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DOI
10.1016/j.wri.2019.100117

Publication date
2020

Document Version
Final published version

Published in
Water Resources and Industry

Citation (APA)
van Linden, N., Shang, R., Stockinger, G., Heijman, S., & Spanjers, H. (2020). Separation of natural organic matter and sodium chloride for salt recovery purposes in zero liquid discharge. *Water Resources and Industry*, *23*, Article 100117. https://doi.org/10.1016/j.wri.2019.100117

Water Resources and Industry 23 (2020) 100117

Contents lists available at ScienceDirect

Water Resources and Industry

journal homepage: http://www.elsevier.com/locate/wri

Separation of natural organic matter and sodium chloride for salt recovery purposes in zero liquid discharge

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ARTICLE INFO

Keywords:
Brine
Separation
Nanofiltration
Electrodialysis
Ion exchange
SALEX

ABSTRACT

The application of zero liquid discharge (ZLD) results in the generation of solid residual streams, which are often not fit for reuse. In this study, we assessed the separation of natural organic matter (NOM) and sodium chloride (NaCl) by nanofiltration (NF), electrodialysis (ED) and ion exchange (IEX) in reverse osmosis brine (RO-brine) and by the extraction of impurities from salt (SALEX) in the generated mixed solids of a full-scale ZLD water treatment plant.

The NaCl recovery by NF, ED and IEX ranged 69-99% and the rejection of NOM ranged 18–19%, 43–65% and 53–76%, respectively. The recovery of NaCl by SALEX ranged 52–99%, while the rejection of NOM ranged 59–92%. The results show that NOM and NaCl can be separated both in RO-brine and mixed solids, opening opportunities for recovery of reusable salt from brines in ZLD.

1. Introduction

1.1. Generation of brines in water treatment

The use of membrane technologies in water treatment results in the generation of residual streams. A major application of membrane technologies is desalination of brackish and saline feed water by reverse osmosis (RO) to provide fresh water for production, cleaning or cooling processes in industry. The generated residual water streams contain the dissolved compounds of the feed stream, but in a higher concentration, because part of the volume of the feed stream is recovered as fresh water. These concentrated residual water streams are called brines and typically have high concentrations of dissolved salts, but also contain other dissolved substances.

1.2. Treatment of brines

In the study of Pramanik et al. [1], various strategies to manage brines are discussed, such as deep-well injection, evaporation ponds and discharge to receiving water bodies. However, deep-well injection and discharge to receiving water bodies could lead to (local) environmental damage [2], while the use of evaporation ponds requires large surface areas and suitable conditions to allow for evaporation. Brines could be used more efficiently, by means of reclamation of the water. The application of zero liquid discharge (ZLD) aims at full water recovery from residual waters and becomes interesting in situations with an excess of waste heat and shortages

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https://doi.org/10.1016/j.wri.2019.100117
Received 27 June 2019; Received in revised form 29 September 2019; Accepted 24 October 2019

Abbreviation list

BV	bed volume
CNF	ceramic nanofiltration
EC	electrical conductivity
ED	electrodialysis
IEX	ion exchange
IEXM	ion exchange membranes
LMW	low molecular weight
MVM	monovalent-selective ion exchange membranes
MW	molecular weight
MWCO	molecular weight cut-off
NF	nanofiltration
NOM	natural organic matter
PNF270	loose polymeric nanofiltration membrane
PNF90	tight polymeric nanofiltration membrane
RO	reverse osmosis
SALEX	extraction of impurities from salt
STM	standard ion exchange membranes
TDS	total dissolved solids
TOC	total organic carbon
UV_{254A}	absorbance of ultraviolet light at 254 nm
ZLD	zero liquid discharge

of (fresh) water sources, since the recovery of water from residual waters by thermal technologies is energy intensive and costly [3]. A drawback of the application of ZLD is the generation of solid residual streams. Because the solids consist of a mixture of substances, they are often not suitable for reuse and therefore sent to a landfill [3]. By means of separating the substances, opportunities for resource recovery emerge.

1.3. Generation of solids in a ZLD water treatment plant

In a full-scale petrochemical industrial water treatment plant, the ZLD strategy is applied to maximise the recovery of water for reuse purposes. Fig. 1 presents the layout of the ZLD water treatment plant. After the removal of most organic substances and suspended solids, reusable water is produced by RO. The generated concentrate (RO-brine) is finally evaporated, resulting in the

