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Performance evaluation of nanofiltration membranes for SWRO brine valorisation: Insights from a pilot plant under real conditions

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ABSTRACT

The success of a desalination brine valorisation process heavily depends on the effectiveness of the pre-treatment stage, which purifies the brine by reducing the concentration of ions that could form insoluble compounds and hinder system performance. This study focused on testing an innovative nanofiltration (NF) pilot plant operating with 144 m^3/d of actual brine from an upstream seawater reverse osmosis (SWRO) pilot plant located in the Canary Islands (North Atlantic Ocean). The NF membranes tested (NE8040-40) played a critical role, demonstrating exceptional rejection rates for divalent ions, therefore also increasing their concentration in the divalent-rich stream, setting the stage for future valorisation of the related by-products. Simultaneously, these NF membranes allowed the achievement of a high-purity monovalent-rich stream with Na^+ and Cl^- concentrations reaching approximately 98 %, potentially enabling the generation of valuable commercial products in subsequent stages. The NF system was thoroughly assessed under different conditions of flow, pressure, and recovery rates, incorporating extensive process monitoring with comprehensive sensor data.

1. Introduction

In an era marked by global water scarcity and the unstoppable effect of climate change, the importance of desalination has never reached the current level of significance. As populations grow, demand for potable, industrial and irrigation water will keep raising, while freshwater resources become insufficient or contaminated [1]. Furthermore, climate change is aggravating this crisis, altering precipitation patterns and intensifying droughts all over the world. Desalination stands as a vital solution to tackle such vital challenge [2].

Reverse osmosis (RO) prevails as the leading technology used in desalination plants already installed worldwide [3], and it is expected to dominate a large percentage of the facilities currently being designed for the coming years. This success is due to the continuous optimisation in energy efficiency. Over the past decades, the Specific Energy Consumption (SEC) has been consistently reduced, even achieving values below 2 kWh/m^3. This remarkable achievement (1.86 kWh/m^3) has been demonstrated recently by the DESALRO 2.0 desalination plant in the Canary Islands [4].

Despite this level of optimisation, there are still remaining challenges for the RO technology, including a) integrating renewable energy sources to reduce its carbon emissions and footprint, and b) transforming the concentrate (brine) produced during the RO process from a waste product discharged back into the sea into a source of valuable by-products, adopting a circular economy strategy. Traditional desalination generates large quantities of brine, which, if discharged inadequately, can harm marine ecosystems due to its high salinity. Through brine valorisation, this by-product can be transformed into a source of valuable minerals and industrial chemicals, alongside additional water recovery. This not only mitigates the environmental impact of

Abbreviations: BMED, Bipolar membrane electrodialysis; CCU, Carbon capture and utilisation; CE, Circular Economy; CP, Chemical precipitation; DB, Desalination brine; DBV, Desalination brine valorisation; EDM, Electrodialysis metathesis; FO, Forward osmosis; FTIR, Fourier-transform infrared spectroscopy; HPP, High pressure pump; HPRO, High Pressure Reverse Osmosis; ICP-OES, Inductively coupled plasma – optical emission spectrometry; IEx, Ion exchange; LSI, Langelier Saturation Index; MD, Membrane distillation; MED, Multi-effect distillation; MLD, Minimal liquid discharge; MSF, Multistage flash distillation; NF, Nanofiltration; OARO, Osmotically assisted reverse osmosis; PRO, Pressure retarded osmosis; RED, Reverse electrodialysis; SWRO, Seawater reverse osmosis; RO, Reverse osmosis; SEC, Specific energy consumption; SED, Selective electrodialysis; TDS, Total dissolved solids; TOC, Total organic carbon; TRL, Technology readiness level; UF, Ultrafiltration; ZLD, Zero liquid discharge; %st, % saturation.

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desalination, but also creates economic opportunities by turning waste into resources, aligning desalination plants with the circular economy principles of resource efficiency and waste minimization.

Water reuse, including brine from desalination plants, is a fundamental pillar of Circular Economy (CE) policies implemented in Europe [5]. Supporting policies like the European Green Deal (EGD) [6], the Circular Economy Action Plan (CEAP), and the Water Framework Directive (WFD) [7] highlight the need for sustainable resource use and promote the recovery of secondary raw materials to protect water bodies. Brine valorisation addresses these policy goals by closing resource loops, minimizing desalination's environmental footprint, and contributing to a responsible water management. Furthermore, this approach aligns with the United Nations Sustainable Development Goals (SDGs) [8], particularly Goals 6 (Clean Water and Sanitation) and 12 (Responsible Consumption and Production), by enhancing water availability and sustainability in water-stressed regions.

Current treatment methods for desalination brine (DB) can be categorised into three main types: disposal, direct reuse, and valorisation [9]. Disposal methods include discharge into surface water, sewer, deep-well injection, pond evaporation, and most commonly, returning it to the sea [10]. Direct reuse involves applications such as energy exchange in an energy recovery device (ERD) [11], microalgae production in aquaculture [12], and use in coastal wetlands [13]. Brine valorisation can be achieved by numerous approaches, such as: extracting minerals and metals [14], producing chemical by-products, generating energy via salinity gradient, and capturing CO_2, among others, most of them while producing additional fresh water [15].

Desalination brine valorisation (DBV) has emerged as a prominent topic at water congresses, attracting attention from academic institutions, technological centres and industry alike. Over the past decade, research efforts dedicated to the development of brine treatment technologies have significantly raised [16,17,18]. Typically, a brine valorisation scheme comprises three stages: pre-treatment, concentration and the final conversion [19], as shown in Fig. 1.

The **pre-treatment** stage main objective is to remove undesired elements from the brine, usually the components with a lower solubility product, prone to form precipitates in the subsequent stages, mainly products linked to divalent ions such as calcium (Ca^{2+}), magnesium (Mg^{2+}) and sulphates (SO_4^{2-}), hence compromising its correct functioning and the performance. Within this pre-treatment stage, valuable by-products can be generated derived from those ions, e.g. magnesium hydroxide ($Mg(OH)_2$), calcium carbonate ($CaCO_3$) or calcium sulphate ($CaSO_4$) [20]. Several processes and technologies have been studied for this stage [21]: chemical precipitation (CP) [22], ion exchange (IEx) resins [23], selective electrodialysis (SED) [24], carbon capture and utilisation (CCU) techniques [25], nanofiltration (NF) [26].

The **concentration** stage is the intermediate phase where the brine, once pre-treated, is concentrated to near saturation levels, simultaneously producing more fresh water, hence increasing the overall recovery of the system. Traditionally, this has been achieved using thermal processes, such as evaporators [27], crystallizers [28,29,30], multistage flash distillation (MSF) [31] and multi-effect distillation (MED) [32]. However, there is a recent trend toward using membrane concentrators, such as osmotically assisted reverse osmosis (OARO) and high pressure reverse osmosis (HPRO), which consume significantly less energy (75–100 kWh/t NaCl) [33]. Additionally, membrane distillation (MD) technology combines both thermal and membrane processes [34,35]. Other technologies like forward osmosis (FO) [36] and electrodialysis metathesis (EDM) have also been employed for this purpose [37].

The final **conversion** stage in any brine valorisation process involves transforming the brine, primarily composed of sodium and chloride at this point, into one or more valuable products, such as solid NaCl of different degrees of purity, $NaHCO_3$ through carbonation, or valuable chemical products like hydrochloric acid (HCl) and sodium hydroxide (NaOH) obtained via bipolar membrane electrodialysis (BMED) or sodium hypochlorite (NaClO) through electrolysis [38,39,40]. Additionally, brine can be a source of lithium and rubidium, which are notable examples of valuable recovered elements [41] for the global economy today. Desalination brine can also be valorised in different ways not involving generating by-products. One example is generating energy through osmotic pressure gradient, like pressure retarded osmosis (PRO) [42] or reverse electrodialysis (RED) [43]. Another example is valorisation through ocean alkalinity enhancement (OAE) [44].

An effective pre-treatment stage is critical for optimising the entire brine valorisation process by enhancing operational performance and ensuring product quality throughout the different stages. **Nanofiltration (NF)** offers a promising solution by allowing selective separation of specific ions, reducing energy consumption due to lower operating pressures, and improving resistance to fouling in high-salinity environments. NF is a membrane filtration process that utilises a semi-permeable membrane with properties between those of between reverse osmosis (RO) and ultrafiltration (UF). NF separates the feed water into two distinct streams: a monovalent-rich stream (mainly Na^+ and Cl^-) that crosses the membrane and a polyvalent-rich stream (mainly Ca^{2+}, Mg^{2+} and SO_4^{2-}) that is retained by the membrane. The pressure required for NF is significantly lower than the pressure applied in RO. The unique selectivity and the lower pressure requirement make NF it particularly useful for applications such as water softening [45], concentration in the food and beverage industries [46], and industrial wastewater treatment [47].

