

An Experimental Investigation of Electrodialysis with Bipolar Membranes Long-Run Performances with Real Solutions from Saltworks

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Electrodialysis with Bipolar Membranes (EDBM) is a promising process to produce acidic and basic solutions that are important in circular treatment chains. However, there is a lack of knowledge regarding the long-run performance of EDBM units fed multi-ionic solutions. This study aims to fill this gap by performing a long-run test, via an innovative feed and bleed configuration, with real brines coming from Trapani (Italy) saltworks and pre-treated to remove Mg and Ca. A laboratory EDBM unit with 5 triplets with an active membrane area of 100 cm² was used. The results show that a steady-state concentration of 0.44 mol/L on average of OH⁻ and H⁺ (in the form of NaOH and HCl) was reached in both acid and base outlet solutions, respectively, with a maximum deviation of 2 %. Stable performances were observed with a current efficiency of 69 % and 56 % and specific energy consumption of 1.78 kWh/kg and 2.19 kWh/kg on average for base and acid, respectively. These results demonstrate the potential of EDBM processes to maintain competitive and efficient performance.

1. Introduction

Electrodialysis with Bipolar Membranes (EDBM) has emerged as a promising technology for circular treatment schemes due to its ability to convert salty streams into acidic and basic streams (Tongwen, 2022). The EDBM stack consists of repeating units of anion exchange, cation exchange, and bipolar membranes (AEM, CEM, and BPM) arranged in triplets and placed between an anode and a cathode (Culcasi et al., 2022). When an electric field is applied, anions move toward the positive anode, while cations move toward the negative cathode. The selectively charged membranes control the transport of ions through them (Parnamae et al., 2021). The BPM generates H⁺ and OH⁻ ions by allowing the water-dissociation reaction to occur at the junction of its cationic and anionic layers (Mareev et al., 2020). EDBM has been proposed for integration into seawater reverse osmosis (SWRO) desalination plants to convert brine into valuable chemicals, including HCl, NaOH, and a diluted brine. Chen et al. (Chen et al., 2018) investigated the use of mono-selective membranes (ACS and CIMS) by Astom to valorize NaCl solutions (105 g/L) in a lab-scale unit (189 cm²). Authors achieved concentrations of 1.9 mol/L HCl and 2.2 mol/L NaOH and evaluated the impact of competing ions, including calcium, magnesium, and sulphate, on the products purity. The base compartment had concentrations below 2 mg/L of calcium and magnesium, while the acidic compartment had 14 mg/L of sulphate, resulting in purities higher than 99.9% for both solutions. Herrero-González et al. (Herrero-Gonzalez et al., 2020) utilized Ralex (CM-PP and AM-PP) and Fumatech (Fumasep FBM) membranes in a lab-scale unit (100 cm²) to generate NaOH and HCl from NaCl solutions. The authors tested different constant and variable current densities ranging from 500 A/m² to 1,000 A/m², with a fixed volume ratio of salt to acid/base of 20. They were able to achieve solutions containing 10.2 wt. % HCl (~3 mol/L) and 9.7 wt. % NaOH (~2.5 mol/L), with a Specific Energy Consumption (SEC) of 43.5 kWh/kg HCl. Song, Chae and Bang (Song, Chae and Bang, 2021) Song, Chae and Bang (Song, Chae and Bang,

2021) carried out tests via EDBM with a post-carbonated brine (0.9–1.2 mol/L NaCl, 74 mg/L Mg) using Neosepta membranes (CMB, AHA, and BP1). The tests were performed at volume ratios of 5:10:2 (salt/acid/base), producing 1.8 mol/L NaOH. The authors reported a Current Efficiency (CE) of 48% and a SEC of 4.85 kWh/kg NaOH. Despite the possibility of valorizing brines, there are still significant knowledge gaps that hinder the large-scale application of EDBM, such as (i) the influence of multi-ionic feed solution on membrane performance, (ii) the lack of data on long-term operation (Blommaert et al., 2021), (iii) the study of scaling forming agents in terms of operational issues, and (iv) the need for developing new membranes with enhanced separation properties, lower costs, and reduced electrical resistance. Long-term tests have been conducted using Reverse Electrodialysis (RED) to produce energy from the salinity gradient (Luque Di Salvo et al, 2018, Cosenza et al., 2022). However, a proper strategy is needed to avoid channel clogging and membrane fouling. The authors recommended daily flushing in short consecutive pulses at very high flow rates to prevent the accumulation of matter inside the channels, alkaline backwashing to remove membrane fouling, and water acidification to avoid scaling. No side effects of the chemical treatments were reported.

