, which is still a drawback for the application of all IEX-processes in full scale water treatment (Verdickt, 2012). In general, saline waste streams are frequently produced in drinking water or industrial water production. Probably the largest amount is produced as a result of seawater desalination (Jones et al., 2019). Other sources of saline waste streams are inland desalinisation installations, such as in the treatment of brackish groundwater with reverse osmosis, and spent regenerants from IEX processes. Conventional methods to dispose brines are landfill, ground storage, deep well injection, evaporation ponds, and discharge in the sewer or, in coastal area, in the sea (Brandt et al., 2016; Neale and Schäfer, 2009; Panagopoulos et al., 2019). However, risks linked to landfill and ground storage include pollution of ground water and salt pollution of soil (Mohamed et al., 2005). In addition, discharge in the sea can have a negative impact on the sea ecology. The brine has different salinity compared to the sea, and may contain pollutants (Neale and Schäfer, 2009). In some cases, zero liquid discharge technologies are used. The goal of zero liquid discharge is to concentrate the dissolved salts as much as possible with technologies as reverse osmosis or electro dialysis (Subramani and Jacangelo, 2014). Finally, an evaporation and a crystallisation technology is used to obtain the dry salt. The drawback of this technology is the energy use of the evaporation and crystallisation step (Panagopoulos et al., 2019).

To the authors` knowledge, there is few literature specific for waste management of brine from IEX for NOM removal for drinking water production. The NOM-rich brine from several pilot and full scale plants with MIEX and conventional IEX has also been reported to be disposed in conventional waste water treatment plants (WWTP) (Schippers et al., 2005; Amini et al., 2015; Arias-Paic et al., 2016). For most of the treatment plants described by Amini et al. (2015), this is done after dilution and slow discharge. However, depending on, e.g., the brine composition and volume, discharge to a municipal

WWTP is often not feasible. Biological treatment can be challenged by the presence of salts (Romero Barranco et al., 2001). Moreover, the specific NOM in the IEX brine is considered not readily biodegradable. The external costs for brines treatment are high, e.g., between 50 and 200 euro/m^3 in the European Flanders region (Ceulemans et al., 2015). In addition, drinking water companies deal with restrictions regarding waste disposal, meaning that brine treatment for reuse and recovery is of interest as a sustainable solution to brine management. Two approaches are used and/or studied to reduce the volume of brine waste: reusing the brine multiple times before disposal, and treating the brine to recover the resources in the brine, for instance the water, the regeneration salts and the NOM.

Regeneration brine has been reused for, e.g., IEX full scale and pilots in the Netherlands, in the United Kingdom, in Belgium, and in the United States (Schippers et al., 2005; Vaudevire and Koreman, 2013; Verdickt et al., 2012; Amini et al., 2015; Verdickt and Schoutteten, 2018). In the water treatment plants described by Amini et al. (2015), portions of low conductivity brine were recycled as raw drinking water, and in some cases the brine was reused until a minimum conductivity was reached. The conductivity in this case can be an indicator of the remaining concentration of NaCl in the brine. In the pilot plant from Schippers et al. (2005), the regenerant was reused three times before disposal. First, the resin bed was regenerated by a three times used solution, and subsequently by a two and one time used solution, and finally with fresh regenerant (10 percent NaCl) (Schippers et al., 2005). For the pilot study of Verdickt et al. (2012), the waste brine was reused after flocculation with 6 g $FeCl_3$/L, filter pressing, and pH adjustment. Verdickt et al. (2012) observed that the sulphate (SO_4^{2-}) accumulated in the reused brine reduced the removal of sulfates, nitrates and alkalinity from the main process water, but this did not affect the NOM removal greatly. Although reusing the brine can reduce the waste volumes and the use of chemicals (Amini et al., 2015; Schippers et al., 2005; Verdickt et al., 2012), this approach has as the main drawback that it creates a limit for the amount of resin per litre of water that can be regenerated (Verdickt and Schoutteten, 2018). The volume of the brine after regeneration is generally larger than the volume of the brine before regeneration, because the resin also needs a rinse with clean water before returning in the ion exchanger. If the resin cannot be rinsed properly, excessive salt ends up in the treated water (Verdickt and Schoutteten, 2018).

Research on NOM-rich brine treatment has been focussed on treatment technologies that use polymeric membranes. For pressure driven membranes, the range of molecular weight cut-off (MWCO) was mostly in the nanofiltration range (Schippers et al, 2005; Vaudevire and Koreman, 2013; Kabsch-Korbutowicz et al., 2011; Leong et al., 2015). The resources that could be recovered from the brine has mainly been the NOM and the regeneration salt (typically NaCl). Concentrated

NOM has been suggested to be used in agriculture and food industry, and the clean regeneration salt solution could be recycled in IEX regeneration itself (Schippers et al., 2005; Leong et al., 2015; Vaudevire and Koreman, 2013; Haddad et al., 2019; Vaudevire et al., 2019). When brine is treated, however, other anions from the raw water could also accumulate in the NaCl regenerant. For instance, in case of raw water containing SO_4^{2-}, this anion has a high affinity for the IEX-resin and also accumulates in the regenerant brine. Therefore, it would be beneficial if the membrane could combine rejection of SO_4^{2-} with NOM rejection, without limiting the passage of Cl^- to the permeate. Polymeric nanofiltration for IEX brine treatment removed NOM by about 90 percent and more (Schippers et al., 2005; Kabsch-Korbutowicz et al., 2011; Vaudevire and Koreman, 2013; Jirícek et al., 2015; Ceulemans et al., 2015). The passage of Cl^- was high, but some of the tightest membranes showed some Cl^- rejection (Kabsch-Korbutowicz et al., 2011; Leong et al., 2015). Where measured, the rejection of SO_4^{2-} was between 75 and 90 percent (Vaudevire and Koreman, 2013; Leong et al., 2015). In case of direct brine reuse after treatment, because of the presence of resin rinse water in the brines, concentration should be included in the treatment. Therefore, dynamic vapour decompression (Vaudevire and Koreman, 2013) and membrane distillation (Jirícek et al., 2015; Ceulemans et al., 2015) have been considered after nanofiltration. Electrodialysis has also been studied as alternative treatment for NOM-rich IEX brine (Kabsch-Korbutowicz et al., 2011; Haddad et al., 2019; Vaudevire et al., 2019). In particular, Vaudevire et al. (2019) were interested in the recovery of concentrated NOM and NaCl water for regeneration reuse. Vaudevire et al. (2019) piloted a two stage process: monovalent selective electrodialysis, with high removal of Cl^- and low removal of NOM; and standard elecrodialysis with removal of inorganic content and conservation of NOM. According to Haddad et al. (2019), monovalent selective electrodialys is a promising option for NOM-IEX brine treatment.

However, an attention point of the technologies that use polymeric membranes is that their performances can decrease in the presence of NOM, e.g., due to fouling, as shown by Gryta et al. (2001), Lindstrand et al. (2000), Lee et al. (2002), and Hong and Elimelech (1997). Therefore, additional technologies were used to counteract NOM fouling in NOM-IEX brine membrane treatment, e.g., frequent feed forward flush during nanofiltration (Vaudevire and Koreman, 2013), and vibratory shear-enhanced processing (VSEP) (Leong et al., 2015). VSEP enhances cross flow using vibrations along the membrane surface.

This paper is focused on ceramic nanofiltration membranes because of their advantages over polymeric membranes, e.g., higher fluxes and lower fouling characteristics (Hofs et al., 2011; AMTA, 2018). In addition, ceramic membranes are supposed to be more durable than the polymeric membranes: both mechanical strength and chemical resistance are better (Sondhi et al., 2003; Van der Bruggen et al., 2003). NOM, removed by IEX, is supposed to be mostly composed of humic substances (Grefte et al., 2011), and therefore bench scale rejection tests were performed with ceramic membranes using NOM that was isolated from IEX brines from two different water treatment plants. In addition, the rejection of NaCl and Na_2SO_4 in NOM rich brine was studied. Waste brine can have varying ionic strengths, depending on the IEX regeneration system and the varying composition of the negative ions in the raw water. To simulate this, different ionic strengths and concentrations of NaCl and Na_2SO_4 were used for testing. In addition, the influence of the zeta potential and the NOM charge on the rejection of NOM and salts from the simulated brines was studied.

2 Materials and Methods

2.1 Characteristics of the membranes

The commercial ceramic membranes (Inopor GmbH, Germany) used in this study have a support layer of Al_2O_3 and a separation layer of TiO_2. According to the manufacturer, the mean pore size of the separation layer was 0.9 nm and the membrane porosity was 30 to 40 percent. For the filtration tests, we used a single channel tubular shaped membrane with an internal diameter of 7 mm and filtration area of 0.00163 m^2. For the zeta potential tests (see section 3.1.2), a flat disk membrane with the same characteristics as the tubular membrane was used.

The MWCO of a membrane is the molecular weight of a compound that shows 90 percent retention. To measure the MWCO of the tubular ceramic membrane for the filtration tests, a solution of demineralized water and a mixture of polyethylene glycol (PEG) of five sizes, (i.e., 200, 300, 400, 600 and 1000 Da) (Sigma-Aldrich, Germany) was filtered. This procedure was similar of those by Shang et al. (2017) and Kramer et al. (2019). The PEG of each size had a concentration of 0.6 g/L in the mixture. The filtration was in cross flow mode and the concentrate was recirculated as feed. After 60, 70 and 80 min of filtration, three permeate samples were collected (temperature range 22 to 25 ^{o}C, trans membrane pressure range 2.9 to 3.1 bar, flux range 41 to 43 LMH, cross flow velocity 1.28 to 1.31 m/s); the feed was sampled twice, during the collection of the first and third permeate. After 0.45 µm filtration, the samples were analysed using high performance liquid chromatography (Prominence, Shimadzu, Japan) with a refractive index detector (RID-20A, Shimadzu, Japan) and two gel permeation chromatography columns for size exclusion (5 µm 30 Å, PSS GmbH, Germany). Knowing the elution time of the single sizes of PEG, the signal of the refractive index detector for permeate and feed samples were compared to calculate the membrane retention of each PEG size.

Further, a streaming potential measurement was used to determine the zeta potential of the membrane. The zeta potential is the potential difference between the slippery plane of the electrical double layer (that consists of the Stern layer and the diffuse layer) of a surface and the surrounding stable electrolyte, and it gives an indication of the charge in the proximity of the membrane. The zeta potential is thus frequently used as a tool to describe the charge of membranes (Hurwitz et al., 2010). The measurement was performed on 0.02 m x 0.01 m dices of a flat disk membrane. The streaming potential was measured by an electrokinetic analyzer (SurPASS, Anton Paar, Austria) with tangential mode. An electrolyte solution passed through the channel formed by two membrane dices. As explained by Chang (2016), an electrolyte solution removes from the surface of the channel the ions with opposite charge compared to the charge of the surface of the channel, causing a difference in the electrical potential between the two ends of the channel. The measured streaming potential (ζ) was used by the electrokinetic analyzer to calculate the zeta potential according to the Helmholtz-Smoluchowski relation (Christoforou et al., 1985), with Equation 1:

$$\zeta = \frac{dI}{dp} \times \frac{\eta}{\varepsilon_r \times \varepsilon_0} \times \frac{L}{A} \qquad (1)$$

Where *dI/dp*= streaming current coefficient, *L*= length of membrane dice, *A*= cross section area of the channel, η= viscosity, ε_0 =vacuum permittivity, and ε_r = relative permittivity of the background solution.

NaCl solutions of 0.01 M and 0.1 M were used to simulate the zeta potential for various brine conditions; it was not possible to measure the zeta potential in a NaCl solution of 1M, because this was outside the measurement range of the instrument. The pH was adjusted manually from 4 to 8 or 9, with a temperature range of 22 to 25 ^{0}C.

The Debye length also gives an indication of the effect of membrane charge. The Debye length is distance in the double layer where the surface electric potential of a charged surface is decreased by 1/e magnitude (Sillanpää and Shestakova, 2017). For different solution ion strengths (0.01, 0.1 and 1 M), we calculated the Debye length (κ^{-1}, m) in water at 20°C was calculated using Equation 2 (Hunter, 1981):

$$\kappa^{-1} = \left(\frac{\varepsilon_0 \times \varepsilon_r \times K_B \times T}{2000 \times N_A \times e^2 \times I}\right) \qquad (2)$$

Where ε_0 = vacuum permittivity (8.85×10^{-12} C V^{-1} m^{-1}), ε_r = relative permittivity of the background solution (80 for water at 20°C), K_B = Boltzmann constant (1.38×10^{-23} JK^{-1}); T = absolute temperature (K); N_A = Avogadro number (6.0×10^{23} mol^{-1}); e = elementary charge (1.6×10^{-19} C), I = ionic strength (mol L^{-1}).

2.2 Character of NOM

Two concentrated NOM samples were provided by two Dutch water companies, Vitens and PWN. Both samples contained NOM that has been recovered from spent IEX regenerant brines, and these samples contained mostly humic substances. The NOM of Vitens had a groundwater origin, while the NOM of PWN had a surface water origin. For the characterisation of NOM, the organic carbon of five NOM fractions was measured by Het Water Laboratorium (the Netherlands), using liquid chromatography- organic carbon detection (LC-OCD) (as described in Huber et al., 2011). The five NOM fractions, i.e., biopolymers, humic substances, building blocks, low molecular weight acids and low molecular weight neutrals, form the chromatographic fractionation of organic carbon (CDOC) (Huber et al., 2011).

2.3 NOM and salt tests

Rejection tests were performed with four membranes, synthetic brines, and waste brines from IEX treatment of different locations. This paper shows only the results of the membrane with the lowest MWCO and the synthetic brines. The other results are shown in the Supplementary Information of Chapter 3 (Chapter 7). The synthetic feed solution for the Vitens and PWN NOM and salts filtration experiments was prepared by adding the NOM into demineralized water with dissolved NaCl and Na_2SO_4 (Sigma-Aldrich, Germany; Carl Roth, Germany) at varying concentrations. Composition, set ionic strength and pH of the feed solutions, used in the filtration experiments, were divided into four series as summarized in Table 1. The filtration was in cross flow mode and the concentrate was recirculated as feed. The experiments could not be repeated using the same membrane; instead, for each experiment, the permeate was sampled at three different times after the system was stable. After 60 minutes of filtration, three permeate samples were collected one after another for 30 minutes; the feed was sampled twice, during the collection of the first and third permeate (temperature range 27 to 42 ^{o}C). With manual adjustment of a needle valve and pump speed, the cross flow velocity and the flux were maintained constant during sampling and were 1.3±0.1 m/s and 31±7 LMH, respectively (except for the 0.1 M experiment at pH 4, which had a flux of 20 LMH). The cross flow velocity provided turbulent flow with a Reynolds number of 9100 inside the tubular membrane. Directly after each experiment, the membrane was flushed forward with demineralized feed water. Before each experiment, after the last experiment of each series and after each experiment at pH 4, the ultrapure water permeability was measured (temperature range 20 to 32 ^{o}C, trans membrane pressure of approximately 3 bar, recirculation cross flow velocity of approximately 1.3 m/s). After the final permeability tests of series 1, series 2, series 3, and the experiments at pH 4, the membrane was cleaned with 2 hours soak in a solution of 0.2 percent NaOCl.

Table 1, NOM and salts rejection tests pre-set concentrations.

Series	pH during sampling	Initial NOM (g/L)	Type NOM	Ionic strength of tests (% ionic strength from Na_2SO_4)*					
				0.1 M (100%)	0.1 M (0%)	1 M (100%)	1 M (0%)	1 M (50%)	0.1 M (50%)
1	7.5-8.1	0.3-0.4	PWN	x	x	x	X	x	x
2	7.5-8.1	0.5-0.6	Vitens	-	x	x	-	x	x
3	7.5-8.1	0	No NOM**	x	x	x	X	x	x
4	3.7-3.8	0.5-0.6	Vitens	-	-	-	-	x	x

*The performed experiments are indicated with "x"; **Demineralized water

NOM was measured as dissolved organic carbon (DOC) in the feed and permeate samples. The samples were measured after 0.45 µm filtration by a total organic carbon (TOC) analyzer (TOC-VCPH, Shimadzu, Japan). The concentration of Na^+, SO_4^{2-} and Cl^- in most of the feed and permeate samples were determined by ionic chromatography (Metrohm AG, Switserland). Anions and cations were identified based on their specific charge groups and interaction with two ion exchange columns (Metrosep C6-150/4.0 and A Supp 150/4.0, Metrohm AG, Switserland). For some of the experiments, only SO_4^{2-} was measured, using a test cell kit (Spectroquant, Merck, Germany). For both ion chromatography and kits, the samples were filtrated with a 0.45 µm filter and diluted according to the measurement range of the instruments.

3 Results and discussion

3.1 Characteristics of the ceramic nanofiltration membrane

3.1.1 MWCO

The measured MWCO of the tightest membrane was 560 Da (Figure 1). Due to the size distribution of the pores, PEGs with lower molecular weight were also (partially) rejected. Other membranes from the same manufacturer, tested in a previous study, had a similar MWCO, in the range of 490 ± 99 Da (average ± standard deviation); however, these membranes had a narrower pore size distribution (Shang et al., 2017). Commercially available ceramic membranes cannot reach very low MWCO. The lowest MWCO for commercial ceramic membranes, approximately 450 Da, seems to be provided by the membranes described by Pühlfurß et al. (2000). As a comparison, polymeric nanofiltration membranes, as described in section 1, cover the range of 200-400 Da. The MWCO of the other membranes is shown in the Supplementary Information of Chapter 3 (Chapter 7).

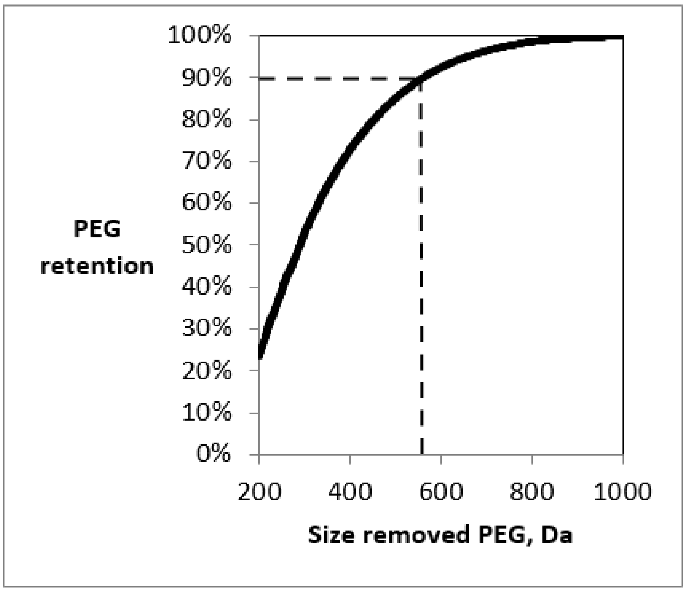

Figure 1, PEG-rejection graph of the commercial membrane. The dashed line shows the PEG size with 90% rejection.

3.1.2 Zeta potential of ceramic membrane at varying ionic strength

The zeta potential of the membrane measured in the NaCl solution was negative (Figure 2). It was dependent on the pH, and the membrane had a less negative zeta potential at lower pH. This behaviour is confirmed by literature for Ti-OH surface groups of TiO_2 (Van Gestel et al., 2002). The membrane's zeta potential was also dependent on the ionic strength of the solution. At 0.01 M ionic strength, the ceramic membrane had more negative zeta potential than at 0.1 M. The decreasing zeta potential is according to the diffuse double layer theory (DLVO-theory). Although the zeta potential at 1M could not be measured, it can be argued that the charge effect of the membrane would be even lower. This hypothesis was confirmed by the calculated, Debye length, which was small (Table 2).

Table 2, Debye length calculated for solutions of ionic strength of 0.01, 0.1 and 1 M, for water at 20^{0}C

Ionic strength (M)	Debye length (nm)
0.01	3.05
0.1	0.97
1	0.31

The effect of the lower zeta potential for the higher ionic strength feed solutions has also been observed (Bagerman et al., 2015) during experiments at nearly saturated salt solutions. Counter-ions, present at higher concentrations, can shield the potential of the electrical double layer of a surface (where the zeta potential is measured), and, consequently, decrease the effect of its charge at the electrokinetic slipping plane where the zeta potential is measured (Skluzacek et al., 2007).

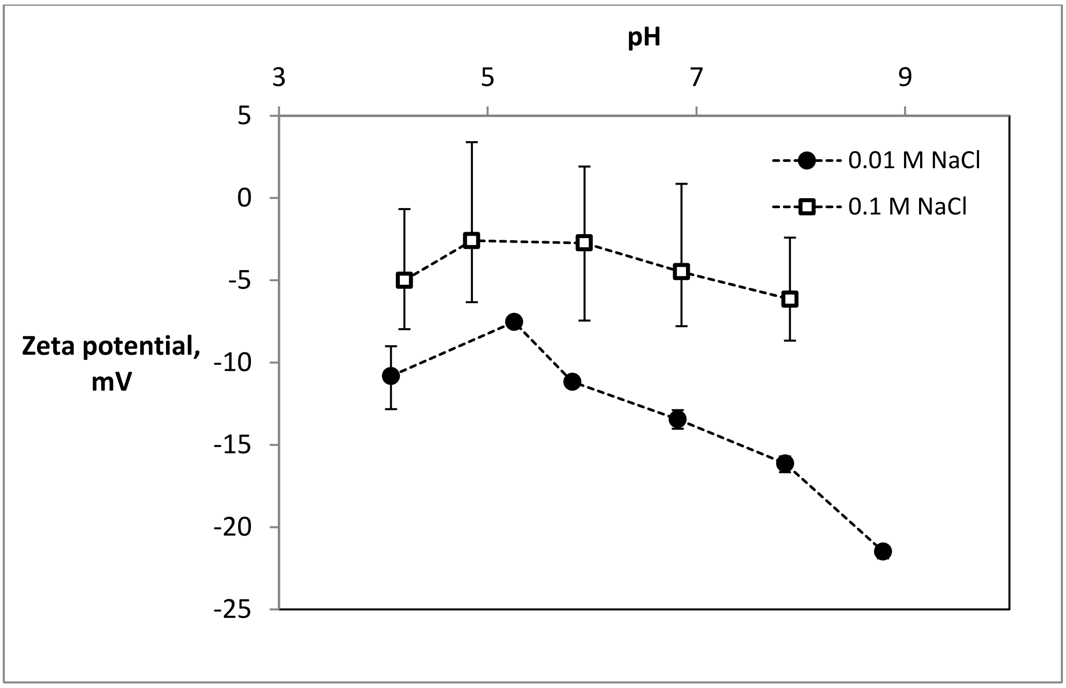

Figure 2, Zeta potential measurement of commercial ceramic nanofiltration membrane, measured in NaCl solutions with ionic strength of 0.01 M (white squares) and 0.1M (black dots).

3.2 Character of NOM

The LC-OCD analyses confirmed that the NOM, provided by Vitens and PWN, abstracted from IEX brines, was mostly humic substances, between 82 percent and 89 percent of the CDOC (Table 3). This was expected because anionic exchange mainly removes NOM by electrostatic interactions (Cornelissen et al., 2008), and humic substances and building blocks are negatively charged (Huber et al., 2011). Minor hydrophobic interactions between NOM and IEX resin (Cornelissen et al., 2008) might explain the presence of very low concentrations of low molecular weight neutrals that are, according to Huber et al. (2011), uncharged. Humic substances are mostly 1000 Da; the smaller fractions, building blocks and low molecular weight neutrals, are in the range of 300 to 500 Da and less than 350 Da, respectively (Huber et al., 2011).