The above-mentioned specific characteristic of the NF membranes (high selectivity and low energy consumption) make them an ideal choice for use as a pre-treatment stage in a desalination brine valorisation scheme [48]. On one hand, these membranes remove most of the

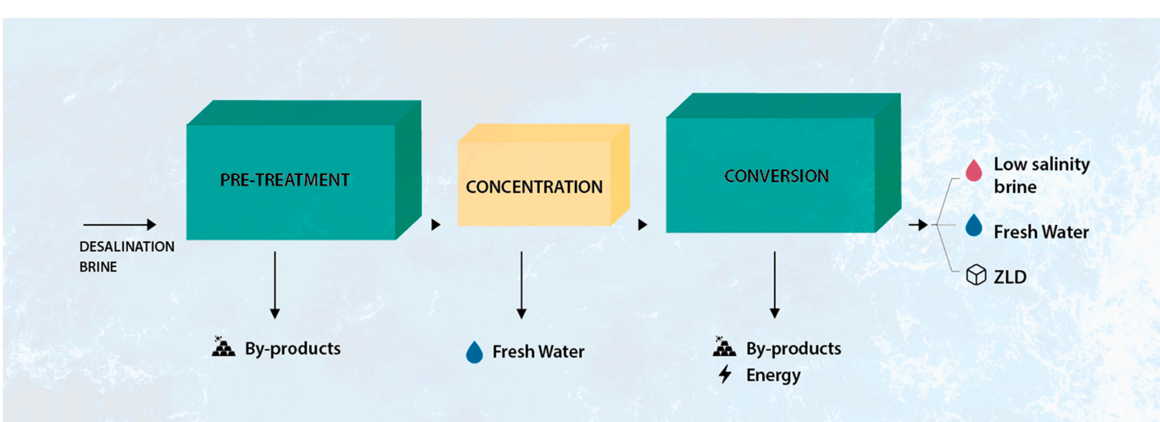

Fig. 1. Schematic diagram of the main stages involved in a desalination brine valorisation process.

ions prone to causing scaling, therefore purifying the monovalent-rich stream for further concentration and valorisation processes. On the other hand, they concentrate valuable divalent ions, such as Mg^{2+}, which is one of the critical raw materials in Europe [49], facilitating the subsequent valorisation of the divalent-rich stream. Moreover, NF produces no residues, if both streams can be valorised [50], while also decreasing the volume processed in subsequent stages, enhancing their efficiency, reducing floor area requirements, and lowering CAPEX.

Multiple scientific articles about desalination brine valorisation and nanofiltration specifically have been published over the past decade. However, a significant lower number of publications are linked to studies carried out in **pilot plants**. This is a crucial step, though, to fully develop a particular technology, becoming essential for advancing and scaling up new technologies. New pilot plants using real SWRO brine (rather than synthetic solutions) are essential, as they provide empirical data, validate theoretical models, and uncover operational challenges such as scaling, maintenance needs, and long-term reliability in realistic conditions. In the field of nanofiltration as a previous step in brine valorisation schemes, only a few pilot plants have been tested. For instance, C. Morgante et al. [51] tested a NF pilot plant with a single membrane, using two different synthetic solutions that mimicked the composition of the Mediterranean seawater and SWRO brine as input, operating at a flow rate of 0.21 m^3/h. Guillem Gilabert-Oriol et al. [52] ran a larger system with a flow rate between 1.30 and 1.98 m^3/h, targeting high magnesium concentration using selective NF membranes. Additionally, Ahmed S. Al-Amoudi et al. [33] tested a pilot plant in Jubail, Saudi Arabia, including a NF pilot plant fed with 16 m^3/h of seawater. These pilot studies are significant for translating laboratory research into viable industrial-scale applications.

This paper aims at providing new insights into the performance of NF membranes in a pilot plant within the Canary Islands Institute of Technology (ITC) brine valorisation open testbed [53] (DESAL + LIVING LAB) [54], using actual SWRO brines, detecting flaws and highlighting potential areas for optimisation, thereby contributing to the advancement and refinement of this technology in the near future. This study not only contributes to the development of more sustainable desalination practices, but also opens new avenues for the industrial exploitation of desalination by-products. This research, along with future studies, can bridge the gap between theoretical potential and practical implementation, enabling SWRO facilities to transform brine from a waste product into a valuable resource, aligning with sustainability and circular economy goals.

2. Materials and methods

This section provides a comprehensive overview of the experimental setup, including detailed information about the feed conditions, equipment and instrumentation used.

2.1. Case study

The Canary Islands, a Spanish archipelago situated near the northwest African coast, in the North Atlantic Ocean, have a significant history in desalination [55]. Their journey began with Europe's first desalination plant, built in the island of Lanzarote in 1964. Over the years, the number of desalination plants in the Canary Islands has increased substantially, reaching more than 300 nowadays [56].

This study is conducted at the Brine valorisation open testbed at the ITC facilities in Pozo Izquierdo (Gran Canaria). This unique experimental area allows the NF plant to be tested under real world conditions, aiming to optimise cutting-edge technologies, embracing circular economy and innovation [53]. By using actual brine instead of synthetic brine solutions, the tests in NF pilot plant provide a more accurate assessment of real-world operational challenges, which are crucial for developing a viable industrial-scale process. Real brine contains a complex mix of ions and organic matter not fully replicable in synthetic solutions, which affects scaling, fouling and contaminant interactions within the membrane system. Moreover, testing with real brine allows for a better understanding of how operational fluctuations, such as temperature or pH, impact system efficiency, thereby informing adjustments necessary to scale up NF technology reliably and effectively in desalination brine valorisation. In conclusion, the use of actual brine offers valuable critical insights into real-world challenges, facilitating more realistic evaluations of system performance and applied research.

Seawater intake comes from a beach well, which provides clear water (SDI < 1) to the RO pilot plant located next to the NF plant. The seawater's salinity is typical for the Atlantic Ocean along the eastern coast of Gran Canaria, between 36 and 38 g/L. Before reaching the RO rack, the seawater passes through a sand filter, it is continuously dosed with an antiscalant, and then goes through a 5 μm cartridge filter. It then reaches the high-pressure pump, which includes energy recovery integrated through rotating pistons. The RO system operates with a range of 80–100 m^3/day of product water with a recovery rate of 40 %. The configuration consists of one pressure vessel with 2 elements and another in series with 5 elements, all containing *Hydranautics SWC4 MAX* spiral wound high rejection membranes. Table 1 shows the physicochemical characteristics of both the seawater intake and the RO brine.

2.2. NF pilot plant description

The NF pilot plant is located downstream of the RO pilot plant, acting as a pre-treatment stage in a desalination brine valorisation scheme, as shown in Fig. 2. The aim is to adapt the brine for subsequent phases by reducing divalent ions in the monovalent-rich stream, thereby increasing their concentration in the divalent-rich stream. This also enhances the ratio of sodium and chloride ions relative to TDS in the monovalent-rich stream. Fig. 3 shows actual pictures of the pilot plant.

An RO-NF distribution was selected as the preferred configuration, due to its ease of implementation in existing desalination plants, making it a more feasible approach than modifying the existing desalination process. Both configurations, RO-NF and NF-RO, offer promising results for new constructions. On the one hand, using NF as a pre-treatment for RO systems can reduce the operating pressures, but it requires higher intake flows to maintain the same fresh water production. On the other hand, placing NF after RO requires higher operating pressures but demands less flow and a fewer number of membranes. The final decision will need to consider several factors (technical, logistic, economical, etc.) particular to each situation, to determine the most suitable option.

The experimental setup shown in Fig. 4 was used to evaluate the performance of seven NE8040-40 membranes in series treating actual SWRO brine. These membranes are high productivity NF elements with low monovalent ion rejection from CSM industry (Toray) under an agreement with Toray Advanced Materials Korea Inc. They are thin-film composite membranes, made of polyamide with a spiral-wound configuration, 8 in. in size, with an active area of 37.2 m^2 (400 ft^2), capable of operating at a maximum pressure of 41.4 bar and a maximum

Table 1
Physicochemical analysis of the seawater and SWRO brine used in this study as feed for the SWRO and NF pilot plants, respectively.

