Separating NOM from salts in ion exchange brine with ceramic nanofiltration

Caltran, I.; Rietveld, L. C.; Shorney-Darby, H. L.; Heijman, S. G.J.

DOI
10.1016/j.watres.2020.115894

Publication date
2020

Document Version
Final published version

Published in
Water Research

Citation (APA)
Caltran, I., Rietveld, L. C., Shorney-Darby, H. L., & Heijman, S. G. J. (2020). Separating NOM from salts in ion exchange brine with ceramic nanofiltration. Water Research, 179, [115894]. https://doi.org/10.1016/j.watres.2020.115894

Important note
To cite this publication, please use the final published version (if applicable). Please check the document version above.
Separating NOM from salts in ion exchange brine with ceramic nanofiltration

I. Caltran a,*, L.C. Rietveld a, H.L. Shorney-Darby b, S.G.J. Heijman a

a Delft University of Technology, Department of Water Management, Stevinweg 1, 2628CN, Delft, the Netherlands
b PWN Technologies, Dijkweg 1, 1619HA, Andijk, the Netherlands

A R T I C L E   I N F O

Article history:
Received 30 October 2019
Received in revised form 23 April 2020
Accepted 26 April 2020
Available online 3 May 2020

Keywords:
NOM-Rich brine
Ceramic nanofiltration
Ion exchange

A B S T R A C T

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 Na2SO4, 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.

© 2020 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

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 Levlchuk 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 (Na2SO4), 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 desalination 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 the 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., 2009). 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/m³ 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 Schoutetten, 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 FeCl3/L, filter pressing, and pH adjustment. Verdickt et al. (2012) observed that the sulphate (SO4 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 Schoutetten, 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 Schoutetten, 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-Korboutowicz 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 SO4 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 SO4 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-Korboutowicz 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 limited Cl- rejection (Kabsch-Korboutowicz et al., 2011; Leong et al., 2015). Where measured, the rejection of SO4 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 decomposition (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-Korboutowicz 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 electrodialysis with removal of inorganic content and conservation of NOM. According to Haddad et al. (2019), monovalent selective electrodialysis 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 Na2SO4 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 Na2SO4 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 Al2O3 and a separation layer of TiO2. According to the manufacturer, the mean pore size of the separation layer was 0.9 nm and the membrane porosity was 30–40 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 m². 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 to 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 22–25 °C), trans membrane pressure range 2.9–3.1 bar, flux range 41–43 LMH, cross flow velocity 1.28–1.31 m/s); the feed was sampled twice, during the collection of the first and third permeate. After 0.4 um 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 (α 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 × 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):

\[ \zeta = \frac{dI}{dp} \times \frac{\eta}{\epsilon_r \times \epsilon_0} \times \frac{L}{A} \] (1)

Where \( dI/dp \) = streaming current coefficient, \( L \) = length of membrane dice, \( A \) = cross section area of the channel, \( \eta \) = viscosity, \( \epsilon_0 \) = vacuum permittivity, and \( \epsilon_r \) = 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 22–25 °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 (\( \kappa^{-1} \), m) in water at 20 °C was calculated using Equation (2) (Hunter, 1981):

\[ \kappa^{-1} = \left( \frac{\epsilon_0 \times \epsilon_r \times K_B \times T}{2000 \times N_A \times e^2 \times I} \right) \] (2)

Where \( \epsilon_0 \) = vacuum permittivity (8.85 × 10^−12 C V⁻¹ m⁻¹), \( \epsilon_r \) = relative permittivity of the background solution (80 for water at 20 °C), \( K_B \) = Boltzmann constant (1.38 × 10⁻²³ J K⁻¹); \( T \) = absolute temperature (K); \( N_A \) = Avogadro number (6.0 × 10²³ 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 Hot Water Labyrinth (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 (CDCO) (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 Data Appendix. 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 Na2SO4 (Sigma-Aldrich, Germany; Carl Roth, Germany) at varying concentrations. Composition, set ionic strength and pH of the feed solutions, were 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 min of filtration, three permeate samples were collected one after another for 30 min; the feed was sampled twice, during the collection of the first and third permeate (temperature range 27–42 °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 20–32 °C, transmembrane 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 h soak in a solution of 0.2 percent NaOCl.

