

Osmotically assisted reverse osmosis: Assessing pretreatment on hypersaline produced water

Masha'el Al-Maas, Joel Minier-Matar, Altaf Hussain, Eman AlShamari, Ramesh Sharma, Samer Adham

Item type

Journal Contribution

Terms of use

This work is licensed under a [CC BY 4.0](https://creativecommons.org/licenses/by/4.0/) license

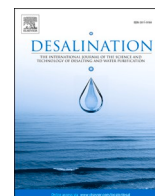
This version is available at

https://manara.qnl.qa/articles/journal_contribution/Osmotically_assisted_reverse_osmosis_Assessing_pretreatment_on_hypersali

Access the item on Manara for more information about usage details and recommended citation.

Posted on Manara – Qatar Research Repository on

2025-02-24



Osmotically assisted reverse osmosis: Assessing pretreatment on hypersaline produced water

Mashaël Al-Maas^a, Joel Minier-Matar^a, Altaf Hussain^a, Eman AlShamari^a, Ramesh Sharma^b, Samer Adham^{a,c,*}

^a ConocoPhillips Global Water Sustainability Center, Qatar Science and Technology Park, P. O. Box 24750, Doha, Qatar

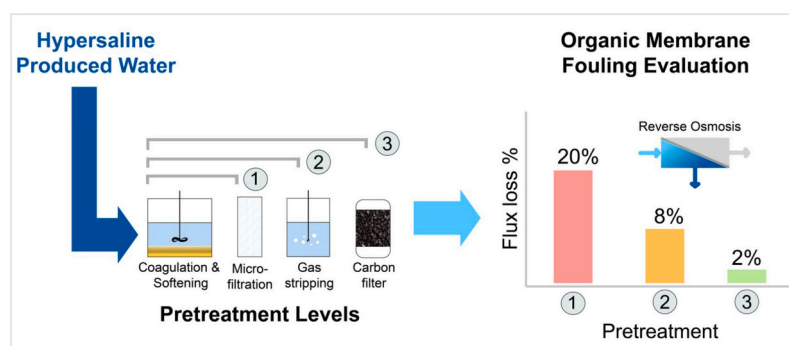
^b Low Carbon Technologies, ConocoPhillips, Houston, TX 77079, United States of America

^c Center for Advanced Materials, Qatar University, PO Box 2713, Doha, Qatar

HIGHLIGHTS

- Investigated desalination via osmotically assisted reverse osmosis (OARO)
- Tested efficacy of multiple pretreatment technologies on saline produced water (PW)
- Improved removal of high fouling potential organics by pretreatment, 17 to 62 %
- Reduced organic membrane fouling by pretreatment; flux loss dropped from 20 % to 2 %
- Generated preliminary product water quality for potential beneficial reuse

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Oil and gas
Produced water
Desalination
Reverse osmosis
Pretreatment
Reuse

ABSTRACT

In a rapidly developing oil and gas industry, sustainable management of produced water (PW) is a key challenge. Due to increasing environmental regulations, the industry is driven towards reducing volumes of PW requiring deep well injection and maximizing beneficial reuse. Among multiple innovative technologies being explored, osmotically assisted reverse osmosis (OARO) has been gaining attention as a possible cost-efficient route for brine concentration. This study addressed key knowledge gaps associated with facilitating the industrial application of OARO for hypersaline PW including a systematic evaluation of pretreatment requirements, membrane organic fouling potential, and product water quality for beneficial reuse applications. A sequence of multiple technologies, including chemical coagulation, softening, microfiltration, stripping, and granular activated carbon (GAC) adsorption, were configured and tested as pretreatment level I, level II, and level III. Approximately 60–70 % of

Abbreviations: PW, Produced water; O&G, Oil and gas; TDS, Total dissolved solids; RO, Reverse osmosis; MLD/ZLD, Minimum/zero liquid discharge; HPRO, High pressure reverse osmosis; OARO, Osmotically assisted reverse osmosis; CFRO, Crossflow reverse osmosis; BWRO, Brackish reverse osmosis; SWRO, Seawater reverse osmosis; EVAP, Evaporators; CRYST, Crystallizers; DOC, Dissolved organic carbon; TOG, Total oil and grease; HPIC, High-pressure ion chromatography; FTIR, Fourier transfer infra-red; SEM, Scanning electron microscope; SPW, Synthetic produced water; MF, Microfiltration; GAC, Granular activated carbon; SCM, Sodium carbonate monohydrate; HOC, Hydrophobic organic carbon; DAF, Dissolved air flotation; UF, Ultrafiltration; NF, Nanofiltration; IX, Ion Exchange; DI, Deionized water; EBCT, Empty bed contact time; MBR, Membrane bioreactor; PFA, Perfluoro alkoxy; CAPEX/OPEX, Capital and operating expenditures.

