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Integration of electrically driven membrane separation processes for water treatment and resources recovery

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"All is water"

(Thales of Miletus)

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Abstract

Nowadays, due to the growing fresh water demand, several processes are used to purify seawater by means of desalination or industrial brackish water by different treatment processes. The main limitation of these techniques is the production of rejected brines. For this reason, new management techniques for brines valorization are being studied to achieve the maximum water recovery, avoid liquid streams disposal and recover the valuable compounds from the concentrated streams. In this thesis, four membrane technologies were used to promote resources recovery, including water, depending on the valorization way of the concentrated stream: electrodialysis (ED) was used for its concentration, nanofiltration (NF) for its purification, selectrodialysis (SED) for its ions separation and ED with bipolar membranes (EDBM) for acid and base production from the brines. The integration of these membrane techniques provided brines reuse and promoted potential circular economy based on solutions where a waste is transformed into a resource.

Seawater reverse osmosis (SWRO) brine was treated by ED in order to concentrate NaCl for the chlor-alkali industry. An ED pilot plant was used to concentrate the brine up to 150-250 g NaCl/L, depending on temperature and current density conditions. Then, a mathematical algorithm was developed to predict the concentration evolution during the ED process. The model was able to describe the NaCl concentration evolution and the energy consumption taking into account temperature changes and longtime operation. Moreover, monovalent selective cationic (MVC) membranes were synthetized using several mixtures of polyvinylidene fluoride (PVDF) and sulfonated PVDF (S-PVDF). Then, surface polymerization of polyaniline (PANi) doped with p-toluene sulfonic acid (pTSA) or L-valine was applied in order to improve their cationic monovalent selectivity. Results indicated that sodium selectivity increased when using doping agents (higher sodium selectivity when using valine than pTSA) or increasing the voltage applied.

Besides, NF was used as a purification treatment for the SWRO brine. Different membrane configurations (flat sheet (FS) and spiral wound (SW)) were tested to study ions rejection behavior. The solution-diffusion-electromigration-film model (SDEFM) was successfully applied in order to fit the experimental rejections and calculate the membrane permeances to each ion. Ions rejection and permeances calculated for both membrane configurations were

similar. These results indicated that lab-scale results could be used for the NF scale up. Also, the dominant salt effect on the trace ion rejection was determined by means of a FS membrane indicating that a higher initial dominant salt concentration implied a lower rejection for the dominant salt itself and also for the trace ions.

Furthermore, two ED-based technologies were used. SED was utilized to separate chloride from sulfate ions of an industrial wastewater rich in sodium chloride and sodium sulfate, achieving separation factors around 80-90 %. EDBM was employed to produce sodium hydroxide/hydrochloric acid from sodium chloride and sodium hydroxide/sulfuric acid from sodium sulfate.

Finally, ED, NF and SED were used as pre-treatments for EDBM. With the NF and EDBM system it was possible to purify the SWRO brine working with NF membranes at 20 bar. However, the permeate stream was treated by chemical precipitation in order to diminish the calcium and magnesium concentration before being introduced in the EDBM system. Maximum NaOH and HCl concentrations of 1 M were obtained. ED was used prior to the EDBM in order to concentrate the SWRO brine up to 200 gNaCl/L and be able to produce 2 M acid and base. SED was used to separate chloride from sulfate ions of an industrial wastewater. Both streams, sodium chloride-rich and sodium sulfate-rich were introduced in the EDBM stack and pure sodium hydroxide, hydrochloric acid (87 %) and sulfuric acid (93 %) were produced.

Summary

Glossary

AAS: Atomic absorption spectrophotometry

AEM: Anion-exchange membrane

APS: Ammonium peroxodisulfate

BM: Bipolar membrane

CAPEX: Capital expenditure

CCD: Central composite design

CEM: Cation-exchange membrane

CF: Concentration factor

Ec: Energy consumption

ED: Electrodialysis

EDBM: Electrodialysis with bipolar membranes

EDM: Electrodialysis metathesis

EDS: Energy dispersion X-ray spectroscopy

FS: Flat-sheet

FTIR: Fourier transform infrared spectroscopy

HX: Acid

IC: Ion conductivity / Ionic chromatography

ICP-OES: Inductively coupled plasma atomic emission spectroscopy

Ie: Current efficiency

IEC: Ion exchange capacity

IEM / IXM: Ion-exchange membrane

LCD: Limiting current density

MED: Multiple-effect distillation

MOH: Base

MSF: Multi-stage flash distillation

MVA: Monovalent selective anionic

MVC: Monovalent selective cationic

MX: Salt

NF: Nanofiltration

NMP: N-methyl-2-pyrrolidone

OPEX: Operating expenditure

PANi: Polyaniline

PC: Potentiostatic conditions

PEC: Polyelectrolyte complex

PEI: Polyethylenimine

PS: Permselectivity

pTSA: p-toluene sulfonic acid

PVDF: Polyvinylidene fluoride

R: Rejection

RO: Reverse Osmosis

RSM: Response surface methodology

SDEFM: Solution-diffusion-electromigration-film model

SED: Selectrodialysis

SEM: Scanning electron microscopy

SKM: Spiegler-Kedem model

S-PVDF: Sulfonated PVDF

SW: Spiral wound

SWD: Seawater desalination

SWD-RO: Seawater desalination reverse osmosis

SWRO: Seawater reverse osmosis

TMP: Trans-membrane pressure

WU: Water uptake

XRD: X-ray diffraction

ZLD: Zero liquid discharge

1. INTRODUCTION

1. Introduction

1.1. Challenges on brines and concentrates management: from disposal to valorization for by-products recovery

As water shortage has become a global issue in the urban and industrial cycles, water reuse, waste water reclamation and desalination of industrial brines are crucial strategies to generate water. In order to attend the growing demand for fresh water, nowadays a large number of treatment processes of industrial brackish water and seawater desalination to produce purified water generate brine rejection streams. Examples of such rich-salt streams are brines generated as by-products by membrane-based technologies such as electrodialysis (ED), reverse osmosis (RO) and nanofiltration (NF) in the desalination field. For example, for seawater RO systems, the typical water recovery varies between 40 and 50 %, so 50 - 60 % of the feed stream is wasted as concentrate. Brackish water RO desalination plants operate at recoveries of 75 - 85 %, but due to scaling or energy saving considerations occasionally some plants operate at only 50 - 65 %. On the other hand, water recovery of brackish water and reclaimed water can increase to 85 - 95 % depending on feed water quality when ED is used [1].

Traditional management of concentrates from desalination plants is mainly conditioned by the location of the plant. In coastal desalination plants, RO concentrates are directly discharged into the sea, while in inland plants the traditional option consists in reducing the concentrate volume prior to disposal [2]. Unfortunately, in both cases, their discharged streams into the environment results in a waste and environmental pollution. One mechanism that has been applied to reduce environmental effects of these brines relies on their dilution either with power plant cooling waters [3] or with seawater or municipal wastewaters to reduce salinity prior to discharge [4,5]. However, the effects of disposal of diluted concentrates can also affect sensitive species so the solution should be appropriate to local conditions [4].

Another important issue that must be taken into account is the cost of brine disposal. This cost depends on the brine characteristics (e.g. salinity), the level of treatment before disposal, brine volume and disposal methods [6,7]. Of course, the cost is higher for inland desalination plants than for costal plants where brine is discharged into the sea [6,8]. Though, the cost of

brine disposal to the sea in coastal desalination plants ranges from 5 to 33 % of the total desalination cost [9].

Then, proper handling and disposal of ED/RO/NF concentrates are being considered a critical environmental issue, particularly for inland communities where disposal of brine is usually problematic and solid by-products can be obtained and further reused. Moreover, the generate brines from inland desalination plants cannot be discharged into the sea and must rely upon disposal alternatives such as sanitary sewer discharge, evaporation pond, deep well injection and land application [10,11]. Each of them has some advantages or benefits, but the challenges and uncertainties are larger as it was summarized by Xu et al. [1] (Table 1).

Table 1. Comparison of concentrate management options [1].

Concentrate management options	Advantages and benefits	Challenges and uncertainties
Surface water discharge to rivers, lakes, ocean, or estuary via a dedicated outfall, or power plant outfall, or blending with wastewater	- Used for facilities of all sizes - Cost effective	- Environmental implications due to the differences in salinity and major ion imbalance between concentrate and ambient surface waters, resulting in adverse impact on aquatic life - Stringent regulations, for example, National Pollutant Discharge Elimination System (NPDES) - Complex and costly permitting
Sewer discharge to an existing wastewater treatment system	- Commonly used for brackish water and wastewater facilities - Low energy use and costs	- Only feasible to small size facilities, limited by the hydraulic capacity of the sewer collection system and by the treatment capacity of the wastewater treatment plant receiving the discharge - May impact the operation of wastewater treatment plant and beneficial use of reclaimed water because of the concentrate salinity and specific constituents, such as sodium, chloride, boron, and bromide in the blended stream due to their potential negative impact on microorganisms, plants, and soil.
Deep well injection into a deep geological formation, that permanently isolates the concentrate from shallower aquifers that may be used as a source of drinking water	- Suitable for inland facilities	- Typically expensive and often used in larger facilities - Requires appropriate geological formation and confined saline water aquifer, not feasible for areas of elevated seismic activity or near geologic faults - Permitting is becoming more stringent because of greater perceived potential for leakage to, and contamination of nearby water supply aquifers
Evaporation ponds	- Suitable for inland and coastal facilities - Easy to implement and low maintenance - Economical if land is inexpensive	- Climate dependent - Large physical footprint - Regulatory permitting may be complicated - Limited to small flows - Need the control of erosion, seepage, and wildlife management
Land application through percolation ponds, or beneficially used for irrigation of lawns, parks, golf courses, or crops	- Relatively easy to implement and low costs - Beneficial use of concentrate	- Limited to irrigation of salt tolerant grass, trees, and plants - Limited to small facilities - Dependent on seasonal irrigation needs and climate - Limited by groundwater protection laws - Potential contamination of soil and groundwater
Thermal zero and near-zero liquid discharge	- Avoid a lengthy and tedious permitting process - Smaller environmental impact - Potential recovery of valuable salts	- Costly, capital and energy intensive - Disposal of the final brine or salt can be expensive - Large carbon footprint

As it can be seen in Table 1, conventional treatments have several disadvantages such as extensive land use and low productivity. Moreover, these alternatives generate solid salts and/or liquid waste that require special handling [12]. Thus, investigation on new options to improve the management of concentrates is a current demand.