Parameter	Units	Seawater	SWRO brine
Conductivity @ 20 °C	μS/cm	51,400	78,500
pH	U. pH	7.22	7.36
TDS	mg/L	37,900	65,184
Chloride	mg/L	20,945	36,107
Sodium	mg/L	11,300	19,906
Sulphate	mg/L	3,100	4,902
Magnesium	mg/L	1,522	2,392
Calcium	mg/L	472	753
Potassium	mg/L	387	704
Silica	mg/L	30	53

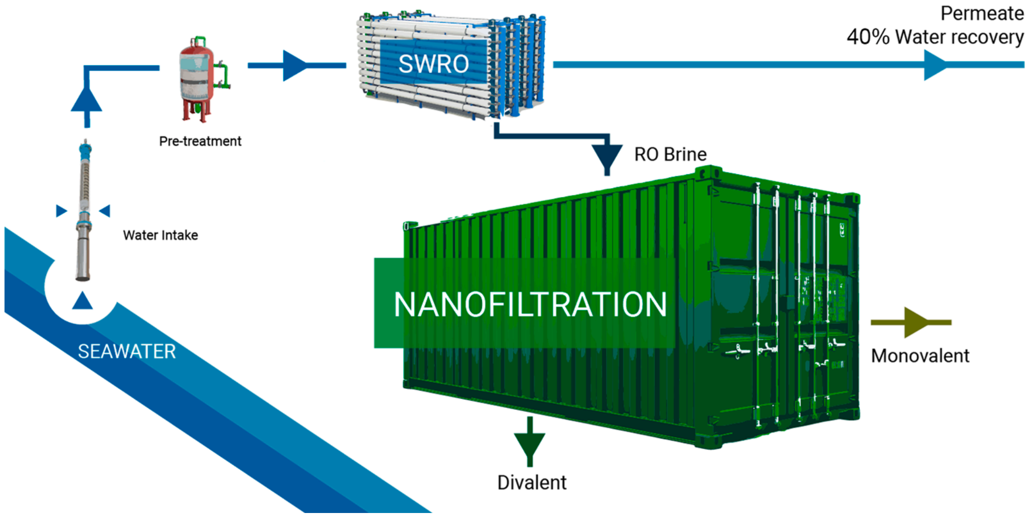

Fig. 2. Basic process diagram of the experimental configuration evaluated in this study.

Fig. 3. Pictures of the nanofiltration pilot plant, including container and its key components.

temperature of 45 °C. The main properties of RO and NF membranes are shown in Table 2, considering test conditions according to membrane supplier information [57,58]:

The NF pilot plant equipment and instrumentation are distributed inside a 20-foot container, mounted on a compact, self-transportable frame with double front and back doors. This container size is a versatile, modular and efficient option for international trade to optimize logistics and commercial operations.

Firstly, the feed tank receives the brine from a SWRO pilot plant (DESAL +) located next to the NF pilot plant. The feed tank is a 2 m^3 polyethylene tank with a filling control system integrated. The feed pump is a vertical multi-stage centrifugal pump of 1.1 kW (Grundfos

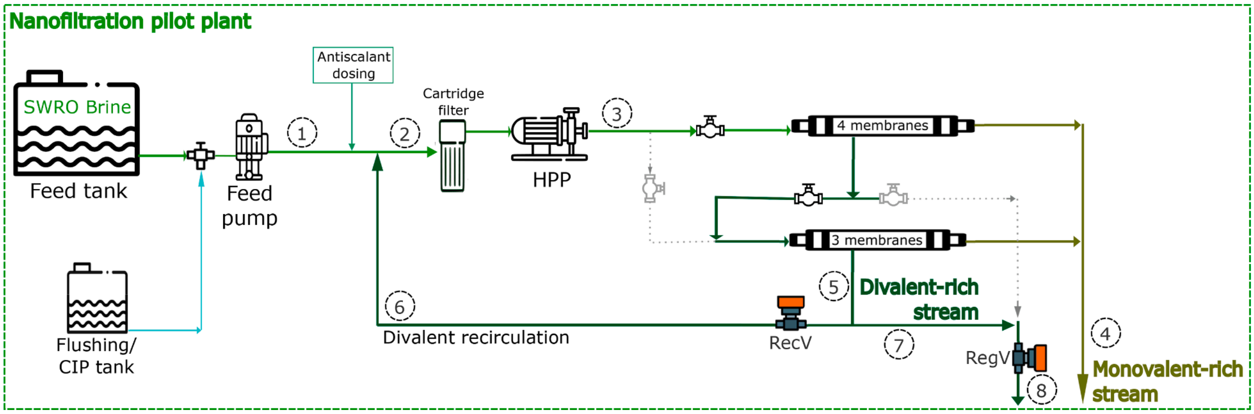

Fig. 4. Process flow diagram of the nanofiltration pilot plant, showing the internal configuration of tanks, valves, and pumps.

Table 2
Technical data about the RO and NF membranes used in this study.

Process	Product	Type of polymer	Weight (kg)	Minimum $MgSO_4$ rejection (%)	NaCl rejection (%)	Maximum pressure (MPa)	Active area (m^2)	Permeate flow rate (m^3/d)
RO*	Hydranautics SWC4 MAX	Composite Polyamide	16.4	–	99.8	8.27	40.9	27.3
NF**	Toray/CSM NE8040-40	Polyamide (PA)	15	98.0	20–40	4.14	37.2	45.4

* Test conditions: 32000 mg/L NaCl solution at 800 psig (5.5 MPa) applied pressure, isothermal process conditions at 25 °C, pH at 6.5–7.0, tests at 10 % permeate recovery.
** Test conditions: 2000 mg/L inlet $MgSO_4$ solution at 75 psig (0.5 MPa) operating pressure, isothermal process conditions at 25 °C, pH at 6.5–7.0, tests at 15 % permeate recovery after 30 min of filtration.

CRT 4-6). An antiscalant solution is dosed after the feed pump as chemical pre-treatment, using a 22 W dosing pump (SEKO, TEKNA APG-603) with the purpose of preventing potential scaling on the membranes surface, mainly when the system is working at higher recoveries. After the feed pump, there are 5 µm cartridges filters to remove any particles from entering the HPP. This high-pressure pump of 11 kW is a positive displacement pump with axial pistons (Danfoss APP 10.2). Both pumps are controlled by variable frequency drives (VFD) (Schneider Electric Altivar 320).

Finally, the pressurised brine passes through seven NF membranes arranged in two PRFV pressure vessels (BEL-8-S-1200): one vessel contains 4 elements, and the other contains 3 elements. The system was designed to achieve the desired flow rates and pressures for the NF process, based on the available flow and concentration of the SWRO brine. The NF pilot plant was designed with a certain flexibility to accommodate its use for research and demonstration purposes. The feed flow range of the system can vary between 72 and 144 m^3/d and the hydraulic lines include the necessary number of electrovalves with automatic actuators, enabling operation with three possible configurations: 4 membranes, 3 membranes or 7 membranes. For all tests described in this paper, the 7-membrane configuration was selected. The system also allows for the recirculation of the divalent-rich stream back to the HPP inlet, as indicated in Fig. 4 (Line 5 – Divalent recirculation).

Several sensors are positioned in different lines throughout the system, including pressure gauges (Wika 263.50), pressure switches (Danfoss KPS), pressure sensors (Hispano Control PCE-28), flow meters (Khrone Optiflux 2050C), pH sensors (Seko SPH2), and conductivity meters (Seko S411). This sensor integration allows for complete monitoring and control, enabling comprehensive evaluation of any particular test.

The recovery rate and operating pressure of the system are regulated by a high-precision motorized needle valve (TECVAL CP-15), which is automatically controlled. It is labelled as RegV in Fig. 4 and is located in the divalent-rich output stream.

The NF pilot plant is fully automated and equipped with all necessary components for manual operation as an alternative, at the operator's discretion. The control architecture, managed through a PLC (Siemens Simatic S7-1200) and an HMI, is connected to all sensors and equipment, to collect data, operational parameters, and internal variables of the plant. Additionally, it includes a network analyser (Schneider Electric EasyLogic PM2200) to measure instantaneous energy consumption (kWh) and accumulated energy (kW), enabling comprehensive energy management of the plant.

On the other hand, the accumulation of working hours produces natural fouling in the membranes, mainly due to contamination with mineral incrustations, organic and biological matter. Chemical cleaning restores basic operating parameters in terms of flow, pressure and water quality. For this reason, a polyethylene 500 L tank is incorporated into the system for flushing and chemical cleaning operations, using the same feed pump than in the NF operation.