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⁺, SO₄²⁻ and Cl⁻ in most of the feed and permeate samples were determined by ionic chromatography (Metrohm AG, Switzerland). 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, Switzerland). For some of the experiments, only SO₄²⁻ 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 (Fig. 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, approximately 450 Da, seems to be provided by the membranes described by PuhlfürB 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 Data Appendix.

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 (Fig. 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 TiO₂ (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).

The effect of the lower zeta potential for the higher ionic strength feed solutions has also been observed (Bargeman et al., 2015) during experiments at nearly saturated salt solutions.

| Series | pH during sampling | Initial NOM (g/L) | Type NOM | Ionic strength of tests (% ionic strength from Na₂SO₄)¹ |
|--------|-------------------|------------------|----------|---------------------------------------------------|
|        |                   |                  |          | 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   | –         | –          | –          | –         | –         | –         |
| 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         |

¹ The performed experiments are indicated with “x”; **Demineralized water.
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 electroskinning slipping plane where the zeta potential is measured (Skluzacek et al., 2007).

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 300–500 Da and less than 350 Da, respectively (Huber et al., 2011).

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 (Schipperes 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 (4–8). The independence of pH and ionic strength shows that the zeta potential (Fig. 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. Fig. 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 300 to 500 Da (~1000 Da) were completely rejected. Due to the pore size distribution mainly to steric hindrance. Fig. 1 shows that the membrane is expected to be negatively charged (Fig. 2). In the mixed NaCl:Na2SO4 solutions without NOM, the rejection of SO4 was 36 percent at 0.1 M, and only 9 percent at 1 M (Fig. 4). Lower SO4 rejection at higher ionic strength was also observed in additional experiments with membranes with a higher MWCO (Supplementary Data Appendix). The negative membrane charge at 0.1 M was confirmed by the Donnan effect, because the retention of SO4 in the mixed feed solution was higher compared to the pure SO4 solution (Fig. 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 SO4. 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; Bargeman et al., 2015). The Donnan effect was not evident in the experiments with the higher MWCO, probably due to the larger pore size (Supplementary Data Appendix).

The rejection of SO4 improved between 2 and 3 times in the presence of NOM. Additional tests with a membrane at higher MWCO also showed this behaviour (Supplementary Data Appendix). 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 SO4 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 SO4 was higher when the pH of the feed was decreased from 8 to 4 (Fig. 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 (Dé Souza and Braganca, 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 Fig. 5 for the NOM experiments at 0.1 M ionic strength. The

| Ionic strength (M) | Debye length (nm) |
|-------------------|-------------------|
| 0.01              | 3.05              |
| 0.1               | 0.97              |
| 1                 | 0.31              |
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-}$, presenting a rejection was between 20 and 80 percent. The composition of the permeates of the experiments with NOM are shown in the Supplementary Data Appendix, and the SO$_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.

### Table 3

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

**Fig. 3.** Membrane permeability of the experiments of series 2. In the legend, the preset ionic strength and the percentage of ionic strength due to Na$_2$SO$_4$ are indicated for each salt experiment.

**Fig. 4.** Na$_2$SO$_4$ 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.
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$_2$SO$_4$ 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 ionic 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.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research is part of the DOC2C’s project. This project has received funding from the Interreg 2 Seas programme 2014–2020 co-funded by the European Regional Development Fund under subsidy contract No 2501-013. The partners of DOC2C’s are companies from water industry (PWN Technologies, South West Water, and De Watergroep) and universities (Lille University, and Delft University of Technology). We thank Bob Siemerink, Iske Achterhuis and Antoine Kemperman from Twente University for the support concerning the zeta potential measurements. We also thank Vitens and PWN for providing us samples of natural organic matter.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2020.115894.
content/uploads/21_Ceramic_Membranes.pdf,

Jiricek, T., De Schepper, W., Ledener, T., Cauwenberg, P., Genne, L. 2015. Recovery of salts from ion-exchange regeneration streams by a coupled nanofiltration-membrane distillation process. Water Technol. 72 (2), 252–259.