Zero liquid discharge (ZLD) or near-ZLD schemes can be used in order to reduce the brine volume after water recovery for reuse and generation of a dry salt waste or a wet salt waste, respectively. The main objective of these schemes is to achieve the maximum water recovery, through several stages of treatment in order to avoid liquid effluent disposal and to recuperate the valuable compounds from concentrates. ZLD systems combining several concentration/separation technologies are seen as a promising methodology for inland desalination. However, these systems are usually expensive and high energy demanding, so are only partially implemented [13].

Favorable reuse of ED/RO/NF brines represents a promising and sustainable alternative to other approaches. It is an opportunity to: a) achieve a ZLD scheme strategy that so far has been applied only on a limited scale because of the large energy needs associated with the process [14] and b) develop a new paradigm of circular economy concept to transform a waste to a resource, which is promoted by the EU commission inside the SPIRE program [15,16].

In the case of industrial brines, there are some potential salts (NaCl, Na_2SO_4, $CaCl_2$, $MgSO_4$, NH_4Cl, NH_4NO_3) whose direct reuse in the process itself is usually the most attractive option as was reported by the Water Supply and Sanitation Technology Platform Report of Brines Management [17]. However there is a limited demand of this kind of streams due to its composition. Research and development is still needed to ensure that the full-scale applications of brine treatment technologies achieve both water treatment and water and waste recycling. Besides, recycling and valorization of salts are having a main challenge to develop selective separation technologies and/or combined treatments in order to enhance the purity of the produced salts. When trying to apply valorization routes, especially for the $NaCl/Na_2SO_4$ mixtures, the desired quality requirements is to separate onto single concentrated streams of NaCl and Na_2SO_4 reducing the presence of other minor ionic or neutral species, and then the main target objective is the separation of Cl^-/SO_4^{2-}.

For this reason, different membranes technologies have been used in this thesis in order to valorize these brines, by means of purification, separation, concentration and/or chemical production from the salt.

1.2. Electrically driven membrane separation processes using ion-exchange membranes (ED/SED/EDBM) for brines purification and concentration

Several separation processes are available for ions separation and fractionation, including solid-liquid extraction (e.g. ion exchange resins), liquid-liquid extraction (liquid ion exchangers), membrane separation processes (e.g. NF and ED) [18–24]. Pressure driven NF membranes, originally designed by Dow-Chem for the selective removal of sulfate ions in the treatment of water generated from the oil extraction wells, do not provide suitable separation factors due to the fact that although more than 99 % sulfate ions are rejected, monovalent ions are rejected in the range 20-60 % depending on the membrane properties and the aqueous solution composition [25,26]. NF has been reported for ions fractionation [27–31] and as reviewed by Van der Bruggen et al. [32] most of the applications have been devoted to organic ions with interest in pharmaceutical, food and sweetener industries. The main limitation of NF membranes is the lack of suitable separation factors even though new NF layer-by-layer or multilayered polyelectrolyte complex (PECs) have been reported to improve separation factors for the separation of Cl^-, SO_4^{2-} and HPO_4^{2-} mixtures (e.g. 86% removal of for SO_4^{2-} and HPO_4^{2-}, and below 25% for Cl^-) [33]. However, higher product purity may be desired in view of potential industrial applications.

In contrast to NF membranes, ion-exchange membrane (IXM), with electrical fixed groups, need an electrical potential as the driving force, which means that the ions are transported through the membrane by an electrical field [34]. There are different kind of IXM, such as, homopolar, bipolar, monovalent ions selective membranes, etc., which will be explained in the next sections.

1.2.1. Electrodialysis

ED is an electrically driven membrane process based on the selective passage of some constituents through an IXM while blocking the passage of others. IXM are generally very dense with the pore size around 1 nm. There are different types of IXM which can be applied in ED, either separately or in combination. Cation exchange membranes (CEM)

(with negative fixed charges, generally $-SO_4^{2-}$, $-PO_3^{2-}$, or $=CO_2^-$) and anion exchange membranes (AEM) (with positive fixed charges, generally, $-NH_4^+$ or $=NH_2^+$), are well known for hindering the passage of co-ions (same charge) while allowing the passage of contra-ions (opposite charge) due to the Donnan repulsion. Figure 1 shows the membrane layout in a conventional ED stack.
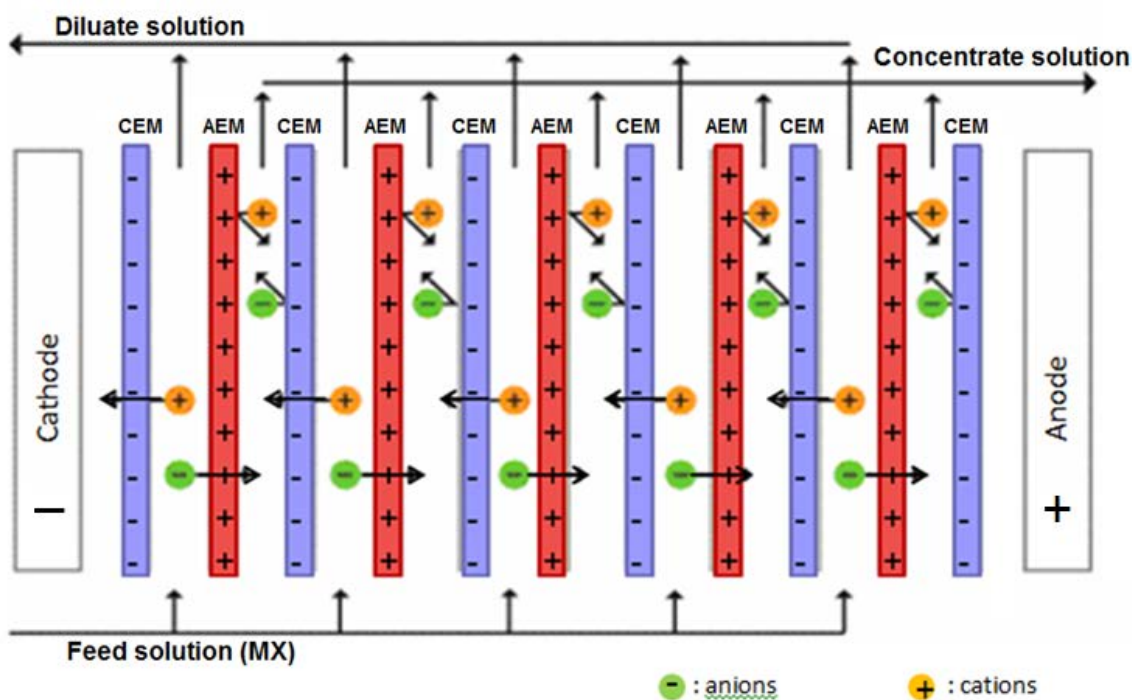
Figure 1. ED membranes layout scheme.

The ion transfer in the ED stack takes place when the driving force is applied between the cathode and the anode. In the ideal case, anions are transported through the AEM and the cations across the CEM.

An electrolyte concentrate solution (MX) is introduced into the "feed compartment", which is limited by the CEM and the AEM, and through direct current supplied by the electrodes, the cations (M^+) are moved towards the cathode (negative), crossing the cationic membranes, but not the anionic ones. For this reason they are retained in the "concentrate compartment", which is delimitated between an AEM and a CEM as it is shown in Figure 1. Similarly, the anions (X^-) are moved towards the anode (positive), crossing the anionic membranes but no the cationic ones. For this reason, they are also retained in the "concentrate compartment". Finally, a concentrate stream is obtained in the concentrate compartment while a diluted salt solution stream is retained in the feed compartment. The transport phenomena called

14

migration flux is the one that makes that charged species in the solution are transported to the cathode or anode through the IXM. Nevertheless, there exist undesired transports of ions trough membranes which reduce the process efficiency [34–36]. For this reason, the migration flux is not the only phenomenon that takes place inside the stack when electrical potential is applied. Due to current intensity applied, an electro-osmosis or water migration flux is created because of migration of water solvating the ions through the IXM. Moreover, two more mass transport phenomena appear after a period of operation caused by the ion concentration gradient appeared between the diluate and concentrate compartments. On the one hand, ion diffusion from the concentrate compartment to the diluate one is known as diffusion flux or back diffusion. On the other hand, water transported from the diluate compartment to the concentrate one is called osmosis flux (Figure 2).