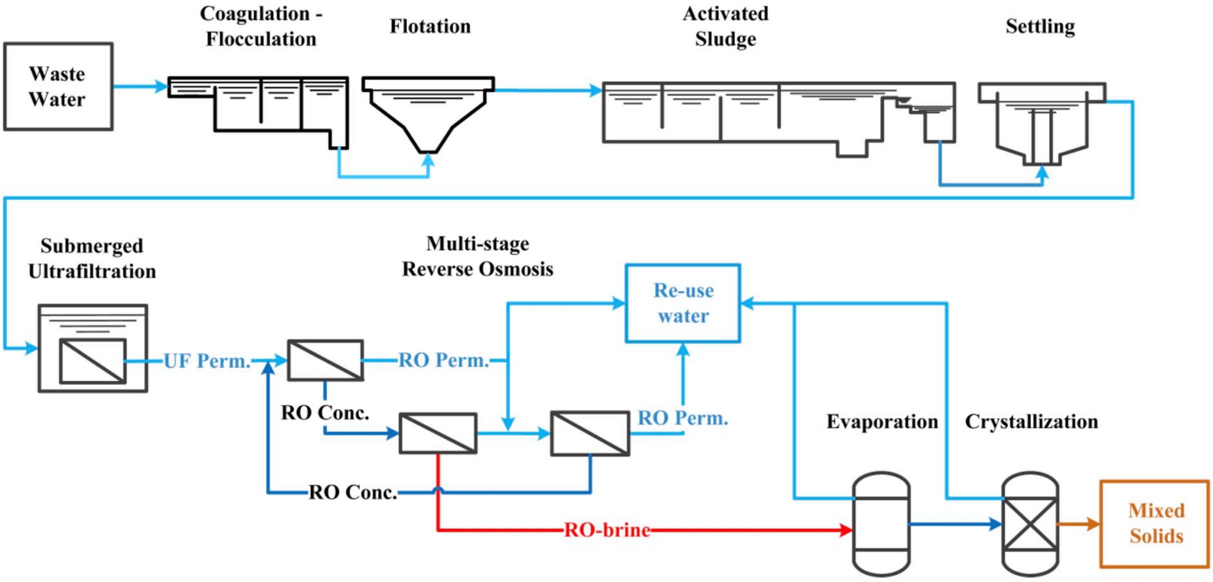

Fig. 1. A schematisation of the ZLD water treatment plant. The water streams are indicated in blue and the RO-brine stream is indicated in red. The mixed solids stream is indicated in brown.

generation of a solid residual stream, consisting of mixed solids. These mixed solids consists of sodium chloride (NaCl) crystals with a distinct brown colour (Fig. 7), making the salt not suitable for reuse.

The colour of the mixed solids is caused by the presence of natural organic matter (NOM), which originate from the activated sludge process. The NOM in the RO-brine is of dissolved nature, because it is not rejected by the submerged ultrafiltration, prior to the multi-stage RO. The generated NaCl crystals can potentially be reused by separation of the NOM and NaCl. This can both be achieved in the dissolved phase (in the RO-brine) or the solid phase (the mixed solids).

1.4. *Natural organic matter in water*

NOM typically refers to a collection of various organic substances and can be divided into various groups [4]. By the characterisation of NOM by liquid chromatography in combination with organic carbon detection (LC-OCD) method, the following groups are generally distinguished: biopolymers, humic acids and low molecular weight (LMW) organics [5]. The characterisation and classification of NOM in water by methods such as LC-OCD is key for the selection of technologies for the treatment of the respective water. According to the study of Huber et al. [6] on the NOM categorisation by LC-OCD of waters with various origins, biopolymers are non-ionic organic molecules with a molecular weight (MW) higher than 10,000 Da. Humic acids cover a wide variety of organic molecules which typically have a negative charge, an MW ranging 350–1000 Da and contain aromatic groups that absorb ultraviolet light at a wavelength of 254 (UV_{254A}) [4–6]. Finally, LMW organics have an MW lower than 350 Da, do not absorb UV_{254} and can be split into two groups: uncharged LMW neutrals and anionic LMW acids, as a function of the solution pH [5].

1.5. *Dissolved phase separation*

To separate NOM and NaCl in the RO-brine, nanofiltration (NF), electrodialysis (ED) and ion exchange (IEX) were considered to be suitable technologies.

1.5.1. *Separation by nanofiltration*

NF membranes allow permeation of monovalent ions and have shown to effectively reject NOM for the production of drinking water and the treatment of sewage effluent for water reclamation purposes [7,8]. Besides, NF has been widely studied and applied to separate organic matter (as dye) and salt in the textile industry [9,10]. However, because the concentrations of organic matter in dyes are in the order of grams per litre and the organic matter often consists of a singular compounds which are well-defined [9,11], the results of previous studies cannot directly be translated to the separation of NOM and NaCl in RO-brine. Furthermore, the actual rejection of NOM depends strongly on the composition of NOM, the membrane characteristics and the feed solution chemistry. Schäfer et al. [12] showed that the fractions of NOM with an MW larger than the MWCO (molecular weight cut-off) of the NF membrane are rejected by size exclusion. The rejection of LMW organics by NF is more challenging [13], because the MW of LMW organics is close to the MWCO of NF membranes. The rejection mechanism of LMW organics relies more on electrostatic repulsion and depends on the solution chemistry, which determines the charge of the LMW organics [12]. Besides the use of polymeric NF (PNF) membranes, a new trend in the application of NF is the use of ceramic NF (CNF) membranes, which can be chemically cleaned. CNF membranes can be coated with selective layers, allowing passage of salt ions and rejection of organics [14]. In fact, CNF membranes proved to be able to reject NOM from pre-sieved sewage without any other pre-treatment [15].

1.5.2. *Separation by electrodialysis*

ED is typically used to concentrate and (partially) desalinate brines, but can also be used as a separation technology [16]. Separation of NOM and salt ions can be achieved by ED by means of transport of salt ions and rejection of NOM through the ion exchange membranes (IEXM). ED has been used to improve the quality of printing dyes by decreasing the salt concentration [17]. However, because the concentration of organic matter in the printing dyes was around 200 $g\,L^{-1}$ and again singular well-characterised organic compounds represented the organic matter, also the results from this study cannot directly be translated to the separation of NOM and NaCl in the RO-brine. Previous research by Lee et al. [18] showed that synthetic humic acids could be well rejected by the IEXM in ED. These results were confirmed by Kim et al. [19], who showed that the rejection of humic acids fraction of NOM originating from a river was high, while a small fraction of the LMW organics was transported from the diluate to the concentrate. In addition, Zhang et al. [20] used ED to separate synthetic LMW organics from salt ions and showed that separation was challenging and depended on the MW and charge of LMW organics. Because LMW acids are negatively charged and have a relatively low MW, they can be transported through the IEXM. The transport of LMW organics, therefore, depends strongly on the MW, the characteristics of the IEXM and the solution chemistry. Sata et al. [21] showed that it is possible to selectively transport anions by using specific anion exchange membranes. Zhang et al. [22] compared standard IEXM with selective IEXM to separate LWM organics and salt ions and found that the selective IEXM had a higher selectivity for transport the salt ions than the standard IEXM.