Table 3, LC-OCD fractionation of organic carbon of the NOM isolated in the spent brine, given as a percentage of the CDOC

NOM sample	Bio-polymers	Humic Substances	Building Blocks	Low molecular weight neutrals	Low molecular weight acids
	>>20000 Da	~1000 Da	300-500 Da	<350 Da	<350 Da
PWN	0.1%	82.2%	12.0%	5.8%	0.0%
Vitens	0.0%	88.7%	6.8%	4.5%	0.0%

3.3 Rejection experiments

3.3.1 NOM rejection at high ionic strength

The experiments showed rejections of NOM of at least 97 percent, with one exception (94 percent), even considering the relatively large MWCO (560 Da) of our ceramic membrane. Other studies with polymeric nanofiltration have reported over 99 percent removal of humic acids, but with smaller pore sizes, between 200 and 400 Da (Schippers et al., 2005; Jirícek et al., 2015).

In our experiments, NOM retention was independent of ionic strength, the NaCl:Na2SO4 ionic strength ratio, and the pH of the feed (4 to 8). The independence of pH and ionic strength shows that the zeta potential (Figure 2), and thus the effect of membrane charge, had no influence on NOM retention.

The MWCO measurements in combination with the LC-OCD measurements suggest that the removal of NOM can be attributed mainly to steric hindrance. Figure 1 shows that the membrane was able to reject 90 percent of polymers larger than approximately 600 Da; therefore, we can assume that humic substances (~1000 Da) were completely rejected. Due to the pore size distribution of the membrane, smaller NOM fractions were also likely partially rejected. The expected rejection of building blocks (from 300 to 500 Da), approximated with the rejection of polymers of 400 Da, could have been nearly 73 percent. The rejection of low molecular weight neutrals (smaller than 350 Da) is expected to be much less, because the rejection for PEG-molecules of 350 Da and 200 Da was only 65 percent and 25 percent, respectively. When these expected rejection percentages are applied to the NOM fraction composition of Table 3, the calculated composite rejection of NOM is between 92 and 97 percent, which is close to the measured NOM-rejection during the filtrations experiments. Additional tests with membranes with larger pore sizes and/or brines from different IEX treatment locations show that the used cut-off measurement method predicted fairly well the retention of NOM, knowing its LC-OCD profile (Supplementary Information of Chapter 3, Chapter 7).

For series 1, 2 and 3, see Table 1, the pH of the feed solutions was pH 8, which is close to the common pH of the waste brine. During the first experiments of these series, the ultrapure water permeability dropped from 13-14.5 LMHbar to 10 LMHbar, and then stabilized at 8 LMHbar (see, e.g., Figure 3 for series 2). The ultrapure water permeability was recovered to at least 8 LMHbar after each NOM and salt tests, using only forward flushing with demineralized water, without the need of chemical cleaning or other fouling treatment. These results suggest the presence of higher osmotic pressure difference between feed and permeate due to rejection of SO_4^{2-} or NOM. The trans membrane pressure during the experiments at pH 8 was between 3 and 7 bar, and the provided and the flux was between 24 and 38 LMH. As a comparison, the flux of the polymeric membrane tested by Vaudevire and Koreman (2013) was approximately five times lower, for IEX brine with the same or lower DOC concentrations and for a higher trans membrane pressure (6 to 10 bar).

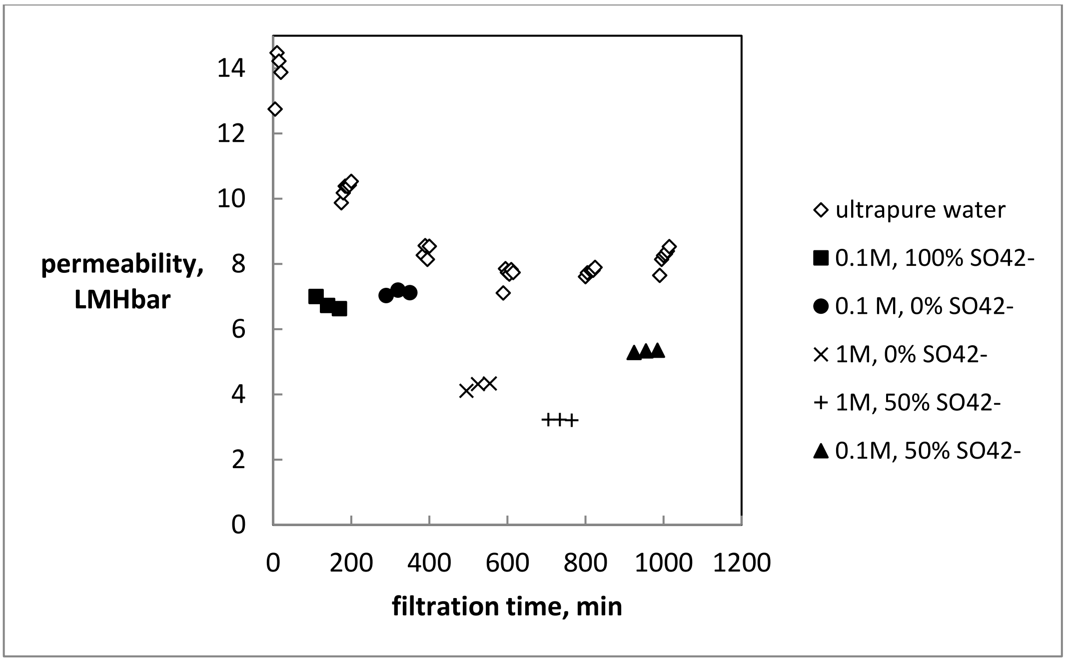

Figure 3, Membrane permeability of the experiments of series 2. In the legend, the pre-set ionic strength and the percentage of ionic strength due to Na_2SO_4 are indicated for each salt experiment.

3.3.2 Influence of NOM on salt rejection

In all the experiments there was a high passage of NaCl, indicated by a Cl^- retention of less than 5 percent. SO_4^{2-} was rejected to a larger extent, compared to Cl^-, because SO_4^{2-} has a larger hydration size and energy (Tansel, 2012), a lower diffusion coefficient (Meihong et al., 2008), and a higher charge valence than Cl^-. In particular, the higher SO_4^{2-} retention at 0.1M compared to 1M showed that charge had an influence at 0.1 M ionic strength, where the membrane is expected to be negatively charged (Figure 2). In the mixed NaCl:Na_2SO_4 solutions without NOM, the retention of SO_4^{2-} was 36 percent at 0.1 M, and only 9 percent at 1 M (Figure 4). Lower SO_4^{2-} rejection at higher ionic strength was also observed in additional experiments with membranes with a higher MWCO (Supplementary Information of Chapter 3, Chapter 7). The negative membrane charge at 0.1 M was confirmed by the Donnan effect, because the retention of SO_4^{2-} in the mixed feed solution was higher compared to the pure SO_4^{2-} solution (Figure 4). According to the Donnan effect, when the membrane is negatively charged, the Na^+ ions easily permeate the membrane. For the permeate to be electrically neutral, anions need to permeate as well. The passage of monovalent Cl^- is preferential because it is less affected by charge repulsion than the divalent SO_4^{2-}. In this case, the rejection of Cl^- in mixed ions solution can even be negative, as frequently observed in literature (e.g., Pérez-González et al., 2015; Bagerman et al., 2015). The Donnan effect was not evident in the experiments with the higher MWCO, probably due to the larger pore size (Supplementary Information of Chapter 3, Chapter 7).

The rejection of SO_4^{2-} improved between 2 and 3 times in the presence of NOM. Additional tests with a membrane at higher MWCO also showed this behaviour (Supplementary Information of Chapter 3, Chapter 7). This has been observed before, by, e.g., Tang et al. (2007). Tang et al. (2007) argued that two mechanisms could be the cause of improved SO_4^{2-} retention in the presence of NOM: membrane pore size reduction by NOM fouling and increased negative charge by NOM in the proximity of the membrane. In the experiments with NOM, the rejection of SO_4^{2-} was higher when the pH of the feed was decreased from 8 to 4 (Figure 4). Humic substances are generally negatively charged at pH 8 and less charged at lower pH; literature reports, e.g., zero charge at pH 3 and less (De Souza and Roca Bragança, 2018; Bratskaya et al., 2008; Saito et al., 2004). Thus, at pH 4 humic substances were nearly uncharged. A lower charge density decreases the repulsion between NOM and membrane wall and, consequently, enhances NOM fouling (Tang et al., 2007) and, likely, pore size reduction. The permeability of the membrane was lower during the experiments at pH 4 compared to pH 8, as shown by Figure 5 for the NOM experiments at 0.1 M ionic strength. The comparison between the experiments at different pH suggests that pore size reduction was the main mechanism involved in the improved SO_4^{2-} rejection in the presence of NOM.

Fouling might thus improve the steric rejection of membranes. However, other mechanisms linked to fouling can have a negative effect on rejection. Hoek and Elimelech (2003) described how cake fouling can enhance concentration polarisation in polymeric membranes by modifying the cross-flow characteristics of the filtration and by inhibiting back diffusion. For ceramic ultrafiltration in the presence of NOM, Shang et al. (2014) observed a lower rejection of phosphate for a background solution with NaCl compared to a background solution with $CaCl_2$ of the same ionic strength. This was attributed to both zeta potential decrease of the NOM and cake-enhanced concentration polarisation due to fouling (Shang et al, 2014), because Ca^{2+} can bind to the acid functional groups of NOM (Li et al., 2011; Shao et al., 2011). In spent IEX brine, however, the cations are mainly Na^+, which can make ceramic nanofiltration suitable for brine treatment at high fluxes. In our experiments, NOM had a positive effect on the removal of SO_4^{2-}, presenting a rejection was between 20 and 80 percent. The composition of the permeates of the experiments with NOM are shown in the Supplementary Information of Chapter 3 (Chapter 7), and the SO_4^{2-} concentrations were between 0.3 and 16.9 g/L. However, the maximum allowed concentration of SO_4^{2-} for direct regenerant reuse of the NaCl solution is not known yet. The limit is influenced by, e.g., the required removal of ions and NOM for water treatment, and the available IEX resin sites, influenced by biological resin binding and resin dosage, which may vary at different locations and IEX systems. However, a study on SIX® spent brine treatment considered that the recovered regenerant was suitable for reuse in a scenario where the contamination of anions and trace pollutants was decreased by more than 90 percent of the original concentration (Vaudevire et al., 2019). Therefore, to recover a clean NaCl solution, other techniques would need to improve the removal of SO_4^{2-}.

Nevertheless, the use of ceramic nanofiltration (with a MWCO of about 600 Da) has two advantages which might be beneficial for separation applications. First, NOM can be concentrated and recovered at high fluxes. Second, the NOM-free permeate can further be treated more efficiently, e.g., by subsequent filtration with tighter polymeric membranes, or by chemical precipitation of SO_4^{2-}. These two options are currently under investigation.

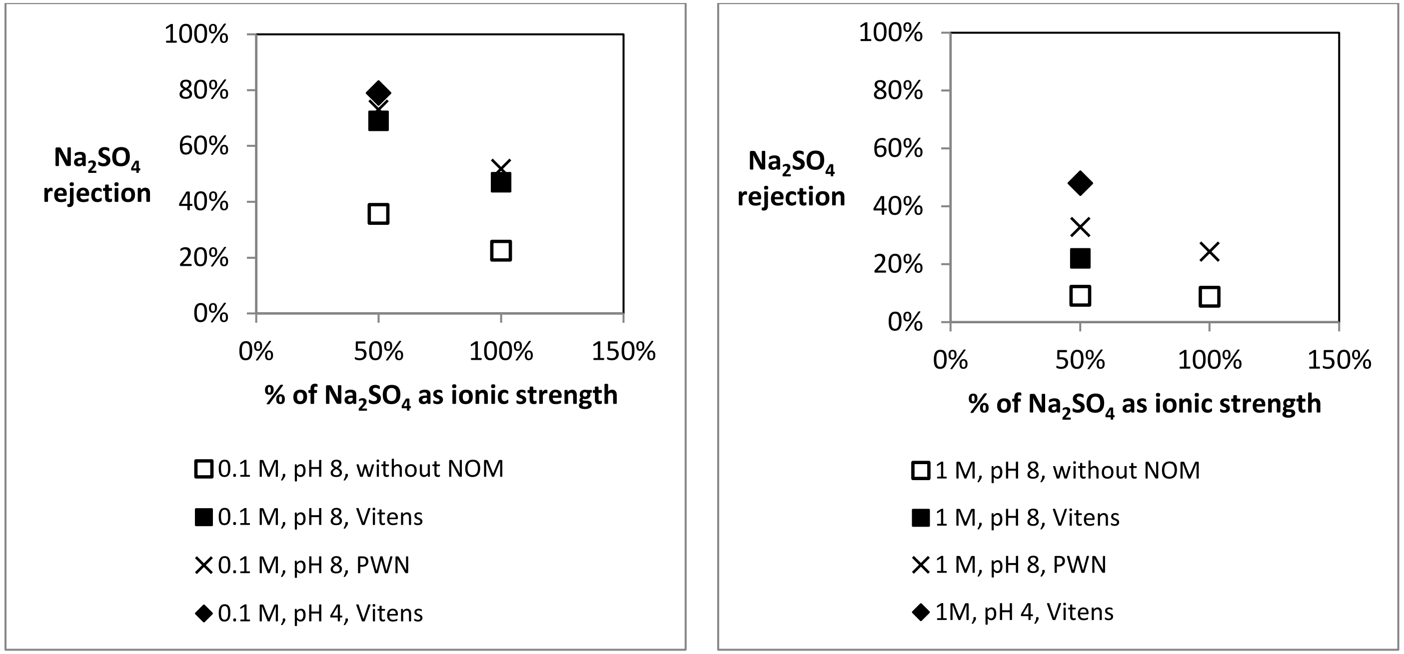

Figure 4, Na_2SO_4 retention with and without NOM, at different pH values, ionic strength and solution composition. Vitens and PWN are two different NOM-samples that were added to artificial brine.

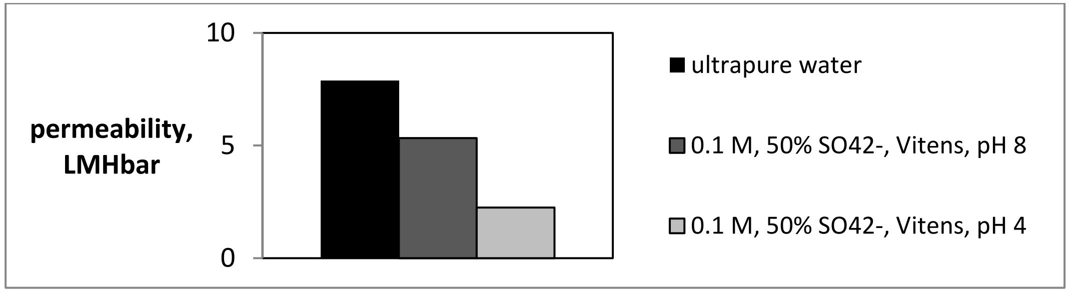

Figure 5, Ultrapure water permeability and permeability during the NOM experiments at pH 4 and 8.

4 Conclusions

Ceramic nanofiltration as a treatment for spent NOM-rich brine from IEX was studied, with the aim to reduce the volume of this waste and recover humic substances and/or regeneration fluid. The aim was, in first instance, to reject and concentrate NOM. The results demonstrated that a commercial ceramic membrane with loose pore sizes (~600 Da) could reject more than 97 percent of the NOM even at high ionic strength, while the passage of NaCl was 95 percent or more. Compared to polymeric nanofiltration, the fouling was limited. The zeta potential at high ionic strength was nearly zero, and this suggests that the rejection mechanism of NOM was steric hindrance. While the steric separation of NOM and inorganic anions could be achieved during loose nanofiltration, the separation between Na_2SO_4 and NaCl was more complicated, specifically in relation to high ionic strength of the brine. At low ionic strength, separation between the divalent anion (SO_4^{2-}) and the monovalent ion (Cl^-) was possible due to the high, negative zeta potential (divalent anions rejection and Donnan effect). At high ion strength, the zeta potential of the membrane decreased, and therefore also the rejection of SO_4^{2-} decreased. In the presence of NOM, however, it was observed that the rejection of SO_4^{2-} slightly increased, probably due to pore size reduction by NOM fouling. To reuse the permeate as a regenerant solution, the concentration of SO_4^{2-} should be further reduced. Polymeric nanofiltration and chemical SO_4^{2-} precipitation are currently under investigation.

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Chapter 4

Sulfate precipitation treatment for NOM-rich ion exchange brines

This chapter is based on

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Sulfate precipitation treatment for NOM-rich ion exchange brines

Abstract

Ion exchange (IEX) resins can remove natural organic matter (NOM) from drinking water sources. However, the IEX system produces a waste brine rich of sodium, chloride, NOM and sulfate. The treatment of the waste brine aims to recover a clean solution rich of sodium chloride, that can be reused to regenerate IEX resin. Previous research showed that ceramic nanofiltration partially removes NOM from the waste brine, but sulfate removal requires additional treatment. Sulfate removal by chemical precipitation was previously studied either on brines with low NOM concentrations or water with low concentrations of NOM and salts. The current work focussed on sulfate removal from NOM-rich brines by chemical dosing of (1) $BaCl_2$, resulting in precipitation of barite ($BaSO_4$), and (2) $CaCl_2$, $Ca(OH)_2$ and $NaAlO_2$, resulting in precipitation of calcium sulfate and, subsequently, ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$). Additionally, the effect of NOM on SO_4^{2-} removal was studied. Modelling and batch experiments were conducted with IEX and synthetic brines within the typical ion strength range of 0.1 to 1 M. With doses of 2.2 g of $BaCl_2$ per g of initial sulfate, $BaSO_4$ precipitation removed more than 83 percent of sulfate, resulting in final concentrations below 0.4 g/L even in the presence of NOM. However, NOM inhibited the precipitation of calcium sulfate and, subsequently, ettringite. With doses of 1.3 g of $CaCl_2$, 0.5-0.7 g of $Ca(OH)_2$ and 0.4-0.6 g of $NaAlO_2$ per g of initial sulfate, calcium sulfate and ettringite precipitation removed between 8 and 95 percent of sulfate from NOM-rich brines, resulting in final concentrations between 0.8 and 2 g/L. As a reference, NOM-free brines required doses of 1.3 g of $CaCl_2$, 0.2-0.7 g of $Ca(OH)_2$ and 0.1-0.6 g of $NaAlO_2$ per g of initial sulfate for 89 to 99 percent of sulfate removal, resulting in final concentrations of 0.2 g/L. The inhibition might be attributed to covering of crystal sites by NOM molecules, and to NOM coagulation with aluminium.

1 Introduction

Anion exchange (IEX) can effectively remove negatively charged natural organic matter (NOM) during drinking water treatment [1]. In IEX processes, resins are reused after cleaning with an electrolyte regenerant solution. In IEX for NOM removal, the regenerant solution is usually NaCl [2, 3, 4]. The regenerant solution is then reused several times before disposal, which increases the concentrations of NOM and anions, like sulfate (SO_4^{2-}) [3, 4, 5]. The composition of spent IEX brines depends on the quality of the water to be treated, the affinity of negatively charged components with the resin, and the specific IEX system operation. Spent IEX brines obtained by four pilot and full-scale installations had concentrations between 0.04 and 1.6 g/L of dissolved organic carbon (DOC), and concentrations of chloride (Cl^-) and SO_4^{2-} in a broad range of 2.6 to 19.1 g/L and 0.3 to 24.3 g/L, respectively (Supplementary information of Chapter 4, Chapter 7).

Discharging waste streams with NOM and salts is often problematic. Therefore, water companies aim to limit waste volumes by recovering some of the spent IEX brine components, such as clean water or concentrated NOM [4, 6, 7]. Additionally, the recovery of clean NaCl regenerant was previously studied [2, 7, 8, 9]. Previous work has also shown that nanofiltration of brines can remove high levels of NOM, humic substances [2, 9, 10]. On the other hand, residual SO_4^{2-} was still present in the nanofiltration permeate, giving potential risk of SO_4^{2-} accumulation in the recovered regenerant.

Chemical precipitation can be an option to remove SO_4^{2-} from spent IEX brine. SO_4^{2-} can precipitate with various cations to form sparingly soluble salts, for instance calcium sulfate, barite ($BaSO_4$), and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$). Calcium sulfate exists in different phases, such as gypsum ($CaSO_4*2H_2O$) and anhydrite ($CaSO_4$). Gypsum precipitates at lower temperatures and NaCl concentrations than anhydrite. Gypsum was found to precipitate below 25^{o}C and with NaCl concentrations below 4M at 25^{o}C [11], and is therefore potentially relevant for treatment of IEX spent regenerant, that has NaCl concentrations below 2 M [2, 3, 4]. A disadvantage of gypsum is its high solubility product, i.e. a log Ksp of -4.31 at 25^{o}C [12], and, thus, the required low SO_4^{2-} concentrations cannot be reached. $BaSO_4$ has a much lower solubility product, i.e. a log Ksp of -9.96 at 25^{o}C [12], but it requires the dosage of toxic $BaCl_2$. An alternative is ettringite precipitation. Ettringite is stable at high alkaline conditions, with an optimum pH close to 12 [13], and its solubility product is low, i.e. log Ksp of -44.91 at 25^{o}C [14]. SO_4^{2-} removal from brines by ettringite precipitation has been frequently studied, mostly subsequent to calcium sulfate precipitation [15, 16, 17, 18, 19]. Generally, very low concentrations of SO_4^{2-} could be obtained by chemical precipitation. However, to the authors' knowledge, brines with high NOM concentrations were not studied before.

Based on other applications, some NOM interference on chemical precipitation could be expected. NOM and polymaleic acid, which is a synthetic surrogate of the fulvic fraction of humic substances [20], for instance, has been found to inhibit chemical precipitation in studies for water recycling in cooling towers [21, 22]. In addition, Banz and Luthi [21] found that NOM of wastewater origin inhibited calcium sulfate precipitation, which was attributed to complexation of Ca^{2+} and NOM.

However, NOM and salts concentrations in cooling tower water are much lower than in spent IEX brine and different mechanisms might be involved.

In the present study we therefore studied chemical precipitation as an alternative to remove SO_4^{2-} from NOM-rich spent IEX brines. In particular, the focus was on the performances of $BaSO_4$ precipitation, and the combination of calcium sulfate and ettringite precipitation to obtain low concentrations of SO_4^{2-}. The impact of NOM on chemical precipitation in brines and the mechanisms involved were also investigated. We studied spent and synthetic brines with varying NOM, sodium (Na^+), Cl^- and SO_4^{2-} concentrations within the typical ion strength range of 0.1 to 1 M, by means of laboratory experiments and modelling.

2 Materials and methods

2.1 Analyses for NOM and ions' concentrations

NOM was measured as dissolved organic carbon (DOC) by a total organic carbon analyser (TOC-VCPH, Shimadzu, Japan) after filtration of the sample. For some of the analyses, the Cl^- and SO_4^{2-} concentrations were determined by ionic chromatography using an ion-exchange column (A Supp 150/4.0, Metrohm AG, Switzerland). Other experiments required direct measurement results for SO_4^{2-}. Therefore, test cell kits (NOVA 60 Spectroquant, Merck, Germany; or LCK 311/153 with spectrophotometer DR 3900, Hach, Germany) were used. For both DOC and anion measurements, the samples were filtered with 0.45 µm filters and diluted when needed.

2.2 Brines

2.2.1 Preparation of synthetic brines

For the synthetic brines, Na_2SO_4 and NaCl were weighted and dissolved in demineralized water. The pre-set anion concentrations divided the synthetic brines into two groups: (1) low concentration brines, in the range of 0.2 to 5 gCl^-/L and 0.2 to 2 gSO_4^{2-}/L; and (2) high concentration brines, in range of 9 to 18 gCl^-/L and 8 to 16 gSO_4^{2-}/L. In addition, for the synthetic brines with NOM, concentrated NOM (HumVi, Vitens) was added to obtain concentrations of 0.5 and 2 gDOC/L. The NOM of HumVi has groundwater origins and was recovered from spent IEX regenerant brine. HumVi was also used and described in previous research [10, 23].