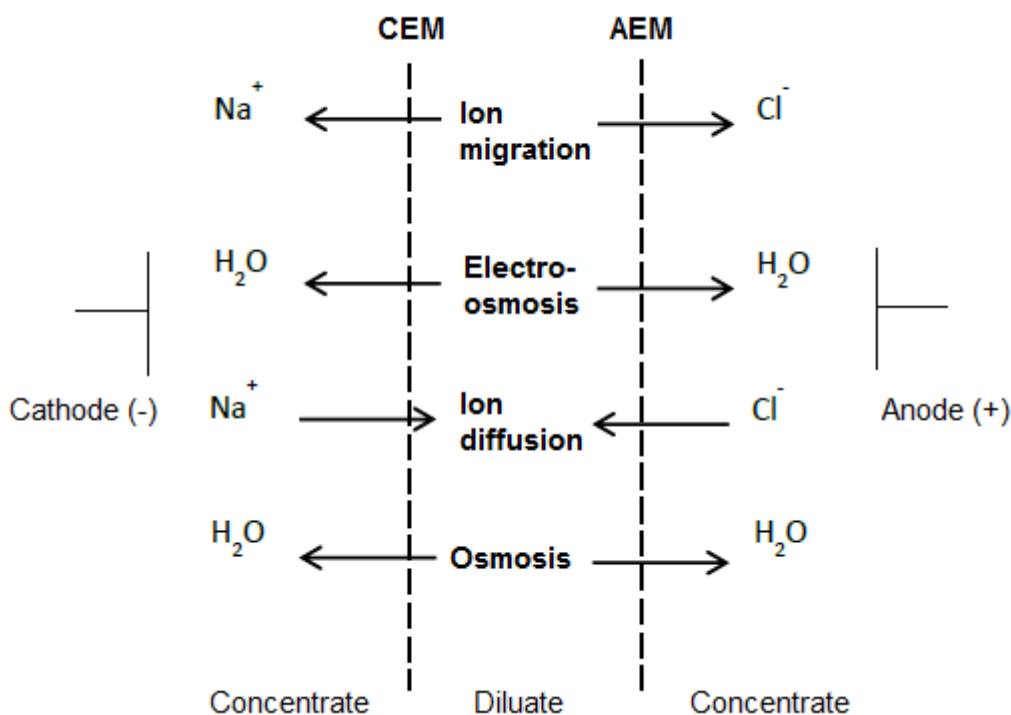Figure 2. NaCl and mass transport mechanisms scheme in an ED cell.

ED technology has been studied for more than 100 years, and has been applied on a large industrial scale. The area of major application of the ED is the desalination of brackish water. It has also been used to produce ultrapure water, remove salt from cheese whey or soy, produce energy through reverse ED, concentrate solutions and brines or produce

organic acids [37,38]. ED technologies are gaining increasing attention in the water resource management field, because they offer promising possibilities: (i) to recover ions in the form of a concentrated stream by conventional ED [39], (ii) to purify solutions separating monovalent from divalent ions by using monovalent selective membranes [40], (iii) to recover and reuse valuable compounds from saline streams by using bipolar membranes [41] or (iv) for power production from saline waters and concentrated brines by using reverse ED [42–46]. ED is considered to be economically advantageous due to the fact that its main characteristic is the ability to concentrate brine at higher concentration than evaporation with less energy consumption [47].

In this thesis, ED technology has been used with the purpose of concentrating the seawater desalination RO (SWD-RO) brines in order to be introduced as feed solution in the chlor-alkali industry to produce NaCl (Publication 1) or in an ED with bipolar membranes (EDBM) system to produce chemicals (Publication 7).

Mathematical modeling of industrial processes is essential to predict the dynamic behavior of the system and optimize its design and operating conditions, so it can be a useful tool to reduce experimental time and costs. ED modelling for desalination has been extensively studied during the last years [48–60]. In the last decade, different models on seawater or high salinity brines have been implemented [60–65]. Sadrzadeh et al. [64] obtained concentration in the diluate compartment for various voltage, flow rates and feed concentration and modeled an one-pass flow process using mass balances. Moon et al. [65] studied the ionic transport across the membranes using a 2D or 3D continuous model. Tanaka [62,66] also studied ED models where current density distribution, mass transport, cells voltage and energy consumption are taken into account. These models have been applied to different ED configurations and lately, they have been applied for seawater concentration modeling by ED. Nevertheless, these models required several experimental parameters that should be determined previously and difficult their application.

Casas et al. [67] described a mathematical model to predict NaCl concentration by means of ED taking into account that temperature remained constant. However, experimental results reported in Publication 1 [68] demonstrated that temperature changes do affect the final concentration obtained. Furthermore, the performance of an ED process is controlled by several designs and operational variables apart from temperature, such as,

membranes selectivity, feed and product concentration, flow rate, current density and voltage applied to the electrodes, etc. For this reason, a mathematical model was developed taking into account mass transport, energy consumption, electric current leakage, temperature changes, concentrate NaCl purity, pressure drop and limiting current density. Then, in this thesis the ED technology was not only evaluated experimentally, but also it was discussed with a computer simulation program (Publication 2).

As it has been explained, standard CEM were used in the experimental part of the thesis for the NaCl concentration by means of ED. Considering the trace ions contained in the SWD-RO brines, such as Ca^{2+} and Mg^{2+}, the possibility of using monovalent selective cationic (MVC) membranes during the ED process was investigated. According to the literature, some attempts have been made to prepare CEM with permselectivity for specific cations. However, the efficiency of the resulting membranes were lower than expected and then ineffective [69,70].

In this thesis, novel MVC with different mixtures of polyvinylidene fluoride (PVDF) and sulfonated PVDF (S-PVDF) were synthesized. The selected composite membranes were modified by surface polymerization of polyaniline (PANi) to improve their monovalent cation selectivity. PANi is an electrically conducting polymer, which is easy to synthesize and has high chemical stability [71]. PANi was doped with p-toluene sulfonic acid (pTSA) or L-valine (2-amino-3-methylbutanoic acid) and the selectivity of each CEM was determined. The newly developed membranes were used for electrodialytic concentration of NaCl from synthetic RO brine (Publication 3).

1.2.2.   Selectrodialysis

In general, IXM do not differentiate between different ions, although some differences in transport rate through the membranes can be observed (some membranes are selective for monovalent anions compared to multivalent anions). These differences, however, do not lead to fractionation of practical use by ED and the separation factor is limited [72] and similar to the effect that can be obtained with NF, as was proven previously by Van der Bruggen et al. [73]. Ion fractionation has a great application potential in various industries but is difficult to achieve, especially to the ions with the same size and charge sign.

A solution to improve ED separation factors was the proposal presented by Van der Bruggen et al. [40], consisting in combining monovalent selective to anions (MVA) membranes and non-selective AEM to introduce improved separation patterns. This integration of selective and non-selective AEM or CEM, recognized as selectrodialysis (SED) or metathesis [74] is based on the same principle than ED, but one more membrane is introduced between the standard AEM and the CEM: a MVA one. Then, two different solutions, one rich in divalent ions and the other rich in monovalent ions, can be obtained [40]. Figure 3 shows the membrane scheme of a SED stack (repeating unit: MVA–AEM–CEM). Again, when electrical current is applied, anions (Cl$^-$ and SO$_4^{2-}$) are attracted by the anode and cations (Na$^+$) by the cathode. Then, in the feed compartment the solution is diluted due to the transport of cations through the CEM to the brine compartment and of anions through the AEM to the product compartment. A MVA membrane is located in the next compartments. In this case, only monovalent anions (Cl$^-$) can pass through it obtaining a NaCl concentrated stream in the brine compartment (monovalent anions-rich) and a Na$_2$SO$_4$ concentrated solution in the product compartment (divalent anions-rich).
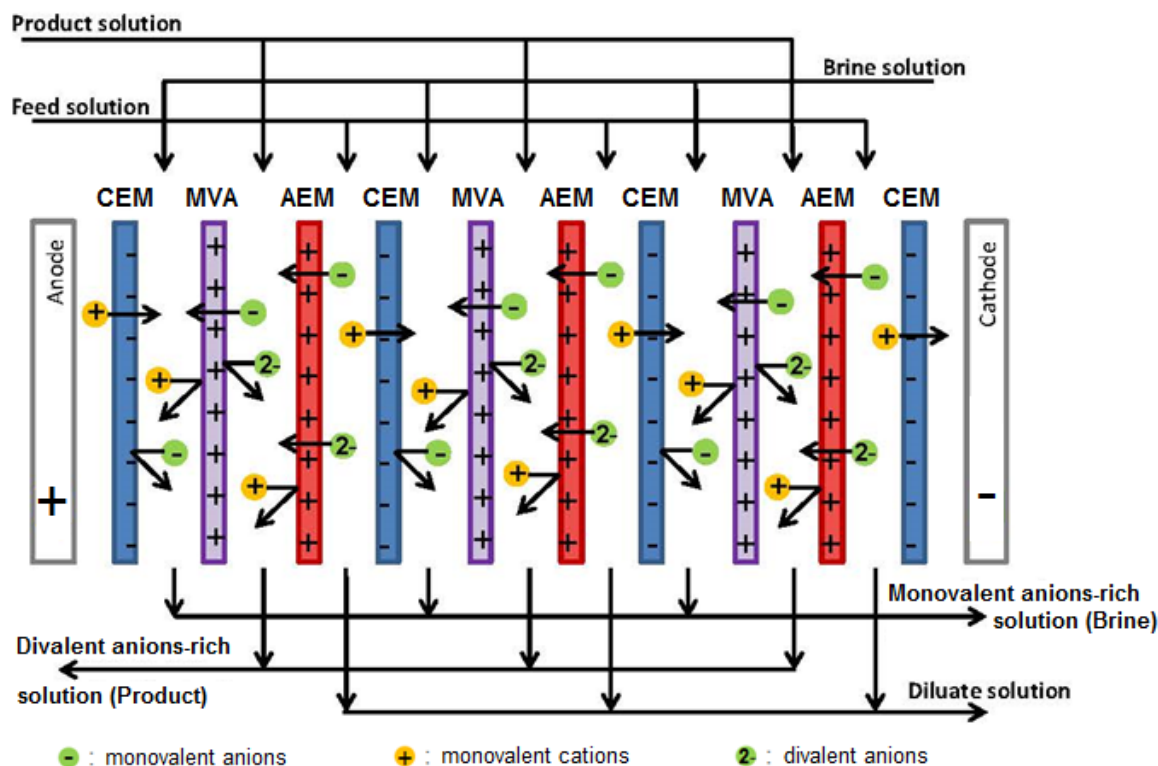

Figure 3. SED membranes layout scheme.