Additionally, the NF pilot plant is equipped with a sampling panel designed for collecting samples from the various streams enumerated in Fig. 4. This panel allows for analysis of the physicochemical characteristics of the samples and also validation of the correct measurement of the inline instrumentation.

2.3. Analytical methodologies

The chemical composition of each sample was analysed by an external certified laboratory to characterize physical and chemical properties of the NF feed solution (SWRO brine) and the two NF outputs (divalent-rich stream and monovalent-rich stream). To achieve this, various samples were collected at different system recovery rates.

The comprehensive study includes a total of 20 parameters: Electrical conductivity @ 20 °C by conductivity meter, pH by electrometer; TDS by calculation; TOC by FTIR; Ba, B and Sr by ICP-OES; Br^-, Ca^{2+}, Cl^-, Mg^{2+}, K^+, Na^+, SO_4^{2-} and hardness by Ion Chromatography; F^-, NO_3^-, PO_4^{3-} and SiO_2 by UV–Vis Spectroscopy; and HCO_3^- by titration.

2.4. Experimental data analysis

A NF system performance depends on process operating parameters, such as feed concentration, flow, temperature, and pressure. However, the evaluation of its performance is typically assessed using the following key performance indicators: permeability and permeate flux, ion rejection, Na + Cl concentration (purity), selectivity factor between monovalent and divalent ions and the concentration factor for divalent ions in the divalent-rich stream. These specific indicators were evaluated due to their direct impact on system efficiency, operational stability and economic viability within the context of a brine valorisation scheme.

2.4.1. Permeability and permeate flux

Permeate flux (J_v) and permeability (k_w) at specific operating pressures were calculated using the following equations. These equations allow for the calculation of J_v and k_w by considering the relationship between the pressure applied during the operation and the resulting flux and permeability values.

$$J_v = \frac{V_p}{A_m * t}\ (LMH) \tag{1}$$

$$k_w = \frac{V_p}{A_m * t * TMP}\ (LMH/bar) \tag{2}$$

where V_p is the volume of permeate (m^3), t is time (h), A_m is the area of the membrane (m^2) and TMP is the transmembrane pressure (bar).

These indicators are fundamental in assessing the system's capacity to produce a monovalent rich-stream efficiently under varying operational conditions. Permeability reflects the ease with which water passes through the membrane under pressure, directly correlating to energy requirements and overall efficiency. Permeate flux, or the flow rate of permeate per unit area, influences the total throughput of the NF system, which is crucial for scalability in large-scale applications.

2.4.2. Ion rejection

The ion rejection rate evaluates the capacity of the NF membrane to reject specific ions, in order to obtain two valuable streams: one enriched with monovalent ions and another one enriched with divalent ions. This separation is vital for subsequent brine concentration stages and is a key factor in reducing operational maintenance and chemical costs, derived from possible scaling or fouling. This involves measuring the concentration of the ion on both the feed and permeate streams, allowing for the calculation of the rejection percentage R_i (%):

$$R_i = \left(1 - \frac{C_{p,i}}{C_{f,i}}\right) * 100 \tag{3}$$

where $C_{p,i}$ is the concentration of ion *i* in the permeate (monovalent-rich) stream (mg/L) and $C_{f,i}$ is the concentration of ion *i* in the feed stream (mg/L).

2.4.3. Selectivity factor

The selectivity factor measures the membrane's capacity to filter between monovalent and divalent ions, which is critical for efficient separation. Higher selectivity ensures that divalent ions are effectively retained in the divalent-rich stream, while monovalent ions pass into the monovalent-rich stream. This makes NF membranes ideal for brine valorisation, as they enhance the purity in the monovalent rich-stream, in Na + Cl concentration terms, and increase the concentration of valuable divalent ions in the divalent rich-stream, optimizing both streams for potential resource recovery.

The selectivity factor is related to the ion rejection, but it calculates the relationship between the rejection rates from different ions or even the average of different groups of elements. In this case, it is evaluated the preference of NF membrane for rejecting multivalent elements than monovalent ones. The selectivity factor is determined by the following equation:

$$S_{i_1/i_2} = \left(1 - \frac{R_{i_2}}{R_{i_1}}\right) * 100 \tag{4}$$

where R_{i1} and R_{i2} are the rejection rates (%) of element i_1 and element i_2, respectively [59].

For this particular case, the selectivity factor is calculated as the ratio between the average rejection of the main monovalent ions and the average rejection of the main divalent ions, as shown in the following equation:

$$S_{mon/div} = \left(1 - \frac{(R_{Na^+} + R_{Cl^-})/2}{(R_{Ca^{2+}} + R_{Mg^{2+}} + R_{SO_4^{2-}})/3}\right) * 100 \tag{5}$$

2.4.4. Na + Cl concentration (purity) in the monovalent-rich stream

Achieving high Na + Cl purity in the monovalent-rich stream is essential for brine valorisation schemes that aim to recover NaCl as a product. High purity is critical for industrial applications requiring high-grade NaCl and directly impacts the economic feasibility of brine valorisation. Consequently, this indicator is highly useful for assessing the purity of the desired stream in terms of Na + Cl concentration. It is calculated by summing the concentration of Na^+ and Cl^- ions (mg/L) relative to the TDS of each stream, as it is shown in the following equation:

$$Purity_{NaCl}(\%) = \frac{[Na^+] + [Cl^-]}{TDS} x100 \tag{6}$$

where $[Na^+]$ is the concentration of sodium ions (mg/L), $[Cl^-]$ is the concentration of chloride ions (mg/L), and TDS is the total dissolve solids (mg/L) in the correspondent stream.

2.4.5. Divalent ions concentration factor in the divalent-rich stream

The divalent concentration factor indicates the degree to which divalent ions are concentrated in the divalent-rich stream, which is an important factor for resource recovery. By concentrating ions like magnesium, the NF system can provide a feasible extraction of valuable by-products, supporting the economic viability of the brine valorisation process and aligning with circular economy goals. A higher concentration factor reduces the volume required for processing these ions in later stages, leading to greater efficiency and lower processing costs.

The concentration factor is calculated to assess the relative concentration of an ion (*i*) in the divalent-rich stream (div) compared to its concentration in seawater (SW):

$$Concentration\ factor_i = \frac{C_{div,i}}{C_{SW,i}} \tag{7}$$

where $C_{div,i}$ is the concentration of ion *i* in the concentrate (divalent-rich) stream (mg/L) and $C_{SW,i}$ is the concentration of ion *i* in the seawater (mg/L).

The specific indicators evaluated in this study provide insights into membrane performance under realistic conditions and ensure that the system meets the demands of industrial-scale desalination and resource recovery applications. This study has compiled the main equations currently used to describe the performance of NF membranes. These equations assume that ions flux is related to a solution-diffusion transport mechanism within the membrane and take into account the electromigration originated by the different transport velocities of ions across the active layer [51].

3. Results and discussion

This section provides a detailed overview of the operation and the results achieved during the experimental process. It also examines the interaction between various critical parameters, emphasizing their interconnections and the effects on the overall results.

As mentioned in Section 2, a configuration with seven nanofiltration NE8040-40 membranes at a constant feed flow rate of 144 m^3/d of SWRO brine was selected for this study. Table 3 presents results for the remaining feed conditions, including flow, temperature, pH, conductivity, TDS and flux.

Initial experiments were conducted to assess the impact of recirculating the divalent-rich stream into the HPP inlet (Line 5 in Fig. 4) on the overall system performance. Consistent with projections made using the CSM software, the only significant difference observed was an increase in energy consumption due to the higher HPP flow. Results from conductivity, pressure and chemical analysis of the samples taken revealed no substantial differences between 0 % and 50 % recirculation. Therefore, all tests presented in this study refer to the setup with 0 % divalent-rich stream recirculation.

In summary, the NF system was tested at different recovery rates ranging from 38 % to 70 %, with a corresponding pressure range in the high-pressure pump outlet (Line 3 in Fig. 4) from 9 to 20 bar and a stable pressure drop of 0.4–0.6 bar between Lines 3 and 5 (Fig. 4). The monovalent-rich stream resulted with flow rates between 1.64 and 4.17 m^3/h, with conductivity values ranging from 73 to 78 mS/cm at a pressure of 0.4 to 1.7 bar (Line 4). The divalent-rich stream exhibited flows between 1.80 and 3.08 m^3/h, with conductivity values ranging from 87 to 101 mS/cm at pressures from 0.3 to 1.5 bar (Line 8). Consequently in relation to the recovery rate, the NF process obtained membrane fluxes from 8 to 16 LMH and a constant permeability of 0.8 to 0.9 LMH/bar, operating at temperatures between 23 and 26 °C and a pH value around 7.