This study aimed to investigate the performance of EDBM in a long-run test using a real saltwork brine previously treated to remove magnesium and calcium. An innovative feed and bleed mode configuration with brine fed to both salt and base compartments was tested. Both dynamic and steady-state phases were investigated, focusing on the concentration profiles, SEC and CE.

1.1 SEArcularMINE project

This study was performed within the framework of the SEArcularMINE project, which is funded by the European Union (<https://searcularmine.eu>). The aim of this project is to develop innovative technologies that can be used to recover valuable minerals from the biterms produced by traditional saltworks in the Mediterranean basin. The project specifically aims to recover critical raw materials (CRMs), such as Mg(II), Li(I), B(III), and trace elements (TEs). To achieve this goal, a circular scheme will be implemented to maximize resource efficiency, recovery efficiency, and economic viability. Additionally, one of the main objectives of the project is to produce the necessary chemicals (HCl and NaOH) on-site from exhausted brines using EDBM.

2. Material and methodology

A long-run experimental campaign was carried out with an EDBM unit fed by real saltwork brine to produce acidic and alkaline solutions at a desired target concentration.

2.1 Material and experimental setup

An ED-100-3-10 EDBM unit (Fumatech, Germany) was assembled using five repeating units, including Fumatech membranes: each repeating unit comprises three membranes (FKB-PK-130 CEMs, FAB-PK-130 AEMs, and FBM-PK BPMs) with an active area of 0.01 m² and three spacer-filled channels. The same type of AEM (i.e. FAB-PK-130 AEMs) was used as end membrane to separate the last compartments from the electrodes. PVC/ECTFE spacers (500 µm thick) were used to separate the membranes and create the solution compartments. Titanium-DSA electrodes were used as both the cathode and anode. To measure the voltage, platinum wires (99.9% metal basis, Alfa Aesar, 127 µm diameter) were assembled in the EDBM stack, excluding the fraction of the total voltage consumed at the electrodic compartments.

The experimental campaign was conducted using real brines from Trapani saltwork, which had been pre-treated to remove magnesium and calcium. The pre-treatment step involved mixing the saltwork bittern with a spiked alkaline solution comprising NaOH micro-pearls (technical grade, Inovyn), NaCl (>99.5% purity, Saline di Volterra s.r.l., Italy), Na₂SO₄ (technical grade, CR GRUPO CRIMIDESA), and KCl (technical grade, Tor). The pre-treatment step resulted in the precipitation of Mg and Ca as Mg(OH)₂ and Ca(OH)₂, separated by sedimentation. The clarified solution was a 0.1 mol/L OH⁻ solution, used as the brine feed for the EDBM unit. Table 1 shows the compositions of the saltwork bittern, the spiked alkaline solution, and the clarified brine. For electrode rinse solution (ERS), a 0.5 mol/L FeCl₂/FeCl₃ (ACS grade, Chemsolute, Germany) and 0.6 mol/L HCl (ACS Reagent 37%, Honeywell, Fluka) was used.

Table 1. Composition of the main elements constituting the solution involved in the pre-treatment step.

Solution	Na ⁺ [mol/L]	K ⁺ [mol/L]	Mg ²⁺ [mol/L]	Ca ²⁺ [mol/L]	Cl ⁻ [mol/L]	SO ₄ ²⁻ [mol/L]	OH ⁻ [mol/L]
Saltwork bittern	2.99	0.27	1.60	4.65 10 ⁻³	5.60	0.45	-
Alkaline spiked solution	3.38	0.53	<lq*	<lq*	3.09	0.32	0.5
Clarified brine	3.74	0.51	<lq*	<lq*	3.06	0.35	0.10

*below quantification limit (lq)

Figure 1 illustrates the experimental setup featuring a feed and bleed configuration for the acid, base, and salt compartments and a closed-loop configuration for the ERS. SEKO Kronos 50 FF10 peristaltic pumps were used to introduce the inlet solution in the feed and bleed configuration. In contrast, YT15 and BT601S (Lead Fluid, CO LTD, China) recirculation pumps were utilized to ensure an inlet flow rate of 75 mL/min for the salt, base, and acid compartments to feed the ERS solution in a closed loop. A higher ERS flow rate of 600 mL/min was established to promote the iron redox reactions at the electrodes.