1.5.3. *Separation by ion exchange*

IEX is a widely applied technology to remove NOM, especially to avoid the formation of disinfection by-products after chlorination during the production of drinking water [23]. NOM rejection by IEX relies on the exchange of organic anions with anions attached to the resin, which have a lower affinity for the resin than the organic anions [24]. No studies that focused on the separation of NOM and NaCl (in RO-brine) were found.

1.6. Solid phase separation

Separation of NOM and NaCl can also be achieved in the solid phase, for example by washing the solid NaCl by using a technique called SALEX, which is an acronym for the extraction of impurities from salt. This process is used to remove impurities from solid salt by means of washing the salt with a saturated salt solution (eluent). The impurities dissolve into the eluent and are subsequently washed away, while the salt remains in solid phase [25]. According to our best knowledge, there are no studies available on the separation of NOM and salt by this technique.

1.7. Research objective

To our best knowledge, there are no studies present that assessed the performance of NF, ED and IEX to separate NOM and NaCl in RO-brine. This study, therefore, focusses on the separation of NOM and NaCl by NF, ED and IEX by assessing both the recovery of NaCl and the rejection of NOM by the respective technologies. We experimentally tested two polymeric NF membranes and one ceramic NF membrane, a standard and a monovalent-selective ED membrane stack and IEX resin in chloride form to separate NOM and NaCl in the RO-brine. Additionally, we experimentally assessed the performance of SALEX to separate NOM and NaCl in the mixed solids

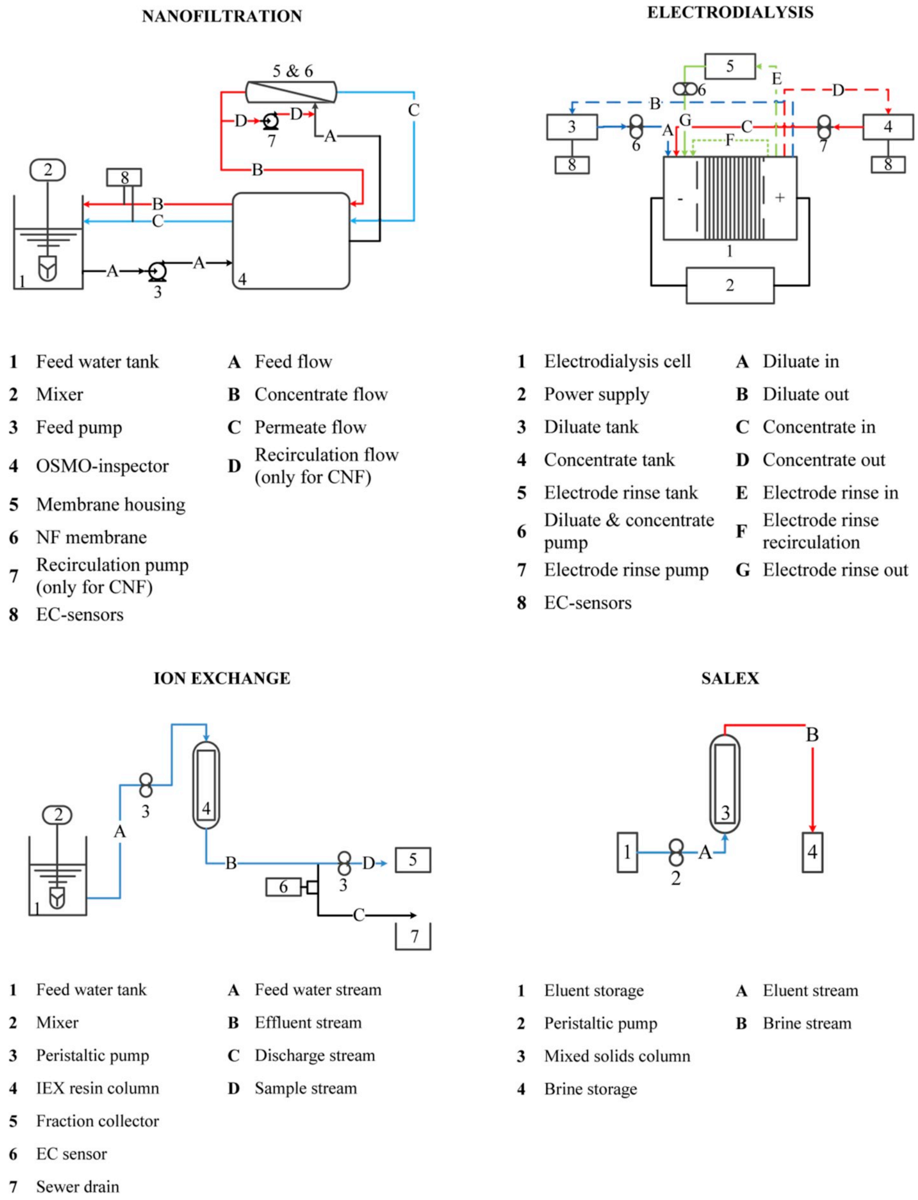

Fig. 2. A schematic representation of the experimental set-ups used for the NF, ED, IEX and SALEX experiments.

generated in the ZLD water treatment plant.