2.2.2 Characterisation of spent IEX brine

A spent IEX brine was provided by a drinking water facility in Sweden (Sweden brine). This facility piloted suspended ion exchange (SIX®), as described by Galjaard and Koreman [24]. The NOM of the brines was characterized using liquid chromatography-organic carbon detection (LC-OCD), according to the procedure from Huber et al. [25]. LC-OCD gave the chromatographic fractionation of organic carbon (CDOC), being the sum of the concentrations of five NOM fractions. In decreasing size, the fractions are biopolymers (BP), humic substances (HS), building blocks (BB), low molecular weight acids (LMWa) and neutrals (LMWn) [25].

2.3 Precipitation experiments

Sweden brine and the synthetic brines of Table 1 were tested in duplicate for $BaSO_4$ precipitation. Samples for NOM and anion measurements were taken before and after precipitation. First, 150 mL of brine in a plastic container was stirred on a magnetic plate (speed 9%, Labinco, the Netherlands). The acidity (measured by Multi 3630 with SenTix 940 electrode, WTW, Germany) was adjusted to pH 8 by adding 0.1M NaOH, to the brines. While stirring, $BaCl_2.2H_2O$, dissolved in ultrapure water, was added in the Ba:SO_4 moles proportion of 1:1, considering the pre-set SO_4^{2-} concentration of the synthetic brines and the initial SO_4^{2-} concentration measured in the Sweden brine. After the $BaCl_2.2H_2O$ was added, the brines were mixed for 30 minutes, and the precipitate was allowed to settle for another 30 minutes. The supernatant was then filtered to collect the samples to be analysed, according to Section 2.1.

Table 1, Synthetic brines (with different ionic strength) and IEX brine tested for $BaSO_4$ precipitation experiments

Brine	Ionic strength, IS (M)	Cl^- (g/L)	SO_4^{2-} (g/L)	NOM (gDOC/L)
1. 0gNOM/L-low IS	0.1	1.8	1.6	0
2. 0gNOM/L-mid IS	0.5	9	8	0
3. 0gNOM/L-high IS	1	18	16	0
4. Sweden brine	~0.2	5	2	0.5

Sweden brine and the synthetic brines of Table 2 were tested for calcium sulfate precipitation and subsequent ettringite precipitation, similar to the work of Almasri et al. [15]. All the experiments were in duplicate. Samples for NOM and anion measurements were taken before calcium sulfate precipitation, and before and after ettringite precipitation. For the calcium precipitation, 150 mL of brine in a plastic container was stirred on a magnetic plate (at 9% speed, Labinco, the Netherlands). While stirring, $CaCl_2$ was added in the Ca:SO_4 moles proportion of 1:1, considering the pre-set SO_4^{2-} concentration of the synthetic brines and the initial SO_4^{2-} concentration of the Sweden brine. The plastic container was closed directly after the addition of $CaCl_2$, and the stirring continued for 2 hours. The pH before the addition of $CaCl_2$ and after precipitation was 7.6 ± 1.2 and 8.3 ± 0.7 (average ± standard deviation), respectively. The solid content in the plastic container after calcium sulfate precipitation was separated using gravity glass fibre filters. The supernatant was then filtered to collect the samples to be analysed, according to Section 2.1. For the subsequent ettringite precipitation, 115 mL of the filtered brine was again stirred on the magnetic plate. While stirring, $NaAlO_2$ and $Ca(OH)_2$ were added as solids in the Al:SO_4 and Ca:SO_4 moles proportion of 0.67:1 and

1:1, respectively, considering the concentration of the brines after gravity filtration. Afterwards, the stirring continued for 2 hours. The supernatant was then filtered to collect the samples to be analysed, according to Section 2.1. The pH before the addition of $NaAlO_2$ and $Ca(OH)_2$ and after precipitation, was 8.2 ± 0.6 and 11.8 ± 0.1 (average ± standard deviation), respectively. The final pH was in the range for ettringite formation according to Almasri et al. [15] without further adjustment, except for Sweden brine. For Sweden brine, the pH before ettringite precipitation was increased from 8.1 to 11.9 with addition of 1M NaOH. The chemicals used for the precipitation experiments have a purity ≥93 percent.

Table 2, Pre-set concentrations of synthetic brines tested for calcium sulfate and subsequent ettringite precipitation experiments

Brine	Ionic strength, IS (M)	Cl^- (g/L)	SO_4^{2-} (g/L)	NOM (gDOC/L)
0gNOM/L-low IS	0.2	5	2	0
0gNOM/L-high IS	1	18	16	0
0.5gNOM/L-high IS	1	18	16	0.5
2gNOM/L-high IS	1	18	16	2
Sweden brine	~0.2	5	2	0.5

2.4 PhreeqC model

The results of the precipitation experiments of the synthetic brines without NOM were compared to the results modelled with PhreeqC, a geochemical modelling software. Solutions with high salinity can be modelled using the Pitzer database, as an alternative for the default PhreeqC database [26]. The PhreeqC script for calcium and ettringite precipitation was validated using the data from Almasri et al. [15]. According to the reasoning in Chapter 1, the calcium sulfate precipitate in the model was gypsum. Our scripts of the models and their validation are presented in the Supplementary Information of Chapter 4, Chapter 7).

3 Results and discussion

3.1 Brines characteristics

The NOM in the Sweden brine and in the synthetic brines consisted mostly of HS and BB (Table 3), because these fractions are preferentially removed by IEX from natural water [27, 28, 29, 30].

Table 3, LC-OCD fractionation of NOM in HumVi (used for the synthetic brines), NOM in the Sweden brine, given as carbon percentage of the CDOC.

NOM sample	Bio-polymers	Humic Substances	Building Blocks	Low molecular weight neutrals	Low molecular weight acids
	>>20000 Da	~1000 Da	300-500 Da	<350 Da	<350 Da
HumVi	0.0%	88.7%	6.8%	4.5%	0.0%
Sweden brine	0.3%	74.7%	16.0%	9.0%	0.0%

3.2 Modelling of sulfate precipitation with BaSO4, calcium sulfate and ettringite

The scripts for the PhreeqC model, and the procedure of its validation are presented in the Supplementary Information of Chapter 4 (Chapter 7). Model simulations are shown in Figures 1, 2 and 3, including the validation points of $BaSO_4$ and calcium sulfate precipitation. The model shows that, in Na_2SO_4 solutions with an ionic strength of 0.1 to 1 M, SO_4^{2-} precipitation with calcium sulfate depends on the initial SO_4^{2-} concentration (Figure 1).

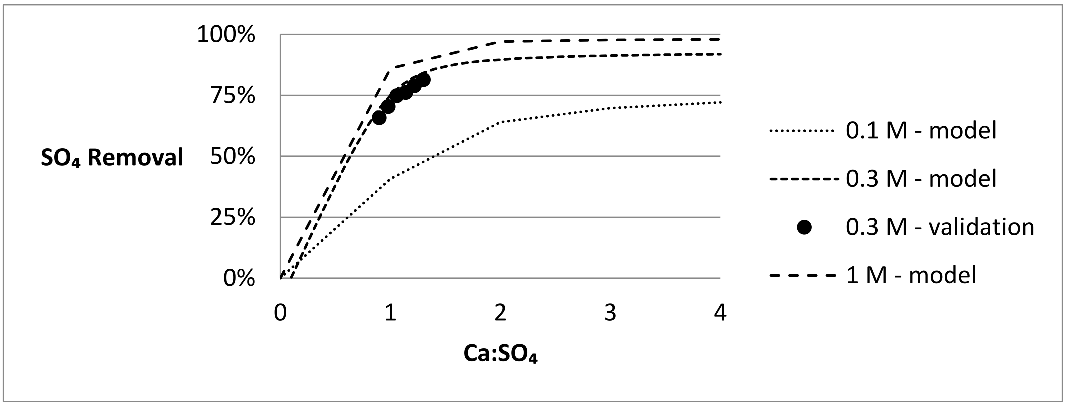

Figure 1, PhreeqC model of calcium sulfate precipitation for Na_2SO_4 solutions with ionic strength between 0.1 and 1 M

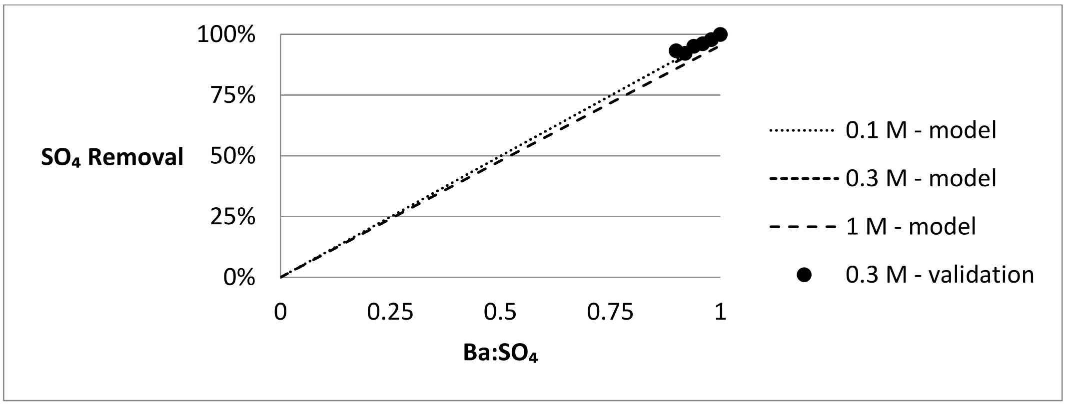

Figure 2, PhreeqC model of $BaSO_4$ precipitation for Na_2SO_4 solutions with ionic strength between 0.1 and 1 M

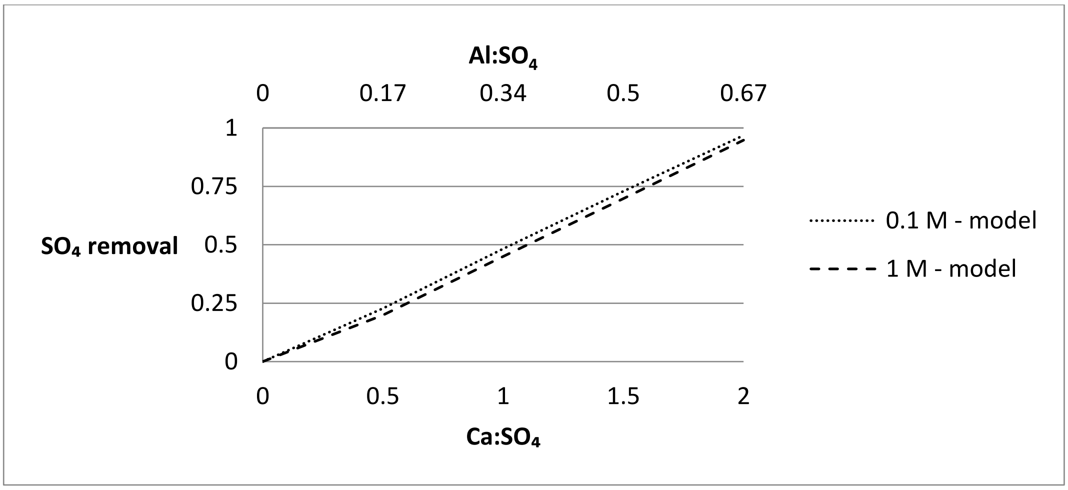

Figure 3, PhreeqC model of ettringite precipitation for Na_2SO_4 solutions with ionic strength between 0.1 and 1 M

The low SO_4^{2-} removal at low ionic strength is explained by the relatively high solubility product of calcium sulfate, that puts a theoretical limit on the achievable minimum concentration of SO_4^{2-} to 1.5 g/L [31]. In the same SO_4^{2-} range, precipitation with $BaSO_4$ and ettringite, that have low solubility products, only depends on stoichiometry (Figures 2 and 3).

3.3 SO_4^{2-} removal and effect of NOM during $BaSO_4$ precipitation

For $BaSO_4$ precipitation, 2.2 g of $BaCl_2$ was dosed per g of initial SO_4^{2-} in the brine. With initial SO_4^{2-} concentrations between 1.3 and 14.5 g/L (and ionic strengths between 0.1 and 1 M), SO_4^{2-} removal from the synthetic brines without NOM was above 98 percent, resulting in SO_4^{2-} concentrations below 0.2 g/L (Table 4). Table 4 includes the SO_4^{2-} concentration of Sweden brine before and after precipitation with $BaSO_4$, and for the modelled brine without NOM as a reference. The SO_4^{2-} of Sweden brine decreased by 84 percent, from 2 to 0.3 g/L, showing that the presence of NOM slightly inhibited $BaSO_4$ precipitation, probably attributed to the antiscalant properties of NOM [32, 33]. During $BaSO_4$ precipitation of Sweden brine, also NOM was removed by 23 percent, which could be a potential problem in case NOM recovery is desired.

Table 4, SO_4^{2-} and NOM concentrations before and after $BaSO_4$ precipitation of brines: brines without NOM, NOM-rich Sweden brine, and PhreeqC-modelled brine without NOM

Brine for $BaSO_4$ precipitation	Ionic strength, IS, (M)	Initial SO_4^{2-} (g/L)	Final SO_4^{2-} (g/L)	Initial NOM (gDOC/L)	Final NOM (gDOC/L)
0gNOM/L-low IS	0.1	1.34	<0.01	0	-
0gNOM/L-mid IS	0.5	7.86	<0.01	0	-
0gNOM/L-high IS	1	14.50	0.19 ± 0.02*	0	-
Sweden brine	~0.2	2.02	0.33± 0.05*	0.44	0.34 ± 0.01*
Model-low IS	0.2	2.00	0.00	0	-

*average ± standard deviation of duplicate measurement

Another application issue is linked to the toxicity of barium. The toxicity is linked to its chemical form [42]. In particular, barium salts with low solubility, such as $BaSO_4$, are generally considered less dangerous than free Ba^{2+} and readily soluble barium salts. Therefore, residual Ba^{2+} in the treated brine should be measured. The EPA drinking water standard for barium from 2002 was 2 mg/L [43]. However, ecotoxicity studies derived lower limits for environmental quality standards [44]. In the Netherlands, the maximum concentration of Ba^{2+} in surface water intended for drinking water production is 200 µg/L [45].

3.4 SO_4^{2-} removal and effect of NOM during calcium sulfate and ettringite precipitation

Calcium sulfate and subsequent ettringite precipitation without NOM, removed 89 to 99 percent of SO_4^{2-}, resulting in a final SO_4^{2-} concentration of 0.2 g/L for synthetic brines of both low and high initial

SO_4^{2-} concentrations (1.8 to 14.8 g SO_4^{2-}/L, with ionic strength between 0.2 and 1 M). However, the presence of NOM affected the precipitation (Figures 4 and 5).

At low initial SO_4^{2-} concentration (Figure 4), calcium sulfate precipitation removed only less than 7 percent of SO_4^{2-} for both synthetic brine without NOM and Sweden brine, due to high solubility of calcium sulfate (see Section 3.2). However, NOM in Sweden brine inhibited the subsequent ettringite precipitation, resulting in an overall SO_4^{2-} removal of only 7.5 percent and a final SO_4^{2-} concentration of 1.7 g/L.

At high initial SO_4^{2-} concentration (Figure 5), calcium sulfate precipitation removed 75 percent of SO_4^{2-} from the synthetic brine without NOM. However, calcium sulfate precipitation was inhibited by NOM, and the average removed SO_4^{2-} dropped to 35 and 6 percent in the synthetic brines with 0.5 and 2 gDOC/L, respectively. Similar to the case of $BaSO_4$, inhibition of calcium sulfate precipitation by NOM was attributed to the antiscalant properties of NOM [34, 35]. Due to the fact that calcium sulfate precipitation only removed 3 to 4 percent of NOM from the synthetic brines, SO_4^{2-} removal by subsequent ettringite precipitation was inhibited by NOM as well. The dose of chemicals for ettringite precipitation was dependent on the remaining SO_4^{2-} concentration after calcium sulfate precipitation. Therefore, considerably more $NaAlO_2$ and $Ca(OH)_2$ were dosed in the NOM-rich synthetic brines than in the brine without NOM (Figure 5). Nevertheless, the overall SO_4^{2-} removal was between 86 and 95 percent, although the final SO_4^{2-} concentrations for the NOM-rich synthetic brines were still above 0.8 g/L.

The overall NOM removal from the NOM-rich brines was between 23 and 67 percent (Table 5). The calcium sulfate precipitation step only removed between 3 and 11 percent of NOM. The ettringite precipitation step removed 14 percent of the residual NOM from Sweden brine with low initial SO_4^{2-}, and between 51 and 65 percent of the residual NOM from the two NOM-rich synthetic brines with high initial SO_4^{2-}, likely due to coagulation of NOM by $NaAlO_2$ [36, 37].

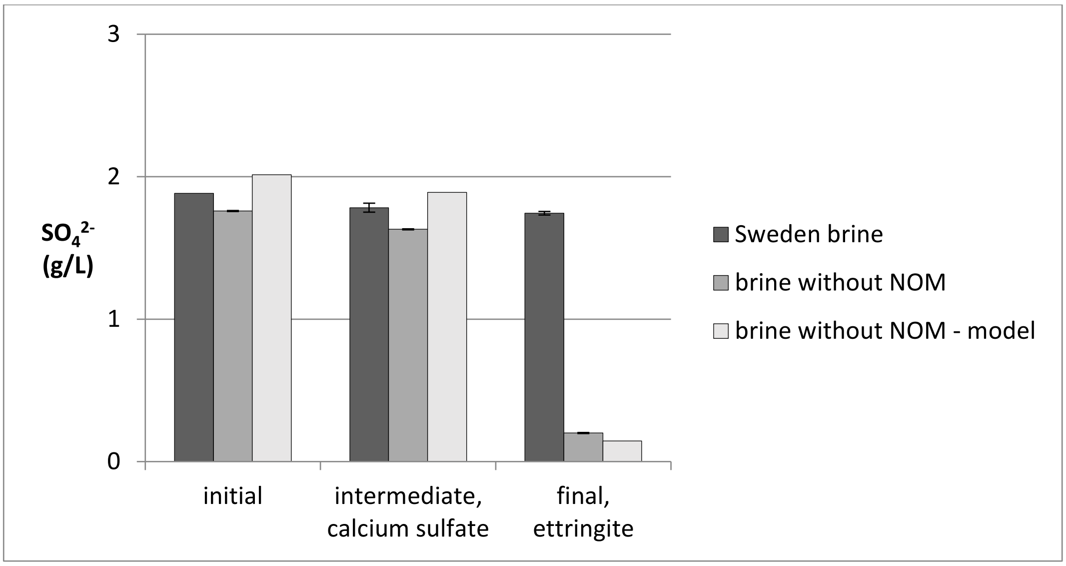

Figure 4, SO_4^{2-} concentration before and after CaSO4 and subsequent ettringite precipitation of brines at low ionic strength: NOM-rich Sweden brine, and synthetic brine without NOM. The doses of chemicals are 2.2 g/L of $CaCl_2$ for the intermediate calcium sulfate precipitation step, and 1.3 to 1.4 g/L of $Ca(OH)_2$ and 1.1 to 1.2 g/L of $NaAlO_2$ for the final ettringite precipitation step. A PhreeqC model calculation of the brine without NOM is included.

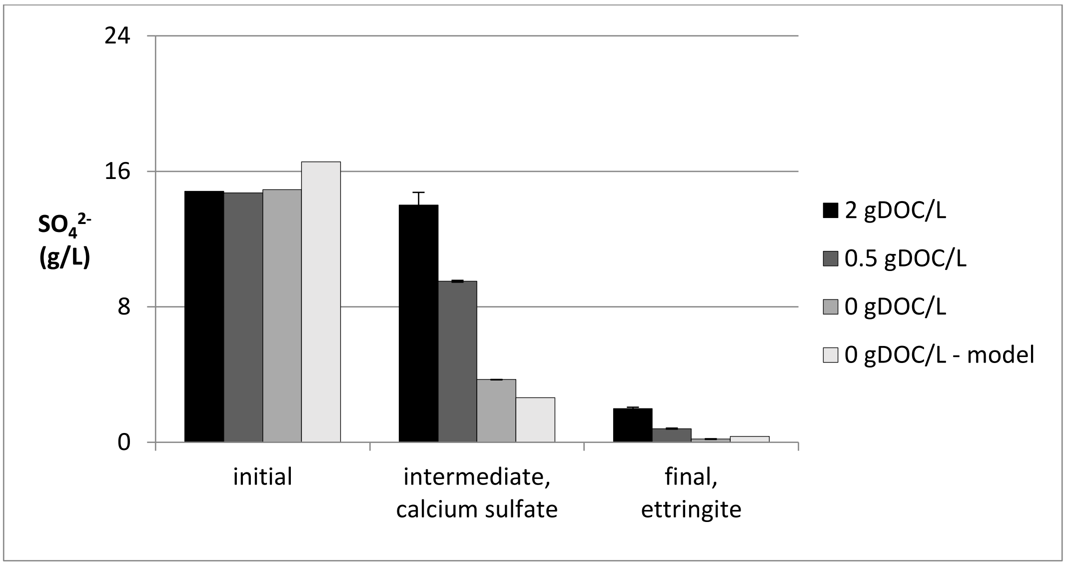

Figure 5, SO_4^{2-} concentration before and after CaSO4 and ettringite precipitation of synthetic brines at high ionic strength (1M) and different NOM concentrations. For the intermediate calcium sulfate precipitation step, the dosed CaCl2 was 20 g/L for all brines. For the final ettringite step, $Ca(OH)_2$ and NaAlO2 were dosed. For the 2 gDOC/L brine, the dose was 11 g $Ca(OH)_2$/L and 9 g NaAlO2/L. For the 0.5 gDOC/L brine, the dose was 8 g $Ca(OH)_2$/L and 6 g $NaAlO_2$/L. For the 0 gDOC/L brine, the dose was 3 g $Ca(OH)_2$/L and 2 g $NaAlO_2$/L. A PhreeqC model calculation of the brine without NOM is included.

Table 5, NOM concentrations during calcium sulfate and subsequent ettringite precipitation

Brine	NOM before $CaSO_4$ precipitation (gDOC/L)	NOM before ettringite precipitation (gDOC/L)	Final NOM (gDOC/L)
Sweden brine, 0.5gDOC/L	0.48	0.43	0.37
High ion strength, 0.5gDOC/L	0.48	0.46	0.16

Table 6, Summary of initial NOM/SO_4^{2-} ratio of the brines, the percentage of SO_4^{2-} removal, and chemicals dosed per amount of initial SO_4^{2-}

Brine	Initial NOM/SO_4^{2-} ratio (gDOC/gSO_4^{2-})	Overall SO_4^{2-} removal (-)	Dose $CaCl_2$ per initial sulfate (g$CaCl_2$/gSO_4^{2-})	Dose $Ca(OH)_2$ per initial sulfate (g$Ca(OH)_2$/gSO_4^{2-})	Dose $NaAlO_2$ per initial sulfate (g$NaAlO_2$/gSO_4^{2-})
NOM-free, high ionic strength	0	99%	1.3	0.2	0.1
NOM-free, low ionic strength	0	89%	1.3	0.7	0.6
0.5 gDOC/L, high ionic strength	0.03	95%	1.3	0.5	0.4
2 gDOC/L, high ionic strength	0.14	86%	1.3	0.7	0.6
Sweden brine	0.25	8%	1.3	0.7	0.6

Table 6 summarises the initial NOM/sulfate ratio of the brines, the percentage of removal and chemicals dosed per initial sulfate concentration (specific dose). Calcium sulfate and subsequent ettringite precipitation is the most suitable for NOM-free brines with high ionic strengths, as indicated by the relatively low specific dose of chemicals and high SO_4^{2-} removal. However, brines with low ionic strength required a relatively high specific dose of $Ca(OH)_2$ and $NaAlO_2$.