The clarified brine was employed as the inlet for both the base and salt compartments. Indeed, in the SEArcularMINE treatment chain, no pure NaOH solution is required. Softened tap water was used as the inlet solution for the acid compartment. Cartridge filters with a 5 μm rating were installed in all lines, downstream the recirculation pumps. Cewal pressure gauges were incorporated upstream the stack inlet to monitor the system pressure drop.

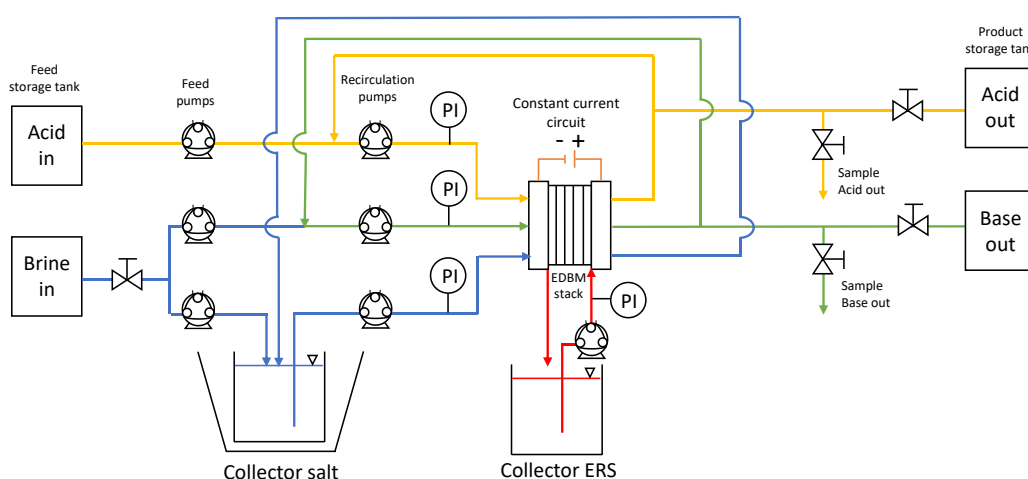


Figure 1. Schematic representation of the experimental setup, including the laboratory EDBM unit and primary auxiliaries.

The long-term experiment was conducted at a current density of 300 A/m^2 using a DC power supply (1902B, B&K precision). Two multimeters (Fluke 175) were connected in series and parallel to the electric circuit to measure the electric current and the corresponding voltages at both platinum wires and electrodes. The sampling points at the outlet of the base and acid solutions were equipped with a T-connection and manual valves. A WTW 314i portable pH and conductivity meter was employed to monitor the evolution of the solutions pH and conductivity. Samples of 40 mL were collected from the outlet sampling point.

2.2 Experimental procedure and analytical techniques

External and internal leakage tests were performed using demineralized water in all the four compartments operated in closed-loop mode at the operating feed flow rates for at least one hour. The mass variation was monitored using precision scales (KERN KB, Max 10,000 g, $d=0.1$ g), and leakage was considered acceptable due to its value below 5% of the relative mass (1,000 g) over one hour.

To evaluate the system long-term performance, a 75-hour feed and bleed experiment was conducted at a current density of 300 A/m^2 , aiming to achieve a steady-state OH^- concentration of 0.5 mol/L. Initially, all compartments were filled with the appropriate inlet solution (the brine for the salt and base compartments and softened tap water for the acid compartment). After purging the system from bubbles, the electric current and inlet flow rates were set (as shown in Table 2). The latter flow rates were estimated using simplified mass balances, assuming a current efficiency of 70%. Specifically, a ~30% lower value of acid flow rate (13 mL/min) compared to the base flow rate (18 mL/min) was set to account for the different inlet concentrations of the acid and base streams. Indeed, the acid and base concentrations were supposed to increase from 0 mol/L to 0.5 mol/L and from 0.1 mol/L to 0.5 mol/L, respectively. Therefore, a lower flow rate of acid was required to ensure a higher concentration difference between the inlet and the outlet streams.

Table 2. Flow rates for acid, base, salt and ERS solutions.