2. Materials and methods

2.1. RO-brine and mixed solids

The RO-brine experiments were conducted with the actual obtained mixed solids, generated by the evaporators in the ZLD water treatment plant. The RO-brine was prepared by dissolving the evaporator mixed solids in demi water. The experiments with mixed solids were conducted with the actual mixed solids from the ZLD water treatment plant, generated by the crystallisers. Fig. 2 presents a schematic representation of the variously used experimental NF, ED, IEX and SALEX set-ups.

2.2. Analytical materials

To characterise the RO-brine and the mixed solids, ICP-MS (Inductively Coupled Plasma Mass Spectrometry) and HPLC (High Performance Liquid Chromatography) were used to detect ions such as sodium and chloride. In addition, the characterisation of NOM was performed by LC-OCD, which makes it possible to distinguish and quantify the presence of various categories of NOM. The EC (electrical conductivity) and pH were measured in all experiments using calibrated TetraCon 925 EC-sensors and IDS SenTix 940 pH sensors, respectively. The automatically logged EC data was stored on a WTW Multi 3630 IDS multi-meter. UV_{254A} was measured by a Thermo Scientific Evolution 60S UV–Visible Spectrophotometer and 50 mm quartz cuvettes, while total organic carbon (TOC) was measured by a Shimadzu TOC-L analyser.

2.3. Nanofiltration

2.3.1. Experimental nanofiltration set-up

The CNF experiments were performed with four tubular TiO_2 Inopor Nano membranes in series, with a total membrane area of 1 m^2 and an MWCO of 450 Da, according to the specifications of the supplier. The PNF experiments were performed with a spiral-wound DOW NF270-2540 (PNF270) and a DOW NF90-2540 (PNF90) polyamide thin-film composite Filmtec membrane, both having a membrane area of 2.6 m^2. The PNF270 membrane is considered to be a loose NF membrane, having an MWCO of 400 Da, while PNF90 membrane is considered to be a tight NF membrane, having an MWCO of 200 Da, according to the specifications of the supplier. The CNF and PNF membranes were placed in stainless steel membrane housings, which were connected to a Divergence OSMO-Inspector, serving as a control system to set the flow rates and pressures.

2.3.2. Methods

To achieve a high NaCl recovery, a water recovery of 70% was maintained for all NF experiments. A Dutchi Motors recirculation pump was used for the CNF experiments to maintain an additional cross-flow rate of 360 $L\,h^{-1}$. The feed flow rate for the CNF experiments was 30 $L\,h^{-1}$ and the permeate flow rate was 21 $L\,h^{-1}$, corresponding to a flux of 19 $L\,m^{-2}\,h^{-1}$. For the PNF experiments, it was not possible to use an additional recirculation pump in the same set-up. Therefore, 50 L of RO-brine was pre-concentrated by 62.5%, by discharging the permeate and recirculating the concentrate to the feed tank. Subsequently, the concentrated RO-brine was used as feed for the PNF membranes at a feed flow rate of 250 $L\,h^{-1}$ and a permeate flow rate of 50 $L\,h^{-1}$, corresponding to a flux of 21 $L\,m^{-2}\,h^{-1}$. The water recovery of the pre-concentration (62.5% of 50 L) and the water recovery during the experiment (20% of 18.75 L) simulated a total 70% water recovery for the PNF experiments.

During the NF experiments, the permeate and concentrate were recombined in the feed tank. Manual samples were taken from the feed, permeate and concentrate during steady-state operation, after a stabilisation period of 4 h. At steady-state, the permeate water flux and pressures were stable for at least 1 h. The temperature, flow rate and pressure of the feed, permeate and concentrate were logged by the OSMO-Inspector. The EC of the feed was continuously measured in the feed tank, while the EC of the permeate and concentrate were continuously measured prior to recombination of these streams in the feed tank.

2.4. Electrodialysis

2.4.1. Experimental electrodialysis set-up

The ED experiments were conducted using a ten cell pair standard ED stack (ED-STM), consisting of ten PC SA standard anion exchange, nine PC SK standard cation exchange and two PC SC cation exchange end membranes. In addition, a ten cell pair monovalent-selective ED stack (ED-MVM), consisting of ten PC MVA monovalent-selective anion exchange, nine PC MVK monovalent-selective cation exchange and two PC SC membranes was used. Both ED stacks were placed in a PC-Cell ED cell with a Pt/Ir coated titanium anode and a V4A steel cathode, having electrode surfaces of $8 \times 8\,cm^2$. The electrodes and membranes were separated by polyethylene/silicone spacers, which also improved the mixing in the diluate and concentrate channels. The spacers had a thickness of 0.5 mm and a void fraction of 59%. The electric current was supplied by a Delta Elektronika direct current supply, with an electric potential range of 0–30 V and an electric current range of 0–0.30 A. Diluate and concentrate solutions were stored in glass bottles and recirculated through the ED cell by a calibrated peristaltic Watson Marlow 520S pump with 313 pump heads, at a flow rate of 5 $L\,h^{-1}$, corresponding to a cross-sectional velocity of 0.7 $cm\,s^{-1}$. RO-brine was used as initial diluate, while a 6.8 $g\,L^{-1}$ NaCl solution was used as an initial concentrate, to measure the transport of NOM and NaCl. A second Watson Marlow 520S pump was used to recirculate the electrode rinse solution, which was also stored in a glass bottle, at a flow rate of 10 L h^{-1}. A 1 M $NaNO_3$ solution was used as electrode rinse solution. All used solutions had an initial volume of 1 L.