Ion transport inside the SED stack follows the same rules as for ED. However, selective transport between monovalent and divalent ions through the MVA membranes arises. Membrane selectivity to different ions needs to be studied in more detail. Zhang et al. [40] postulated that charge differences and/or hydrophilicity difference between monovalent and divalent ions, size exclusion, or other membrane or ions characteristics might be the reason of the membrane selectivity.

SED is a recently postulated technique which is still under development and for this reason few applications can be described so far. SED has been used for ion fractioning purposes, such as high salinity wastewater desalination [40] or phosphate streams pretreatments [75] and its subsequent recuperation as calcium phosphate [76].

Another application for SED is inside a ZLD circuit. In this case, Bond et al. [77] used a combination of CEM, AEM, MVA and MVC membranes named electrodialysis metathesis (EDM). By means of this membranes combination it is possible not only to separate different valence anions but also different valence cations. Then, on the one hand, a concentrated stream with all the anions accompanied by sodium is obtained, while on the other hand, all cations are accompanied by chloride. Moreover, because cations and anions are separated in two different compartments, precipitation problems, such as $CaCO_3$ precipitation are solved and the majority of components can be recovered for its subsequent use in the ZLD unit [77].

In this thesis, SED has been used as a separation technique for different valence anions in order to use the two streams obtained (one rich in monovalent ions and one rich in divalent ions) separately as feed solution for the EDBM and be able to produce monovalent acid or divalent acid and base (Publication 8).

1.2.3.   Electrodialysis with bipolar membranes

A new application area of ED since 1980 is EDBM. Apart from CEM and AEM, a third type of IXM is used in EDBM: the bipolar membranes (BM). BM are used to cause water splitting inside them. Bipolar membranes were first developed in the 1950s although this technology has gained more attention in the last two decades since it was first introduced in industrial-scale processes in 1980s. Figure 4 shows the evolution on the number of publications on EDBM in the last five decades.
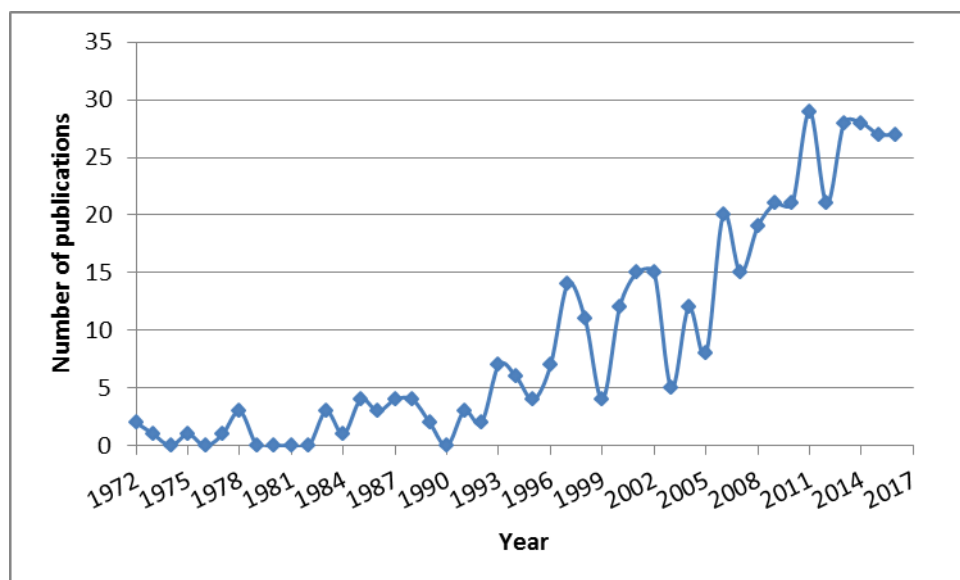
Figure 4. Chronology of EDBM publications according to Scopus Data Base [78].

The BM is a membrane that consists of a layered ion-exchange structure composed of a cation selective layer (with negative fixed charges) and an anion selective layer (with positive fixed charges) with a contact region between them. This interfacial layer facilitates the BM's main function when it is subjected to a reverse potential bias: water splitting [79]. The desired water dissociation reaction occurs in the transition region when the electric potential is applied. The water splits into H^+/OH^- [38,80–84]. As it can be seen in Figure 5, the EDBM consists of a repeated unit BM-CEM-AEM-BM. An electrolyte concentrate solution (MX) is introduced into the "feed compartment", which is limited by the CEM and the AEM, and through direct current applied by the electrodes, water splitting is produced inside the BM. Protons (H^+) formed are moved towards the cathode and hydroxyl ions (OH^-) towards the anode. At the same time, due to the electric current, cations (M^+) are moved towards the cathode (negative), crossing the cationic membranes, but not towards the anionic ones. Then, they are retained in the "basic compartment", which is delimitated between the anionic permeable side of the BM and the CEM. Similarly, anions (X^-) are moved towards the anode (positive), crossing the anionic membranes but not towards the cationic ones. They are then retained in the "acid compartment", which is delimitated by an AEM and the cationic permeable side of a BM. Finally, the products are formed: MOH (in the basic compartment) and HX (in the acid compartment). Also, there is a diluted salt solution stream in the feed compartment [35,37,79,85–87]. For this reason, EDBM may

have the potential to be environmentally sustainable and economically beneficial due to the fact that it is capable to create an acid and a base from its corresponding salt, by the union of its ions with the H^+ and OH^- ions supplied by the water splitting in the BM.
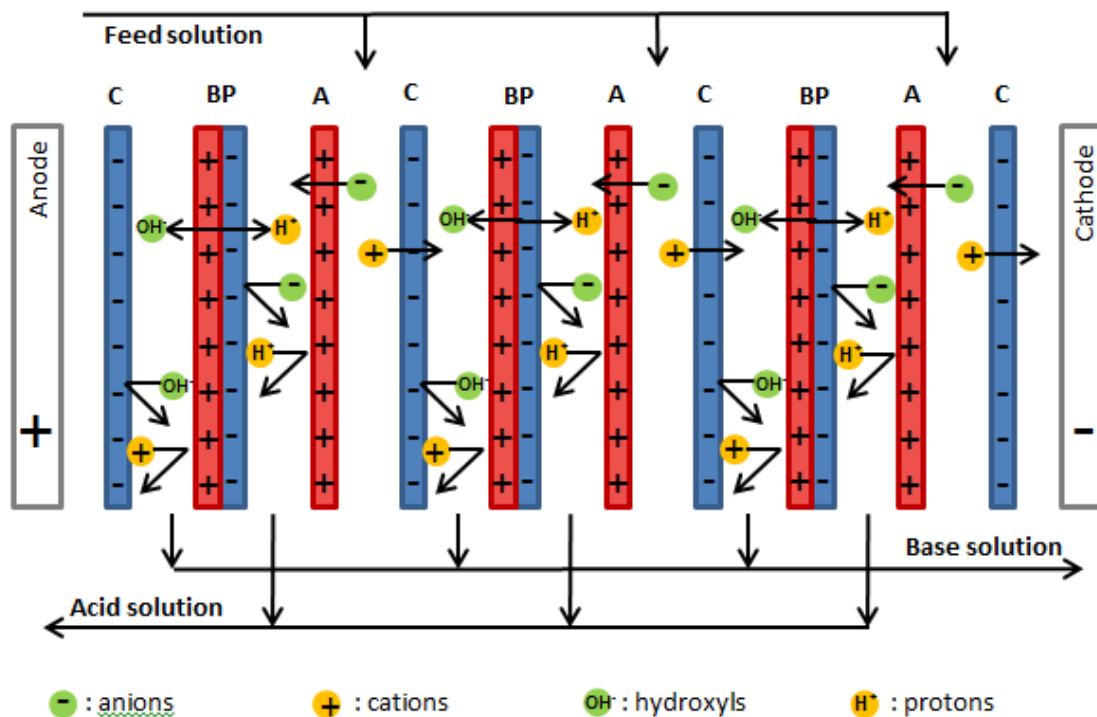

Figure 5. EDBM membranes layout scheme.

EDBM, as all processes, has many advantages but also some disadvantages. On the one hand, during the EDBM process the water dissociation is accelerated up to 50 million times compared to the rate of water dissociation in aqueous solutions. Therefore, the produced H^+ and OH^- ions can be used to generate acid (HX) and base (MOH) from salts (MX), for example NaCl from the chemical industry to produce HCl and NaOH, without production of hydrogen, oxygen or undesirable products. Moreover, it has low voltage drop, maximal energy utilization, space saving, easy installation and operation, low start-up and running costs and last but not least, it can provide products of high quality. On the other hand, EDBM is not as economically competitive as other membrane separation technologies, due to the high cost of electrodes and IXM, relatively short life time of membrane and high capital cost. Despite this economical limitation, all the features previously commented have made EDBM an environmentally friendly technology with potential applications in many fields [12,34,81,88].