Solution	Acid	Base	Salt	ERS
Feed and bleed [mL/min]	13	18	6	-
Inlet to the stack[mL/min]	75	75	75	500

Samples were collected every 30 minutes in the first two hours and then every hour for the first dynamic part of the test in which the OH⁻ and H⁺ concentrations increased. The total dynamic part was completed in 6 hours as it can be observed in Figure 2. Then, the stability of the steady-state concentration over time was monitored by taking samples twice per day. The stability of inlet/outlet feed and bleed flow rates were checked twice per day by manual measurements of the outlet volume for 90 minutes. Voltage values at both stack and platinum wires were measured during the sampling procedure. Manual titration with standard solutions of 0.05 mol/L Na₂CO₃ and 0.1 mol/L HCl were used to measure the acid and base concentration. Methyl Orange solution (ACS dye content at 85 % wt., SIGMA ALDRICH) at 10 % wt. was used as a pH indicator. Metrohm 882 compact IC was used for ion chromatograph analysis. Metrosep C 4. 250/4.0 and Metrosep A Supp 5 – 250/4.0 were assembled in the IC as cation and anion columns. The mobile eluents of the IC were 5.5 mmol/L H₃PO₄ for the cation column and a mixture of 1.0 mmol/L NaHCO₃ and 3.2 mmol/L Na₂CO₃ for the anion column.

2.3 Performance parameters

The Current Efficiency (CE), expressed as a percentage, represents the proportion of applied current converted into the production of H⁺ and OH⁻ ions in the acid and base compartments, respectively. CE can be calculated using Equation (1):

$$CE = \frac{z F Q_{sol} (C_{sol,out} - C_{sol,in})}{3,600 N I} 100 \quad (1)$$

where z (-) is the ion valence, F is the Faraday constant (equal to 96,485 C/mol), Q_{sol} (L/h) is the volumetric flow rate averaged between the inlet and outlet of the feed and bleed system, $C_{sol,in}$ and $C_{sol,out}$ (mol/L) indicate the solution concentrations of acid or base at the inlet and outlet of the feed and bleed system, respectively, N is the number of triplets, and I (A) is the applied current.

The Specific Energy Consumption (SEC), expressed in kWh/kg, represents the energy required by the EDBM unit to produce 1 kg of product (HCl or NaOH). SEC can be calculated using Equation (2):

$$SEC = \frac{I U}{M_w Q_{sol} (C_{sol,out} - C_{sol,in})} \quad (2)$$

where U (V) is the voltage at the platinum wires, and M_w (g/mol) is the molecular weight (for HCl or NaOH). The use of the voltage at the platinum wires allows for the exclusion of the contribution of the electric compartments, which can have a high impact on the total voltage of a laboratory-scale unit, as in the present case, while they can be negligible at the pilot or industrial scale.

3. Result and discussion

Figure 2a illustrates the concentration profiles of OH⁻ and H⁺ ions as a function of time. At the beginning of the test, the concentration profile increased from 0.1 mol/L and 0 mol/L for OH⁻ and H⁺, respectively, up to a steady-state value. Initially, a large portion of the solution exiting the stack was recirculated and mixed with the low concentrated inlet solution of the feed and bleed system. This caused the concentration of the solution entering the stack to increase, raising the outlet concentration to a steady-state condition. The dynamic part of the test lasted for about three hours. After that, the acid and base streams reached an average concentration of 0.44 mol/L, slightly lower than the expected 0.5 mol/L target. The concentration was kept constant with a maximum deviation of 2% for both solutions. Importantly, these steady-state product concentrations were obtained using two different values of the inlet flow rates for the acid and base solutions as mentioned in Section 2.

Figure 2b shows the CE profile during time for both the base and acid compartments. Similarly to the concentration profile, CE increased during the dynamic part of the test due to the increase in the outlet concentration. In the steady-state regime, CE was 61–75 % and 49–61 % for the base and acid compartments, respectively. The relatively low efficiency could be attributed to non-ideal phenomena such as diffusion and partial neutralization of the produced solution. Additionally, the feed and bleed configuration forces the system to constantly operate at the target concentration, favouring non-ideal phenomena that are typically the higher, the higher the concentration. The higher CE for the base compared to the acid can be explained by the larger mobility of H⁺ compared to OH⁻.

This observation was supported by the transport of H^+ towards the salt compartment, which neutralized and acidified the slightly alkaline brine, used as the inlet solution of the salt compartment, from pH 13 (0.1 mol/L OH^- concentration as reported in Table 1) to pH 1.1 (i.e., H^+ concentration of 0.08 mol/L).