When applied to NOM-rich brines, calcium sulfate and subsequent ettringite precipitation removed hardly any SO_4^{2-} at high initial NOM/sulfate ratio, or required a relatively high dose of chemicals.

The potential effect of the initial NOM/sulfate ratio in practice was to see in our experience with additional spent IEX brines. The percentage of sulfate removed was higher in brines with less NOM and higher initial sulfate concentration than Sweden brine (Supplementary Information of Chapter 4, Chapter 7), indicating that calcium sulfate and ettringite precipitation were more suitable for IEX brines with low initial NOM/sulfate ratio.

The inhibition of precipitation of Ca^{2+} or SO_4^{2-} crystals caused by NOM and organic acids could be attributed to Ca^{2+} complexation or covering of nucleation and growth crystal sites [33, 35, 38, 39, 40].

Table 7 shows that the Ca^{2+} that can potentially be consumed by complexation was negligible compared to the available Ca^{2+}, i.e. below 10 percent. Therefore, similar to the experiments of Lee et al. [35], covering of crystal site by NOM molecules is suggested as precipitation inhibition mechanism during our experiments. PhreeqC models the interaction between NOM and ions is modelled as complexation and the antiscalant properties of NOM are not considered. Therefore, PhreeqC could not be used to model the NOM-rich brines of our experiments.

Table 7, Calculation of the charge potentially consumed by NOM in several brines, compared to the charge of dosed Ca^{2+}

Brine	NOM (gDOC/L)	Charge density NOM (-meq/gDOC)	Charge NOM (-meq/L)	Dosed Ca^{2+} (mmol/L)	Charge Ca^{2+} (meq/L)	Charge NOM/ Charge Ca^{2+}
Sweden brine, 0.5gDOC/L	0.5	5-15*	2-7	20 ($CaCl_2$) 19 ($Ca(OH)_2$)	76	3-9%
High ion strength, 0.5gDOC/L	0.5	5-15*	2-7	153 ($CaCl_2$) 99 ($Ca(OH)_2$)	505	0-1%
High ion strength, 2gDOC/L	2	5-15*	10-30	154($CaCl_2$) 146 ($Ca(OH)_2$)	600	2-5%

*charge density range for humic substances according to Edzwald [41]

An application issue is linked to the purity of the chemical used for the precipitation of the sulfate salts. Natural limestone (calcium carbonate) contains magnesium in case of dolomitization [46], and therefore, Mg^{2+} ions can be present as impurity in the produced $CaCl_2$. In our experiments, $CaCl_2$ had high purity, but the presence of Mg^{2+} should be checked in application. Previous studies showed that Mg^{2+} can maintain SO42- in the soluble form $Mg(SO_4)$ [47, 48].

4 Conclusions

Chemical precipitation of SO_4^{2-} to $BaSO_4$, calcium sulfate and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$) was studied for brines with varying NOM and ionic strengths, and initial concentrations between 2 and 16 gSO_4^{2-}/L. Sulfate removal with $BaSO_4$ precipitation was above 98 percent for NOM-free brines, and 84 percent for the NOM-rich spent IEX brine. This resulted in final concentrations below 0.4 g SO_4^{2-}/L, even in the presence of NOM. In addition, 23 percent of NOM was removed from the spent IEX brine, which could decrease the potential for NOM recovery. For application, the residual concentration of dissolved barium, that is toxic, should also be investigated.

At low initial SO_4^{2-} concentration, calcium sulfate and subsequent ettringite precipitation removed overall 89 percent of SO_4^{2-} from the NOM-free brine, resulting in a final concentration of 0.2 g SO_4^{2-}/L. However, the calcium sulfate precipitation step was limited by its high solubility, and the subsequent ettringite precipitation step required a relatively high dose of $NaAlO_2$ and $Ca(OH)_2$. In the NOM-rich spent IEX brine, hardly any removal of SO_4^{2-} was observed at low initial SO_4^{2-} concentration.

At high initial SO_4^{2-} concentration, inhibition of calcium sulfate and subsequent ettringite precipitation by NOM was observed as well. Without NOM, the overall SO_4^{2-} removal was 99 percent, resulting in a final concentration of 0.2 gSO_4^{2-}/L. When NOM was present, SO_4^{2-} removal was between 86 and 95 percent, with final concentrations above 0.8 g SO_4^{2-} /L, even with a relatively high dosage of chemicals for the ettringite precipitation. The inhibition might be attributed to covering of crystal sites by NOM molecules, and to NOM coagulation with aluminium.

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Chapter 5

Integrated treatment for NOM and sulfate removal from ion exchange brines using ceramic nanofiltration and chemical precipitation

This chapter is based on

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Integrated treatment for NOM and sulfate removal from ion exchange brines using ceramic nanofiltration and chemical precipitation

Abstract

Ion exchange (IEX) with an anionic resin removes natural organic matter (NOM) from drinking water sources. However, the regeneration of the resin produces a liquid waste, called spent IEX brine, which is rich in NOM, sodium, chloride and other anions, such as sulfate. Previous work on synthetic solutions and brines showed that (1) ceramic nanofiltration has the potential to remove and concentrate valuable humic substances, and (2) chemical precipitation with barite or calcium sulfate and ettringite could result in low sulfate concentrations in the sodium chloride solution to be used for subsequent regeneration. In this work, we integrated ceramic nanofiltration and chemical precipitation to achieve both goals when treating spent IEX brines. Ceramic nanofiltration at laboratory and pilot scale removed 72 to 91 percent of NOM. Sulfate was hardly removed by ceramic nanofiltration. Consequently, the sulfate concentration did not increase in the humic substances-rich concentrate. Further, unlike barite, calcium sulfate and ettringite precipitation was largely inhibited by NOM, even at low ratio of initial NOM to sulfate concentration. However, removal of NOM by pre-nanofiltration and excess calcium dose substantially improved the sulfate removal.

1 Introduction

Ion exchange (IEX) with anionic resin removes negatively charged natural organic matter (NOM) from drinking water sources (Grefte et al., 2011; Verdickt et al., 2012; Metcalfe et al., 2015). Anions are also removed in this process, while chloride (Cl^-) is released from the resin to the treated water. The resin is periodically regenerated, typically in a concentrated NaCl solution, to partially restore the released Cl^-. Resin regeneration of IEX for NOM removal produces a spent brine stream rich of NOM, Na^+, Cl^-, and other anions removed from the drinking water source. Sulfate (SO_4^{2-}) has high affinity with the resin and it was found in high concentrations in spent IEX brines for surface water treatment

(Verdickt et al., 2012; Vaudevire et al., 2019). Several studies and applications focussed on reusing NaCl or clean NaCl solution in the IEX regeneration process, or recovering NOM as a product (Schippers et al., 2005; Leong et al., 2015; Vaudevire et al., 2019; Haddad et al., 2019). Concerning the recovery of NOM, humic substances can be potentially applied in, for example, medicines as antibiotics or anti-inflammatory means (Klöcking et al, 2002; Van Rensburg, 2015), food industry as food supplement (Ozturk et al., 2010; Bai et al., 2013), agriculture for crops and soil improvement (Suh et al., 2014; Canellas et al., 2015; Zanin et al., 2019), and membrane applications as antiscalant (Bremere et al., 2003; Haidari et al., 2019).

Our previous work on ceramic nanofiltration of brines has shown that NOM, especially humic substances, was largely removed during laboratory experiments, while high passage of NaCl was maintained, and was thus suitable to concentrate and recover humic substances. However, extra treatment was suggested to lower the SO_4^{2-} concentration and recover a clean NaCl solution (Caltran et al., 2020). In a following study (Chapter 4), SO_4^{2-} was partially removed from brines using barite ($BaSO_4$) precipitation, or using calcium sulfate ($CaSO_4$) and subsequent ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$) precipitation.

When NOM was not present in the brines, the removal of SO_4^{2-}, using stoichiometric doses of chemicals, was above 89 percent. This resulted in final SO_4^{2-}concentrations of 0.2 g/L. The presence of NOM did not greatly influence $BaSO_4$ precipitation. However, NOM heavily inhibited $CaSO_4$ and subsequent ettringite precipitation. Considering the influence of NOM, solubility limitations, and toxicity of chemicals, the preferred precipitation treatment were (1) $BaSO_4$ precipitation, for IEX brines with low SO_4^{2-} and high NOM concentrations, and (2) $CaSO_4$ and ettringite precipitation, for IEX brines with high SO_4^{2-} and low NOM concentrations.

The present study focused on a hybrid system consisting of ceramic nanofiltration and sulfate precipitation, to remove both sulfate and NOM from the brine, while producing a concentrated stream of humic substances. The removal of NOM and SO_4^{2-} was studied at laboratory and pilot scale for two integrated options: (1) low SO_4^{2-}- IEX brine with high ratio of NOM/SO_4^{2-}, for $BaSO_4$ precipitation followed by nanofiltration; (2) high SO_4^{2-}- IEX brine with low ratio of NOM/SO_4^{2-}, for integrated nanofiltration and subsequent precipitation of $CaSO_4$ and ettringite.

2 Materials and methods

2.1 Spent IEX brines and their characterisation

Several spent IEX brines from drinking water treatment plants were provided. The main anions of the brines, SO_4^{2-} and Cl^-, were measured with ionic chromatography (Metrohm AG, Switserland), using the same procedure as described by Caltran et al. (2020). The NOM of the brines was measured with dissolved organic carbon (DOC) analysis (see Section 2.4) and characterized with liquid chromatography-organic carbon detection (LC-OCD) by Het Waterlaboratorium (the Netherlands) using the procedure of Huber et al. (2011). The NOM fractions measured by LC-OCD are biopolymers, humic substances, building blocks, low molecular weight (LMW) acids, and LMW neutrals. The measurements are presented in the Supplementary information of Chapter 5 (Chapter 7). Further characterisation of NOM by humic and fulvic acids extraction, using the New Standardized Method (NSM) of Lamar et al. (2014), was performed by the University of Udine (Italy), and can also be found in the Supplementary Information of Chapter 5 (Chapter 7).

Brines from two locations were further selected for the integrated nanofiltration and SO_4^{2-} precipitation experiments:

1. Sweden brine, with low SO_4^{2-} content and high ratio of NOM/SO_4^{2-}, for integrated $BaSO_4$ precipitation followed by nanofiltration; and
2. Netherlands brine, with high SO_4^{2-} content and a low ratio of NOM/SO_4^{2-}, for integrated nanofiltration and subsequent precipitation of $CaSO_4$ and ettringite.

2.2 Ceramic nanofiltration setups

Two setups were used for the ceramic nanofiltration treatment experiments. For both of them, pH and temperature were measured with a multimeter (Multi 3630 with SenTix 940 electrode, WTW, Germany), the recirculation flow was measured by a flow meter (Sea, China), and the trans membrane pressure was measured using two pressure meters (GS4200-USB0016AB, ESI, UK).

A laboratory scale setup (Figure 1) was located at the Waterlab of Delft University of Technology (the Netherlands). The setup had one feed pump, was operated in cross flow mode at low recoveries, and the concentrate was recirculated to the feed tank. The desired flux, pressure, and the recirculating cross flow were adjusted manually by operating a needle valve and by adjusting the rotations per minute (rpm) of the pump. To measure the permeate flux, the amount of permeate collected within known time intervals was weighted.

A pilot setup (Figure 2) was located at the water company PWN in Andijk (the Netherlands). The pilot was operated in cross flow mode at high recoveries. A dosing pump provided a constant feed flow. The permeate flux, the concentrate flow and the pressure could be regulated by the concentrate valve and the rpm of the recirculation pump. The concentrate flow was monitored by weighing the concentrate tank at regular intervals.

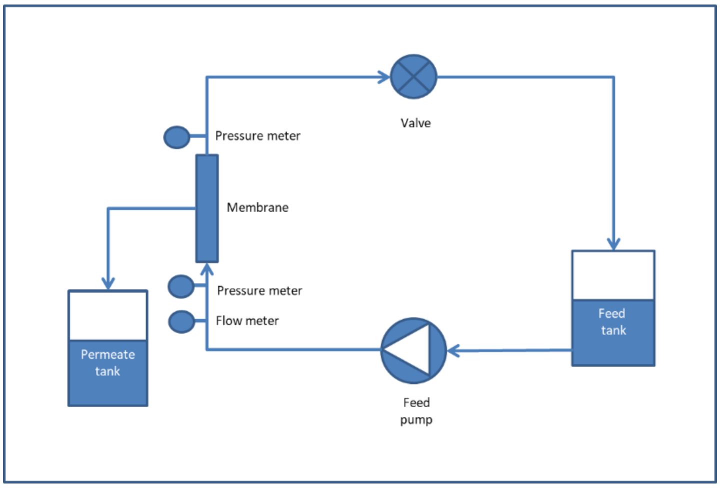

Figure 3, Laboratory scale setup of ceramic nanofiltration

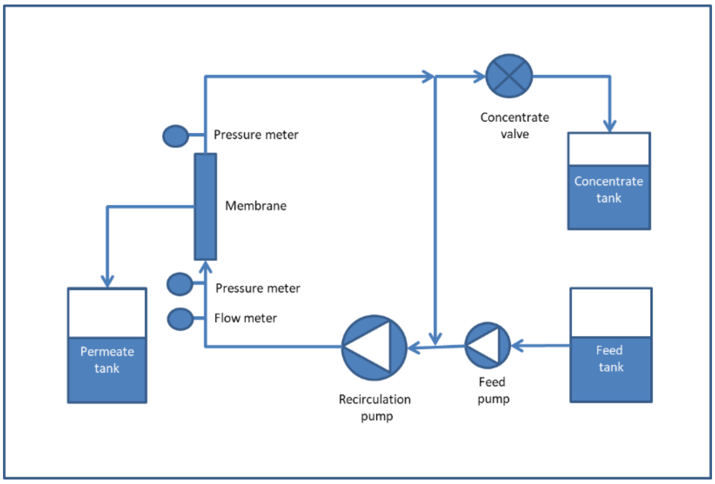

Figure 4, Pilot setup of ceramic nanofiltration

2.3 Characterisation of the ceramic membranes

The used ceramic membranes (Inopor GmbH, Germany) had a TiO_2 separation layer on an Al_2O_3 support layer, with a mean separation pore size of 0.9 nm and porosity of 30 to 40 percent, according to the manufacturer. The molecular weight cut-off of the membranes was measured by filtering a solution of demineralized water and polyethylene glycol (PEG) of 200, 300, 400, 600 and 1000 Da (Sigma-Aldrich, Germany). As in previous studies (Shang et al., 2017; Kramer et al., 2019; Caltran et al., 2020), samples were collected before and after nanofiltration, they were analysed with a high performance liquid chromatography (Prominence, Shimadzu, Japan) using a refractive index detector (RID-20A, Shimadzu, Japan) and size exclusion gel permeation chromatography columns (5 µm 30 Å, PSS GmbH, Germany). Using the known elution times of the various sizes of PEG, the signals before and after nanofiltration were compared to calculate the membrane rejection of each PEG size. The molecular weight of the PEG that was rejected by 90 percent was taken as the molecular weight cut-off (MWCO) of the membranes, as suggested by Shang et al. (2017).

The membranes of the laboratory scale setup were tubular, with 7 mm internal diameter and 0.00163 m^2 filtration area. In the PEG mixture, each PEG size had a concentration of 0.6 g/L. Because of the low recovery of the system, it was assumed that the concentrations in the feed and concentrate were the same. Three permeate samples were collected after 90, 120 and 150 min of filtration, and two feed samples were collected after about 90 and 150 min of filtration. During the sampling, the temperature was 20.1 to 21.2 ^{0}C, the trans membrane pressure was 3.1 to 3.2 bar, the flux was 42 to 44 LMH, and the cross flow velocity was 1.3 m/s, resulting in a Reynolds number of approximately 9100. The recovery was negligible (less than 0.04 percent).

The membranes of the pilot setup were multi-channel, with 19 channels with 3.5 mm internal diameter and 0.1045 m^2 filtration area. In the feed PEG mixture, each PEG size had a concentration of 0.2 g/L. Three permeate samples and three concentrate samples were collected during the filtration intervals of 145 to 150 min, 175 to 180 min, 205 to 210 min. During the sampling, the temperature was 20.3 to 20.5 ^{0}C, the trans membrane pressure was 3.4 to 3.7 bar, the flux was 40 to 46 LMH, and the cross flow velocity was 0.65 m /s, resulting in a Reynolds number of approximately 2300. The recovery was 75 ± 4 percent (average ± standard deviation).

2.4 Integrated NOM and sulfate removal

2.4.1 Analyses

Before and after the nanofiltration and precipitation experiments, the NOM was measured as DOC after 0.45 µm filtration (ChromafilXtra, MN, Germany), using a total organic carbon analyser (TOC-VCPH, Shimadzu, Japan). SO_4^{2-} was measured with test cell kits (NOVA 60 Spectroquant, Merck, Germany; or LCK 311/153 with spectrophotometer DR 3900, Hach, Germany).

2.4.2 Simultaneous chemical precipitation of $BaSO_4$ and ceramic nanofiltration

For the $BaSO_4$ precipitation step, a volume of 8 L of Sweden brine was collected in a plastic tank. The concentration of SO_4^{2-} was measured to determine the weight of $BaCl_2 \cdot 2H_2O$ (Sigma-Aldrich, Germany) required for a dose of 1:1 mol of [Ba]:[SO4]. The required $BaCl_2 \cdot 2H_2O$ was then dissolved into 0.12 L of ultrapure water, and added to the plastic tank. After mixing for 10 min with a stirrer (RZR 1, Heldolph Instrument, Germany), and a waiting time of 30 min, the supernatant was transferred with a tube to another container.

The supernatant from the $BaSO_4$ precipitation step was then treated by ceramic nanofiltration in the laboratory setup. As reference, a test using Sweden brine without the $BaSO_4$ precipitation step was performed (Table 1), using the same setup and the same membrane. The experiments were not duplicated; instead, for each experiment, the permeate was sampled after 90, 120 and 150 min of filtration. In addition, two feed samples were collected after about 90 and 150 min of filtration. During the sampling, the temperature was 26.7 to 28.3 ^{o}C, the trans membrane pressure was 2.6 to 4.2 bar, the flux was 29 to 32 LMH, and the cross flow velocity was 1.3 m/s, resulting in a Reynolds number of approximately 9100. The recovery was negligible. The pH during the experiment was 8.2 to 8.5.

Table 1, Tests of the experiment with chemical precipitation of $BaSO_4$ and ceramic nanofiltration

Test	Brine	Nanofiltration	$BaSO_4$ precipitation
1	Sweden	Yes, membrane CNF-1	Yes, $BaCl_2$ dose 1:1 mol of [Ba]:[SO_4]*
2	Sweden	Yes, membrane CNF-1	No

*[SO_4] is the concentration in the brine before precipitation

2.4.3 Sequential NOM removal by nanofiltration and sulfate precipitation to $CaSO_4$ and ettringite

Ceramic nanofiltration with the pilot setup was performed in duplicate on Netherlands brine. Six permeate samples, six feed samples and six concentrate samples were collected at 10, 70, 130, 190, 250 and 310 min. During the sampling, the temperature was 18.1 to 19.7 ^{o}C, the trans membrane pressure was 6 to 8.3 bar, the flux was 30 to 50 LMH, and the cross flow velocity was 0.67 m/s. The Reynolds number was approximately 2300. The recovery was 76 ± 5 percent (average ± standard deviation).

The permeate of the ceramic nanofiltration step was used for the $CaSO_4$ and subsequent ettringite precipitation step. As a reference, a test using Netherlands brine without the ceramic nanofiltration step was also performed. Table 2 shows the dose of chemicals added for precipitation. In test 3, the dose was stoichiometric, as in the work of Almasri et al. (2015). In test 4, the dose of $Ca(OH)_2$ was doubled. This higher dose of Ca^{2+} was selected by trial and error to obtain a final concentration of SO_4^{2-} of 0.4 g/L or below. Test 5 had the same dose of chemicals as test 4. For $CaSO_4$ precipitation, $CaCl_2 \cdot 2H_2O$ (Merck, Germany) was added to plastic containers with 0.15 L of nanofiltration permeate or Netherlands brine and mixed for 120 min. Subsequently, the supernatant was passed through gravity glass fibre filters (Merck, Ireland). The obtained solutions were placed in other containers and used for the subsequent ettringite precipitation of the residual SO_4^{2-}. $Ca(OH)_2$ and $NaAlO_2$ (Sigma-Aldrich, Germany) were added and mixed for 120 min. Then the supernatant was filtered over 0.45

µm filters. Both $CaSO_4$ and ettringite precipitation tests were performed at room temperature. The initial pH was 7.6 to 8.6 and the final pH was 12 to 12.4.

To monitor the removal of different NOM fractions during nanofiltration and precipitation, LC-OCD analyses were performed for one feed and one permeate sample of the ceramic nanofiltration step at 75 percent of recovery, and for the supernatant of the ettringite precipitation step from test 3.

Table 2, Tests of the experiment with ceramic nanofiltration and chemical precipitation of $CaSO_4$ and ettringite

Test	Brine	Nanofiltration	$CaSO_4$ and ettringite precipitation		
			Dose $CaCl_2$	Dose $Ca(OH)_2$	Dose $NaAlO_2$
3	Netherlands	Yes, membrane CNF-4	1:1 mol of [Ca]:[SO_4]*	1:1 mol of [Ca]:[SO_4]^	0.67:1 mol of [Al]:[SO_4]^
4	Netherlands	Yes, membrane CNF-4	1:1 mol of [Ca]:[SO_4]*	2:1 mol of [Ca]:[SO_4]^	0.67:1 mol of [Al]:[SO_4]^
5	Netherlands	No	Same concentration as test 4	Same concentration as test 4	Same concentration as test 4

*[SO_4] is the concentration in the brine before precipitation

^ [SO_4] is the concentration in the brine after $CaSO_4$ precipitation and before ettringite precipitation

3 Results and discussion

3.1 Molecular weight cut-off of the ceramic membranes

The MWCO of the ceramic membranes used in these experiments were 870 and 630 Da for the laboratory scale setup and for the pilot setup, respectively. The membranes can thus be considered as “loose” nanofiltration, as the nanofiltration range MWCO is generally from 150 to 2000 Da (Paul and Jons, 2016). The membrane retention curves, that give the membrane rejection of each PEG size, are shown in Figures S1 and S2 of the Supplementary Information of Chapter 5 (Chapter 7).

3.2 Simultaneous sulfate precipitation to $BaSO_4$ and NOM removal at high NOM/SO_4^{2-} ratio

3.2.1 Characterisation of NOM in spent brine

Sweden brine had a NOM concentration of 0.5 gDOC/L, and the concentration of the main anions, Cl^- and SO_4^{2-}, was 5 and 2 g/L, respectively. The LC-OCD characterisation shows that almost all the NOM was negatively charged, mostly humic substances (75 percent of DOC) and building blocks (17 percent of DOC) (Figure 3). Similar NOM characterisation was observed in the spent IEX brines from other locations as well (Table S1 of Supplementary Information of Chapter 5, Chapter 7). The results are in accordance with other research, since IEX mostly removes NOM by charge interactions (Cornelissen et al., 2008).