2.4.2. Methods

To achieve a high NaCl recovery, the diluate EC was reduced to 1 mS cm^{-1}. Prior to the ED experiments, a relationship between the limiting current density (LCD) and the diluate EC was determined. The applied current density during ED should always be below the LCD, to avoid the dissociation of water [26]. For the determination of this relationship, diluted RO-brine solutions of 1x, 0.8x, 0.6x, 0.4x, 0.2x and 0.1x were prepared, while the concentrate consisted of a 6.8 g L^{-1} NaCl solution. By stepwise increasing the electric current with 0.05 A per minute and logging the electric potential, the LCD for each RO-brine dilution was determined according to the empirical method of Cowan and Brown [27]. During the ED experiments, an initial current density of 47 A m^{-2} was applied, until the LCD was exceeded. The current density was subsequently adjusted according to by "the linear ($R^2 = 0.95$) relationship between between the LCD and the diluate EC (current density = 10.4 · EC). Before and after each ED experiment, the samples were taken from the diluate, concentrate and electrode rinse solutions and the volumes were measured. The EC of the diluate and concentrate was continuously measured in the respective bottles. The electric current and electric potential were manually logged throughout the experiments.

2.5. Ion exchange

2.5.1. Experimental ion exchange set-up

The IEX experiments were conducted in a column set-up, filled with 20 cm Lewatit VP OC 1071 strong base anion exchange resin, having a bed volume (BV) of 51 mL. The resin consisted of crosslinked polyacrylamide, with a quaternary amine function group and an average bead size of 1.4–1.6 mm, according to the specifications of the supplier. For the IEX experiments, the resin was in chloride form, allowing for exchange of NOM with chloride. A calibrated peristaltic Watson-Marlow 120S pump was used to pump the RO-brine through the IEX resin.

2.5.2. Methods

RO-brine was fed top-down over the IEX resin for 600 BV, corresponding to a volume of 31 L. The flow rate through the resin was 30 BV·h^{-1}, to provide a contact time of 2 min, as recommended by the supplier. The EC of the RO-brine was again continuously measured in the feed tank, while the EC of the effluent was continuously measured in the effluent, prior to discharge. The effluent samples were automatically taken to determine the rejection of NOM every 60 BV in 7.5 mL glass vials, using a Biorad 2110 fraction collector and an additional Watson-Marlow 120S pump.

2.6. Experimental SALEX set-up and methods

SALEX experiments were conducted in column set-up with a BV of 51 mL. The column was filled with mixed solids and washed with a saturated NaCl solution (400 g L^{-1}), to avoid dissolution of the mixed solids in the eluent. The mixed solids were washed in a bottom-up configuration with one, two and three bed volumes of eluent, at a bed expansion of 0%, 25% and 50%. After elution, the treated solids were dried and weighed, to determine the NaCl recovery. The NOM content in the solids was determined by dissolving 5 g L^{-1} of treated solids in demi water and measuring the TOC concentration. Also, the TOC concentration of the SALEX-brine was determined, to close the mass balance and determine the NOM rejection by SALEX.

2.7. Performance indicators

For the dissolved phase separation technologies (NF, ED and IEX), the recovery of NaCl (Eq. (1)) was determined by using the water recovery and the rejection of TDS.

$$Y_{NaCl,i} = Y_{H_2O,\mathrm{i}} \cdot (1 - r_{TDS,i}) \tag{1}$$

Where $Y_{NaCl,i}$ = recovery of sodium chloride (unitless), $Y_{H2O,i}$ = water recovery (unitless) and $r_{TDS,i}$ = rejection of TDS by nanofiltration, electrodialysis and ion exchange.

The NaCl recovery (Eq. (2)) and the rejection of NOM (Eq. (3)) by SALEX were determined by using the NaCl masses and the measured TOC concentrations, respectively.

$$Y_{NaCl,SALEX} = \frac{m_{NaCl,ts}}{m_{NaCl,ms}} \tag{2}$$

Where $Y_{NaCl,SALEX}$ = recovery of NaCl by SALEX (unitless), $m_{NaCl,ts}$ and $m_{NaCl,ms}$ = NaCl mass of the treated solids and of the mixed solids, respectively (in g).

$$r_{NOM,SALEX} = 1 - \frac{c_{TOC,ts}}{c_{TOC,ms}} \tag{3}$$

Where $r_{NOM,SALEX}$ = rejection of natural organic matter (unitless), $c_{TOC,ts}$ and $c_{TOC,ms}$ = concentration of total organic carbon per gram of treated solids and the mixed solids, respectively (in mg·g^{-1}).

3. Results and discussion

3.1. Characterisation of RO-brine and mixed solids

The TDS concentration of the RO-brine was 6.9 g L^{-1} and was for 98% represented by NaCl according to the measurements by ICP-MS. The concentration of NOM, expressed as TOC, in the RO-brine was 35 mg L^{-1}, corresponding to a NOM concentration of 5 mg per gram of NaCl. Fig. 3 presents the results of the characterisation of NOM by LC-OCD and shows that 73% of the NOM in the RO-brine was present as humic acids and 23% was present as LWM neutrals, making up the majority of the NOM. The residual fraction (4%) of the NOM was present as hydrophobic NOM, biopolymers and LMW acids. The LMW organics were dominated by LMW neutrals, based on the pH of the RO-brine (8.1). The low fraction of biopolymers is a result of treatment of the activated sludge effluent in the ZLD water treatment plant by ultrafiltration prior to RO.