Jones, E., Qadir, M., Vliet, V., Smakhtin, V., Kang, S., 2019. The state of desalination and brine production: a global outlook. Sci. Total Environ. 657, 1343–1356.

Kachb-Korbutowicz, M., Wisniewski, J., Lakomska, S., Urbanowska, A., 2011. Application of UF, NF and ED in natural organic matter removal from ion-exchange spent regenerant brine. Desalination 280 (1), 428–431.

Kramer, F., Shang, R., Scherrenberg, S., Rietveld, L., Heijman, S., 2019. Quantifying defects in ceramic tight ultra- and nanofiltration membranes and investigating their robustness. Separ. Purif. Technol. 219.

Lee, H., Kim, D., Cho, J., Moon, S., 2002. Characterization of anion exchange membranes with natural organic matter (nom) during electro dialysis. Desalination 151 (1), 43–52.

Leong, J., Tan, J., Heitz, A., Ladewig, B.P., 2015. Performance of a vibratory shear membrane filtration system during the treatment of magnetic ion exchange process concentrate. Desalination 365, 196–203.

Levchuk, I., Rueda Márquez, J., Sillanpää, M., 2018. Removal of natural organic matter (nom) from water by ion exchange - a review. Chemosphere 192, 90–104.

Li, S., Heijman, S., Verberk, J., Le Clech, P., Lu, J., Kerpman, A., Amy, G., Van Dijk, J., 2011. Fouling control mechanisms of deminerlized water backwash: reduction of charge screening and calcium bridging effects. Water Res. 45 (19), 6289–6300.

Linstrand, V., Sundström, G., Jönsson, A., 2000. Fouling of electrodialysis membranes by organic substances. Desalination 128 (1), 91–102.

Matilainen, A., Sillanpää, M., 2010. Removal of natural organic matter from drinking water by advanced oxidation processes. Chemosphere 80 (4), 351–365.

Meihong, L., Sanchuan, Y., Yong, Z., Congjie, G., 2008. Study on the thin-film composite nanofiltration membrane for the removal of sulfate from concentrated salt aqueous: preparation and performance. J. Membr. Sci. 310 (1–2), 289–295.

Mohamed, A.M.O., Maraqa, M., Al Handhaly, J., 2005. Impact of land disposal of reject brine from desalination plants on soil and groundwater. Desalination 182 (1), 411–433.

Morran, J.L., Bursill, D.B., Drikas, M., Nguyen, H., 1996. A new technique for the removal of natural organic matter. In: Proceedings of the AWWA Watertech Conference (Sydney, Australia).

Neale, P.A., Schafer, A.L., 2009. Magnetic ion exchange: is there potential for international development? Desalination 248 (1–3), 160–168.

Panagopoulos, A., Haralambous, K., Louzado, M., 2019. Desalination brine disposal methods and treatment technologies - a review. Sci. Total Environ. 693.

Perez-González, A., Ibáñez, R., López, P., Urtiaga, A.M., Ortiz, I., Iriáin, J.A., 2015. Nanofiltration separation of polyvalent and monovalent anions in desalination brines. J. Membr. Sci. 472, 16–27.

Puhlflurß, P., Voigt, A., Weber, R., Morbé, M., 2000. Microporous titania membranes with a cut off. J. Membr. Sci. 174 (1), 123–133.

Romero Barranco, C., Brenes Balbuena, M., Garca Garcúa, P., Garrido Fernández, A., 2001. Management of spent brines or osmotic solutions. J. Food Eng. 49 (2), 237–246.