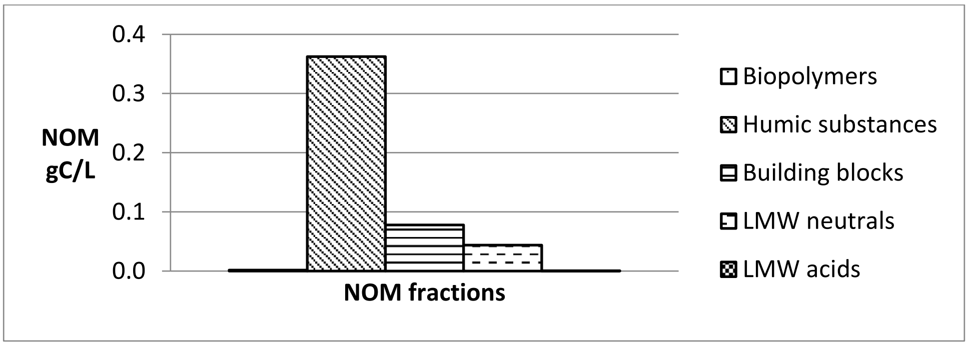

Figure 5, LC-OCD characterisation of NOM for Sweden brine

3.2.2 NOM and sulfate removal by $BaSO_4$ precipitation and ceramic nanofiltration

The $BaSO_4$ precipitation step removed 27 percent of NOM (Figure 4). However, $BaSO_4$ precipitation in the integrated treatment with ceramic nanofiltration did not result in more NOM removal compared to treatment consisting of ceramic nanofiltration alone. The overall NOM removal in both cases was 85 to 91 percent (Figure 4). This result shows that NOM removed by precipitation, is also rejected by the membrane.

For NOM in the nanofiltration step, the removal (the concentration difference between the feed and the permeate, divided by the concentration of the feed) was the same as the membrane rejection (the concentration difference between the recirculation loop and the permeate, divided by the concentration in the recirculation loop). This was due to the negligible recovery of the laboratory scale setup. For nanofiltration in the treatment without precipitation, the membrane rejection of NOM of 91 percent could be predicted, knowing the size of the NOM fractions (measured by LC-OCD) and the membrane PEG retention curve. The prediction method and calculation, for several brines and membranes, is shown in Figure S3 of Supplementary information of Chapter 5 (Chapter 7). A similar method was used by Caltran et al. (2020) for synthetic brines and suggested that NOM is mostly removed by steric hindrance. For nanofiltration in the integrated treatment, the membrane rejection of NOM was only 79 percent, suggesting that precipitation changed the fractionation of NOM by preferential removal of the larger fraction of NOM, i.e. humic substances. As shown by previous research (Van Dijk, 1971; Pagenkopf and Whitworth, 1981), Ba^{2+} and humic substances can bind to form, for instance, barium humate. This potentially decreases the recovery of humic substances concentrate by ceramic nanofiltration, but this problem could be solved by applying $BaSO_4$ precipitation after nanofiltration.

Sweden brine had a low initial SO_4^{2-} concentration of 2 g/L and high NOM to initial SO_4^{2-} ratio of 0.2 gDOC/gSO_4^{2-}. Nevertheless, the removal of SO_4^{2-} by the integrated treatment was 86 percent and mostly due to the $BaSO_4$ precipitation step, resulting in a final concentration below 0.4 g/L (Figure 4). Ceramic nanofiltration, both with and without precipitation, removed hardly any SO_4^{2-}, as expected from previous work with synthetic brines and similar membranes (Caltran et al., 2020).

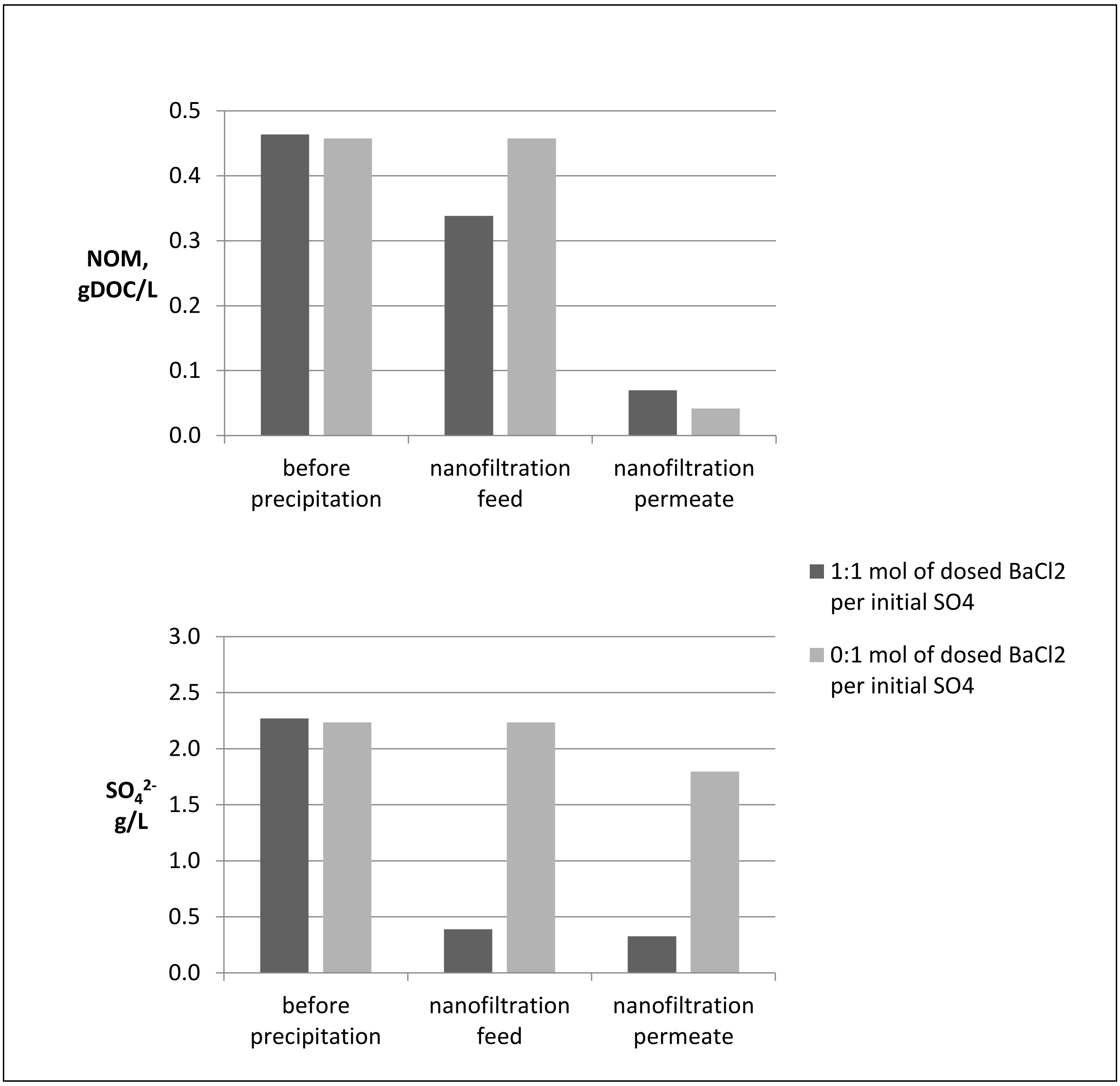

Figure 6, Removal of NOM and SO_4^{2-} from Sweden brine, using low-recovery nanofiltration with or without $BaSO_4$ precipitation

3.3 Sequential NOM rejection and sulfate precipitation to $CaSO_4$ and ettringite removal at low NOM/SO_4^{2-} ratio

3.3.1 NOM removal by ceramic nanofiltration

As in the case of the laboratory scale setup previously described, the concentration of Cl^- and SO_4^{2-} of Netherlands brine with the pilot setup were only slightly affected by direct ceramic nanofiltration treatment of the brine (Figure 5). Also, nanofiltration removed a large portion of NOM (Figure 5).

The average NOM removal, or the difference between the NOM concentration of feed and permeate divided by the NOM concentration of the feed, was 72 percent (Figure 5) with an average water recovery of 76 percent in the pilot setup. The NOM removal is lower than in the laboratory scale setup (Section 3.2.2) because the pilot setup was operated at higher recovery. The average NOM rejection of the membrane (the difference between the NOM concentration of recirculation loop and permeate divided by the NOM concentration in the recirculation loop) was 89 percent (Figure 5).

The LC-OCD analysis of one feed and one permeate samples shows that ceramic nanofiltration removed preferentially the larger NOM fraction in the brine, i.e. humic substances. This is in accordance with the related findings from Section 3.2.2 and our previous work (Caltran et al., 2020).

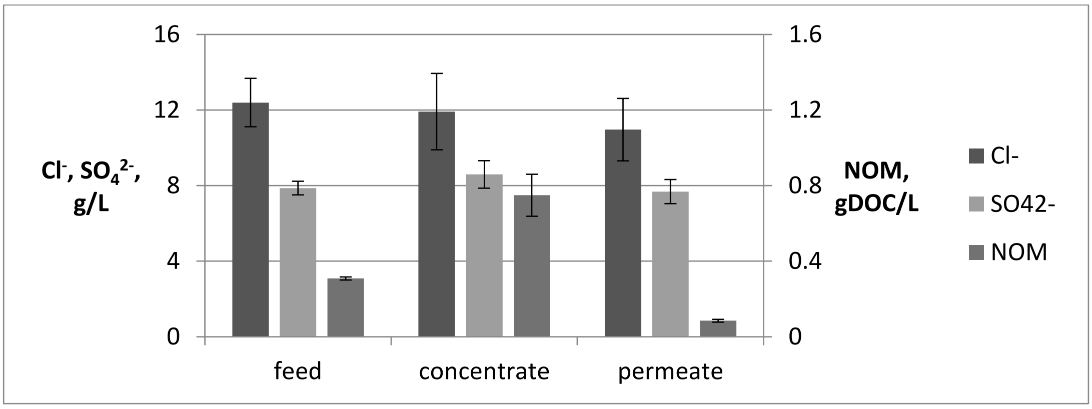

Figure 7, Cl^-, SO_4^{2-} and NOM concentration of feed, concentrate and permeate of the high recovery nanofiltration pilot for the treatment of Netherlands brine.

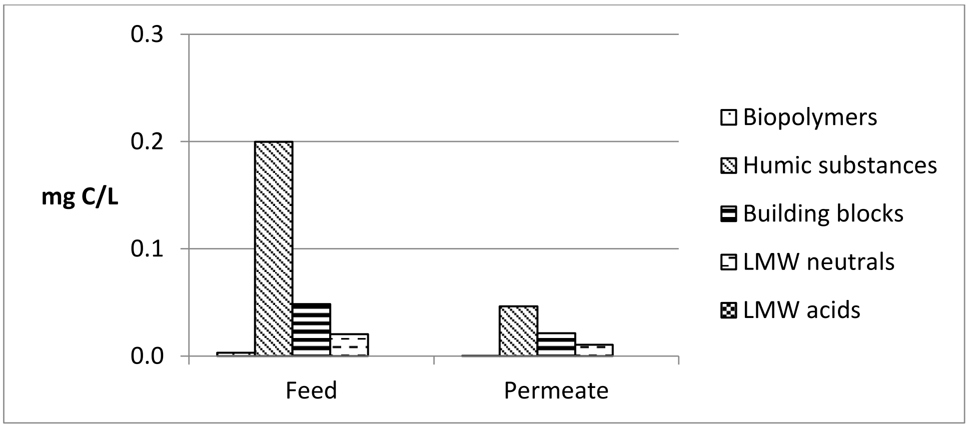

Figure 8, LC-OCD analysis of one feed and one permeate of the high recovery setup (recovery 75 percent)

3.3.2 Effect of NOM on sulfate removal by $CaSO_4$ and subsequent ettringite precipitation

After nanofiltration, $CaSO_4$ and subsequent ettringite precipitation removed only a small amount of NOM, i.e. less than 7 percent of the initial DOC concentration in Netherlands brine. The removed NOM mostly consisted of humic substances (Figure 7).

The nanofiltration permeate of Netherlands brine had a high SO_4^{2-} concentration of approximately 8 g/L and a low NOM to initial SO_4^{2-} ratio of 0.01 gDOC/gSO_4^{2-}. With stoichiometric dosage of $CaCl_2$ for $CaSO_4$ precipitation, the removal of SO_4^{2-} from the nanofiltration permeate was only 17 percent, from 8.1 to 6.7 g/L (Figure 8). In comparison, the removal of SO_4^{2-} from a model Na_2SO_4 solution with similar concentration of SO_4^{2-} was approximately 70 percent (Chapter 4). The inhibition was likely caused by the residual NOM, in accordance with previous experiments (Chapter 4). Previous research showed that NOM can cause inhibition of precipitation of Ca^{2+} or SO_4^{2-} crystals by complexing with Ca^{2+} or by covering nucleation and growth crystal sites (Wada et al., 1993; Le Gouellec and Elimelech, 2002; Bremere et al., 2003; Lee et al., 2009; Li and Zhang, 2020). In our experiments, the Ca^{2+} that can potentially be consumed by complexation was calculated assuming a maximum density charge of humic substances of -15 meq/gDOC, according to Edzwald (1993). The potential Ca^{2+} concentration consumed by NOM is then 2.3 mmol/L for 0.3 gDOC/L, which is less than 3 percent of the dosed Ca^{2+} for $CaSO_4$ precipitation, i.e. 84 mmol/L. Therefore, covering of crystal sites is probably the main mechanism of NOM inhibition, as also suggested by Lee et al. (2009) and Chapter 4.

By dosing chemicals in stoichiometric proportion, the ineffective $CaSO_4$ precipitation step impacted the subsequent ettringite precipitation. With a dose of 0.83 mol of $Ca(OH)_2$ and 0.56 mol of $NaAlO_2$ per mol of initial SO_4^{2-}, the overall SO_4^{2-} removal after $CaSO_4$ and subsequent ettringite precipitation was 72 percent, resulting in a final concentration of 2.3 g/L (Figure 8). Using a double $Ca(OH)_2$ dose for the ettringite step precipitation limited the inhibition on SO_4^{2-} precipitation. An overall SO_4^{2-} removal of 95 percent was obtained, resulting in a final concentration as low as 0.4 g/L (Figure 8). The result suggests that inhibition is due to Ca^{2+} shortage, likely consumed by NOM. Excess of Ca^{2+} has also been used by other authors (Tait et al., 2009) to obtain low SO_4^{2-} concentrations in the presence of impurities in a solution.

NOM removal by nanofiltration improved the removal of SO_4^{2-} by $CaSO_4$ and subsequent ettringite precipitation, as shown in Figure 8. Compared to the nanofiltration permeate, unfiltered Netherlands brine had approximately the same initial concentration of SO_4^{2-} but a higher NOM to initial SO_4^{2-} ratio, i.e. 0.04 gDOC/gSO_4^{2-}. With the same dose of chemicals, the removal of SO_4^{2-} from unfiltered brine was only 70 percent.

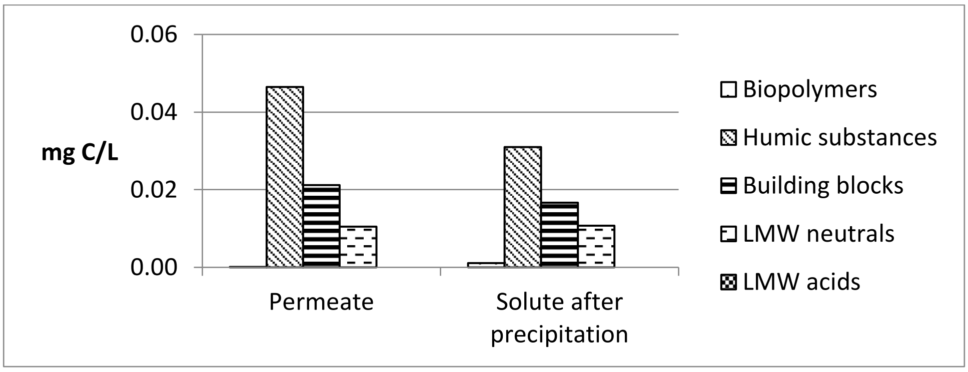

Figure 9, LC-OCD analysis of nanofiltration permeate of the high recovery setup and the solute after subsequent ettringite precipitation (mol dosed chemical per initial SO_4^{2-}: 1:1 of $CaCl_2$; 0.83:1 of $Ca(OH)_2$; 0.56:1 of $NaAlO_2$).

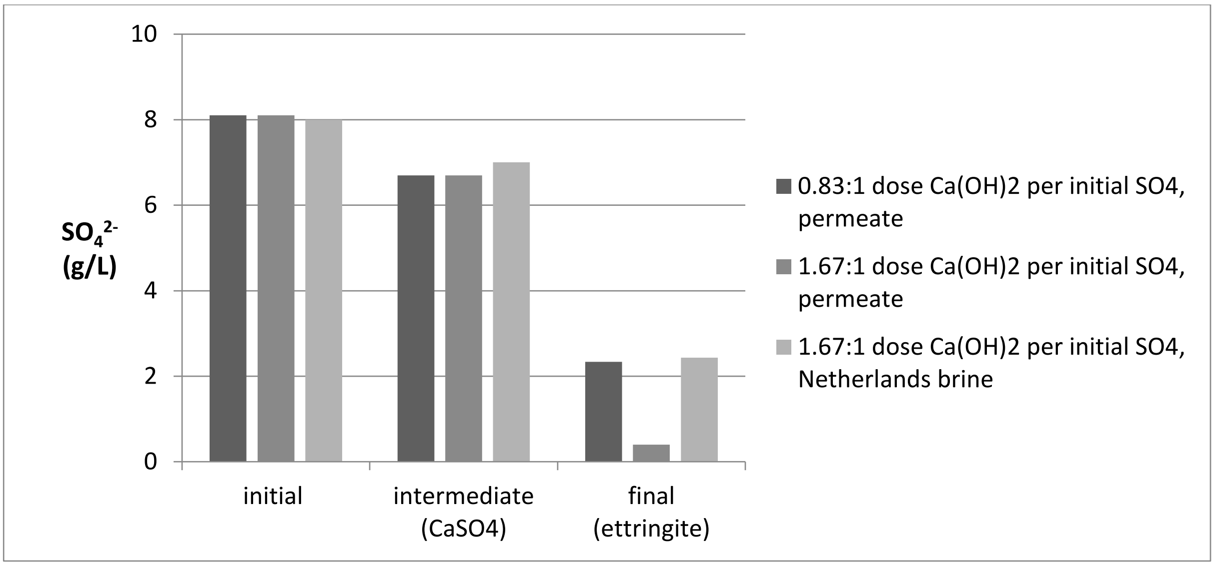

Figure 10, SO_4^{2-} concentration before and after $CaSO_4$ and subsequent ettringite precipitation of Netherlands brine and its permeate from nanofiltration treatment, with different $Ca(OH)_2$ doses. The dose of the other chemicals per mol initial SO_4^{2-} is 1:1 of $CaCl_2$ and 0.56:1 of $NaAlO_2$.

4 Conclusions

Ion exchange treatment (IEX) for NOM removal from surface water produces spent brine that contains, amongst others, NaCl, NOM and Na_2SO_4. Integrated treatment with chemical precipitation and ceramic nanofiltration aims to reduce the IEX waste by recovering (1) a concentrate stream of humic substances, and (2) a NaCl-solution with low sulfate and NOM concentration, that can be reused for IEX regeneration.

In the studied integrated treatment, ceramic nanofiltration alone mostly removed humic substances, the larger NOM fraction of the spent brine, by steric rejection. The NOM removal was 72 to 91 percent and was dependent on the recovery of the system. To a minor extent, precipitation partially removed NOM as well, likely including humic substances in the precipitate. Sulfate and chloride were hardly removed by ceramic nanofiltration and, consequently, the accumulation in the concentrate stream was minimal.

Integrated barite precipitation with subsequent laboratory scale ceramic nanofiltration removed 86 percent of sulfate, resulting in a final concentration below 0.4 gSO_4^{2-}/L. This was even the case with a spent IEX brine with high NOM to sulfate concentration ratio. Nearly all sulfate removal was due to the barite precipitation step.

In integrated pilot scale nanofiltration system with subsequent calcium sulfate and ettringite precipitation, NOM largely inhibited precipitation likely by depleting calcium. Sulfate removal from a spent brine with a low NOM to initial sulfate ratio was improved after decreasing this ratio by NOM removal and dosing excess Ca^{2+}. This resulted in an overall sulfate removal of 95 percent and a final concentration of 0.4 gSO_4^{2-}/L.

The presented study showed that the NOM to initial sulfate ratio of a spent IEX brine is an important parameter to decide whether applying barite or calcium sulfate and ettringite precipitation to obtain low concentrations of sulfate. Environmental considerations should also influence this decision. Barite precipitation requires the use of toxic barium chloride, but calcium sulfate and ettringite precipitation may consume high quantities of chemicals. Moreover, preceding ceramic nanofiltration can decrease NOM hindrance on sulfate removal by subsequent calcium sulfate and ettringite precipitation. To maximise the recovery of humic substances, ceramic nanofiltration should be also considered before barite precipitation.

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Chapter 6

Conclusions and outlook

6 Conclusions and outlook

6.1 Conclusions

6.1.1 Impact of ion exchange for NOM removal from surface water treatment

Drinking water companies in the European North Sea region have applied ion exchange (IEX) with anion resin to remove natural organic matter (NOM) from surface water. Using IEX in the early stage of treatment without fouling was possible with non-fixed bed configurations. Bench and pilot scale IEX removed typically 40 to 60 percent of NOM. The targeted NOM fraction were humic substances and building blocks, which are negatively charged, while biopolymers were hardly removed. The case study revealed the following effects of IEX in surface water treatment:

- IEX before coagulation resulted in lower doses of coagulants;
- IEX pre-treatment had a limited influence on improving fouling of ceramic microfilters;
- IEX removed precursors of assimilable organic carbon, which are formed during advanced oxidation, improving biological stability of treated drinking water; and
- IEX removed NOM and nitrate, resulting in lower energy consumption during advanced oxidation.

Moreover, concerning the water quality after the treatment,

- IEX contributed to lower the formation of disinfection byproducts; and
- integrated IEX, coagulation and ceramic microfiltration outperformed conventional treatment.

A drawback of IEX for NOM removal is the production of spent IEX brines, rich in NOM, sodium sulfate and sodium chloride. Nanofiltration has been considered as a possible treatment for this waste, with the aim to recover humic substances concentrate and sodium chloride permeate to use as regeneration fluid. Additionally, sulfate should also be removed.

6.1.2 Effect of brines’ ionic strength on NOM removal with loose ceramic nanofiltration

Several commercial ceramic nanofiltration membranes in the loose molecular weight cut-off range of 600 to 900 Da were used to treat spent IEX brines and synthetic brines. The resulting NOM removal (the concentration difference between the feed and the permeate, divided by the concentration of the feed) was between 72 to 99 percent, also depending on the recovery of the nanofiltration system. The NOM rejection (the concentration difference between the recirculation loop and the permeate, divided by the concentration in the recirculation loop) was above 90 percent and the membranes removed mostly humic substances.

The impact of ionic strength on the rejection of NOM and sulfate was studied for 600 Da commercial ceramic nanofiltration. The results demonstrated that more than 97 percent of the NOM was rejected at several ionic strengths, while the passage of sodium chloride was 95 percent or more. This was also the case at high ionic strength, when the zeta potential of the nanofiltration membrane was nearly zero. This suggested that the rejection mechanism of NOM was steric hindrance.

6.1.3 Effect of brines' ionic strength on sulfate removal with loose ceramic nanofiltration

While the steric rejection of NOM could be achieved during loose nanofiltration, the rejection of sulfate was more complicated, specifically in relation to high ionic strength of the brine. At low ionic strength, rejection of sulfate was possible due to the high, negative zeta potential of the ceramic membranes. At high ion strength, the zeta potential of the membrane decreased, and therefore also the rejection of sulfate decreased. In the presence of NOM, however, it was observed that the rejection of sulfate slightly increased, probably due to pore size reduction by NOM fouling.

6.1.4 Effect of NOM on precipitation of barium sulfate, calcium sulfate and ettringite

Chemical precipitation of sulfate with barium ($BaSO_4$), calcium sulfate ($CaSO_4$) and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$) was studied for synthetic and IEX brines with varying ionic strengths and NOM concentrations, and initial concentrations of sulfate between 2 and 16 g/L.