* Corresponding author at: Center for Advanced Materials, Qatar University, PO Box 2713, Doha, Qatar.

E-mail address: sadham@qu.edu.qa (S. Adham).

<https://doi.org/10.1016/j.desal.2025.118724>

Received 14 November 2024; Received in revised form 18 February 2025; Accepted 18 February 2025

Available online 19 February 2025

0011-9164/© 2025 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

the dissolved organic carbon (DOC) in the PW originated from organic acids, which were proven to exhibit low membrane fouling potential. The remaining DOC (30–40 %), composed of other constituents including the high-fouling potential hydrophobic organic carbon (HOC), were reduced by ~17 %, ~38 %, and ~62 % via application of pretreatment level I, level II, and level III, respectively. Membrane fouling tests using level I PW quality resulted in immediate fouling and a flux drop of ~20 %. A flux loss of ~8 % was obtained using level II PW quality which was reduced to ~4 % by application of level III pretreatment. Generated results were used to depict the fouling mechanism for the different DOC fractions in the PW including, organic acids (electrostatic), HOC (adsorption), and uncharged/neutrals (diffusion). The study also shared preliminary insights on the expected product water quality and discussed implications for reuse applications including posttreatment, toxicological evaluations, and regulatory requirements.

1. Introduction

Produced water (PW) is the naturally existing saline water generated during the extraction of oil & gas (O&G). Typically, volumes of PW can range between an average of 3–4 barrels per barrel of oil and can reach up to 10 barrels for some locations [1–6]. In the United States, approximately ~20 billion barrels per year of PW are produced by onshore O&G activities, with >15 million barrels generated daily in the Permian Basin [7]. Large volumes of PW require efficient management to reduce handling or disposal costs and associated environmental risks. Current PW management practices involve underground injection for either disposal, pressure maintenance, and/or water flooding for enhanced oil recovery in active formations [8]. Limited reuse of PW is also considered after minimal treatment for industrial applications. Adopting treated PW effluents for reuse outside the O&G industry requires addressing several challenges including the complex water quality, the limited toxicity data, and the knowledge gaps for adequate regulatory responses and risk assessment frameworks [9]. Only for specific high-quality PWs and/or some locations, other non-industrial PW reuse applications can include landscape irrigation and livestock watering [10]. Nevertheless, with increasing environmental regulations and concerns associated with induced seismicity, there are stringent constraints on the PW discharge quality and injection volume, respectively. These factors have globally driven the O&G industry towards reducing the PW volume requiring disposal via developing fit-for-purpose PW beneficial reuse solutions [11,12].

PW possesses a complex composition of organics and inorganics governed by several factors like hydrocarbon type, location, and age of reservoir. Organics include oil, present as free, dispersed/emulsified, and dissolved, as well as some chemical additives and their associated transformational byproducts during interactions with the formation water. Inorganics cover suspended particles, dissolved solids (known as total dissolved solids (TDS), precipitated solids (i.e., scales), and metals. TDS is considered one of many challenging contaminants hindering the treatment and reuse applications of PW. A gas field PW typically has relatively low TDS (i.e., <10 g/L) compared to >100 g/L TDS expected for oil field PWs [1–3]. Membrane desalination by reverse osmosis (RO), driven by applied pressure overcoming the osmotic pressure, has been proven to be one of the most energy efficient processes for desalinating streams of TDS concentrations up to ~70 g/L [13–22]. The relatively low TDS PWs (i.e., less than seawater salinity of 35–40 g/L) demonstrate higher opportunities for desalination application at lower specific energy consumption (< 5 kWh/m³) [23,24].