EDBM has been applied to or studied for many purposes, such as chemical and food processing, biochemical industries and environmental protection. The technology of EDBM is presented as an alternative in fields such as the recovery or the valorization of residues or the production of certain chemistry products, leading to its growing implementation in many industries [12,89–93].

However, the EDBM technology has not been developed at a desirable pace. On one hand, there is a lack in recognition of the role EDBM plays in industrial ecology and sustainable development. On the other hand, there exist some hurdles to cross when bringing this technology to practice [82,94].

A clear application of EDBM is, thus, the salt-rich waste valorization for the production of acids and bases. Few authors [11,12,89–91,95] have been working with saline water to create acid and base with EDBM at lab or pilot scale. For instance, Badruzzaman et al. [12] treated RO concentrate in an EDBM pilot plant with an active membrane area of 64 cm^2 and 0.2 M of mixed acid and base was obtained in 10 h of operation. Ibañez et al. [95] used synthetic RO brines as feed solution in an EDBM pilot plant of 200 cm^2 of membrane area and 1 M of acid and base concentration was produced. Table 2 summarizes the main results and references dealing with EDBM at lab-scale and batch mode for acid and base production from brines.

Table 2. State of the art of acid and base production from salt using EDBM.

Authors	Feed saline water	Material and methods	Study	Results
Koter and Warszawski, 2006 [90]	Industrial brine (NaCl)	- TS001 FuMATech - 1250 A/m^2 - Active membrane area: 49 cm^2	- NaOH and HCl production	- Bipolar membrane efficiency 85 - 90% - AEM lower selectivity than CEM
Badruzzaman et al., 2009 [12]	1) Synthetic brine solution (NaCl) 2) RO concentrate (Ca^{2+}, Mg^{2+}, Ba^{2+}, K$^+$, Fe$^{2+/3+}$, SiO$_2$, Na$^+$, Mn^{2+}, Sr^{2+}, As^{2+}, B^{3+}, Cl$^-$, SO$_4^{2-}$, NO$_3^-$, PO$_4^{3-}$)	- PCCell ED 64-4 - 100 to 900 A/m2 - Active membrane area: 64 cm^2	1) Determine optimal operation parameters 2) Mixed acid and base production	1) - Higher current density → more concentrated acid and base → current efficiency decrease - Concentration < 4g·L^{-1} → constant current density (100 A/m^2) 2) *Divalent ions are removed in a pre-treatment step - 0.2 M of mixed acid and 0.2 M of mixed base in 10h - Salt concentration reduction from 9 to less than 2 mS·cm^{-1} in 10h
Ghyselbrecht et al., 2013 [91]	Industrial saline water (Cl$^-$, SO$_4^{2-}$, Na$^+$, K$^+$, Ca^{2+})	- PCCell ED 64-4 - 594 and 641 A/m^2 - Active membrane area: 64 cm^2	- Limiting current - Desalination and membrane selectivity - Current efficiency	*Ca(OH)$_2$ precipitation → 5mg·L^{-1} maximum feed solution - No limiting current was observed - Concentration reduction in the diluate (Cl$^-$: 91%; SO$_4^{2-}$: 82%; Na$^+$: 83%; K$^+$:92%) → Non selective membranes - Anions and cations current efficiency: 47 - 73% - Mixed acid (HCl, H$_2$SO$_4$) and base (NaOH, KOH) production
Ibañez et al., 2013 [95]	Synthetic RO brines (HCO$_3^-$, CO$_3^{2-}$, Cl$^-$, SO$_4^{2-}$, K$^+$, Na$^+$) without Ca^{2+}, Mg^{2+}.	- Elektrolyse Project - 250 to 1000 A/m^2 - Active membrane area: 200 cm^2	- Salt removal - Determine acid and base concentration	* Pre-treatment step must be done - Salt conductivity decrease (80%) faster at higher current densities - Acidification of the stack (pH 2-1.5) whatever current density used - HCl and NaOH production is faster at higher current density - Approx. 0.8 M acid and 1 M base concentration produced - Current efficiency 50-80%
Yang et al., 2014 [89]	1) Synthetic NaCl, Na$_2$SO$_4$ 2) RO seawater concentrate (Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, Cl$^-$, SO$_4^{2-}$, Br$^-$, CO$_3^{2-}$)	- Shandong Co. - 340 to 570 A/m^2 - 2) Batch & continuous mode - Active membrane area: 88 cm^2	1) Operation parameters optimization 2) Acid and base production	* Pre-treatment to avoid Ca^{2+} and Mg^{2+} precipitation (pH=2) 1) – Optimal current density: 57mA/cm^2 - No difference between NaCl or Na$_2$SO$_4$ 2) – Acid compartment: anions (<< cations) - Base compartment: cations (<< anions) - Salt compartment: OK (low levels of ions)
David et al., 2015 [96]	Synthetic NaCl solutions mimicking RO or evaporating cools	- PCCell EDQ380 - 26 to 260 A/m^2 - Active membrane area: 380 cm^2	- Effect of feed salt concentration	- Higher acid (0.3 M HCl) and base (0.3 M NaOH) concentration production at higher feed NaCl concentration (0.4 M NaCl) - Current use increased with increasing feed salt concentration - The energy required per mole of acid or base produced increased linearly with increasing current density
Ghyselbrecht et al., 2013 [97]	Saline water (NaCl and organic matter)	- PCCell ED 64-4 - 523 to 769 A/m^2 - Active membrane area: 64 cm^2	- Electrical resistance & current efficiency of 2 kind of BM: 1) Fumasep 2) PCA	- Almost complete desalination was achieved 1) Fumasep BM: - Better electrical resistance & current efficiency - 1.6 M HCl and 1.7 M NaOH production 2) PCA BM: - Slightly higher current densities - 1.8 M HCl and 2 M NaOH production

In this thesis, EDBM technology has been studied as a final treatment combined with other membrane processes in order to produce acid and base (Publication 6, 7 and 8).

1.3. Integration of membrane technologies as pre-treatment for chemicals production

One option for water treatment and resources recovery could be the membrane technologies integration. EDBM can be used for acid and base production, although a pre-treatment of the feed mixed solution, such as SWD-RO brines, may be needed.

As explained before, ED or SED can be applied as a pre-treatment for brines concentration or monovalent from divalent ions separation, respectively. In this thesis, it was possible to pre-concentrate the SWD-RO brines by means of ED before being introduced in the EDBM system. If a NaCl concentrate stream is used, it is possible to purify the divalent concentration in the concentrate stream while concentrating the NaCl. Then, the concentrate NaCl solution can be introduced in the EDBM and HCl and NaOH can be obtained (Publication 7). On the other hand, SED could be applied as a separation pre-treatment of a high salinity effluent (NaCl and Na_2SO_4). After applying SED technology, a NaCl-rich stream and a Na_2SO_4-rich solution could be separated, apart from obtaining a diluate solution. Then, each stream obtained by SED could be used as feed solution for EDBM, producing HCl/NaOH from the first one and H_2SO_4/NaOH from the second one (Publication 8).

Another membrane technique that can be used as SWD-RO purification pre-treatment is nanofiltration (NF). This membrane process is well known as a divalent purification technique in between RO and ultrafiltration. NF membranes are capable to reject divalent ions up to 99 %, although rejecting less monovalent ions (from 20 to 70 %) [26,98,99]. Apart from high multivalent ions retention, NF has many other advantages, such as low operational pressure, high flux, relatively low investment (capital expenditure (CAPEX)) and low operation and maintenance costs (operating expenditure (OPEX)). NF has been studied for the production of potable water, because the remineralization process of the obtained water by means of NF can be reduced compared to the current treatment after RO [100,101]. Besides, NaCl rejection by NF membranes has been widely studied [102–106].

In this thesis, NF has been used as a purification step previous to the EDBM (Publication 6). By means of NF it could be reasonable to concentrate divalent ions, but not monovalent ones. Then, the NaCl-rich stream filtered by NF can be used as feed solution for the EDBM to obtain HCl and NaOH. Firstly, ion rejection was studied in a flat-sheet (FS) and spiral wound (SW) NF configuration membranes (Publication 4). Synthetic solutions were prepared in this case using a dominant salt and trace ions mimicking natural waters. Then, the dominant salt effect on the trace ions was investigated in this thesis (Publication 5). In both publications, the solution-diffusion-electromigration-film model (SDEFM) was used in order to describe the experimental data of electrolyte mixtures transport through the NF membrane [107,108]. This model assumes that ion transport through the NF membrane occurs via solution-diffusion, electric migration phenomena within the active layer and takes into account the external

concentration polarization [107]. By means of the SDEFM it is possible to describe and fit the experimental rejection curves of both dominant salt and trace ions and also from these fittings, the membrane permeance with respect to each ion can be estimated [108].

1.4. References

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34

2. THESIS OVERVIEW

2. Thesis overview

In this work, membrane technologies have been used for water treatment and resources recovery. Mainly, ED was studied as concentration treatment of the brines in order to produce NaCl for the chlor-alkali industry (Publication 1). Moreover, modelling was used in order to understand the behavior of the process (Publication 2). Besides, MVC membranes were synthetized in order to perform ED experiments (Publication 3).

Furthermore, a purification step was studied by means of NF. Ion rejection by means of NF was studied by means of different membrane configurations (Publication 4) and the dominant salt effect on the trace ion rejection was also investigated (Publication 5).

SED was studied to understand its capacity in separating monovalent from divalent anions, such as Cl^- and SO_4^{2-}. And EDBM was used in order to produce acid and base from its corresponding salt.