The Langelier saturation index (LSI) and the degree of concentrate saturation ($CaSO_4$) were also evaluated through the membrane manufacturer projection, giving values of LSI < 2 and %st $CaSO_4$ < 200. These parameters are important to control membrane scaling as they offer predictive and quantitative assessments of the scaling potential.

The following results show the influence of the system recovery value, which is the process set-point, on other parameters such as the high-pressure value at the HPP outlet, conductivity values, specific energy consumption (SEC), and the chemical composition of monovalent and divalent enriched streams.

3.1. Correlation between recovery rate and HPP outlet pressure value

The range of recovery rates tested varied from 38 to 70 %, with working pressures between 9 and 20 bar. Fig. 5 shows the pressure measured at the HPP outlet (Line 3) for different tests carried out at various initially set recovery rates. As expected, a linear ascending trend is observed for both parameters across all the tests, for a constant feed flow, due to the direct relationship between the applied operating pressures and permeate flux.

In this study, the pressure is directly proportional to the recovery rate due to its configuration. It was decided not to exceed the 20 bar pressure threshold, due to concerns about potential concentration polarisation, possibly causing a decrease on the rejection of multivalent elements and compromising selectivity of the membranes, as previously reported for C. Morgante et al [51]. Other theoretical studies have worked with higher pressure values, up to 30 bar [59], but it was possible to

Table 3
Feed conditions of the experimentation done in the NF pilot plant.

Parameters	Units	Value
Flow	m^3/d	144
Temperature	°C	23–26
pH	U. pH	7.0–7.5
Conductivity @ 25 °C	mS/cm	82–86
TDS	mg/L	64–66
Flux	LMH	8–16

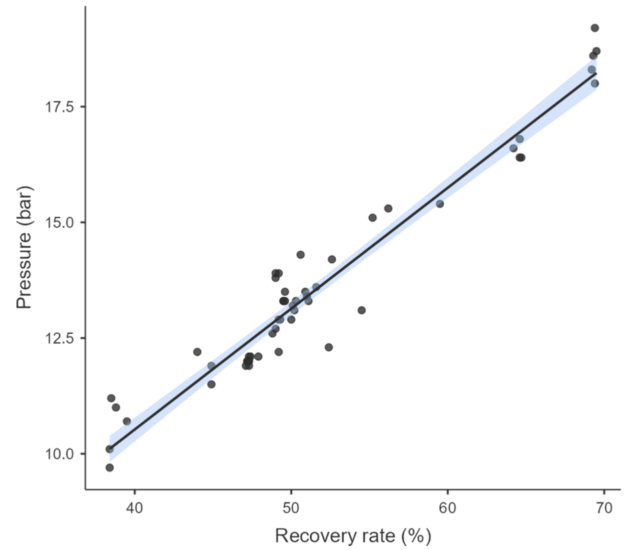

Fig. 5. Analysis of the correlation between recovery rate and operational pressure in the nanofiltration process.

corroborate the decrease in the rejection of multivalent elements for pressure values higher than 20 bar. Additionally, increasing the pressure would also escalate system energy consumption and recovery rates, potentially reaching concentrations where precipitations might occur or requiring significant amounts of antiscalant.

3.2. Influence of recovery rate on conductivity values

The conductivity values from the NF feed (Line 1), the monovalent-rich stream (Line 4), and the divalent-rich stream (Line 8) are represented in Fig. 6, illustrating their behaviour depending on the recovery values achieved by the NF system.

These in-situ conductivity values @25 °C serve as a real-time indicator on performance of the system. Although they do not provide a complete chemical analysis, they are useful for evaluating the effects of adjustments made to the system, allowing for immediate action and decision-making, without the need of waiting for the laboratory analysis, helping the optimisation of the system. Additionally, they could serve as indicators for long-term tests, especially in cases where there are significant discrepancies, helping to identify and address potential issues quickly.

In this case, a strong correlation between the different values is noticed. Across all tests, the conductivity of the feed remains fairly constant, as the SWRO brine conditions are not expected to change significantly from test to test. For the output streams, the conductivity of the monovalent-rich stream also remains stable, despite changes in flow associated with the variation on different recovery rates. This situation can be clarified because monovalent ions, such as sodium and chloride, are not heavily rejected by the membrane, so their concentration remains similar even at different flow rates. However, the conductivity of the divalent-rich stream increases as the recovery rate rises. This phenomenon can be explained by the fact that the rejection rate of monovalent ions is minimal, whereas divalent ions, like calcium and magnesium, are predominantly rejected by the membrane, and consequently, accumulate in higher concentration in the divalent-rich stream. When the recovery rate increases, the flow decreases, leading to a higher concentration of these divalent ions in the stream, which causes the conductivity to increase.

3.3. Influence of recovery rate on specific energy consumption (SEC)

SEC values plays a significant role in determining future operational

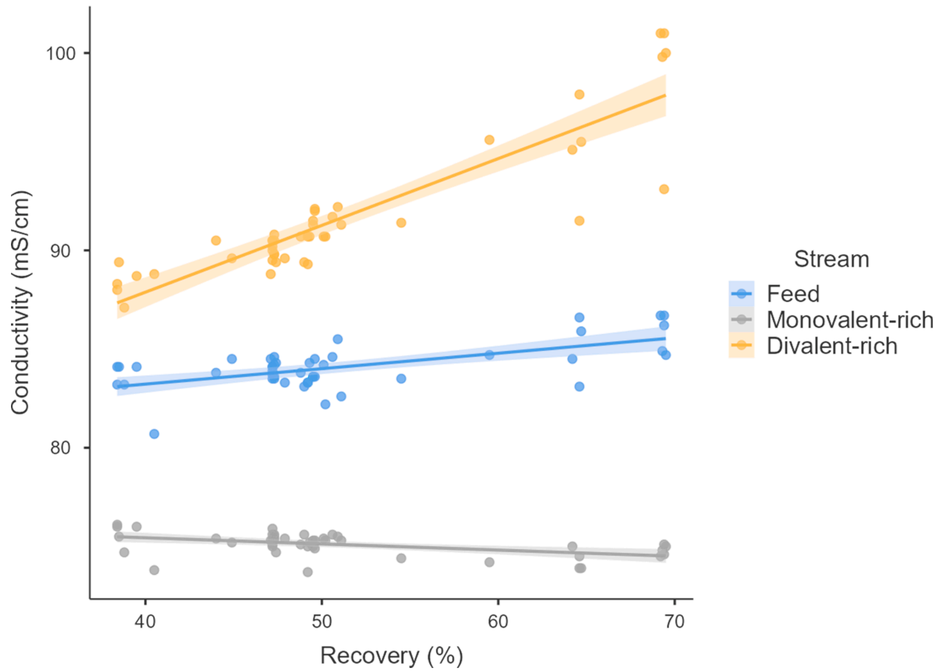

Fig. 6. Conductivity measurements for NF feed, monovalent-rich, and divalent-rich streams at various recovery rates.

costs and overall efficiency of a NF plant, where energy costs are a significant portion of the operational expenses. This parameter measures the amount of energy required per unit of water processed, in this case, the monovalent-rich stream. Achieving lower SEC values is essential for ensuring the economic feasibility of large-scale NF applications, making the overall operation more cost-effective and environmentally friendly, and enhancing the competitiveness of NF-based brine valorisation compared to traditional disposal methods. Furthermore, a reduction in energy use lowers the environmental impact, as it decreases associated carbon emissions and supports alignment with circular economy principles. Thus, by optimizing SEC, NF plants can more sustainably operate at scale, offering financially viable solutions for transforming desalination brine into valuable resources.

To determine the SEC values (kWh/m^3) in the NF system of this study, the energy consumption measured by the energy analyser installed as specified in Section 2.2, is then divided by the flow rate of the monovalent-rich stream.

The results observed in Fig. 7 illustrate that the SEC value decreases as the system recovery rate increases, stabilising at around 1.25 kWh/m^3 at approximately 65–70 % recovery rate. Despite higher energy consumption at increased recovery rates due to the higher operating pressure, the flow rate of the monovalent-rich stream also increases, offsetting the energy increase. This trend has also been observed in a theoretical study [60], where an energy consumption as low as 0.5 kWh/m^3 was calculated, achieving recovery rates exceeding 70 % at an operating pressure of 10 bar. Comparing the data from this study with the previous theoretical research, the energy consumption at recovery rates between 60 and 70 % with an operating pressure of 20 bar, was around 1.20–1.30 kWh/m^3.