High NOM concentrations did not affect barite precipitation to a large extent. The barite precipitation in a spent NOM-rich IEX brine with low initial sulfate concentration resulted in a sulfate removal above 84 percent. In comparison, barite precipitation in synthetic brines without NOM with same chemical dose resulted in sulfate removal above 98 percent. However, the final concentration of sulfate in the treated IEX brine was low, i.e. 0.3 to 0.4 g SO_4^{2-} /L.

Calcium sulfate and subsequent ettringite precipitation were heavily hindered by the presence of NOM. At low initial sulfate concentration, hardly any removal of sulfate was observed from the spent IEX brine. In brines with high initial sulfate concentration, in the presence of NOM, sulfate removal was between 86 and 95 percent, with final concentrations above 0.8 g SO_4^{2-} /L. In comparison, for brines without NOM, the removal of sulfate was above 99 percent despite of a lower dose of chemicals. The inhibition might be attributed to covering of crystal sites by NOM molecules, and to NOM coagulation with aluminium. Considering that calcium sulfate is also limited by its solubility, this precipitation treatment is more suitable for brines with low NOM and high sulfate concentrations.

6.1.5 Towards practice: Integrated ceramic nanofiltration and chemical precipitation for IEX-brines treatment

Integrated nanofiltration and chemical precipitation for sulfate removal are proposed as a treatment for spent IEX brines. The treatment aims to reduce liquid waste by producing concentrate NOM, and by recovering a NaCl solution that can be reused as IEX regenerant.

The targeted NOM fraction for recovery is humic substances and this fraction was largely retained by ceramic nanofiltration. In the meantime, compared to previous studies with polymeric nanofiltration, the fouling was limited. The concentrate can be treated further to reduce sodium, chloride and sulfate. The preferred settings to concentrate NOM are the following:

- *high recoveries*. At higher recoveries, the rejected humic substances are more concentrated than using lower recoveries. A concentrated product is usually more valuable and easier to transport;
- *loose nanofiltration*. With membranes of large pore sizes, chloride and sulfate are less likely to be rejected and to accumulate in the humic substances concentrate, also considering the high ionic strength of the IEX brine; and
- *nanofiltration before precipitation*. The preferential NOM fraction removed by precipitation is likely humic substances. Therefore, with precipitation before nanofiltration, there would be less humic substances available for concentration.

However, nanofiltration should also remove sufficient NOM to enhance sulfate removal by subsequent precipitation. In brines with high initial sulfate, the removal of sulfate by precipitation of calcium sulfate and ettringite decreased when the ratio of initial NOM to added calcium increased (Figure 1). The precipitation and removal of sulfate from a spent IEX brine improved by removing 72 percent of the NOM with ceramic nanofiltration (at 75 percent recovery and molecular weight cut-off of 630 Da) and by increasing the calcium dosage, resulting in a removal of sulfate of 95 percent and in a final sulfate concentration of 0.4 g/L. Low final sulfate can thus be obtained by lowering NOM or increasing calcium.

Removal of sulfate by barite precipitation requires toxic chemicals, which can make the treatment less attractive to implement. Nevertheless, barite seems to be effective for brines at low sulfate and high NOM initial concentrations, and can be used as an alternative when calcium sulfate and ettringite precipitation are not feasible. The proposed treatment is shown in Figure 2.

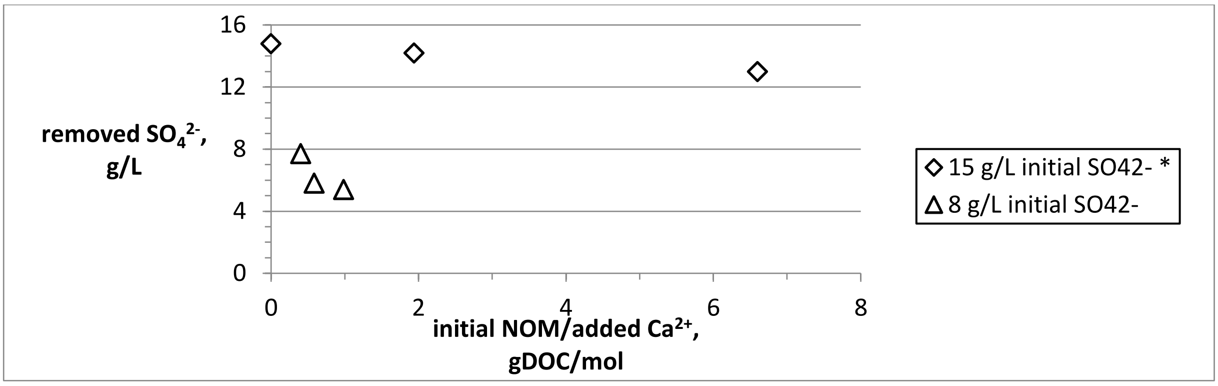

Figure 11, Removed sulfate (SO_4^{2-}) by calcium sulfate and ettringite precipitation using brines with several initial concentrations of sulfate for the ratio of initial NOM and added calcium (Ca^{2+}).

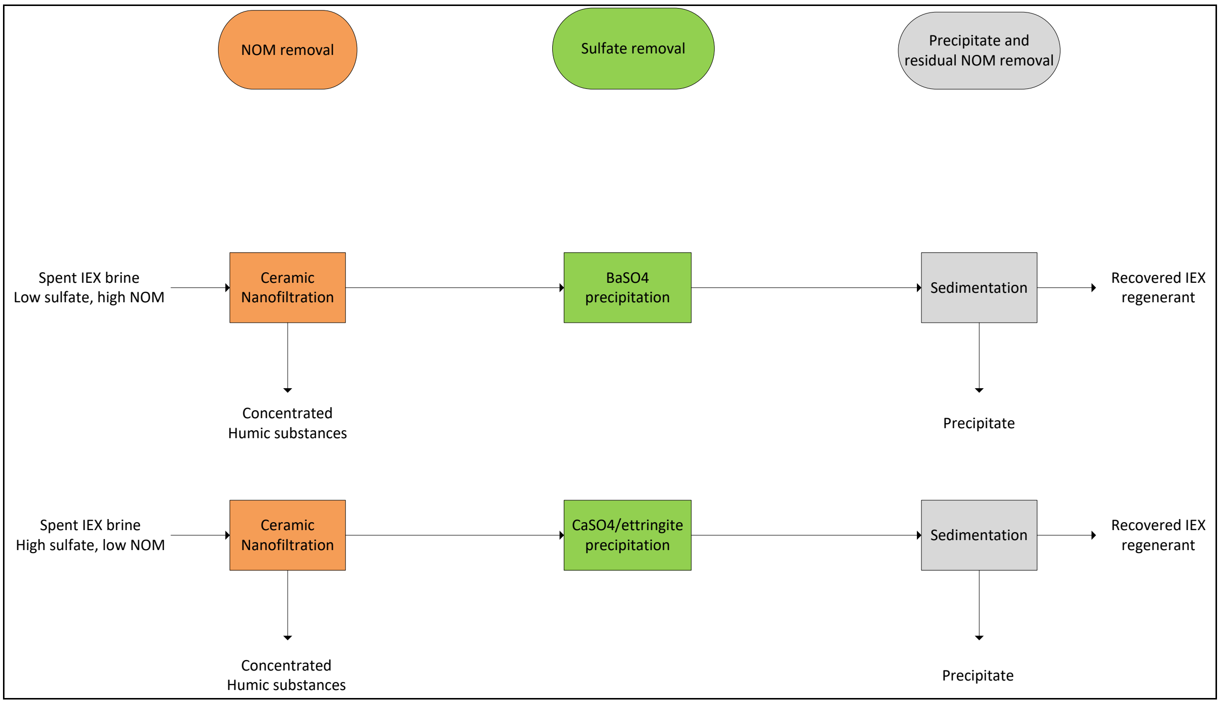

Figure 12, Proposed treatment of spent IEX brines

6.2 Outlook

6.2.1 Quality of recovered ion exchange regenerant

NOM and sulfate should be removed from spent IEX brines to obtain a clean sodium chloride regenerant. However, the allowed residual concentrations are yet unknown. Maximum NOM and sulfate concentrations depend on characteristics related to the location and on the used IEX system, e.g. the required NOM and ions removal for the drinking water treatment, and the available IEX resin sites. If needed, tighter ceramic membranes and more chemicals could be used to remove more NOM and sulfate, respectively. Moreover, the regenerated IEX resin requires rinsing with clean water before reuse. When IEX brines are diluted by rinse water, the clean sodium chloride solution could be too weak for direct reuse as regenerant solution. To avoid an extra concentration step of the sodium chloride solution, rinse water should not be mixed with the IEX brine and recycled or treated separately.

Further studies should be done to determine the local requirements of the recovered ion exchange regenerant for reuse, and optimize operational parameters. Research streams should focus on the effect on operation of brine dilution, accumulation of residual sulfate and NOM, but also of other ions. In particular, accumulation of bicarbonate is seen as a potential risk in nanofiltration treatment of ion exchange brine (Vaudevire and Koreman, 2013). What would be the effect on ion exchange treatment if the composition of the regenerant solution is partially changed from NaCl to $NaHCO_3$?

6.2.2 Purpose and quality of recovered NOM

Similar as in the case of recovered regenerant, knowing the desired quality of the NOM and humic substances in a specific situation is necessary to decide the required treatment steps. A product with high NOM and low salt concentrations has been considered of higher quality. Therefore, research should focus on, e.g., recovery of highly concentrated humic substances with low sodium, chloride and bicarbonate content. As an example, diafiltration has been applied to nanofiltration concentrate to reduce the salts concentration and obtain a marketable product (“Vitens: Circularity in drinking water production”, 2019). Alternatively, the use of humic substances as anti-scalant (Haidari et al., 2019) could be studied, where the presence of salts is of less importance.

6.2.3 Customisation of ceramic membranes

Previous research showed that narrow polymeric membranes rejected sulfate from almost saturated chloride solution (Bargeman et al., 2015). Narrow ceramic nanofiltration could combine sulfate and chloride separation with low membrane fouling and low pressures. Recent research successfully reduced the pore size of ceramic nanofiltration membranes by applying atomic layers of titanium dioxide on commercial ceramic nanofiltration prototypes at bench scale (Shang et al., 2017). However, the substrate ceramic membranes should be defect-free, have a narrow pore size distribution and a sufficient small pore size, and, to the author’s knowledge, they are currently not available in the market.

6.3 References

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Chapter 7

Supplementary Information

7 Supplementary Information

7.1 Supplementary Information of Chapter 3

S1 Molecular weight cut-off and PEG retention of membranes

The paper showed the results for membrane 1, that had a molecular weight cut-off (MWCO) of 560 Da. Membranes 2, 3 and 4 had a MWCO of 850 Da, 910 Da and 840 Da, respectively. The PEG removal of these membranes is shown in Figure S1.

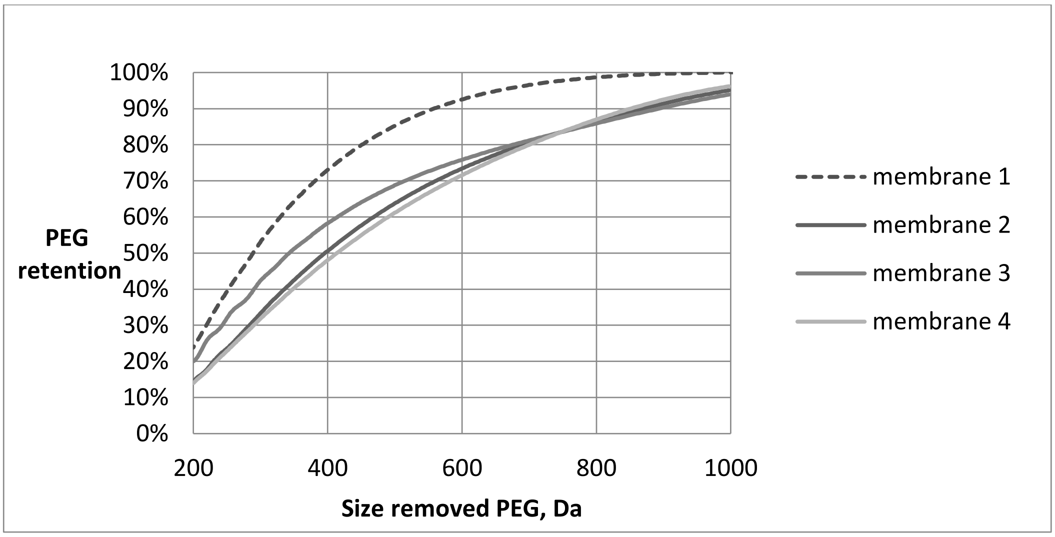

Figure S1, PEG retention of the tested ceramic membranes.

S2 NOM fractionation with LC-OCD

The LC-OCD fractionation of NOM is shown in table S1, for the NOM extracted from IEX brines and used in the synthetic brines, and for four IEX spent brines.

Table S1, LC-OCD fractionation of organic carbon of the NOM isolated from the spent brine, given in percentage of the CDOC

NOM sample	Bio-polymers	Humic Substances	Building Blocks	Low molecular weight neutrals	Low molecular weight acids
	>>20000 Da	~1000 Da	300-500 Da	<350 Da	<350 Da
PWN	0.1%	82.2%	12.0%	5.8%	0.0%
Vitens	0.0%	88.7%	6.8%	4.5%	0.0%
IEX Brine 1	1.8%	71.6%	15.4%	11.2%	0.0%
IEX Brine 2	0.7%	64.7%	18.6%	16.0%	0.0%
IEX Brine 3	0.3%	74.7%	16.0%	9.0%	0.0%
IEX Brine 4	0.9%	80.2%	9.7%	9.3%	0.0%

S3 Experiment pre-settings

The synthetic brines experiment pre-settings for each membrane are shown in tables S2, S3, S4 and S5. The list of spent IEX brine experiments is shown in table S6.

Table S2, Experiment pre-settings for membrane 1 with artificial brines

Type NOM	pH	Initial NOM (g/L)	Ionic strength of tests (% ionic strength from Na_2SO_4)*					
			0.1 M (100%)	0.1 M (0%)	1 M (100%)	1 M (0%)	1 M (50%)	0.1 M (50%)
PWN	8	0.5	x	x	x	X	x	x
Vitens	8	0.5	-	x	x	-	x	x
Vitens	4	0.5	-	-	-	-	x	x
No NOM**	8	0	x	x	x	X	x	x

*The performed experiments are indicated with “x”; **Demineralized water

Table S3, Experiment pre-settings for membrane 2 with artificial brines

Type NOM	pH	Initial NOM (g/L)	Ionic strength of tests (% ionic strength from Na_2SO_4)*					
			0.1 M (100%)	0.1 M (0%)	1 M (100%)	0.5 M (50%)	1 M (50%)	0.1 M (50%)
No NOM**	8	0	x	-	x	x	x	x

*The performed experiments are indicated with “x”; **Demineralized water

Table S4, Experiment pre-settings for membrane 3 with artificial brines

Type NOM	pH	Initial NOM (g/L)	Ionic strength of tests (% ionic strength from Na_2SO_4)*					
			0.1 M (100%)	0.1 M (0%)	1 M (100%)	0.5 M (50%)	1 M (50%)	0.1 M (50%)
No NOM**	8	0	x	-	x	-	x	x

*The performed experiments are indicated with “x”; **Demineralized water

Table S5, Experiment pre-settings for membrane 4 with artificial brines

Type NOM	pH	Initial NOM (g/L)	Ionic strength of tests (% ionic strength from Na_2SO_4)*					
			0.1 M (100%)	0.1 M (0%)	1 M (100%)	1 M (0%)	1 M (50%)	0.1 M (50%)
Vitens	8	0.5	-	-	-	-	x	x

*The performed experiments are indicated with “x”

Table S6, Experiment with spend IEX brines

Brine	Membrane*			
	Membrane 1	Membrane 2	Membrane 3	Membrane 4
Brine 1	-	-	-	X
Brine 2	-	-	-	X
Brine 3	-	X	X	X
Brine 4	-	-	-	X

*The performed experiments are indicated with “X”

S3 Anion removal synthetic brines experiments

The measured Cl$^-$ and SO_4^{2-} removal of synthetic brines experiments for each membrane are shown in tables S7, S8, S9, S10.

Table S7 (part 1), Cl$^-$ and SO_4^{2-} removal for the experiments of membrane 1

NOM type	experiment	ph	Cl$^-$ feed mg/L	Standard deviation mg/L	Cl$^-$ permeate mg/L	Standard deviation mg/L	Cl$^-$ retention	SO_4^{2-} feed mg/L	Standard deviation mg/L	SO_4^{2-} permeate mg/L	Standard deviation mg/L	SO_4^{2-} retention
No NOM	0.1M (0%)	8	3170	1	3076	4	3%	-	-	-	-	-
	0.1M (100%)	8	-	-	-	-	-	3130	13	2426	20	22%
	0.1M (50%)	8	1565	35	1657	1	-6%	1459	26	939	13	36%
	1M (0%)	8	33009	423	32336	584	2%	-	-	-	-	-
	1M (100%)	8	-	-	-	-	-	28812	258	26295	320	9%
	1M (50%)	8	15387	351	15821	146	-3%	14233	351	12942	64	9%

Table S7 (part 2), Cl^- and SO_4^{2-} removal for the experiments of membrane 1

NOM type	experiment	ph	Cl^- feed mg/L	Standard deviation mg/L	Cl^- permeate mg/L	Standard deviation mg/L	Cl^- retention	SO_4^{2-} feed mg/L	Standard deviation mg/L	SO_4^{2-} permeate mg/L	Standard deviation mg/L	SO_4^{2-} retention
PWN	0.1M (0%)	8	2787	8	2671	32	4%	-	-	-	-	-
	0.1M (100%)	8	-	-	-	-	-	2379	66	1153	15	52%
	0.1M (50%)	8	1369	14	1411	30	-3%	1253	3	339	15	73%
	1M (0%)	8	24739	284	24700	212	0%	-	-	-	-	-
	1M (100%)	8	-	-	-	-	-	22279	136	16893	80	24%
	1M (50%)	8	14676	1433	13811	189	6%	13191	1219	8631	132	35%
Vitens	0.1M (0%)	8	3237	6	3115	38	4%	-	-	-	-	-
	0.1M (100%)	8	-	-	-	-	-	2538	36	1354	18	47%
	0.1M (50%)	8	1024	60	1091	271	-7%	848	31	262	113	69%
	1M (0%)	8	32914	182	33055	190	0%	-	-	-	-	-
	1M (50%)	8	13369	330	15186	620	-14%	10867	291	8491	497	22%
	0.1M (50%)	4	n.a.	n.a.	n.a.	n.a.	n.a.	1130	31	234	27	79%
	1M (50%)	4	n.a.	n.a.	n.a.	n.a.	n.a.	14750	1061	7733	351	48%

Table S8, SO_4^{2-} removal for the experiments of membrane 2

NOM type	experiment	SO_4^{2-} mg/L					Removal
		Permeate 1	Permeate 2	Permeate 3	Feed 1	Feed 2	
No NOM	0.1 M (50%)	1.2	1.1	1.2	1.5	1.5	22%
	0.5 M (50%)	6.6	6.8	6.9	7.2	7.4	8%
	1 M (50%)	13.0	11.6	12.8	13.1	12.8	3%
	0.1 M (100%)	2.1	2.4	2.1	2.8	2.8	21%
	1 M (100%)	22.9	23.6	23.9	25.0	24.2	5%

Table S9, SO_4^{2-} removal for the experiments of membrane 3

NOM type	experiment	SO_4^{2-} mg/L					Removal
		Permeate 1	Permeate 2	Permeate 3	Feed 1	Feed 2	
No NOM	0.1 M (50%)	1.1	1.1	1.1	1.5	1.5	23%
	0.5 M (50%)	7.9	8.1	8.1	8.0	8.6	3%
	1 M (50%)	14.4	14.1	14.4	14.0	15.8	4%
	0.1 M (100%)	2.3	2.4	2.4	3.2	3.1	25%
	1 M (100%)	28.9	28.2	28.8	27.9	31.5	4%

Table S10, Cl^- and SO_4^{2-} removal for the experiments of membrane 4

NOM type	experiment	SO_4^{2-} mg/L					Removal
		Permeate 1	Permeate 2	Permeate 3	Feed 1	Feed 2	
Vitens	0.1 M (50%)	826	802	882	1308	1330	37%
	1 M (50%)	12303	11868	12317	12917	15181	13%
NOM type	experiment	Cl^- mg/L					Removal
		Permeate 1	Permeate 2	Permeate 3	Feed 1	Feed 2	
Vitens	0.1 M (50%)	1689	1661	1706	1652	1670	-1%
	1 M (50%)	17314	15737	17388	15915	18477	2%

S4 NOM removal

The measured NOM removal of synthetic brines experiments for each membrane are shown in tables S11 and S12. The NOM removal for the experiments with spent IEX brines are in table S13.

Table S11, NOM removal for the synthetic brine experiments of membrane 1

NOM type	experiment	ph	DOC feed mg/L	Standard deviation mg/L	DOC permeate mg/L	Standard deviation mg/L	DOC retention
PWN	0.1M (0%)	8	370	15	9	1	98%
	0.1M (100%)	8	340	2	8	1	98%
	0.1M (50%)	8	383	5	6	0	99%
	1M (0%)	8	270	1	16	1	94%
	1M (100%)	8	277	3	9	0	97%
	1M (50%)	8	279	8	8	0	97%
Vitens	0.1M (0%)	8	551	4	11	2	98%
	0.1M (100%)	8	533	2	14	3	97%
	0.1M (50%)	8	517	2	9	1	98%
	1M (0%)	8	509	2	12	1	98%
	1M (50%)	8	476	3	12	0	98%
	0.1M (50%)	4	481	6	6	0	99%
	1M (50%)	4	457	7	14	1	97%

Table S12, NOM removal for the synthetic brine experiments of membrane 4

NOM type	experiment	DOC mg/L					Removal
		Permeate 1	Permeate 2	Permeate 3	Feed 1	Feed 2	
Vitens	0.1 M (50%)	10	9	9	457	469	98%
	1 M (50%)	27	18	17	470	465	96%

Table S13, NOM removal for the spent IEX brine experiments of membranes 2, 3 and 4

Brine	Membrane	DOC mg/L					Removal
		Permeate 1	Permeate 2	Permeate 3	Feed 1	Feed 2	
Brine 1	Membrane 4	21	23	22	167	162	87%
Brine 2	Membrane 4	6	5	7	43	44	86%
Brine 3	Membrane 2	41	41	43	461	455	91%
	Membrane 3	38	32	33	472	492	93%
Brine 4	Membrane 4	127	126	121	1659	1717	93%

7.2 Supplementary Information of Chapter 4

S1 Characteristics of spent brines from ion exchange for NOM removal

S1.1 Brines

Four drinking water treatment companies in Europe provided spent brines from ion exchange (IEX) treatment for NOM removal.

S1.2 Material and methods

NOM was measured as dissolved organic carbon (DOC) by a total organic carbon analyzer (TOC-VCPH, Shimadzu, Japan). For some of the analyses, the Cl^- and SO_4^{2-} concentrations was determined by ionic chromatography using an ion exchange column (A Supp 150/4.0, Metrohm AG, Switserland). Otherwise, test cell kits were used (NOVA 60 Spectroquant, Merck, Germany; or LCK 311/153 with spectrophotometer DR 3900, Hach, Germany). For both DOC and anion measurements, the samples were filtrated with 0.45 µm filters and diluted when needed.

S1.3 Characteristics of brines

NOM, Cl^- and SO_4^{2-} concentrations are shown in Figure S1. These are examples of concentration ranges that could be expected for spent IEX brines. We were particularly interested in the inhibition of NOM by sulfate precipitation. Therefore, we worked with Sweden brine because this brine has the highest NOM to sulfate ratio. The removal of sulfate removed by calcium sulfate and ettringite precipitation was easier in brines with less NOM and higher initial sulfate concentration than Sweden brine. The data for Netherlands brine is shown in Figure S2.