Figure 2c reports the SEC trend during the time referred to NaOH or HCl products. In the dynamic part of the test, a significant reduction of SEC was observed, which could be attributed to a reduction of the voltage measured at the platinum wires, referred to the 5 triplets, from 13.2 V up to 8.5 V, due to the initial increase in acid conductivity, and an increase in the efficiency with which NaOH or HCl were produced. The SEC trend mirrored the CE behaviour, and higher values of SEC were always observed for the acid, which showed lower CE than the base. In the second part of the test, SEC was 1.56–1.84 kWh/kg and 1.94–2.35 kWh/kg for NaOH and HCl products, respectively. It is worth noting that in the acid solution, Cl^- was the major anion present as it represented ~99 % of the total anions in the solution, while SO_4^{2-} reached a maximum concentration of 0.01 mol/L. Conversely, apart from the H^+ produced via water dissociation in the BPM, Na^+ and K^+ were present at 0.09 mol/L and 0.01 mol/L, respectively, as they diffused from both the saline and alkaline channels.

Overall, Figure 2 shows stable performances for all investigated parameters. No scaling or fouling effects were observed, when the stack was inspected, and the pressure drop remained stable.

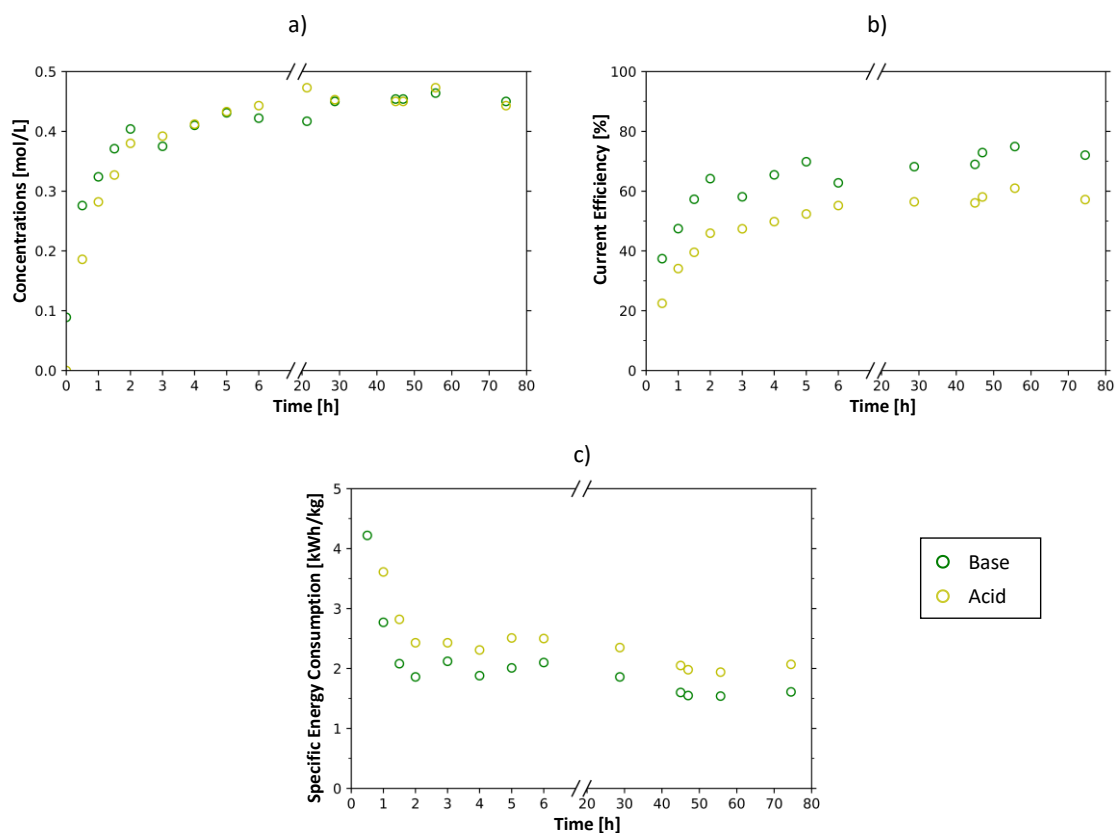


Figure 2. a) Concentration, b) Current Efficiency and c) Specific Energy Consumption as functions of time for both acid and base solutions. A different abscissa was used to magnify the long-run test first hours, where the system dynamic behaviour was observed.

4. Conclusions

In this study, a laboratory-scale EDBM unit was tested in feed and bleed operation mode for 75 hours using pre-treated real brine from a saltwork. A new configuration for the EDBM was presented that utilized the concentrated pre-treated brine as feed for both salt and base compartments.