This makes NF a cost-effective pre-treatment process for brine valorisation in existing SWRO desalination plants. While it only raises the overall desalination process by 25–35 %, which typically ranges from 3.5 to 4.5 kWh/m^3 [61,62] (including intake, pre-treatment and post-treatment processes), it also generates two potentially valuable output streams. These additional benefits, make the NF system a profitable solution, despite the moderate increase in energy consumption.

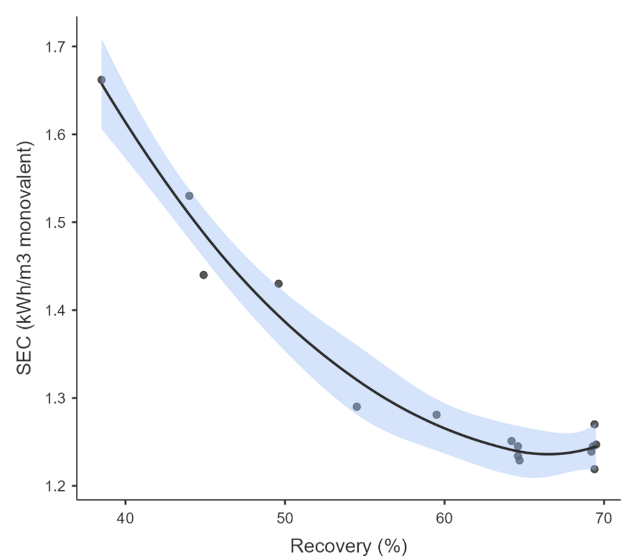

Fig. 7. Specific Energy Consumption (SEC) values at various recovery rates for the nanofiltration process.

3.4. *Influence of recovery rate on chemical composition*

The chemical composition of the different streams (inlet and two outlets) within the NF system of this study, was determined by an external certified laboratory, following the methods described in Section 2.3.

Table 4 shows the 21 parameters analysed for each of the streams: average values for the monovalent-rich and the divalent-rich streams at three different recovery rates (50, 60 and 70 %), and ranges of values for the feed stream.

From the concentration results shown in Table 4 can be calculated the ion rejection values of the NF membranes tested in this study, which outcomes are illustrated in Fig. 8. The other main NF characteristics for major ions will be analysed in more detail in Section 3.5, using the data analysis methods described in Section 2.4.

Table 4
Chemical composition of NF streams: range of values for NF feed, and average composition of major and minor ions in the monovalent-rich and divalent-rich streams, according to the experimental tests done at 50%, 60%, and 70% recovery rates in the pilot plant set-up.

Parameter	Units	Feed	50 % recovery		60 % recovery		70 % recovery	
			Monov.	Div.	Monov.	Div.	Monov.	Div.
Conductivity at 20 °C	mS/cm	78–80	69.9	84.8	71.3	89.5	70.3	92.1
pH	U.pH	7.2–7.5	7.3	7.3	7.1	7.2	7.2	7.3
Temperature	°C	24–25	23.9	23.9	25.1	25.0	25.2	25.6
TOC	mg/L	0.7–0.9	0.24	1.28	0.16	1.68	0.06	1.85
Silica	mg/L	55–60	58.9	59.6	58.4	59.9	56.5	57.6
Boron	mg/L	6.2–7.7	7.33	7.40	6.19	6.20	7.08	7.18
Chloride	mg/L	35,600–36,200	32,923	41,506	31,904	42,487	32,805	45,548
Sodium	mg/L	19,800–20,300	20,219	20,726	19,850	20,224	20,015	19,669
Sulphate	mg/L	4,900–5,100	22.4	10,275	22.1	12,547	23.2	16,033
Magnesium	mg/L	2,300–2,500	140.5	4,550	139.0	5,728	143.6	7,701
Calcium	mg/L	700–800	171.2	1,359	166.1	1,677	171.6	1,966
Potassium	mg/L	650–750	716.5	762.5	625.5	675.7	632.9	709.0
Bicarbonate	mg/L	165–235	145.7	299.1	147.4	351.9	152.5	428.1
Bromide	mg/L	120–140	129.0	148.5	117.5	133.5	108.5	138.5
Strontium	mg/L	12–15	1.8	28.9	1.4	30.8	1.8	40.2
Fluoride	mg/L	4–6	0.39	5.75	1.76	8.60	0.82	10.73
Nitrate	mg/L	4.5–6.5	4.21	5.02	6.04	7.35	5.96	7.68
Phosphate	mg/L	0.18–0.23	0.00	0.39	0.14	0.51	0.00	0.66
Barium	mg/L	0.18–0.21	0.02	0.38	0.02	0.57	0.03	0.62
Hardness	DegF	1,100–1,200	100.5	2211	98.6	2775	101.9	3659
TDS	mg/L	64,500–65,300	54,343	79,492	52,861	83,364	53,945	92,077

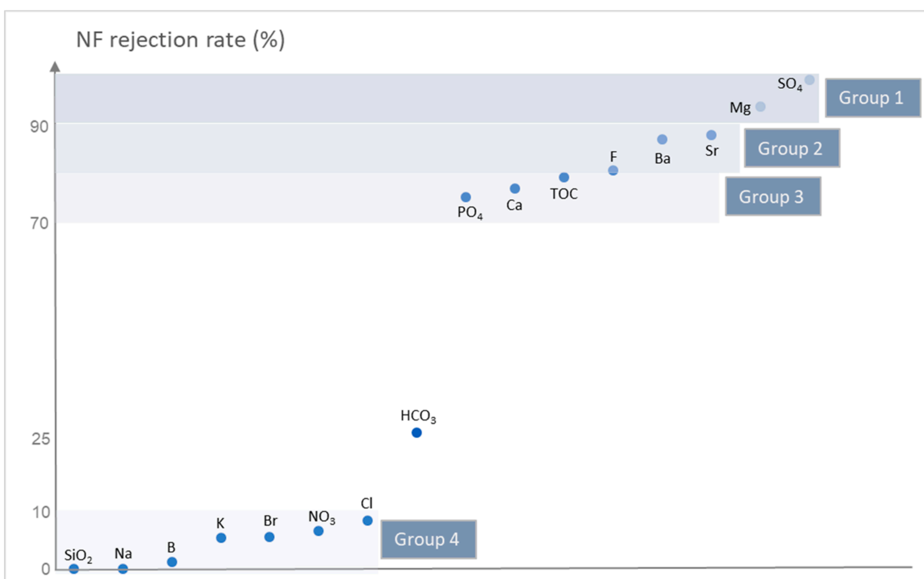

Fig. 8. Categorisation of major and minor ions into four groups based on the rejection rate achieved with the tested NF membranes.

In order to establish an ion classification, according to their rejection rate, Fig. 8 categorises elements into four groups based on their rejection levels by the NF membranes. Group 1 includes elements that are extremely well rejected by the NF membranes ($R_i > 90$ %); Group 2 involves ions with very high rejection values (80 % $< R_i <$ 90 %), Group 3 contains the elements with moderately high rejection values (70 % $< R_i <$ 80 %), and Group 4 includes elements with very low rejection values ($R_i < 10$ %). As particular fact, the rejection rate for bicarbonate ions falls between Groups 3 and 4, indicating a medium rejection rate.

From these categories, it can be concluded that magnesium and sulphate are the main rejected ions of the NF membranes tested, corresponding to the first group. Calcium is moderately high rejected in the NF system, thus it is contained in Group 3. Main monovalent ions, such as Na^+, Cl^- and K^+, are part of Group 4, with a very low rejection rate as expected.

A notable characteristic of the seawater from beach wells in the Canary Islands is its high silica content, due to the volcanic nature of the archipelago. Fig. 8 shows that the tested NF membranes do not reject silica. It can be also observed from Table 4 that the silica concentration remains the same in the feed and in both output streams across all tests done at different recovery rates. This behaviour can be explained by the formation of different Si species ($Si(OH_4)$ or H_4SiO_4) when the pH is below 7.5, which may reduce the effectiveness of removal through the charge repulsion mechanism of the negatively charged NF membrane, according to the membrane manufacturer. Additionally, the NF membrane's molecular weight cut-off (MWCO) range of 200–300 Da may also play a role. This MWCO range is small enough to reject larger ions and molecules, such as multivalent ions, while allowing smaller molecules, like monovalent ions and uncharged species, to pass through, explaining why silica concentrations remained unchanged in both output streams.

3.5. Evaluation of experimental data

This section focuses on the evaluation of the performance indicators described in Section 2.4, using the experimental data obtained. This evaluation assesses how effectively the system behaves and how it compares to other published studies on this topic, providing a broader context for understanding the NF membranes performance.