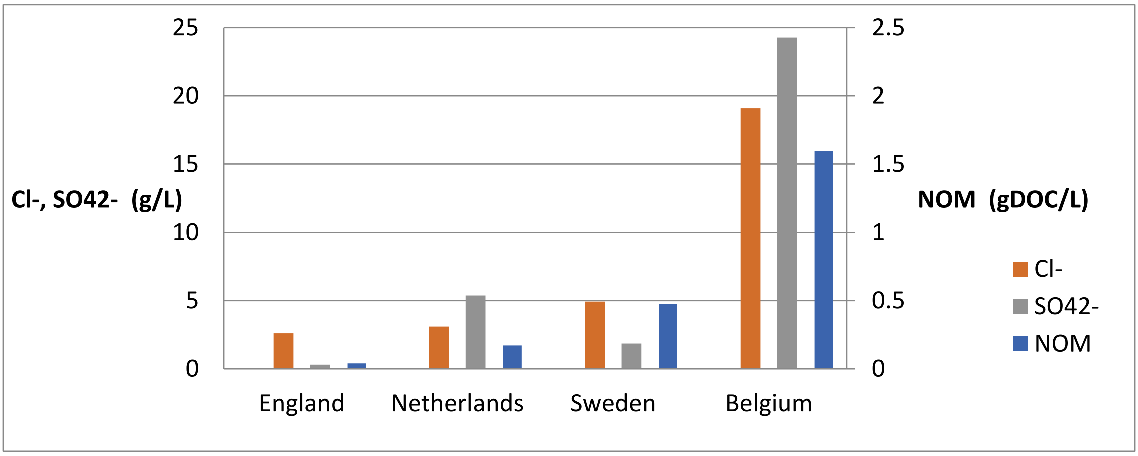

Figure S1, NOM, Cl^- and SO_4^{2-} concentrations of spent brines from IEX for NOM removal

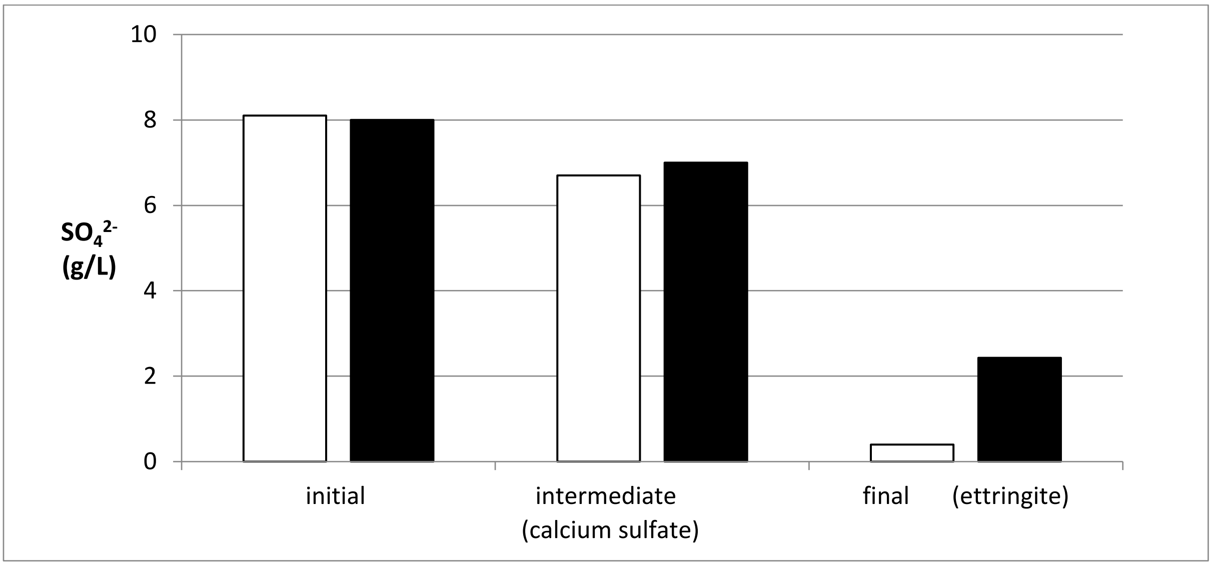

Figure S2, SO_4^{2-} concentration before and after calcium sulfate and subsequent ettringite precipitation of Netherlands brine with approximately 0.3 g/L of DOC (black columns) and of Netherlands brine after NOM removal (white columns, residual NOM approximately 0.1 g/L of DOC). The dose of the chemicals for precipitation per mol initial SO_4^{2-} is 1:1 of $CaCl_2$, 1:67:1 of $Ca(OH)_2$ and 0.56:1 of $NaAlO_2$.

S2 PhreeqC model and validation

S2.1 $CaSO_4$ and $BaSO_4$ Precipitation

To model the high salinity solution, the Pitzer database was used instead of the default PhreeqC database. Pitzer database origins from Pitzer modelling which provides more accurate calculation by measuring the activity coefficients that affect the solubilities in concentrated solutions (Appelo, 2015). This model proposes an approach of ion-interaction which relies on empirical coefficients in describing the ion complexation at high ionic strength (Dudal & Gérard, 2004). All scripts of PhreeqC modelling of this research can be found in this supplementary Information document.

S2.1.1 Material and methods

In the purpose of investigating the suitable dosage of barium and calcium salts for barite ($BaSO_4$) and calcium sulfate ($CaSO_4$) precipitation, several Ba:SO_4 and Ca:SO_4 ratios are simulated using PhreeqC. The model was set in a certain condition as indicated in Table S1. The result of the model was validated whether it represents the actual condition through laboratory experiment by imitating the model and the model's condition.

Table S1. Condition set up for precipitation modelling

Parameter	$BaCl_2.2H_2O$	$CaCl_2.2H_2O$
Ba:SO_4 or Ca:SO_4	0.90-1.10	0.90-1.30
SO_4 concentration	~ 10 g/L	
pH	~8	
Temperature (°C)	20	

The experiments were performed using a plastic beaker and the solutions were stirred using magnetic stirrer with the working volume of 160 ml, consists of 150 ml synthetic brine and 10 ml barium or calcium salt (dissolved in ultrapure water). Prior to salt addition, all the beakers were mixed for a few minutes to ensure all the beakers had approximately the same agitation. After the salts were added, the solutions were mixed for 30 minutes. Subsequently, the mixing was terminated, and the solutions were kept for another 30 minutes to settle the precipitate. Samples were taken from each beaker using a 10 ml syringe and filtered using 0.45 µm before it was transferred to the sample bottles.

S2.1.2 Sulfate removal model

The results of precipitation modelling are depicted in Figure S3 for $BaSO_4$ precipitation and Figure S4 for $CaSO_4$ precipitation. These modelling results were confirmed by validating the modelling through experiments, because the results of the experiments were almost the same as the prediction by the model. Even though not all the experimental results perfectly fitted to the model results, the maximum deviation for both models were only 3%. The model shows that sulfate removal was effective using barium salt, almost 100% removal with a molar dose ratio $Ba:SO_4$ of 1, while calcium salt was less effective, with 75% sulfate removal with a molar dose ratio $Ca:SO_4$ of 1.

Depending on attached water molecule, calcium and sulfate precipitate in different forms of $CaSO_4.nH_2O$, i.e. anhydrate (n=0), hemihydrate (n=0.5), and gypsum (n=2) (MacAdam & Jarvis, 2015). In this case, it was considered as gypsum, due to the temperature of the experiment. Based on a previous study, the transition temperature between gypsum and anhydrate is 58°C in pure water and decreases to 25°C in NaCl electrolyte of 6 molal (He, et al., 1994). The composition of NaCl in the synthetic brine in the experiment was way lower than 6 molar, therefore, at room temperature, it can be assumed that only gypsum was generated in the precipitation process. Consequently, the properties of gypsum was used to compare the sulfate removal from the brine over the properties of $BaSO_4$ precipitation.

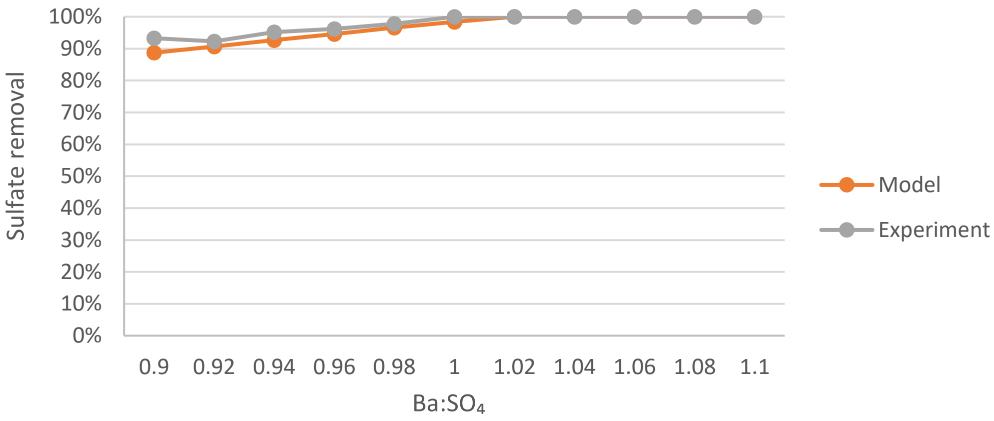

Figure S3. Modelling result of sulfate removal efficacy using barium salt

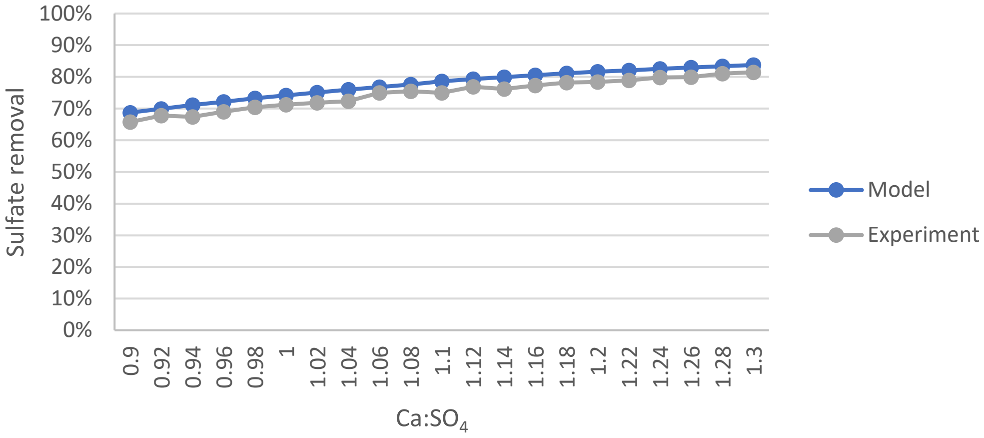

Figure S4. Modelling result of sulfate removal efficacy using calcium salt

Based on Figure S3 and Figure S4, the differences of the removal efficacy between barium and calcium salt addition are evident. In the precipitation process, solubility product is the key for removing the sulfate through chemical precipitation. The solubility product of gypsum is 4.9 x 10^{-5}, while the solubility product of barite is 1.1 x 10^{-10} (Hendricks, 2006). Gypsum solubility is 10^5 higher than barite which means the required molar ratio between calcium and sulfate will be higher compared to barium and sulfate ratio to have similar amount of sulfate to be removed. Next to the removal efficacy, the remaining ions concentration in the brine is also interesting to be considered to choose which chemical is preferred to remove the sulfate. The concentration of the remaining calcium, sulfate and barium in the brines were also modeled with PhreeqC and validated through experiment as shown in Figure S5 and Figure S6.

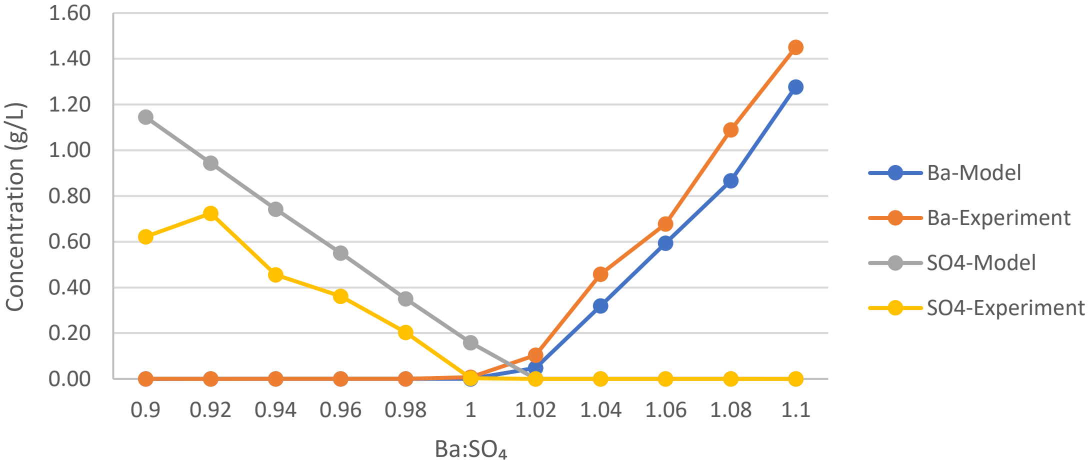

Figure S5. Remaining concentration of sulfate and barium in the brine

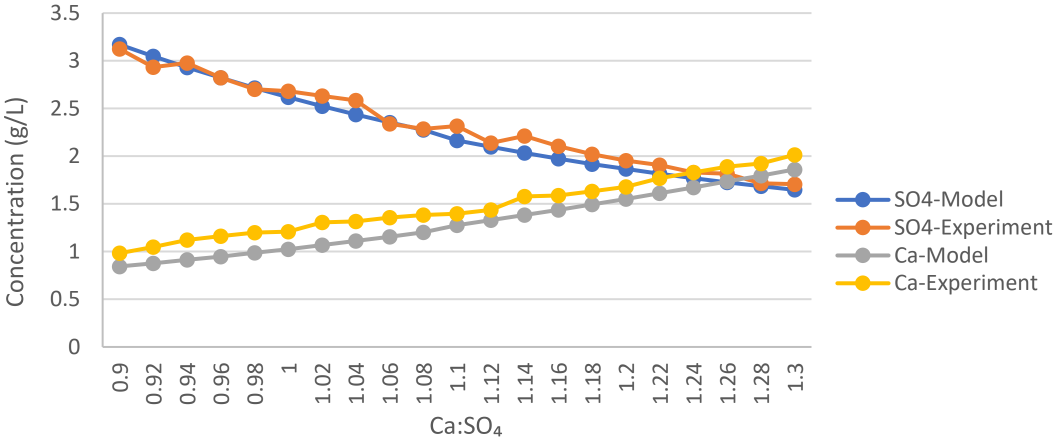

Figure S6. Remaining concentration of sulfate and calcium in the brine

Figure S5 and Figure S6 show that the addition of barium salt was effective to completely remove the sulfate from the brine. When Ba:SO_4=1, all sulfate was completely removed based on the result of the experiment. In the case of calcium salt addition, the remaining sulfate concentration was still above 1 g/L even when the ion ratio is 1.3. In order to achieve very low sulfate concentration with calcium salt, an overdose was thus required. Yet, based on Figure S6, once the sulfate concentration was very low, there was an excess of calcium ions which may lead to scaling problems in further treatment

S2.2 Ettringite

The model for ettrigite was validated using the data from the work of Almasri et al. (2015).

S2.2.1 Material and methods

For modelling ettringite precipitation, the Pitzer database had to be modified because the speciation of aluminum and ettringite phase were not available in the database. The additional data were extracted from llnl.dat, which is a large database containing minerals in a large range and the additional data can be found in PhreeqC manuscripts section of this supplementary information document. An initial model was thus performed to validate the modified database. This initial model was made by imitating the previous experimental work of Almasri, et al. (2015) and the result of the model was compared to the results of the experimental work. The description and the result of the model is indicated in Table S2 and Table S3.

Table S2. Ettringite precipitation description (Almasri, et al., 2015)

Model description	Sulfate removal from synthetic NF reject brine using calcium salt and ettringite precipitation in 2 stages.
Stage 1	Reducing initial sulfate concentration from 97 mM to 12.1 mM using $CaCl_2$ with ion ratio of 2. In this stage $CaSO_4$ formed.
Stage 2	Subsequent ettringite precipitation by adding lime ($Ca(OH)_2$) and sodium aluminate ($NaAlO_2$). Ion ratio between lime and sulfate was 1 and between sodium aluminate and sulfate is 0.67. Final sulfate concentration was 4 mM.

Table S3. Comparison of initial model and previous experiment result

Stage	Almasri, et al. (2015)		Initial Model	
	SO_4^{2-} (mmol/L)	SO_4^{2-} removal	SO_4^{2-} (mmol/L)	SO_4^{2-} removal
Initial	97	-	97	-
Stage 1	12.1	87.5%	11.3	88.3%
Stage 2	4	66.9%	3.5	69%
Overall	95.9%		96.3%	

The difference between the results of the initial model and the previous study was small, therefore the modified database was considered reliable for further modelling of ettringite precipitation. Ettringite precipitation is pH dependent and it is stable in high pH. Ettringite is stable at pH above 10.7 (Germishuizen, et al., 2018), but Almasri, et al. (2015) found that the optimum pH is between 11 and 12.5, which is also supported by a study from Fang, et al. (2018). Beside pH, ion ratio between sulfate, lime, and sodium aluminate are also important. Experiment of Almasri, et al. (2015) used 100% and 67% of sulfate concentration for lime and sodium aluminate dosage, respectively, due to the stoichiometry of the ettringite empirical formula. Adding the salts above these number will not give significant sulfate removal.

S2.2.2 Improvement on sulfate removal using ettringite precipitation

Ettringite precipitation was considered to improve sulfate removal using calcium salt addition. Therefore, ettringite precipitation was modelled to improve the sulfate removal that is indicated previously (see Figure S4). The model set up is shown in Table S4 and the improvement of sulfate removal with ettringite precipitation is depicted in Figure S7. The sulfate removal was improved by applying ettringite precipitation after gypsum precipitation.

Table S4. Setup of sulfate removal modelling with ettringite

Parameter	Value
Initial pH	8
Initial sulfate concentration	104 mmol/L (10 g/L)
$Ca:SO_4$ (Stage 1)	0.90-1.30
Lime ratio (Stage 2)	1
Sodium aluminate ratio (Stage 2)	0.67
Working temperature	23°C

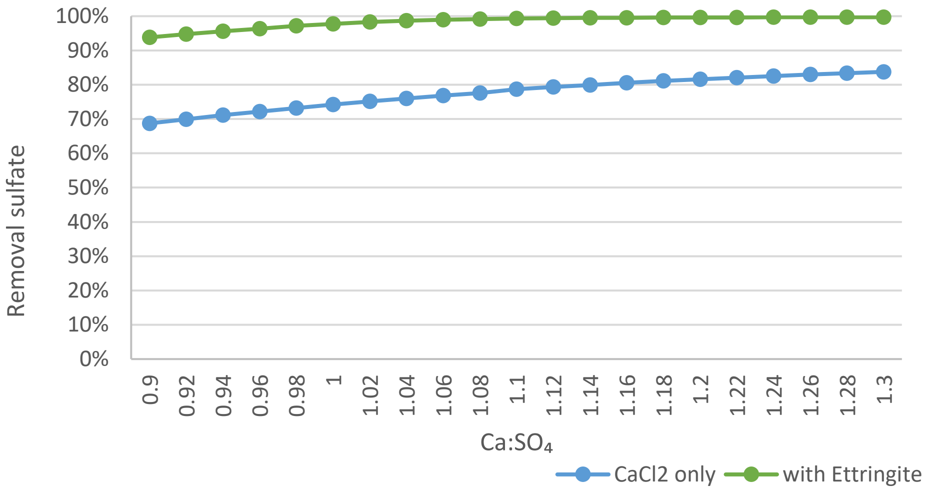

Figure S7. Improvement on sulfate removal using ettringite precipitation

S2.3 References:

Almasri, D., Mahmoud, K. A., & Abdel-Wahab, A. (2015). Two-stage sulfate removal from reject brine in inland desalination with zero-liquid discharge. *Desalination, 362*, 52-58. doi:10.1016/j.desal.2015.02.008

Appelo, C. A. (2015). Principles, caveats and improvements in databases for calculating hydrogeochemical reactions in saline waters from 0 to 200°C and 1 to 1000 atm. *Applied Geochemistry, 55*, 62-71. doi:10.1016/j.apgeochem.2014.11.007

Dudal, Y., & Gérard, F. (2004). Accounting for natural organic matter in aqueous chemical equilibirum models: A review of the theoris and applications. *Earth-Science Review, 66*, 199-216. doi:10.1016/j.earsciev.2004.01.002

Fang, P., Tang, Z.-j., Chen, X.-b., Huang, J.-h., Tang, Z.-x., & Cen, C.-p. (2018). Removal of high-concentration sulfate ions from the sodium alkali FGD wastewater using ettringite precipitation method: Factor assessment, feasilibity, and prospect. *Journal of Chemistry*. doi:10.1155/2018/1265168

Germishuizen, C., Franzen, S., Grobler, H., Simate, G., & Sheridan, C. (2018). Case study modelling for an ettringite treatment process. *Water SA, 44*(1), 86-92. doi:10.4314/wsa.v44i1.10

He, S., Oddo, J. E., & Tomson, M. B. (1994). The inhibition of gyspum and barite nucleation in NaCl brines at temperature from 25 to 90°C. *Applied Geochemistry, 9*, 561-567.

Hendricks, D. (2006). *Water Treatment Unit Processes Physical and Chemical.* Boca Raton, Florida, United States: CRC Press.