Treatment of high salinity PWs, for purposes of complying with emerging brine management strategies and/or minimum/zero liquid discharge (MLD/ZLD) targets, is typically more challenging and energy intensive [25,26]. This is due to the elevated boiling points, for thermal processes, or osmotic pressures, for membrane processes for high TDS streams. Such waters have been traditionally desalinated or concentrated using thermal processes such as multi-effect distillation, falling-film evaporators, or mechanical vapor compression [11,27–30]. However, thermal processes are relatively expensive and highly energy intensive (> 30 kWh/m³) [23]. Recently, non-thermal membrane desalination has been suggested for the treatment of high salinity

wastewater, including high-pressure reverse osmosis (HPRO) and osmotically assisted reverse osmosis (OARO) [31–34]. As shown in Fig. 1, the HPRO process allows for treating salinities ranging between 70 g/L to ~120 g/L. However, HPRO requires operating at elevated hydraulic pressures to overcome the hypersaline PW osmotic pressure. The high-pressure requirement by the HPRO might in some cases restrict the process applicability due to membrane pressure tolerance [35]. Several recent studies have demonstrated the substantial reduction in membrane performance due to compaction [35]. A study by Anvari et al. [36], focused on assessing the viability of HPRO processes in concentrating feedwaters up to 250 g/L, concluded that the development of pressure-resistant membranes is crucial for expanding the boundaries of HPRO commercial application. On the other hand, OARO is a unique membrane process that fills in the energy gap between the conventional RO and thermal evaporative processes. The process overcomes challenges associated with excessive pressure requirements while simultaneously treating high TDS waters of up to ~200 g/L [37–41]. The OARO process features two saline solutions of similar osmotic pressure subjected to both sides of the RO membrane, referred to as “feed” and “sweep”. The main function of the saline sweep solution is to reduce the osmotic pressure differential across the membrane which results in lowering the required RO feed pumping energy. In other words, upon feeding identical salinity solutions on both sides of the membrane, the osmotic differential across the membrane would be minimum, hence water permeation will solely be dependent on the applied pressure and not the initial concentration of the feed. This makes the OARO process applicable for concentrating high salinity wastewaters without requiring operation at extreme pressures [14,37,42,43].

Research studies assessing OARO for brine concentration have been focused on theoretical modeling and performance predictions [39,42–47], investigation of OARO practical application via bench and/or pilot scale tests [37,38,48–52], and membrane development or optimization to address mechanical stability, structural parameters, and external/internal concentration polarization [38,48,53]. However, similar to other membrane-based processes, development of effective pretreatment strategies to prevent membrane fouling is crucial for minimizing constraints on achievable recoveries and enabling cost effective application [54–56]. Existing OARO studies were found to be mostly focused on the use of either synthetic solutions or pretreated seawater with limited data available on real industrial wastewater. Although insights on the fouling behavior of inorganics and/or selected model organics were provided [57,58], the behavior and impact of complex organic constituents, typically present in real wastewater, on the OARO performance remain underexplored. Furthermore, data regarding the generated water quality and implications for beneficial reuse were found to be lacking. A recent pilot study by Houghton et al. [35] investigated one OARO configuration using a hypersaline PW (TDS = 133 g/L) from the Permian Basin. Although several pretreatment technologies were considered to avoid impacting the process performance, the study concluded that additional pretreatment is still required to enhance the process efficiency. Also, details on the applied pretreatment efficiency and associated impacts on membrane fouling were found to be inadequately demonstrated. Therefore, this study focused on addressing key research gaps associated with facilitating the OARO

industrial application for desalinating hypersaline PW via presenting a systematic evaluation of pretreatment requirements, membrane organic fouling potential, membrane cleaning efficiency, and product water quality for reuse. Specific objectives were defined to highlight the novel aspects of the study which include:

- Characterizing the organic constituents of real hypersaline PW samples from an oil and gas production operation.
- Assessing the efficiency of several pretreatment technologies with focus on enhancing the removal of organic constituents.
- Evaluating membrane performance, fouling potential, and chemical cleaning efficiency through bench scale RO tests conducted at relevant industrial conditions.
- Generating preliminary product water quality data and discussing potential for reuse applications.

2. Materials and methods

2.1. Analytical & characterization methods

Multiple analytical and characterization techniques were applied for the comprehensive analysis of PW quality, assessment of pretreatment efficiency, and evaluation of membrane fouling.

2.1.1. Basic analytical methods

pH and conductivity were analyzed using an Orion 3 Star meter. Dissolved ions and total elemental content were measured using Ion chromatography (ICS 6000, Thermo Scientific) and inductively coupled plasma (5900 SVDV, Agilent), respectively. Dissolved organic carbon (DOC) and inorganic carbon were analyzed by a combustion method using a TOC Analyzer, TOC-V, Shimadzu. Total oil and grease (TOG) content was measured by Horiba extraction methods (US EPA test method 413.2 solvent) using OCMA-350 spectrophotometer. Hach turbidimeter was used for turbidity measurements. DR6000 UV VIS Spectrophotometer by Hach was used for ammonium analysis (Ammonia TNT 831, Hach).