3.5.1. Permeability and permeate flux

The flux values (Fig. 9) follow the same trend than Fig. 5, where a linear relationship between pressure applied and recovery rate was shown. In this case, permeate flux is directly proportional to the recovery rate since the area of the membranes used and the feed flow remain constant throughout the process. However, when representing the permeability values (Fig. 9), a fairly constant value of 0.80–0.95 is achieved independently from the pressure applied, showing a consistent performance of the NF membranes.

The performance of the membranes tested in this NF pilot plant shows similarity to the analysis from other authors, where VNF1 membranes from Vontron (China) were used [51]. In that study, a flux value around 9 LMH were achieved at 10–11 bar of operating pressure, while it reached approximately 16 LMH at higher pressures (17–20 bar), for treating SWRO brines.

3.5.2. Ion rejection and selectivity factor

The monovalent-rich stream should ideally leave the NF system with the lowest concentration possible of the divalent ions to avoid precipitation on future stages. In this section, the main divalent ions (Ca^{2+}, Mg^{2+}, SO_4^{2-}) are evaluated based on their rejection rates by the NF membranes. The selectivity factor is also calculated and added to the results shown in Table 5.

Based on the average results from three studies [63,64,65], among others, the ion rejection rates typically range as follows: SO_4^{2-} is usually between 75–96 %, while for the divalent cations (Ca^{2+} and Mg^{2+}), the rejection rates are generally lower. Specifically, calcium normally does not exceed 45–50 %, whereas magnesium rejection rate range from 60 % to 90 %.

In NF membranes, the rejection rates of divalent ions vary due to differences in their size, charge density and interactions with the membrane surface. Generally, magnesium and sulphate are more effectively by NF membranes than calcium due to their higher charge densities, larger hydrated radius, and stronger electrostatic interactions with the membrane, all of which restrict their passage through the membrane pores more than calcium. This difference in ion rejection is governed by the principles of Donnan exclusion and size exclusion, both of which play key roles in NF membrane performance [66].

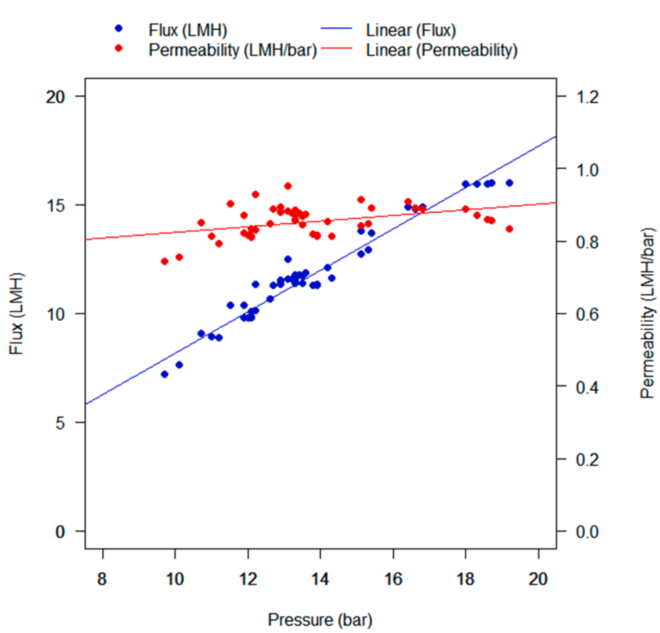

Fig. 9. Flux values and permeability rates under different operating pressures in the nanofiltration process.

Table 5
Ion rejection rate and selectivity factor of main divalent ions in experimental tests carried out at 50%, 60% and 70% recovery rates.

NF recovery (%)	Calcium	Magnesium	Sulphate	Selectivity factor
50	75.7	94.1	99.5	9.4
60	78.4	94.1	99.6	10.0
70	78.2	94.1	99.5	10.3

Recent projections carried out using various programs owned by different NF membrane manufacturers indicates slightly upgraded rejection rates for calcium, around 70–75 %, which is a considerable improvement. More recent studies, using new-generation nanofiltration membranes, show higher calcium rejection rates, although synthetic solutions have been used. It is essential to test these membranes with actual SWRO brines. Sulphate rejection levels are expected to range between 95–99 %, while magnesium rejection is projected to be around 74–90 %, depending on the membrane manufacturer.

The performance of the NF membrane in this system, in terms of selective ion rejection at various recovery rates (Table 6), demonstrates improved behaviour compared to results from other studies and even software projections mentioned above. Regarding to its performance related to the recovery rate, the ion rejection rate remains constant for magnesium and sulphate, whereas calcium rejection slightly increases at 60 % and 70 % recovery rates. Additionally, the selectivity factor also exhibits a slight increase as recovery rates rises.

The rejection of the divalent ions, especially Mg^{2+} and SO_4^{2-}, remain invariable with the changes in recovery rates. This has also been observed in specific NF membranes from another research [26].

At the operating parameters tested in this study, concentration polarisation has not been noticed, since there has not been any decrease in the rejection rate of multivalent elements. Consequently, there has been no compromise in selectivity factors. Other studies have reported observing this phenomenon after exceeding 20 bar of pressure [51].

3.5.3. Na + Cl concentration (purity) in the monovalent-rich stream

Simultaneously, maximising the percentage of sodium and chloride ions in the monovalent-rich stream is crucial for the success of subsequent stages in a brine valorisation scheme. Seawater and SWRO brine typically contain around 85–86 % of these ions.

Three different recovery rates were evaluated in the NF system and the results are presented in Table 7, showing a very stable value of nearly 98 % of Na^{+}+Cl^{-} in the output monovalent-rich stream.

In this study, NaCl purity values demonstrate a low, but significant improvement compared to other current studies. For instance, a purity of 96.85 % was reported after applying a two-stage NF system on seawater [33]. Moreover, purities ranging from 96 to 98 % have been achieved when treating RO brines using diverse commercial membranes [26,51,59]. These results can conclude with an outstanding performance of NE8040-40 membranes tested in this study.

The final purity of the NaCl obtained will determine its ultimate application. For example, the requirement for food-grade salt quality is a purity of at least 97 %, according to the Codex Alimentarius [67]. Pharmaceutical industries, on the other hand, require salt purity levels above 99 %, while for other chemical industries, the acceptable range for salt quality typically spans from 96.0 to 99.7 % [68].

3.5.4. Divalent ions concentration factor in the divalent-rich stream

The concentration factor is an indicator of the effectiveness of NF in concentrating valuable multivalent ions in the divalent-rich stream. It

Table 6
Comparison of Ca^{2+}, Mg^{2+} and SO_4^{2-} rejection between different studies about diverse NF membranes used in a pre-treatment process of a brine valorisation scheme, considering operational pressure of **20 bar**.

Membrane	Manufacturer	Feed	Ca^{2+} rejection (%)	Mg^{2+} rejection (%)	SO_4^{2-} rejection (%)	Study
NE8040-40	TORAY (CSM)	SWRO brine	75	94	99	This paper
NF270	Filmtec (Dupont)	Synthetic brine*	50	71	91	[59]
PRO-XS2	Hydranautics	Synthetic brine*	63	87	>98	[59]
Fortilife XC-N	Dupont	Synthetic brine*	77	87	>95	[59]
NF90	Dow Filmtec	Synthetic brine*	97	95	97	[51]
NFS	Synder Filtration	Synthetic brine*	87	94.6	>97	[51]
NFX	Synder Filtration	Synthetic brine*	>91	>97	>97	[51]
VNF1	Vontron	Synthetic brine*	87	94.6	97.5	[51]
DK	Veolia	Synthetic brine*	>91	>97	98	[51]

* Studies using synthetic desalination brine solutions prepared with deionized water, NaCl and other reagents. Tests done in a flat-sheet (one membrane) experimental set-up.

Table 7
Na + Cl concentration (purity) from NF feed and monovalent-rich stream, operating the NF pilot plant at 50 %, 60 % and 70 % recovery rates.

NF feed	50 % recovery	60 % recovery	70 % recovery
86.1	97.8	97.9	97.9

quantifies the degree to which these ions (mainly Ca^{2+}, Mg^{2+}, and SO_4^{2-}) are concentrated during the process. Fig. 10 shows the gradual concentration increase for those main divalent ions starting from seawater, through the initial concentration in the SWRO process, concluding in the high concentration values achieved in the divalent-rich stream of the NF system.

Higher operating pressures and recovery rates increase the concentration factor, by pushing more water flow through the membrane from feed to the monovalent-rich stream, affecting the concentration and composition of the consequent divalent-rich stream.