The mixed solids consisted for 97% of NaCl and had a NOM concentration (as TOC) of 1.3 mg per gram of NaCl. The NOM in the mixed solids also consisted mainly of humic acids (56%) and LMW neutrals (32%). The differences in concentration of NOM per gram of NaCl between the RO-brine and the mixed solids indicates that evaporation and crystallisation processes in the ZLD water treatment plant affected the amount of NOM per gram of NaCl.

3.2. Separation by nanofiltration

3.2.1. Recovery of NaCl by nanofiltration

Fig. 4A presents the rejection of TDS from the RO-brine by the various NF membranes. The PNF90 membrane rejected 89% of the TDS, while the rejection of TDS by the PNF270 and CNF membranes was negligible (1%). The difference in TDS rejection by the two PNF membranes was a result of the different MWCOs of these membranes. Besides the difference in TDS rejection, the applied pressure to maintain a flux of 21 L m^{-2} h^{-1} was different for the PNF membranes. The applied pressure for PNF270 membrane was 10 bar, while the applied pressure for PNF90 membrane was 17 bar. The higher applied pressure was both a result of the osmotic pressure difference that needed to be overcome and the higher membrane resistance for the more tight PNF90 membrane. In terms of TDS rejection, the CNF membrane performed similarly to the PNF270 membrane, while a pressure of only 4 bar was applied to maintain a stable flux, indicating that the CNF membrane had a higher water permeability than the PNF270 membrane. Since a 70% water recovery was applied for all NF experiments, the recovery of NaCl by PNF270 and CNF was 69% and 68%, respectively (Fig. 4B).

3.2.2. Rejection of NOM by nanofiltration

The PNF90 membrane rejected UV$_{254A}$ by 83% and TOC by 77%, respectively (Fig. 5A–B). The fraction of NOM permeating through the PNF90 membrane consisted probably of LMW organics, which made up 25% of the NOM and have an MW close to the MWCO of the PNF90 membrane. The rejection of NOM by the PNF270 membrane was only 51% as UV$_{254A}$ and 18% as TOC, while the CNF membrane had a NOM rejection of 47% as UV$_{254A}$ and 19% as TOC. The rejection of UV$_{254A}$ by the PNF270 and CNF membranes was more than twice as high as the rejection of TOC. Because UV$_{254A}$ is typically absorbed by humic acids [6], the PNF270 and CNF membranes preferentially rejected humic acids from the RO-brine, which can be explained by the higher MW of humic acids than of LMW organics. These findings are in line with the findings of Lin et al. [11], who found that relatively large (MW = 990 Da) organic compounds in dyes are well rejected by NF membranes. The results indicate that a fraction of the humic acids still permeated through the PNF270 and CNF membranes, as only 18–19% of the TOC was rejected and the humic acids made up 73% of the NOM in the RO-brine.

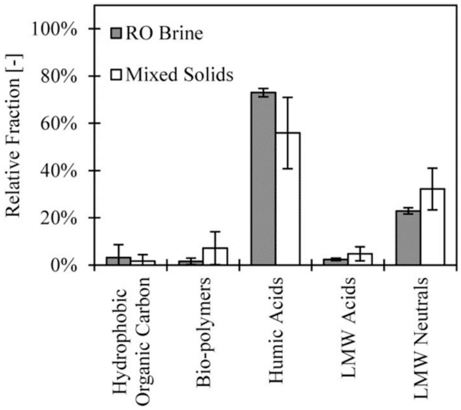

Fig. 3. The categorisation of NOM in the RO-brine and the mixed solids from the ZLD water treatment plant. The error bars represent standard deviations for triplicate measurements.

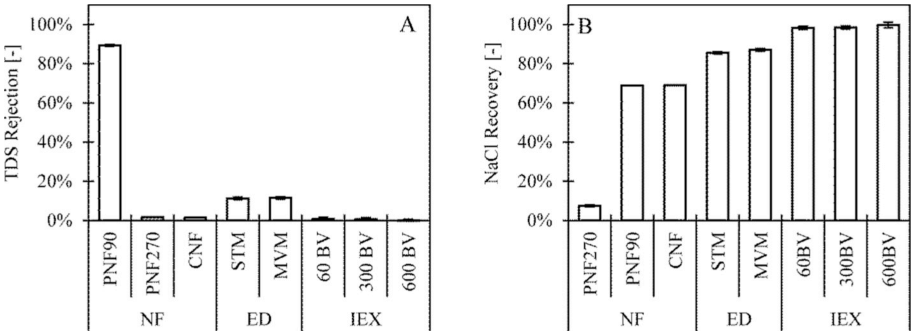

Fig. 4. The rejection of NaCl as TDS (A) and the NaCl recovery (B) by the various separation technologies. The error bars represent standard deviations for triplicate experiments.