2.1.2. Advanced characterization

For in-depth analysis of DOC, the Thermo Scientific Dionex Integrion high-pressure ion chromatography (HPIC) system (Dionex IonPac ICE-AS1) coupled with a Dionex™ AS-DV Autosampler and suppressed conductivity detection was applied for organic acid analysis. Other advanced tools also included Fourier transfer infra-red (FTIR) and

scanning electron microscope (SEM) analyses, which were applied to study the surface morphology and properties of the RO membrane.

2.2. Feedwater samples

2.2.1. PW samples

PW samples, referred to as PW 1 and PW 2, from unconventional O&G operations in the Permian Basin were collected. The samples, collected from different locations, were characterized upon receipt and stored in a refrigerated environment at 4 °C to avoid changes in chemical composition. Water quality analyses were also conducted prior to each assessment for quality assurance and control. A summary of the average initial PW quality, based on three analytical measurements per PW (i.e., $n = 3$), is presented in Table 1. For salinity (i.e., TDS), it ranged between ~80,000 for PW 1 up to ~120,000 mg/L for PW 2. The PW samples

Table 1

Average quality of PW samples, based on three analytical measurements per PW ($n = 3$).

Parameter	Unit	PW 1	PW 2
pH	–	6.7 ± 0.2	6.7 ± 0.1
Conductivity	ms/cm	124 ± 4	142 ± 15
Alkalinity	mg/L as CaCO ₃	299 ± 1	250 ± 6
Turbidity	NTU	240 ± 7	214 ± 5
UV254	–	0.312 ± 0.005	0.166 ± 0.005
TDS	mg/L	85,483 ± 2305	112,259 ± 1417
DOC	mg/L	127 ± 6	47 ± 6
TOG	mg/L	113 ± 1	191 ± 57
Bicarbonate (HCO ₃ ⁻)	mg/L	163 ± 1	234 ± 5
Chloride (Cl ⁻)	mg/L	52,319 ± 437	68,374 ± 927
Sodium (Na ⁺)	mg/L	28,745 ± 210	37,272 ± 1179
Bromide (Br ⁻)	mg/L	459 ± 3.4	504 ± 12
Potassium (K ⁺)	mg/L	517 ± 15	617 ± 14
Calcium (Ca ²⁺)	mg/L	2615 ± 136	3329 ± 23
Magnesium (Mg ²⁺)	mg/L	324 ± 16	475 ± 50
Sulfate (SO ₄ ²⁻)	mg/L	370 ± 3	75 ± 8
Ammonium (NH ₄ ⁺)	mg/L	514 ± 23	688 ± 9
Barium (Ba)	mg/L	2.2 ± 0.3	29 ± 1
Lithium (Li)	mg/L	22 ± 1	37 ± 1
Iron (Fe)	mg/L	17 ± 1	21 ± 3
Manganese (Mn)	mg/L	0.40 ± 0.2	0.53 ± 0.05
Strontium (Sr)	mg/L	527 ± 15	1085 ± 47
Boron (B)	mg/L	104 ± 0.5	76 ± 1
Silicon (Si)	mg/L	22 ± 5	16 ± 1
Acetic acid	mg/L	198 ± 4	65 ± 7
Propionic acid	mg/L	15 ± 3	<0.1