During the transient start-up, which lasted approximately three hours, the acid and base concentrations increased to a steady-state value of 0.44 mol/L on average, with a maximum deviation of 2 %. CE reflected the ion concentration trend, with an initial increase up to 61–75 % and 49–61 % for base and acid, respectively. The lower CE of the acid compartment can be attributed to the high mobility of H^+ ions, which partially diffused towards the salt compartment, resulting in the acidification of the salty stream from pH 13 to pH 1.1 (i.e., 0.08 mol/L H^+).

SEC reduced during the transient start-up of the test due to increased production and lower voltage, resulting into steady-state values of 1.56–1.84 kWh/kg and 1.94–2.35 kWh/kg for NaOH and HCl products, respectively. Importantly, no performance loss (e.g. pressure drop increases) were recognized during the long-run. Overall, this study demonstrates the potential of EDBM units to be integrated into circular treatment chains, producing continuous acidic and alkaline solutions while maintaining stable performance.

Nomenclature

AEM – anion exchange membrane	F – Faraday constant, C/mol
BPM – bipolar membrane	I – current intensity, A
CEM – cation exchange membrane	N, number of triplet, -
EDBM – Electrodialysis with bipolar membrane	M_w – molecular weight, g/mol
RED – reverse Electrodialysis	Q – volumetric flow rate, L/h
SWRO – seawater reverse osmosis	SEC – specific energy consumption, kWh/kg
sol - solution	U – voltage, V
in – inlet of the feed and bleed system	z – ion valence, -
out – outlet of the feed and bleed system	
C – molar concentration, mol/L	
CE – current efficiency, %	

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References

- Blommaert, M. A. *et al.* (2021) 'Insights and Challenges for Applying Bipolar Membranes in Advanced Electrochemical Energy Systems', *ACS Energy Letters*, 6, pp. 2539–2548. doi: 10.1021/acsenergylett.1c00618.
- Chen, B. *et al.* (2018) 'Selectrodialysis with bipolar membrane for the reclamation of concentrated brine from RO plant', *Desalination*. Elsevier B.V., 442, pp. 8–15. doi: 10.1016/j.desal.2018.04.031.
- Cosenza, A. *et al.* (2022) 'Power Production from Produced Waters via Reverse Electrodialysis: A Preliminary Assessment', *Energies*, 15(11). doi: 10.3390/en15114177.
- Culcasi, A. *et al.* (2022) 'A comprehensive multi-scale model for bipolar membrane electrodialysis (BMED)', *Chemical Engineering Journal*. Elsevier B.V., 437(P1), p. 135317. doi: 10.1016/j.cej.2022.135317.
- Herrero-Gonzalez, M. *et al.* (2020) 'Highly concentrated HCl and NaOH from brines using electrodialysis with bipolar membranes', *Separation and Purification Technology*. Elsevier B.V., 242, p. 116785. doi: 10.1016/j.seppur.2020.116785. <https://searctularmine.eu>, accessed in March 2022.
- Luque Di Salvo, J. *et al.* (2018) 'Long-run operation of a reverse electrodialysis system fed with wastewaters', *Journal of Environmental Management*. Elsevier Ltd, 217, pp. 871–887. doi: 10.1016/j.jenvman.2018.03.110.
- Mareev, S. A. *et al.* (2020) 'A comprehensive mathematical model of water splitting in bipolar membranes: Impact of the spatial distribution of fixed charges and catalyst at bipolar junction', *Journal of Membrane Science*. Elsevier B.V., 603(December 2019), p. 118010. doi: 10.1016/j.memsci.2020.118010.
- Pärnamäe, R. *et al.* (2021) 'Bipolar membranes: A review on principles, latest developments, and applications', *Journal of Membrane Science*, 617. doi: 10.1016/j.memsci.2020.118538.
- Song, K., Chae, S. C. and Bang, J. H. (2021) 'Separation of sodium hydroxide from post-carbonation brines by bipolar membrane electrodialysis (BMED)', *Chemical Engineering Journal*. Elsevier B.V., 423(May), p. 130179. doi: 10.1016/j.cej.2021.130179.
- Tongwen, X. (2002) 'Electrodialysis processes with bipolar membranes (EDBM) in environmental protection - A review', *Resources, Conservation and Recycling*, 37(1), pp. 1–22. doi: 10.1016/S0921-3449(02)00032-0