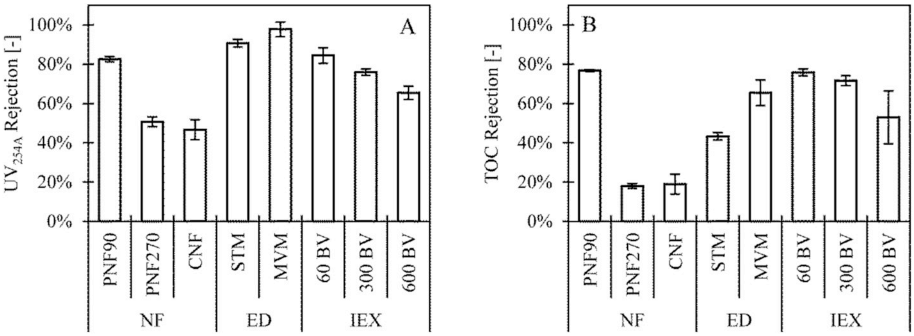

Fig. 5. The rejection of NOM as UV$_{254A}$ (A) and TOC (B) by the various separation technologies. The error bars represent standard deviations for triplicate experiments.

3.3. *Separation by electrodialysis*

3.3.1. *Recovery of NaCl by electrodialysis*

The rejection of TDS by both ED stacks was limited to 11% (Fig. 4A), because the EC of the diluate was decreased from 9 to 1 mS cm^{-1}. The water recovery for ED-STM and ED-MVM was 96% and 98%, respectively. The loss of recovered water from the diluate was caused by both osmosis and electro-osmosis. Electro-osmosis is the transport of water in the hydration shells of transported ions (in this case NaCl) and osmosis is the transport of water from the diluate to the concentrate, as a result of an osmotic pressure gradient between the diluate and concentrate [28]. Because the ion concentration in the diluate decreased and the ion concentration in the concentrate increased throughout the experiments, an ion concentration (and thus an osmotic pressure) gradient established, resulting in osmotic water transport from the diluate to the concentrate. By taking the water recovery into account, the NaCl recovery by ED-STM and ED-MVM was 86% and 87% (Fig. 4B), respectively.

3.3.2. *Rejection of NOM by electrodialysis*

Fig. 5A–B shows that ED-STM rejected UV$_{254A}$ and TOC by 91% and 43%, respectively. ED-MVM rejected UV$_{254A}$ by 98% and TOC by 65%. The high UV$_{254A}$ rejection suggests that almost no humic acids were transported from the diluate to the concentrate by both ED stacks. However, the TOC rejection of ED-STM indicates that more than half of the NOM from the RO-brine was transported from the diluate to the concentrate. This fraction represented NOM that does not absorb UV$_{254}$ and either migrated under the influence of the electric current or diffused from the diluate to the concentrate. LMW organics can be transported through IEXM, due to their low MW [20], while a part of the humic acids probably had an MW that was also low enough to permeate through the IEXMs. The monovalent-selective membranes proved to be more selective to NOM transport, because the rejection of NOM as both UV254 and TOC were higher than for the standard membranes. This can be caused by improved size exclusion or electrostatic repulsion of the IEXMs in the ED-MVM stack, compared to the IEXMs used in the ED-STM stack [22]. The results show that besides separation of organic matter and salts in dyes [17], ED is also able to separate organic matter as NOM from NaCl in RO-brine at much lower organic matter concentrations compared to dye treatment.

For both ED stacks, the TOC mass balance of triplicate experiments did not fit (19% error). After visual inspection of the membranes, decolouration of the anion exchange membranes was observed for both ED stacks, while no noticeable differences were observed on the cation exchange membranes. The decolouration of the anion exchange membranes can be related to adsorption of NOM, indicating that part of the rejection mechanism can be attributed to adsorption of NOM on the anion exchange membranes. It is expected that the adsorption is reversible, as Lee et al. [18] showed that only 0.1% of the humic acids was irreversibly attached to the anion exchange membranes used in their experiments.

3.4. Separation by ion exchange

3.4.1. Recovery of NaCl by ion exchange

The rejection of TDS from the RO-brine by IEX was negligible (<1%). The rejection of NaCl is presented in Fig. 4A for a fresh resin (60 BV) and after the treatment of 300 and 600 BVs. Because the anion exchange resin was already in chloride form, no removal of chloride took place. The water recovery of IEX was 100%, because the feed flow was equal to the effluent flow. In combination with a negligible TDS rejection, the NaCl recovery of IEX was 99% throughout the treatment of 600 BVs of RO-brine (Fig. 4B).

3.4.2. Rejection of NOM by ion exchange

After the treatment of 60 BVs of RO-brine, the rejection of NOM by IEX as UV_{254A} and TOC was 84% and 76% (Fig. 4A and B), respectively. After treatment of 300 BVs of RO-brine, the rejection of NOM decreased to 76% and 72% as UV_{254A} and TOC, respectively. This decrease was caused by saturation of the resin with NOM, resulting in a lower capacity to exchange NOM for chloride. Finally, after 600 BV, the rejection of NOM as UV_{254A} decreased further to 65% and to 53% as TOC, indicating that the resin was getting more saturated with NOM.

Similar to the rejection of NOM by NF and ED, the rejection of UV_{254A} by IEX was consistently higher than the rejection of TOC, which is in line with the findings of Comstock et al. [29]. However, the differences between the rejection of UV_{254A} and TOC by IEX were less obvious than for NF and ED. The high rejection of NOM as TOC can be explained by the negative charge of both humic acids and LMW acids. The residual fraction of NOM that was not removed could be represented by LMW neutrals, which are uncharged and made up 23% of the NOM in the RO-brine. Uncharged NOM is not likely to be removed by IEX, because removal of NOM solely relies on the actual ion exchange mechanism, rather than adsorption for the removal of NOM [24].