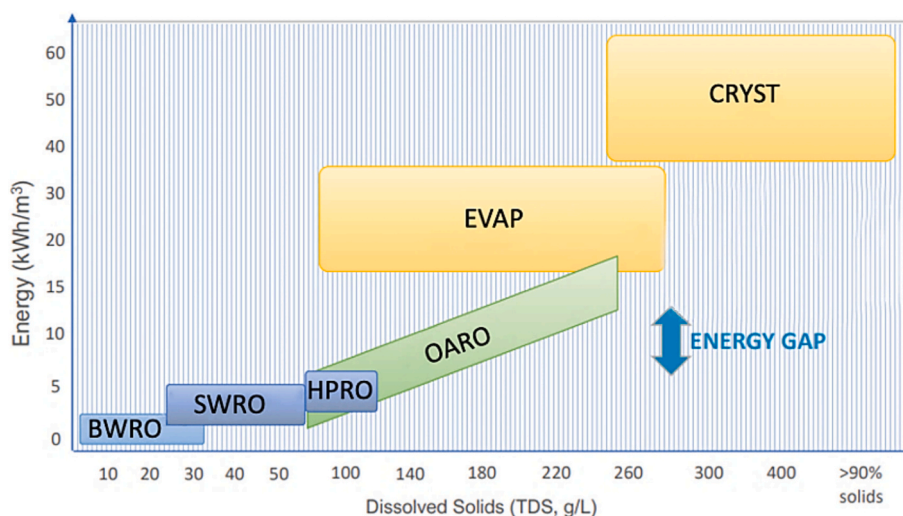


Fig. 1. Comparison of saline water treatment technologies in terms of energy consumption and feedwater TDS including brackish water RO (BWRO), seawater RO (SWRO), HPRO, OARO, evaporators (EVAP) and crystallizers (CRYST) [59,60].

showed similar pH values, close to the neutral range, at ~ 6.5 . Hardness levels were found to exceed 6000 mg/L CaCO_3 , which classifies both PW samples as “very hard” [61]. Organic content, in terms of DOC, differed between PW 1 and PW 2. The average DOC content in PW 1 was measured at ~ 127 mg/L, whereas PW 2 showed ~ 42 mg/L. Deviation in the PW DOC content can be attributed to the location, geological formation, and hydrocarbon type. Most of that DOC was confirmed to come from organic acids, primarily acetic acid (representing ~ 60 – 65 % of total DOC). Other organic acid constituents such as formic and butyric acids were found to be close to detection levels (i.e., <1 %). Differences in average concentrations of several elements (e.g., strontium, iron, lithium, and manganese) and ions (e.g., chloride, sodium, ammonium, magnesium, sulfate, calcium, and barium) were also observed. In most cases, except for sulfate, boron, and silicon, PW 2 was found to contain higher ionic fractions than PW 1. Other not reported constituents were either close to detection levels or not analyzed.

2.2.2. Synthetic solutions

Synthetic solutions were also used in selected membrane fouling evaluations for optimization and benchmarking purposes. Synthetic NaCl solutions at $\sim 40,000$ mg/L and synthetic produced water (SPW) solutions mimicking the composition of real PW were tested. The NaCl solutions were primarily used for the benchmark tests as a performance “Baseline”. For the SPW solutions, they were utilized for assessing fouling impacts of specific constituents in the PW. This technique was adapted to aid in focusing the fouling tests, performed using real PW, on evaluating organic membrane fouling. Two SPW recipes were formulated based on the attained pretreated PW quality. SPW 1, to only mimic the inorganic fraction in the PW (i.e., no organics), and SPW 2 to target a known fraction of organics while maintaining a similar inorganic matrix to SPW 1. This strategy will allow for using the real PW to evaluate fouling caused by unidentified organic species.

2.3. Pretreatment technologies

Various technologies were considered for PW pretreatment. The selection was based on several considerations, including the type of contaminants in PW as well as the applicability range and efficiency of the pretreatment technology. Typically, conventional pretreatment technologies applied for RO can include coagulation- flocculation, media

filtration, dissolved air flotation (DAF), lime/soda ash softening, ozonation, membrane processes (microfiltration (MF), ultrafiltration (UF), nanofiltration (NF)), biological processes, and adsorption/ion exchange (IX) [62]. Depending on several factors including feedwater quality, reuse application, cost, and others, a sequence of pretreatment technologies is applied to sustain the RO operation. In this study, a combination of sequential physical and/or chemical processes targeting different pretreatment levels (i.e., primary to advanced) was selected for qualification on hypersaline PW. Test protocols were developed and/or optimized to assess the pretreatment efficiency, which was verified via water quality analyses performed before and after each treatment step. Fig. 2 describes the selected technologies which included:

2.3.1. Chemical coagulation

Chemical coagulation is one of several primary methods applied for the removal of suspended solids and oils from PW [63]. Tests were performed using a Platypus 4G Jar Tester (Australian Scientific Pty). Iron III chloride (FeCl_3 , >97 % purity, Merck) was used as a coagulant. Previously, optimization tests were conducted by assessing the impact of coagulant dosage on the removal efficiency. Dosages between 120 and 500 mg/L were tested with pH adjustment to 8.5, mixing speed of 200 rpm for 15 min, and finally settling time of 2 h, as developed in earlier studies [64,65]. The supernatant was then collected and analyzed to assess DOC, turbidity, & Fe removal efficiencies. A coagulant dosage of 200 mg/L was determined optimum based on obtained removal efficiencies.