MacAdam, J., & Jarvis, P. (2015). Water-Formed Scales and Deposits: Types, Characteristics, and Relevant Industries. In Z. Amjad, & K. Demadis (Eds.), *Mineral Scales and Deposits* (pp. 3-23). Elsevier. doi:10.1016/B978-0-444-63228-9.00001-2

S2.4 Scripts PhreeqC model

S2.4.1 Example SO_4^{2-} removal with $BaSO_4$ precipitation

```
DATABASE PITZER.DAT

SOLUTION 1

-units mg/L

pH 8
```

```
S(6) 10000
Na 4786.791
END
USE SOLUTION 1
EQUILIBRIUM_PHASES 1
Barite 0 0
REACTION 1
BaCl2:2H2O 1
9.37e-2 9.58e-2 9.79e-2 9.99e-2 1.02e-1 1.04e-1 1.06e-1 1.08e-1
1.1e-1 1.12e-1 1.15e-1
REACTION_TEMPERATURE 1
20
SELECTED_OUTPUT
-file so4concentration.txt
-molalities SO4-2
END
```

S2.4.2 Example SO$_4^{2-}$ removal with CaSO$_4$ precipitation

```
DATABASE PITZER.DAT
SOLUTION 1
-units mg/L
pH 8
S(6) 10000
Na 4786.791
END
USE SOLUTION 1
EQUILIBRIUM_PHASES 1
Gypsum 0 0
REACTION 1
CaCl2:2H2O 1
9.37e-2 9.58e-2 9.79e-2 9.99e-2 1.02e-1 1.04e-1 1.06e-1 1.08e-1
1.1e-1 1.12e-1 1.15e-1 1.17e-1 1.19e-1 1.21e-1 1.23e-1 1.25e-1
1.27e-1 1.29e-1 1.31e-1 1.33e-1 1.35e-1
REACTION_TEMPERATURE 1
20
SELECTED_OUTPUT
-file so4+ca_concentration.txt
```

```
-molalities SO4-2 Ca+2
END
```

S2.4.3 Ettringite model: additional data for Pitzer database

```
SOLUTION_MASTER_SPECIES
Al      Al+3  0.0   Al         26.9815
SOLUTION_SPECIES
Al+3 = Al+3
   log_k 0.0
   -gamma     9.0   0.0
   -dw   0.559e-9
#aqueous speciesAl+3 + H2O = AlOH+2 + H+
   log_k -5.0
   delta_h 11.49   kcal
   -analytic  -38.253 0.0      -656.27 14.327
Al+3 + 2 H2O = Al(OH)2+ + 2 H+
   log_k -10.1
   delta_h 26.90   kcal
   -analytic  88.50 0.0   -9391.6 -27.121
Al+3 + 3 H2O = Al(OH)3 + 3 H+
   log_k -16.9
   delta_h 39.89   kcal
   -analytic  226.374 0.0      -18247.8   -73.597
Al+3 + 4 H2O = Al(OH)4- + 4 H+
   log_k -22.7
   delta_h 42.30   kcal
   -analytic  51.578     0.0   -11168.9   -14.865
PHASES
Ettringite
   Ca6(Al(OH)6)2(SO4)3:26 H2O + 12 H+ = 2 Al+3 + 3 SO4-2 + 6 Ca+2
+ 38 H2O
   log_k            62.5362
   -delta_H   -382.451   kJ/mol     # Calculated enthalpy of
reaction Ettringite
#  Enthalpy of formation:     -4193 kcal/mol
```

```
        -analytic -1.0576e+003 -1.1585e-001 5.9580e+004 3.8585e+002 1.0121e+003
#       -Range:  0-200
```

S2.4.4 Example SO_4^{2-} removal with $CaSO_4$ and subsequent ettringite precipitation

```
DATABASE PITZER.DAT
SOLUTION 1
-units mmol/L
pH 8
S(6) 104
Na 208
END
USE SOLUTION 1
EQUILIBRIUM_PHASES 1
Gypsum 0 0
REACTION 1
CaCl2:2H2O 1
1.35e-01 #input based on lattice ion ratio between calcium and sulphate in stage 1
REACTION_TEMPERATURE 1
23
SAVE SOLUTION 2
END
USE SOLUTION 2
EQUILIBRIUM_PHASES 2
Ettringite 0 0
REACTION 2
Ca(OH)2 1.74e-02 #input based on remaining sulphate in stage 1 (100% of sulphate)
NaAlO2 1.74e-02 #input based on remaining sulphate in stage 1 (67% of sulphate)
REACTION_TEMPERATURE 1
END
```

7.3 Supplementary Information of Chapter 5

S1 Molecular weight cut-off of the ceramic membranes

The retention curve of several polyethylene glycol (PEG) sizes in the range of 200 to 1000 Da, for the membranes used in filtration tests with the low-recovery setup (CNF-1, CNF-2 and CNF-3), are shown in figure S1. For the calculation of the retention curves, the analysis of feed and permeate samples have been used, because the recovery of the setup is very low, and the quality of the feed and the concentrate are assumed to be the same. The molecular weight cut-off (MWCO) of the membranes is in the range of 860 to 870 Da.

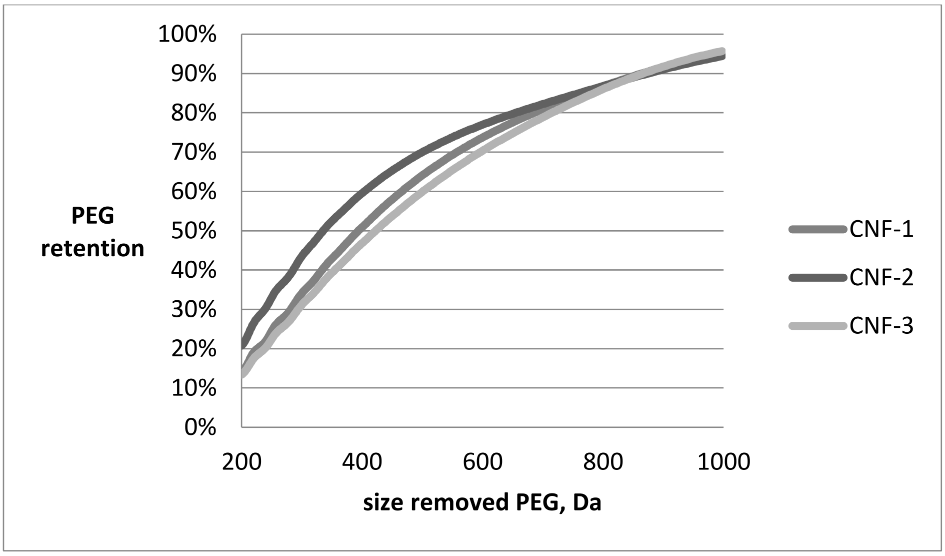

Figure S1, Retention curve of the membranes of the low-recovery setup

The retention curve for the ceramic membrane used in the high-recovery setup (CNF-4) is shown in figure S2. For the calculation of the retention curves, the analysis of concentrate and permeate samples have been used. The MWCO is 630 Da.

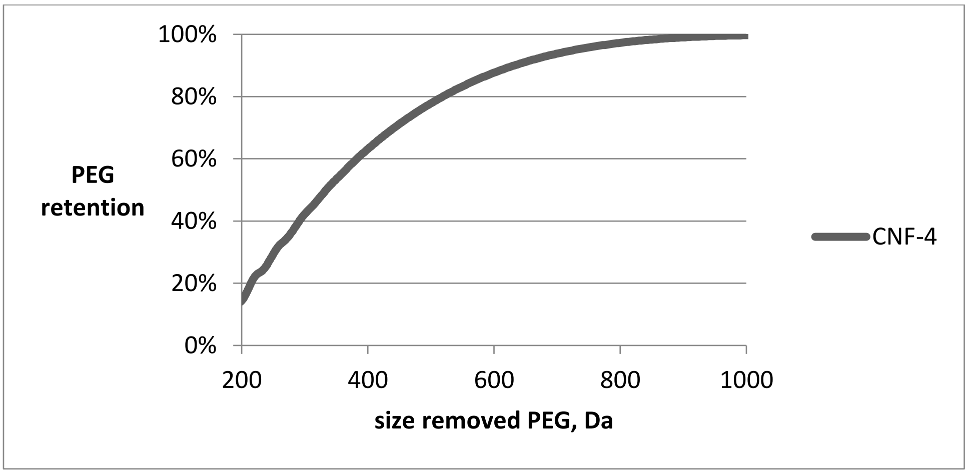

Figure S2, Retention curve of the membrane of the high-recovery setup

S2 Characterisation of NOM in spent brines (low-recovery setup)

The spent anion exchange brines from four locations (England, Sweden, Netherlands and Belgium) had NOM concentrations between 0.04 and 1.6 g/L of dissolved organic carbon (DOC), and Cl^- and SO_4^{2-} concentrations 2.6 to 19.1 g/L and 0.3 to 24.3 g/L, respectively (figure S3). The LC-OCD characterisation (Huber et al., 2011) shows that NOM was mostly from the charged fractions, i.e., humic substances and building blocks (table S1). However, the definition of NOM fractions was different depending on the characterisation method used. With the NSM characterisation method (Lamar et al., 2014), less humic substances were detected. Most of the humic substances were fulvic acids (figure S4).

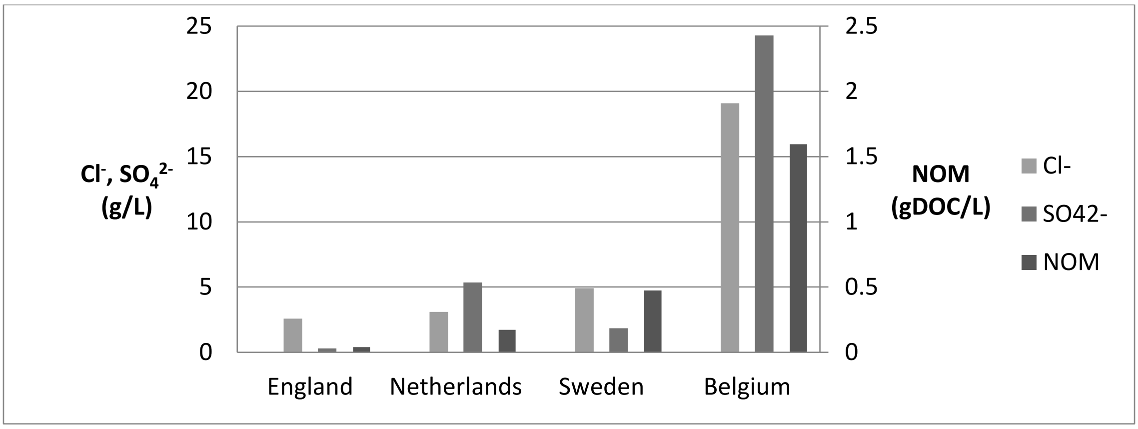

Figure S3, Concentration of SO_4^{2-}, Cl^- and NOM of the spent brines for the low-recovery setup

Table S1, LC-OCD fractions of organic carbon of the NOM isolated from the spent brine, given in percentage of the CDOC

NOM sample	Bio-polymers	Humic Substances	Building Blocks	Low molecular weight neutrals	Low molecular weight acids
	>>20000 Da	~1000 Da	300-500 Da	<350 Da	<350 Da
England	1,8%	71,6%	15,4%	11,2%	0,0%
Netherlands	0,7%	64,7%	18,6%	16,0%	0,0%
Sweden	0,3%	74,7%	16,0%	9,0%	0,0%
Belgium	0,9%	80,2%	9,7%	9,3%	0,0%

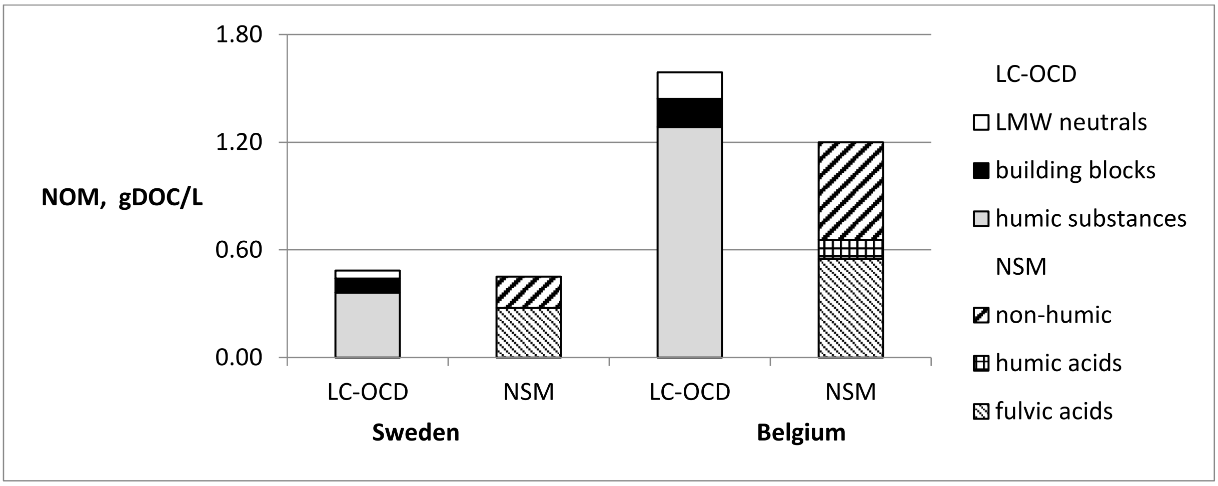

Figure S4, LC-OCD and NSM characterisation of NOM for Sweden and Belgium brine (England and Netherlands brines had not enough NOM for NSM characterisation)

S2.1 Predicting NOM removal by ceramic nanofiltration

For the membranes used the low-recovery setup, the rejection of NOM was in the range of 83 to 90 percent (figure S5). Similarly as in previous work (Caltran et al., 2020), NOM rejection could be predicted with the retention curves of the membranes (figure S1) and the LC-OCD characterisation of the brines (table S1). The rejection of each LC-OCD fraction was approximated by the rejection of the PEG with corresponding molecular weight, in percentage.

Two scenarios for steric hindrance have been used (table S2), firstly because LC-OCD gives an approximation range for the size of the NOM of the different fractions. Moreover, retention curve of the membranes flattens when the PEG size increases, but it seems not able to reach the 100 percent removal. That could indicate the presence of local defects (Kramer et al., 2019). During filtration, large components obstruct the defects or reduce pores size of the membrane, improving steric rejection. In Scenario-1, (1) the bio-polymers are all removed; (2) the humic substances are all removed; (3) the building blocks have the largest size of their range, i.e., 500 Da; and (4) the low molecular weight neutrals and acids have the largest size of their range, i.e., 350 Da. In Scenario-2, (1) the bio-polymers are all removed; (2) the humic substances are 1000 Da; (3) the building blocks have the smallest size of their range, i.e., 300 Da; and (4) the low molecular weight neutrals and acids are not removed. Scenario-1 gave the best prediction for NOM removal (figure S5).

Table S3, Scenario`s used to simulate NOM removal by steric effect

NOM fraction	Bio-polymers	Humic Substances	Building Blocks	Low molecular weight neutrals	Low molecular weight acids
Scenario - 1	>>20000 Da	>>1000 Da	500 Da	350 Da	350 Da
Scenario - 2	>>20000 Da	1000 Da	300 Da	<<350 Da	<<350 Da

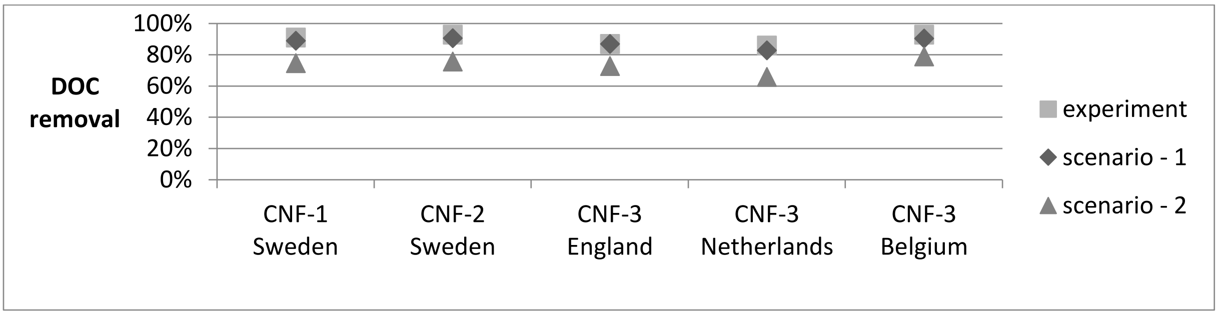

Figure S5, Removal of NOM with the ceramic membrane at low recovery, according to the experiment and according to prediction with different scenarios of steric effect.

S3 References

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Summary

Natural organic matter (NOM) in drinking water sources causes several problems in water consumption and distribution, and decreases the efficiency of water treatment steps. Ion exchange (IEX) with anion resin can be used to remove NOM in combination with or as an alternative to other techniques, such as coagulation and activated carbon.

IEX resins require periodic regeneration with an electrolyte solution that is usually made of sodium chloride. A crucial problem of IEX for NOM removal is related to waste management of the regenerant electrolyte. The regenerant solution is reused several times before disposal, which increases the concentrations of NOM and anions like sulfate. The resulting spent IEX brine is a pollutant and is expensive to dispose, which hampers full-scale applications.

In this research, we proposed a spent IEX brine treatment that is based on ceramic nanofiltration. Ceramic membranes have potential advantages over polymeric membranes, such as higher fluxes and lower fouling characteristics. The treatment aims to recover a permeate of a reusable IEX regeneration salt solution, which is typically sodium chloride, by removing NOM and other anions from the spent IEX brine. Also, concentrated NOM could be used in agriculture and industry, due to the presence of humic substances.

Currently, commercially available ceramic nanofiltration membranes have pore sizes above 450 Da, which is a loose size in the nanofiltration range. This can be favorable when a high passage of sodium chloride in the permeate is desired for IEX regeneration purposes. However, some small NOM fractions and other ions might not be rejected. In particular, sulfate has a high affinity to the anion IEX resin and might be present at high concentrations in the spent IEX brine. Therefore, additional sulfate removal treatment by chemical precipitation was also proposed.

Treatment of high salinity spent IEX brine with commercially available ceramic nanofiltration and chemical precipitation can lead to interactions between the high concentrations of NOM and the chemicals in precipitation processes. Understanding these mechanisms could be a step towards the feasibility of the treatment and the disposal of the spent IEX brine and thus the application of IEX for NOM removal during water treatment.

First, the performance of IEX for NOM removal from surface water was explored using a case study on drinking water companies in the European North Sea region. Bench and pilot-scale IEX typically removed 40 to 60 percent of NOM which consisted mostly of humic substances. IEX resulted in lower consumption of coagulants and energy for advanced oxidation. Moreover, IEX improved the

biological stability of the treated drinking water and lowered the formation of disinfection by-products.

Further, the effect of ionic strength on NOM and sulfate removal by loose ceramic nanofiltration, in the range of 600 to 900 Da, was studied through laboratory-scale experiments. The results showed high NOM removal at several ionic strengths, combined with a high passage of sodium chloride. This was also the case at high ionic strength, when the zeta potential of the nanofiltration membrane was nearly zero. This suggested that the rejection mechanism of NOM was based on steric hindrance. However, the rejection of sulfate was much lower, specifically in relation to the high ionic strength of the brine. At high ion strength, the zeta potential of the membrane decreased, and therefore also the rejection of sulfate decreased.

Then, laboratory studies on the effect of NOM in synthetic and IEX brines on the chemical precipitation of sulfate with barium, calcium sulfate, and ettringite were performed. High NOM concentrations did not affect barite precipitation to a large extent. On the contrary, calcium sulfate and subsequent ettringite precipitation were heavily hindered by the presence of NOM. Also, calcium sulfate precipitation was limited by its high solubility.

Finally, an integrated system with ceramic nanofiltration and chemical precipitation of sulfate was tested on spent IEX brines at pilot scale. The results of these tests gave new practical insights on the performance of treatment for NOM- and sulfate-rich IEX brines. To maximize the recovery of concentrated humic substances, we suggested to apply nanofiltration before chemical precipitation, run the system at high recoveries, and use membranes with loose nanofiltration pore size. For the chemical precipitation, we suggested to apply calcium sulfate and ettingite precipitation. When the brine has low initial sulfate concentration and the NOM to sulfate concentration ratio is high even after nanofiltration, barite precipitation can be used as an alternative.

Samenvatting

Natuurlijke organische stof (NOM) in drinkwaterbronnen veroorzaakt verschillende problemen bij het waterverbruik en -distributie, en vermindert de efficiëntie van waterbehandelingsstappen. Ionenwisseling (IEX) met anion hars kan worden gebruikt om NOM te verwijderen in combinatie met andere technieken, zoals coagulatie en actieve kool, of als alternatief.

IEX-hars vereist periodieke regeneratie met een elektrolytoplossing die meestal gemaakt is van natriumchloride. Een cruciaal probleem van IEX voor NOM-verwijdering is het afvalbeheer van de regenererende elektrolyt. De regenererende oplossing wordt meerdere keren hergebruikt, waardoor de concentraties van NOM en anionen zoals sulfaat toenemen. Het resulterende afval, IEX-brijn, is een vervuilende stof en is duur om te behandelen, wat een volledige toepassing belemmert.

In dit onderzoek hebben we een IEX-brijnbehandeling voorgesteld die gebaseerd is op keramische nanofiltratie. Keramische membranen hebben potentiële voordelen ten opzichte van de meest voorkomende polymere membranen, zoals hogere fluxen en lagere vervuilingseigenschappen. De behandeling is bedoeld om een permeaat van een herbruikbare IEX-regeneratiezoutoplossing, wat typisch natriumchloride is, terug te winnen door NOM en andere anionen uit de afval IEX-brijn te verwijderen. Geconcentreerde NOM zou ook gebruikt kunnen worden in de landbouw en industrie, vanwege de aanwezigheid van humusstoffen.

Commercieel verkrijgbare keramische nanofiltratie membranen hebben poriegroottes van meer dan 450 Da, wat een losse maat is in het nanofiltratiebereik. Dit kan gunstig zijn wanneer een hoge doorgang van natriumchloride in het permeaat gewenst is voor IEX-regeneratiedoeleinden. Het is echter mogelijk dat kleine NOM-fracties en andere ionen niet worden afgestoten. Een van deze ionen is sulfaat. Sulfaat heeft een hoge affiniteit voor de anion IEX-hars en kan het in hoge concentraties aanwezig zijn in afval IEX-brijn. Daarom werd ook een aanvullende behandeling voor het verwijderen van sulfaat door chemische precipitatie voorgesteld.

De behandeling van IEX-brijn met een hoog zoutgehalte met commerciële keramische nanofiltratie en chemische neerslag kan leiden tot interacties tussen de hoge concentraties van NOM en de chemicaliën in de neerslagprocessen. Kennis van deze mechanismen ondersteunt het beheren van de afval IEX-brijn, en dus de toepassing van IEX voor NOM-verwijdering tijdens waterbehandeling.

Allereerst zijn de prestaties van IEX voor NOM-verwijdering uit oppervlaktewater onderzocht aan de hand van een casestudy met drinkwaterbedrijven in de Europese regio van Noordzee. Bench- en pilot-schaal IEX verwijderde doorgaans 40 tot 60 procent van de NOM die voornamelijk uit

humusstoffen bestond. Het tovoegen van IEX aan het zuiveringproces resulteerde in een lager verbruik van coagulanten en een lagere energieconsumptie voor geavanceerde oxidatie. Bovendien verbeterde IEX de biologische stabiliteit van het behandelde drinkwater en verminderde de vorming van desinfectiebijproducten.

Verder werd het effect van ionsterkte op NOM en sulfaatverwijdering door losse keramische nanofiltratie, in het bereik van 600 tot 900 Da, bestudeerd door middel van experimenten op laboratoriumschaal. De resultaten lieten een hoge NOM-verwijdering zien bij verschillende ionsterktes, gecombineerd met een hoge doorlating van natriumchloride. Dit was dus ook het geval bij hoge ionsterkte, toen de zeta-potentiaal van het nanofiltratie membraan bijna nul was. Dit suggereerde dat het afwijzingsmechanisme van NOM gebaseerd was op sterische belemmering. De afstoting van sulfaat was echter veel lager, met name in verband met de hoge ionsterkte van de brijn. Bij hoge ionensterkte nam de zeta-potentiaal van het membraan af, en dus ook de afstoting van sulfaat.

Vervolgens werden laboratoriumstudies uitgevoerd om het effect van NOM in synthetische en IEX-brijnen op de chemische precipitatie van sulfaat met barium, calciumsulfaat en ettringiet te onderzoeken. Hoge NOM-concentraties hadden geen grote invloed op de neerslag van bariet. Integendeel, calciumsulfaat en de daaropvolgende neerslag van ettringiet werden zwaar gehinderd door de aanwezigheid van NOM. Ook werd calciumsulfaatprecipitatie beperkt door zijn hoge oplosbaarheid.

Ten slotte werd een geïntegreerd systeem met keramische nanofiltratie en chemische precipitatie van sulfaat getest op gebruikte IEX-brijnen op pilootschaal. De resultaten van deze tests gaven nieuwe praktische inzichten over de prestatie van de behandeling van NOM- en sulfaatrijke IEX-brijnen. Om het herstel van geconcentreerde humusstoffen te maximaliseren, stelden we voor om nanofiltratie toe te passen vóór chemische neerslag, het systeem met hoge terugwinningen te laten draaien en nanofiltratie membranen te gebruiken met een losse poriegrootte. Voor de chemische neerslag stellen we voor om precipitatie van calciumsulfaat en ettingiet toe te passen. Wanneer de brijn een lage initiële sulfaatconcentratie heeft en de NOM tot sulfaatconcentratieverhouding hoog is, zelfs na nanofiltratie, kan barietprecipitatie als alternatief gebruikt worden.

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