During the IEX experiments, the colour of the resin changed from white to dark brown/black, which was caused by the adsorption of humic acids. The change in colour does not mean that the resin cannot be reused after regeneration, but the regeneration of IEX resin saturated with humic acids can be challenging [23].

3.5. Separation of NaCl and NOM by SALEX

3.5.1. Recovery of NaCl by SALEX

The recovery of NaCl by SALEX using one BV of eluent ranged 91–99% for the various bed expansions, as presented in Fig. 6A. For the use of two BVs of eluent, the NaCl yield ranged 75–96% and for the use of three BVs, the NaCl yield ranged 52–95%. No clear relation between the NaCl recovery and bed expansion was found for the various BVs used.

3.5.2. Rejection of NOM by SALEX

The rejection of NOM from the mixed solids by SALEX deviated over the amount of used BVs eluent, as can be seen in Fig. 6B. By using one BV of eluent, 58–75% of the NOM was rejected. When more than one BV of eluent was used, the rejection of NOM increased, since for two BVs and three BVs, 75–80% and 88–92% of the NOM was rejected respectively. By using more BVs of eluent, more time was available for the NOM to dissolve into the eluent and the NOM concentration gradient between the mixed solids and the eluent was higher. The use of various bed expansions did not result in clear differences in NOM rejection for using the same amount of eluent. This is because the NOM was not present as particulate or suspended solids, which could be washed out by expanding the mixed solids. The NOM was present on the outside of the NaCl crystals and dissolved in the eluent and was washed away in the SALEX brine, resulting in white NaCl crystals, as presented in Fig. 7.

4. Conclusions

Based on the experiments with the various dissolved and solid phase technologies to separate NOM and NaCl, several conclusions can be drawn.

The PNF90 (the tight PNF) membrane proved to be unsuitable for the separation of NOM and NaCl in RO-brine, because this membrane did not allow permeation of NaCl. On the other hand, the PNF270 (loose PNF) and CNF membrane allowed NaCl to permeate, but only had a limited NOM rejection. For ED, the use of a membrane stack with MVM resulted in a higher rejection of NOM, compared to the use of a membrane stack with STM, while both membrane stacks had an equal NaCl recovery. Furthermore, full recovery of NaCl was achieved by treating the RO-brine by IEX, while the rejection of NOM decreased of the amount of volume treated RO-brine. All dissolved phase technologies preferentially rejected the humic acids part of NOM in the RO-brine, based on the consistently higher rejection of UV_{254A} than the rejection of TOC. Finally, SALEX showed to be able to recover NaCl and reject NOM, by means of washing the mixed solids with a saturated NaCl solution as eluent.

The results showed that it is possible to separate NOM and NaCl, both in RO-brine and mixed solids, allowing for the generation of reusable solid NaCl. By means of opening opportunities for reuse of NaCl, the drawback of having to landfill the generated solid streams in ZLD applications can be avoided. Besides, the obtained results can potentially be translated to the separation of organic matter and salts in textile and printing industry, when concentrations of organic matter in the order of $mg \cdot L^{-1}$ are present.

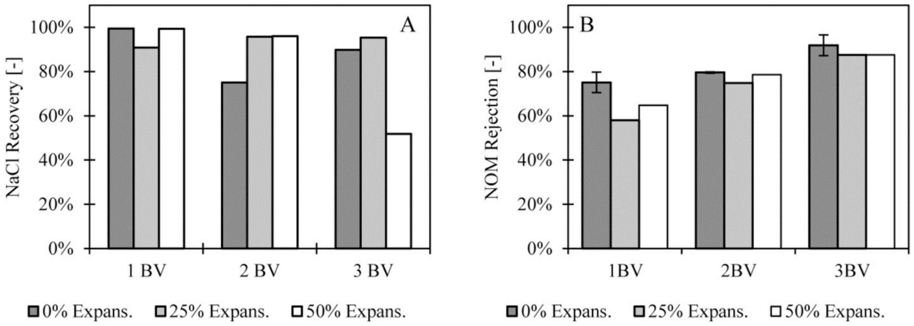

Fig. 6. The NaCl recovery (A) and NOM rejection by SALEX (B) at various bed expansions and BVs of eluent. Error bars represent the minimum and maximum values of NOM rejection.

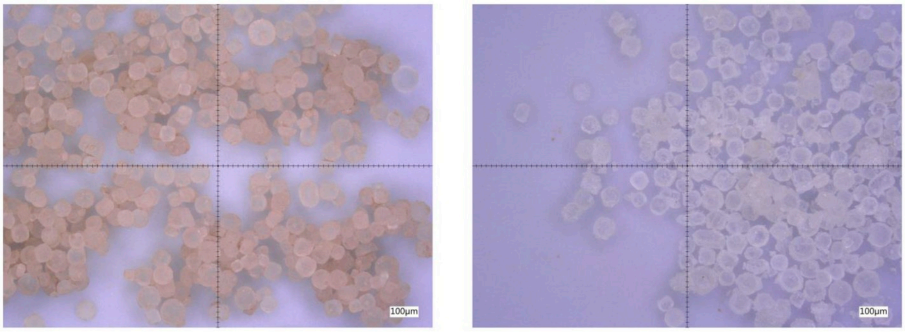

Fig. 7. Microscopic pictures of the actual mixed solids from the ZLD water treatment plant (left) and the obtained NaCl crystals after SALEX treatment (right).

Declaration of competing interestCOI

The authors declare no competing financial interest.

Acknowledgements

No sources of public funding were used to conduct this study.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wri.2019.100117.

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