ED, NF and SED have been used as pre-treatments for EDBM. Then, by integration of two of these membrane processes, it could be possible to pretreat the feed brines and promote circular economy in the same company. Firstly, NF and EDBM were integrated in order to purify and produce acid and bases from the brines (Publication 6). Also, ED and EDBM were used together in order to concentrate the feed brine and then produce acid and base from them (Publication 7). Finally, SED and EDBM were integrated in order to separate different charge anions from a high salinity wastewater effluent and to produce acid and base (Publication 8).
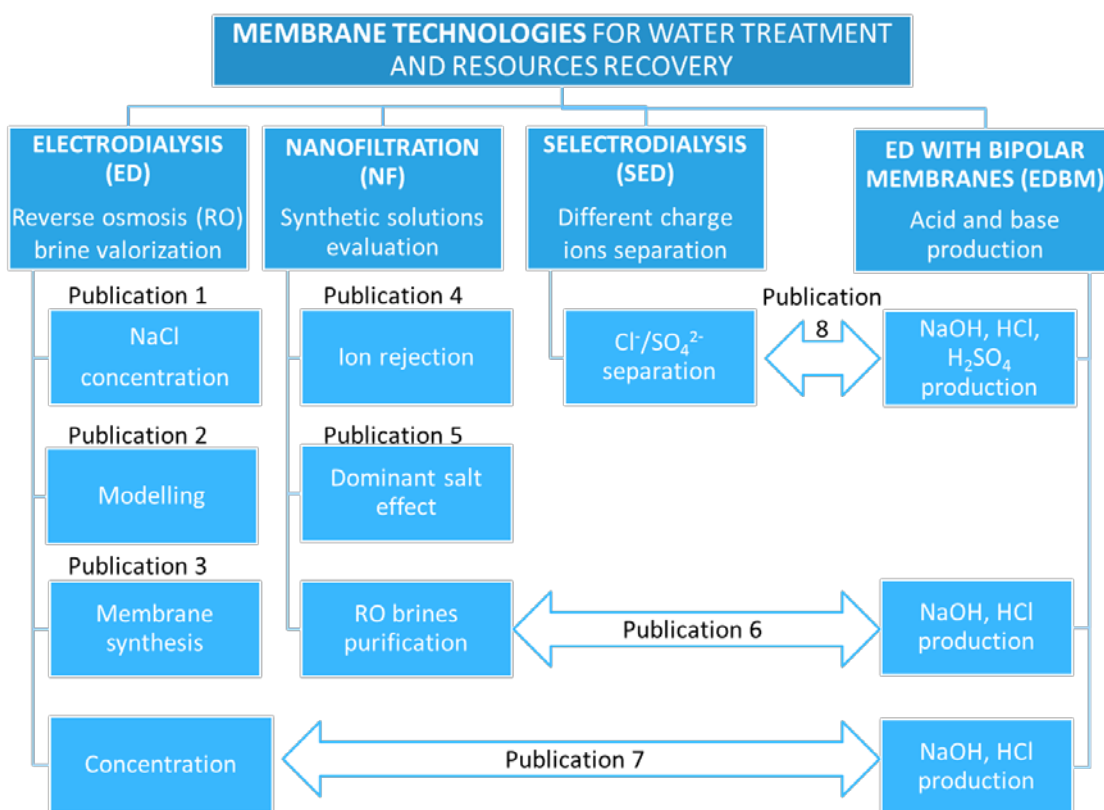
Figure 6. Thesis overview.

Publication 1: Mònica Reig, Sandra Casas, Carlos Aladjem, César Valderrama, Oriol Gibert, Fernando Valero, Carlos Miguel Centeno, Enric Larrotcha, José Luis Cortina. *Concentration of NaCl from seawater reverse osmosis brines for the chlor-alkali industry by electrodialysis*. Desalination 342, (2014), 107–117

Publication 2: Tanaka, Y., Reig M., Casas S., Aladjem C., Cortina J.L. *Computer simulation of ion-exchange membrane electrodialysis for salt concentration and reduction of RO discharged brine for salt production and marine environment conservation*. Desalination. 367, (2015), 76-89.

Publication 3: Reig M., Farrokhzad, H., Van der Bruggen, B., Gibert, O., Cortina, J.L. *Synthesis of a monovalent selective cation exchange membrane to concentrate reverse osmosis brines by electrodialysis*. Desalination. 375, (2015), 1-9

Publication 4: Mònica Reig, Neus Pagès, Edxon Licon, César Valderrama, Oriol Gibert, Andriy Yaroshchuk, José Luis Cortina. *Evolution of electrolyte mixtures rejection behaviour*

using nanofiltration membranes under spiral wound and flat-sheet configurations. Desalination and water treatment, 56 (13), (2015), 3519-3529.

Publication 5: Mònica Reig, Edxon Licon, Oriol Gibert, Andriy Yaroshchuk, José Luis Cortina. *Rejection of ammonium and nitrate from sodium chloride solutions by nanofiltration: Effect of dominant-salt concentration on the trace-ion rejection.* Chemical Engineering Journal. 303, (2016), 401–408.

Publication 6: Reig M., Casas S., Gibert, O., Valderrama C., Cortina, J.L. *Integration of nanofiltration and bipolar electrodialysis for valorization of seawater desalination brines: Production of drinking and waste water treatment chemicals.* Desalination. 382, (2016), 13-20.

Publication 7: M. Reig, S. Casas, C. Valderrama, O. Gibert, J.L. Cortina. *Integration of monopolar and bipolar electrodialysis for valorization of seawater reverse osmosis desalination brines: Production of strong acid and base.* Desalination, 398, (2016), 87–97.

Publication 8: Mònica Reig, César Valderrama, Oriol Gibert, José Luis Cortina. *Selectrodialysis and bipolar membrane electrodialysis combination for industrial process brines treatment: Monovalent-divalent ions separation and acid and base production.* Desalination, 399, (2016), 88–95.

3. Objective

The main objective of the current PhD thesis was to study, understand and integrate different membrane technologies for water treatment and resource recovery.
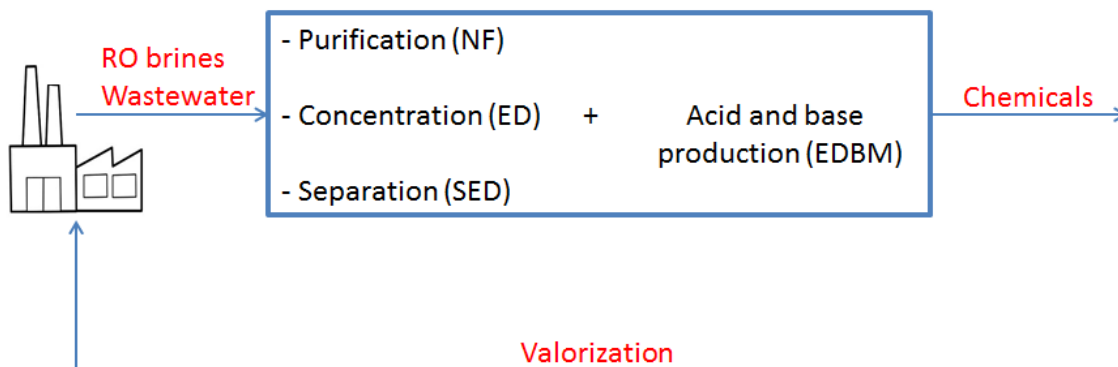

Figure 7. Thesis diagram scheme: membrane integration for resource recovery.

As it is shown in Figure 7, EDBM process has been used as main technology for the valorization of SWD-RO brines producing acid and base in order to achieve a circular economy scheme using NF, ED and SED as pre-treatments.

3.1. Specific objectives

The specific objectives were to find optimal operation conditions of the valorization process, to determine final acid and base concentration and to calculate specific energy consumption when using pretreatment concentration (ED), purification (NF) or separation (SED) steps to treat the SWD-RO brines.

Table 3 summarizes the specific objectives depending on the membrane technology studied:

Table 3. Specific objectives depending on the membrane technology.

Membrane technology	Specific objective
ED	- To produce NaCl for the chlor-alkali industry by ED concentration - To understand the behavior of the process by modelling - To synthetize cationic monovalent selective membranes
NF	- To understand ion rejection by means of different membrane configurations - To study the dominant salt effect on the trace ion rejection
SED	- To quantify the capacity in separating monovalent from divalent ions - To evaluate the best initial product composition and concentration
EDBM	- To produce acid and base from its corresponding salt - To estimate the NaOH, HCl and H_2SO_4 concentration reached
Membrane technology integration	
NF + EDBM	- To purify brines and produce acid and base
ED + EDBM	- To concentrate brines and produce acid and base
SED + EDBM	- To separate different charge ions from wastewater and produce acid and base

4-11 PUBLICATIONS

Chapters 4 to 11 of the thesis contain the magazine articles cited in the list. For respecting the rights of the publisher, you should consult them on your website

Chapter 4, Publication 1:

M. Reig, S. Casas, C. Aladjem, et al. *Concentration of NaCl from seawater reverse osmosis brines for the chlor-alkali industry by electrodialisys. Desalination, vol. 342, 2014, p. 107-117*
Doi: 10.1016/j.desal.2013.12.021
http://www.sciencedirect.com/science/atyicle/pii/S0011916413006073

Chapter 5, Publication 2:

Y.Tanaka, M.Reig, S.Casas, et al. *Computer simulation of ion-exchange membrane electrodialysis for salt concentration and reduction of RO discharged brine for salt production and marine environment concentration. Desalination, vol. 367, 2015, p.76-89*
Doi: 10.1016/j.desal2015.03.022
http://www.sciencedirect.com/science/article/pii/S001196415001897

Chapter 6, Publication 3:

M. Reig, H Farrokhzad, B.Van der Bruggen, et al. *Synthesis of a monovalent selective cation exchange membrane to concentrate reverse osmosis brines by electrodialysis. Desalination vol.375, 2 Nov. 2015, p.1-9*
Doi: 10.1016/j.desal.2015.07.023
http://www.sciencedirect.com/science/article/pii/S001191641530031X

Chapter 7, Publication 4:

M. Reig, N. Pagès**, E. Licon**, et al*. Evolution of electrolyte mixtures rejection behaviour using nanofiltration membranes under spiral wound and flat-sheet configurations. Desalination and Water Treatment vol.56, 2015 #13.*
Doi: 10.1080/19443994.2014.974215
http://www.tandfonline.com/doi/full/10.1080/19443994.2014.974215

Chapter 8, Publication 5:

M. Reig, E. Licon, O. Gibert. *Rejection of ammonium and nitrate from sodium chloride solutions by nanofiltration: Effect of dominant-salt concentration on the trace-ion rejection. Chemical Engineering Journal vol. 303, 1 Nov 2016, p. 401-408*
Doi: 10.1016/j.cej.2016.06.025
http://www.sciencedirect.com/science/article/pii/S1385894716308324

Chapter 9, Publication 6:

M. Reig, S. Casas, O. Gibert, et al. *Integration of nanofiltration and bipolar electrodialysis for valorization of seawater desalination brines: Production of drinking and waste wàter treatment chemicals.* Desalination 382 (2016) 13–20
Doi: 10.1016/j.desal.2015.12.013
http://www.sciencedirect.com/science/article/pii/S001191641530148X

Chapter 10, Publication 7:

M. Reig , S. Casas, C. Valderrama, et al. *Integration of monopolar and bipolar electrodialysis for valorization of seawater reverse osmosis desalination brines: Production of strong acid and base.* Desalination, vol. 398, 15 November 2016, p. 87-97
Doi: 10.1016/j.desal.2016.07.024
http://www.sciencedirect.com/science/article/pii/S0011916416308591

Chapter 11, Publication 8:

M. Reig, C. Valderrama, O. Gibert, et al. *Selectrodialysis and bipolar membrane electrodialysis combination for industrial process brines treatment: Monovalent-divalent ions separation and acid and base production.* Desalination vol. 399, 1 December 2016, p. 88-95
Doi: 10.1016/j.desal.2016.08.010
http://www.sciencedirect.com/science/article/pii/S0011916416303587

12. RESULTS

12. Results

The most relevant results of each technology are discussed below.

12.1. Key findings in electrodialysis (ED)

ED was a suitable membrane process to concentrate NaCl from SWRO brine providing a suitable feed solution for the chlor-alkali industry. By means this membrane technology it was possible to increment the NaCl concentration up to 150 - 220 g NaCl/L depending on the intensity and temperature conditions. During the summer time (higher inlet temperatures), lower NaCl concentrations were obtained, although lower energy consumption values were reached. The best conditions tested (higher NaCl concentration and lower energy consumption) were working at 0.35 kA/m^2 and 27 ºC concentrating NaCl up to 185 g/L with an energy consumption of 0.12 kWh/kg NaCl. Besides, because SWRO brine contains more elements than NaCl, it was proved that ED was capable to purify this brine from polyvalent ions (Ca^{2+}, Mg^{2+}, SO_4^{2-}, …), which were diluted due to osmosis and electro-osmosis phenomena (except nickel and copper, which were in the form of single charged compounds in the operation pH and they were able to pass through the membranes).

A mathematical modeling of the system was developed to predict the concentration evolution of the NaCl in SWRO brines using an ED pilot plant. This model took into consideration the effect of temperature and electric current density. In the program, the algorithm computed not only mass transport and energy consumption, but also electric current leakage and pressure drop. Although the experimental results fluctuated due to temperature changes and longtime pilot plant operations, the numerical algorithm provided a good description of the NaCl concentration evolution and also the energy consumption by ED operation. By means of the computer simulation program, a prediction was carried out decreasing the linear velocity of desalting cells (from around 10 to 1 cm/s) keeping the temperature at 25 ºC and the current density at 4 A/dm^2. Results demonstrated that it was possible to increase the RO recovery by working at a desalting ratio of 0.5 and recirculating the desalted ED solution into the RO system. Then, NaCl concentration could be reduced to seawater levels (around 30 g/L), although the energy consumption increased (0.19 kWh/kg NaCl). As a summary, ED allowed to concentrate

SWRO brine and produce NaCl, which could be competitive in the edible market by acceptable energy consumption. Unfortunately, for industrial use of NaCl, higher concentrations and lower energy consumption values should be obtained to be competitive.

As it has been mentioned, SWRO brine contained some divalent ions, whose presence should be reduced to trace levels when applied in the chlor-alkali industry. It is known that ED membranes typically exhibit moderate selectivities between monovalent and divalent ions. For this reason, novel MVC membranes were synthetized by surface polymerization of polyaniline (PANi) with two different doping agents (pTSA and L-valine) on s-PVDF/PVDF composite membranes. The formation of the PANi layer on the membrane surface modified the functional groups and ordered its structure. These properties were corroborated by FTIR and XRD, respectively. A PVDF solution mixed with 30 % of S-PVDF was used as base solution (S-30) due to the fact that the related CEM was found in a previous work to have the lowest divalent selectivity. It was though that this initial mixture could be the best option to obtain high monovalent cation selectivity after surface modification by pTSA or valine (especially for NaCl saturation for chlor-alkali application). In both cases, results showed that the hypothesis was true: sodium selectivity increased when doping agents were introduced in the membrane structure. All the synthetized membranes were tested by an ED lab-scale set-up by means of a synthetic solution mimicking SWRO brine (containing Na^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}). Higher Na^+ selectivity results were obtained for S30-valine (S_{Na}^{Mg} =0.09, S_{Na}^{Ca} =0.8) than for S30-pTSA (S_{Na}^{Mg} =0.13, S_{Na}^{Ca} =3.59), although both were better than for the composites ones (S_{Na}^{Mg} =0.63, S_{Na}^{Ca} =6.82). In all cases, better Na^+ to Mg^{2+} selectivity than Na^+ to Ca^{2+} were achieved. Moreover, valine surface polymerization did not decrease the Na^+ concentration and kept the Na^+ flux, the surface hydrophobicity and the IEC value as high as S-30. Finally, the influence of the applied voltage in ED was also studied finding that an increase of it (from 5 to 7 V) resulted in an increase of the selectivity for monovalent ions due to the fact that a lower flux of divalent cations appeared at the higher voltage (more powerful attraction of cations by the cathode).

12.2. Key findings in nanofiltration (NF)

NF was studied first at lab-scale with a FS module by means of synthetic solutions composed of a dominant salt and trace ions. Then, the same initial solutions were used to feed a small pilot plant set-up working with a NF SW membrane. Because different membrane configurations and different scales were used in each set-up, results were compared and the reliability of the data obtained was studied. Comparing the rejections and permeances obtained for both configurations, it could be said that, in general terms, both configurations had a similar behavior. Of course, this is a positive conclusion for testing NF membranes at lab-scale, but implementing them in an industrial scale NF system. The only difference between both configurations was the higher trans-membrane flux when working with the FS configuration. The SDEFM was used to fit the experimental rejections as a function of the trans-membrane flux and to calculate the membrane permeances to each ion taking into account the polarization layer and the effect of the arising electric field during the NF process.

On the other hand, the dominant salt effect on the trace ions rejection was studied using synthetic feed solutions containing NaCl as dominant salt and NH_4^+ and NO_3^- (ions associated with fertilizer pollution of groundwater) as trace ions by a FS configuration set-up. Utilizing different NaCl concentrations (from 0.05 to 0.3 M) it was observed that higher rejections of both dominant salt and trace ions were achieved when using the lowest initial concentration. Again, SDEFM was implemented to fit the experimental results satisfactorily even for negative rejections (NO_3^-) and also to calculate the membrane permeances to each ion. Results showed that the dominant salt also affected those permeance values: because the membrane permeances differed depending on the dominant ions (permeance was higher toward Na^+ than toward Cl^-), an electric field appeared causing negative rejections for the NO_3^- ions (accelerating them) and increasing the NH_4^+ rejections due to the fact that the electric filed retarded these cations.

12.3. Key findings in selectrodialysis (SED)

The main purpose of using SED was to improve separation factors of common monovalent/divalent ion mixtures typically found in many industrial process waters (e.g. SO_4^{2-}

and Cl⁻, or Na⁺ and Ca²⁺ and Mg²⁺). In this case, the potential separation of Cl⁻ and SO_4^{2-} ions from a chemical industry waste effluent was evaluated as a model example. For this reason, MVA membranes were used in the SED stack between the standard AEM and CEM. In first place, the optimal initial composition for each stream of the SED process was investigated in order to obtain the maximum monovalent/divalent separation. NaCl, Na_2SO_4 and a mixture of both salts were tested. The best separation factors were obtained when using the single NaCl (50 % Cl⁻ in the monovalent anion-rich stream (brine) and 50 % SO_4^{2-} in the divalent anion-rich stream (product)), although they seemed to be far from the total separation. The incorporation of sulfate in the product stream increased its diffusion through the MVA membrane. Then, different NaCl concentrations were tested and the best separation was reached when using double Cl⁻ concentration than in the feed solution. With this initial composition it was possible to increase the purity of each stream and obtain a monovalent brine stream with 80 % Cl⁻, while producing a divalent product stream containing 90 % SO_4^{2-}. Moreover, it can be concluded that concentrations in the brine and product stream increased over time, but when they reached a steady stage, the energy consumption of the SED system increased drastically. Operation ranges that make SED economically affordable were determined.