Therefore the NF pilot plant successfully demonstrates the efficient concentration of multivalent ions in the divalent-rich stream, achieving approximately 4 times higher calcium concentration and 5 times higher magnesium and sulphate concentrations compared to their concentrations in initial seawater, operating at 70 % recovery rate.

A higher concentration factor reflects the effectiveness of nanofiltration in concentrating valuable elements within the divalent-rich stream. This issue indicates that the NF membranes tested have both exceptional selectivity, favouring the retention of divalent ions, and have a high permeability, allowing the efficient separation of these ions form the initial feeding solution. In essence, the higher the concentration factor, the better the NF system is at isolating and enriching these valuable elements in the divalent-rich stream, for further desired steps in the brine valorisation scheme.

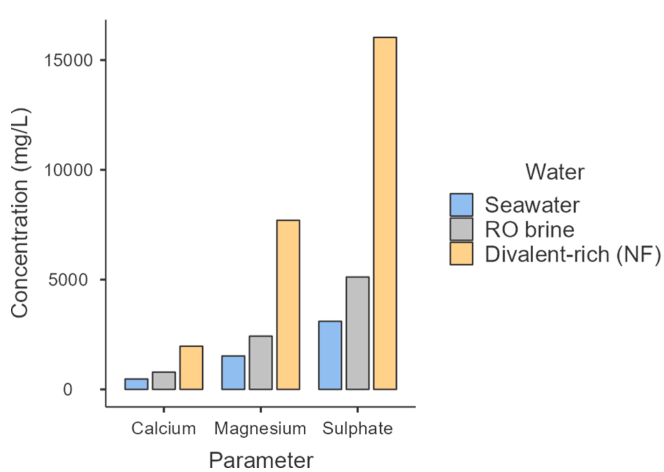

Fig. 10. Concentration factor of major divalent ions in the divalent-rich stream and SWRO brine relative to the initial seawater feeding the entire system.

3.6. Future research

In order to proceed with the research established on this paper, the authors consider the following topics important to address and focus to future efforts on:

3.6.1. New NF membranes

A diverse range of NF membranes will be assessed and compared based on their performance. This evaluation will include both commercially available membranes from various manufacturers and new developments in their fabrication, such as the inclusion of nanomaterials. The primary objective is to enhance the knowledge and understanding of NF technology, aiming to identify the most effective solutions. This study will seek to optimise the use of NF membranes for the specific application of pre-treatment within a desalination brine valorisation scheme.

3.6.2. Energy recovery device (ERD)

Commercial manufacturers are developing new energy recovery devices for pilot plants and low pressure applications. The implementation of these systems has the potential to significantly reduce the energy consumption of the process, and improve the evaluation of their effect on large scale systems to reduce the SEC below 1 kWh/m^3.

3.6.3. Integrate brine concentration and brine mining processes

The optimisation of the NF system needs to be related to the subsequent processes, either brine concentration for the monovalent-rich stream or any type of mineral extraction for the divalent-rich stream. Knowing the needs for an optimum input for those processes can direct the research on the NF membranes, in order to match those needs directly without requiring further stages, if possible.

3.6.4. New feed (2-stage SWRO brine)

In relation to the previous topic, testing different RO brines as NF feed can optimise the overall system. For instance, using a 2-stage SWRO brine which is more concentrated than usual, with typically 50–55 % recovery rate due to its second-stage RO configuration. The SWRO brine from the first stage undergoes through another set of RO membranes, increasing its concentration to 70 – 75 g/L, while producing more desalinated water. The goal would be to test the NF membrane capabilities and performance with this high-concentration feed from a 2-stage RO process.

3.6.5. Long-term tests

Once the optimal configuration of the system is determined, a long-term evaluation would be needed to thoroughly assess the performance of the NF membranes over several months of operation. This extended assessment would involve continuous monitoring and testing of key performance indicators to understand how the membranes behave over time. By evaluating these indicators throughout the extended period, a comprehensive analysis of the membranes' durability, efficiency, and overall effectiveness in the specific application can be achieved.

3.6.6. Different configurations

Testing various configurations of the NF system can also provide insight on this topic. For instance, incorporating a second pass to evaluate the improvement in rejection values or adding a second stage to further concentrate divalent ions in the divalent-rich stream could enhance valorisation processes. Another configuration worth evaluating is positioning the NF pilot plant before the RO rather than after. This could be analysed through a techno-economic comparison for new plants, as implementing an intermediate stage in existing plants would be challenging.

4. Conclusion

This study evaluated the effectiveness of NF membranes as a pre-treatment stage for SWRO brine valorisation processes, providing valuable performance data from a pilot plant using 6 m^3/h of real SWRO concentrate as feed, rather than synthetic solutions. The tested NF membranes demonstrated outstanding performance, particularly in rejecting divalent ions, which is crucial for preventing scaling and other operational challenges in downstream processes. The results highlighted the membranes' ability to efficiently separate multivalent ions, with remarkably high rejection rates for sulphates (99.5 %), magnesium (94.1 %), and calcium (78.2 %).

One of the major advantages observed was the effectiveness of the NF membranes in significantly increasing the concentration of $Na^+ + Cl^-$ in the monovalent-rich stream to nearly 98 %, starting from 86 % in the SWRO brine. The enhancement in NaCl purity is particularly advantageous for several industrial applications, positioning NF as a highly viable choice for integration into existing desalination plants. Besides, this selective ion separation directly enhances the economic viability of subsequent concentration processes, as well as a reduction in waste volumes by minimizing undesirable by-products, which are typically managed at a high cost.

The versatility of the NF pilot plant enabled testing under different recovery rates, with thorough evaluation of several parameters. Remarkably, the NF membranes maintained consistent ion rejection and NaCl concentration across varying recovery rates, while specific energy consumption (SEC) decreased at higher recovery rates. The optimal recovery rate was identified as 70 %, with a SEC of 1.25 kWh/m^3 permeate, representing only an additional 25–30 % increase over the energy consumption of an existing desalination plant. In terms of scalability and implications for large-scale operations, the pilot plant's ability to maintain consistent ion rejection and NaCl concentration across various recovery rates, highlights the robustness of NF membranes in handling high brine volumes with limited fluctuation in performance, at a low energy consumption.

Beyond the potential valorisation of the monovalent-rich stream, the NF membranes effectively concentrated the divalent-rich stream, achieving up to 5 times higher concentrations of sulphate and magnesium, and 4 times higher concentrations of calcium, compared to seawater. This capability is especially vital for magnesium, a critical raw material for Europe, highlighting the strategic importance of securing new sources of production.

Given the promising results gathered from the NF membranes evaluated in this study, future research could explore the use of advanced NF membranes with nanomaterials, integration of novel energy recovery devices for low-pressure applications, combining brine concentration with valorisation of NF output streams, testing new feed sources like 2-stage SWRO brines, and conducting long-term tests to assess system robustness and potential concentration polarisation.

Overall, the tested NF membranes in this study demonstrated exceptional monovalent/multivalent selectivity and rejection, confirming the suitability of nanofiltration as a pre-treatment technology for SWRO brines, a critical step in ensuring the success of desalination brine valorisation schemes at any scale, promoting sustainability, resource efficiency and economic feasibility in desalination operations.

Looking ahead, future research on NF membranes for brine valorisation is vital for enhancing sustainable desalination practices, particularly in real-world applications involving SWRO brines. NF membranes provide a promising pre-treatment stage that can selectively remove specific ions, reduce scaling potential, and improve the efficiency of subsequent brine valorisation processes. However, challenges remain in optimizing NF membrane performance under the high-salinity and complex composition of actual SWRO brines, as laboratory conditions do not fully replicate the harsh and variable nature of operational environments. Addressing issues such as membrane fouling, selective ion separation efficiency, and energy consumption under these real-world conditions is essential for making NF-based brine valorisation feasible at industrial scale. Optimizing this technology can help transforming brine from waste into a valuable resource, thereby supporting sustainability and circular economy in desalination.

CRediT authorship contribution statement

A. Rivero-Falcón: Resources, Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Validation, Writing – original draft, Writing – review & editing, Visualization. **Y. López-López:** Resources, Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Validation, Writing – original draft, Writing – review & editing, Visualization. **B. Peñate Suárez:** Conceptualization, Methodology, Formal analysis, Validation, Writing – review & editing, Supervision, Project administration. **N. Melián-Martel:** Conceptualization, Methodology, Validation, Supervision.

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Declaration of competing interest

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

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Data availability

Data will be made available on request.

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