Saito, T., Koop, L., Riemsdijk, V., Nagasaki, S., Tanaka, S., 2004. Adsorption of humic acid on goethite: isotherms, charge adjustments and potential profiles. Langmuir 20 (3), 689–700.

Schippers, D., Kroo, M., Sjoerdsma, P., De Bruijn, F., 2005. Colour removal by ion exchange and reuse of regenerant by means of nanofiltration. Water Sci. Technol. Water Supply 4 (5–6), 57–64.

Shang, R., Verließde, A., Hu, J., Heijman, S., Rietveld, L., 2014. The impact of EFOM, NOM and cations on phosphate rejection by tight ceramic ultrafiltration. Separ. Purif. Technol. 132, 289–294.

Shang, R., Goulas, A., Tang, C., De Frias Serra, X., Rietveld, L., Heijman, S., 2017. Atmospheric pressure atomic layer deposition for tight ceramic nanofiltration membranes: synthesis and application in water purification. J. Membr. Sci. 528, 163–170.

Shao, J., Hou, J., Song, H., 2011. Comparison of humic acid rejection and flux decline during filtration with negatively charged and uncharged ultrafiltration membranes. Water Res. 45, 473–482.

Sillanpää, M., Shestakova, M., 2017. Electrochemical Water Treatment Methods: Fundamentals, Methods and Full Scale Applications. Butterworth-Heinemann, an imprint of Elsevier, Oxford, United Kingdom (2017). Retrieved September 16, 2019, from TU Delft Library.

Skluzacek, J.M., Tejedor, M.L., Anderson, M.A., 2007. NaCl rejection by an inorganic nanofiltration membrane in relation to its central pore potential. J. Membr. Sci. 289 (1–2), 32–39.

Sondhi, R., Bhave, R., Jung, G., 2003. Applications and benefits of ceramic membranes. Membr. Technol. 2003 (1), 5–8.

Subramani, A., Jaconello, J., 2014. Treatment technologies for reverse osmosis concentrate volume minimization: a review. Separ. Purif. Technol. 122, 472–489.

Tang, C., Kwon, Y., Leckie, J., 2007. Fouling of reverse osmosis and nanofiltration membranes by humic acid—effects of solution composition and hydrodynamic conditions. J. Membr. Sci. 290 (1–2), 86–94.

Tansel, B., 2012. Significance of thermodynamic and physical characteristics on permeation of ions during membrane separation: hydrated radius, hydration free energy and viscous effects. Separ. Purif. Technol. 86, 119–126.

Van Der Bruggen, B., Vandecasteele, C., Van Gestel, T., Doyen, W., Leysen, R., 2003. A review of pressure-driven membrane processes in wastewater treatment and drinking water production. Environ. Prog. 22 (1), 46–56.

Van Gestel, T., Vandecasteele, C., Buekenhoudt, A., Dotremont, C., Luynen, J., Leysen, R., Van der Bruggen, B., Maes, G., 2002. Salt retention in nanofiltration with multilayer ceramic TiO2 membranes. J. Membr. Sci. 209 (2), 379–389.

Van de Velde, E., Koreman, E., 2013. Ion exchange brine treatment: closing the loop of NaCl use and reducing disposal towards a zero liquid discharge. In: Win4Life Conference. Tinos Island, Greece, 2013.

Van de Velde, E.M.H., Radmanesh, F., Koltkin, A., Vughs, D., Cornelissen, E., Post, J., van der Meer, W.G.J., 2019. Fate and removal of trace pollutants from an anion exchange spent brine during the recovery process of natural organic matter and salts. Water Research 154, 34–44.

Verdict, L., 2012. Verwijdering van NOM door middel van i onenwisseling. In: Report Vlaamse Maatschappij Voor Water Voorziening.

Verdict, L., Closet, W.D., D’Haelesleer, V., Crompton, J., 2012. Applicability of ion exchange for NOM removal by means of coagulation/ flotation for Enhanced Natural Organic Matter Removal in Drinking Water Treatment. IWA World Water Congress & Exibition, Tokyo, 2018.