12.4. Key findings in ED with bipolar membranes (EDBM)

It was proved that EDBM is a suitable method for desalinating salt solutions producing acid and base: in this thesis HCl and NaOH were obtained from NaCl, while H_2SO_4 and NaOH from Na_2SO_4. As it was seen before, EDBM requires initial acid and base solutions apart from the feed solution for an electrical current to be applied. Voltage and initial acid and base concentration effect on the final concentration obtained were evaluated. With regard to the effect of voltage and current density, it was found that an increase of both parameters implied higher acid and base concentration. Besides, initial acid and base concentrations represented no substantial effect on the overall performance. For this reason, the minimum initial acid and base concentrations were advised to be used as initial solutions. Finally, the dependence on the initial salt concentration for the acid and base production was studied. A directly proportional relation between initial NaCl concentration and final acid and base production was observed. Results showed that it was possible to produce HCl and NaOH up to 2 M from 200 g NaCl/L working at constant voltage of 9 V. Depending on the voltage and the initial concentrations used, energy consumption values for NaOH production from NaCl were

ranged from 1.8 to 3.6 kWh/kgNaOH. Furthermore, by using a factorial design a general lineal model was defined considering the initial acid (HCl), base (NaOH) and salt (NaCl) concentration. A minimum energy consumption of 1.7 kWh/kg NaOH was calculated working at constant voltage of 9 V, an initial concentration of 104 g NaCl/L, and 0.24 M HCl and NaOH. Acid and base produced by means of EDBM could be used in-situ in the factory or industry to adjust the pH in their own processes.

12.5. Key findings in membrane technology integration

After each membrane technology was tested and analyzed separately, NF, ED and SED were used one by one as a pre-treatment for EDBM to promote resources recovery as a potential example of circular economy by using SWRO brines or industrial streams as waste sources.

NF was used to purify SWRO brines and create a NaCl-rich stream suitable for HCl and NaOH production by EDBM. Working at 20 bars, NF was capable to reject divalent ions more than monovalent ones, obtaining a NaCl purity up to 98 %. However, a chemical purification step was needed to reduce Ca^{2+} and Mg^{2+} concentration of the final NF permeate solution before being introduced in the EDBM process. By means of precipitation with Na_2CO_3 and NaOH removals higher than 95 % were achieved. The benefit of purifying the SWRO brine by NF and chemical precipitation was to produce low concentration HCl and NaOH (around 1 M) from SWRO brines by EDBM.

ED was also used as pretreatment, but in this case to concentrate the SWRO brines before being introduced in the EDBM stack. ED assays were carried out using an initial NaCl stream in the concentrate loop and varying the brine stream temperatures conditions (summer and spring-winter season). Results showed that concentrations around 200 g NaCl/L were achieved working at lower temperatures (15-18 ºC) and approximately 100 g NaCl/L were reached at summer time (22-28 ºC). The initial NaCl stream in the concentrate loop was suitable to reduce the divalent ions levels in the final ED concentrated stream, which was appropriated to be introduced as feed solution in the EDBM stack. ED energy consumption was calculated during both seasons working at 0.30 – 0.40 kA/m^2 and the values varied from

0.10 to 0.17 kWh/kg NaCl produced. The advantage of concentrating the initial EDBM feed by ED was a higher acid and base concentration (up to 2 M) when using the EDBM.

Finally, SED was also used as a pretreatment step to separate monovalent from divalent ions (SO_4^{2-} / Cl^-) from a chemical industry process wastewater effluent with high salinity (containing NaCl and Na_2SO_4). By means of SED it was possible to separate anions resulting in a monovalent anion-rich stream with around 90 % Cl^- and also a divalent anion-rich stream with more than 90 % SO_4^{2-} by using an initial NaCl solution in each stream. Energy consumption in this case was acceptable until the product and brine concentration reached a constant value, then the energy consumption increased drastically. After the SED treatment, each stream was introduced separately in the EDBM stack to produce HCl and NaOH from the monovalent anion-rich stream and H_2SO_4 and NaOH from the divalent anion-rich solution. Because the feed salt streams introduced in the EDBM were not pure in only one anion, pure NaOH was produced in both cases in the base tank, although a mixture of both acids (HCl and H_2SO_4) was obtained in the acid compartment in both cases. These acids were HCl-rich (up to 87 %) in the monovalent case and H_2SO_4-rich (up to 93 %) for the divalent test. Then, it could be concluded that SED was a viable pretreatment before EDBM to separate anions from an industrial brine rich in Cl^- and SO_4^{2-} ions and also to valorize these effluents as pure NaOH and a mixture of acids, which could be used in the same industry.

13. CONCLUSIONS

13. Conclusions

Nowadays there is an increase of industrial process water and wastewater effluents and many of them are not sufficiently well managed. While organic pollution has been removed traditionally by biological processes, total dissolved solids (e.g. salinity and organic and inorganic micropollutants) should be removed using membrane technologies. RO has been widely used in desalination of industrial effluents due to its strong deployment in seawater desalination. However, it is associated with the drawback of the concentrated waste generated. Traditionally, the industrial concentrates are discharged into natural water bodies (with or without dilution depending on the discharge regulations) or treated by evaporation. The former method is not environmentally friendly and the latter process is very costly due to the high energy consumption, although it is promoted as an alternative to recover water and salts under the ZLD concept. ZLD processes for concentrates recovery (thermal evaporators, crystallizers, brine concentrators and spray dryers) are technically feasible but more efforts have to be done to reduce the capital and operational cost. Although they provide a solution to reduce the volume of concentrates, with feed water recovery ratios of 95-98%, they are considered as an uneconomical option and are employed in limited cases.

Then, a new paradigm of circular economy has been postulated through the EU SPIRE program for resource recovery in the industry. In this thesis, the valorization of concentrated dissolved salts has been implemented promoting the development of new technological pathways.

In this thesis, several membrane processes (ED, NF, SED and EDBM) have been studied for industrial process water treatment and resource recovery in order to provide more sustainable treatment trains and potential management solutions. For this reason, NF, ED and SED have also been integrated separately with EDBM to obtain chemicals and close a circular economy loop reusing a waste water effluent of an industry. Particularly, it was proved that:

a) It was possible to concentrate the SWD-RO brine up to 200 g NaCl/L by means of ED and then to produce HCl and NaOH up to approximately 2 M. Also, it was possible to purify the brine removing its divalent ions by ED, although higher divalent cations removal would be

obtained using MVC membranes. For this reason, synthesis of novel MVC membrane was carried out and tested by ED providing higher sodium selectivity results than commercial membranes. Also, the ED technology results were modeled in order to predict the NaCl concentration evolution.

b) SWD-RO brine purification of divalent ions was done by NF and chemical precipitation. NF membranes were tested to pretreat the SWD-RO obtaining a high NaCl purity, although magnesium and calcium concentrations were not low enough to be introduced in the EDBM stack. Then, chemical precipitation was used achieving a 95 % of calcium and magnesium removal. After that, it was possible to produce HCl and NaOH up to 1 M. Moreover, several experiments were carried out to understand the NF process by means of different membrane configuration indicating that qualitatively both configurations provided the same ion rejections results. Also, experiments with different feed solution concentrations were conducted obtaining lower rejections when using the higher initial concentration. NF rejection results were modeled by the SDFM and the membrane permeabilities to each ion were calculated.

c) SED was used to separate monovalent from divalent ions (Cl^- from SO_4^{2-}). SED was used as a membrane technology which allowed separation factors around 90 %. Then, both streams were used separately as feed solution for the EDBM producing pure NaOH in both cases. The acids obtained were a mixture of HCl and H_2SO_4 in both cases, although a rich HCl (87 % purity) was produced with the NaCl-rich stream from SED and a rich H_2SO_4 acid (93 % purity) from the SED Na_2SO_4-rich stream.

As a final conclusion, it can be said that this work has demonstrated that solutions to provide brines valorization routes could be developed by integration of membrane driven process with physicochemical processes. Membrane processes (ED, NF, SED and EDBM) are attractive as they fulfill the requirements of process intensification and process integration: shrinking equipment size, boosting plant efficiency or minimizing waste production, which eventually result in smaller, cleaner, more energy efficient and higher productive technologies. Different examples where membrane technologies, such as ED, NF, SED and EDBM, have been coupled and provided solutions to industrial brines management generating resources recovery alternatives.

14. FUTURE RESEARCH

14. Future research

After the results obtained in this thesis, some recommendations for future research to answer some arising questions can be done. Between them, the most relevant ones are listed below:

➢ To enhance ions selectivity coefficients of IXM in order to improve the SED separation between monovalent and divalent ions by developing new membranes or modifying commercial ones.

➢ To study the temperature and pH influence on ions transport with IXM (e.g. SED and EDBM).

➢ To develop a mathematical model to describe ions transport on IXM in SED and EDBM configurations.

➢ To redesign the experimental ED-based units to evaluate higher voltages, a higher number of membranes inside the stack and/or different types of membranes from different companies.

➢ To test different NF, ED, EDBM and SED membranes to increase ion rejection by NF, salt concentration by ED, acid and base production by EDBM or ion selectivity by SED.

➢ To study the fouling and scaling phenomena on brines concentration and valorization with IXM-based process, to identify the need of purifying (i.e. removing divalent ions) from brines: determination of membranes life time.

➢ To determine ions separation and ions selectivity factors for common ionic species in industrial brines by means of SED.

➢ To experimentally determine further energy consumption values in ED, SED and EDBM technologies when applied on brines concentration and valorization.

➢ To compare the energy and chemicals consumption values of electrically membrane driven processes with conventional treatment processes for brines concentration and valorization.