2.3.2. Softening and MF

Softening was applied targeting the removal of hardness. Water hardness typically originates from the existence of cations like calcium and magnesium. Conventional methods applied for water softening primarily involve chemical precipitation. Commonly used chemicals are lime (calcium hydroxide) or caustic and soda ash (sodium carbonate). The PW used in this study has both carbonate and non-carbonate (dominant) types of hardness. Therefore, the chemical treatment required the presence of two components: hydroxyl ions (OH^-) to raise the pH and remove carbonate hardness and carbonate ions to remove the non-carbonate hardness. In this study, sodium hydroxide (NaOH) and sodium carbonate monohydrate (SCM) were used for the PW softening treatment. As verified with OLI Systems [66], while calcium

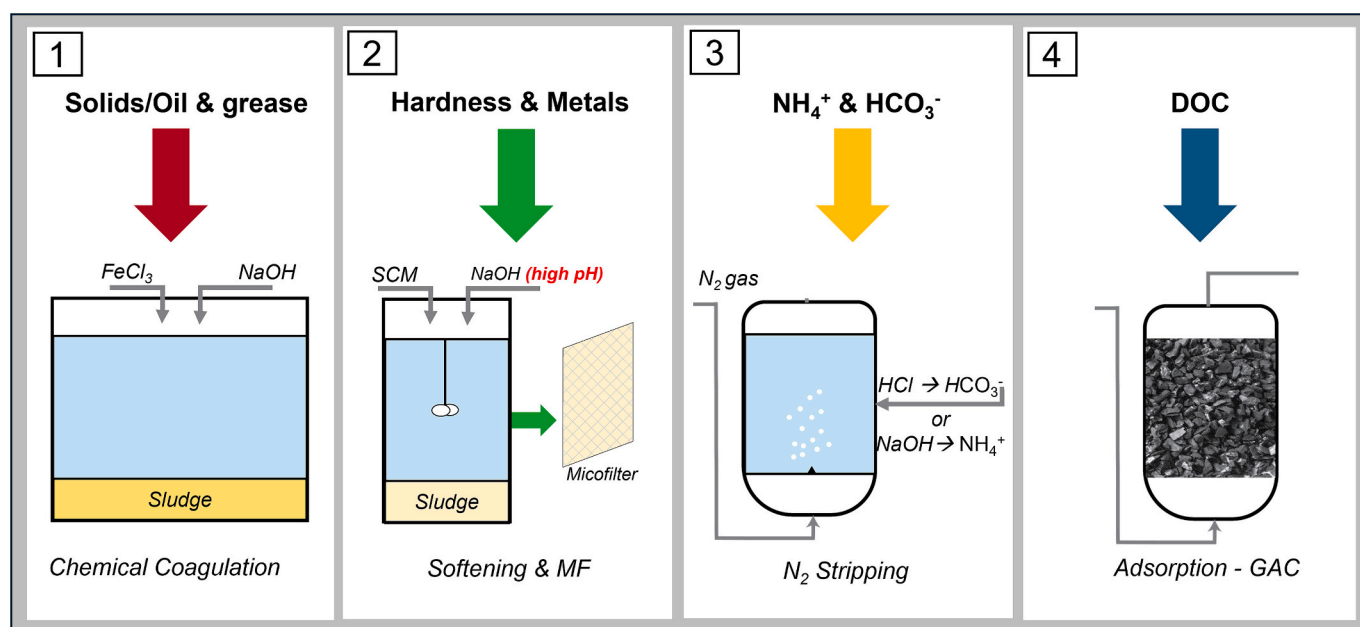


Fig. 2. A diagram depicting the PW target contaminants (top) and the corresponding applied pretreatment technologies (bottom).

carbonate precipitation occurs at pH \sim 9–9.5, waters with high magnesium content require pH above \sim 11 for the precipitation of magnesium hydroxide [67]. Accordingly, 5 M NaOH solution was used to raise the PW pH to \sim 11.5–11.8. Based on the measured hardness levels in the PW and theoretical softening reactions [68], required amounts of SCM were calculated as \sim 9000 mg/L for PW 1 and \sim 12,500 mg/L for PW 2. After adding SCM to the PW, the mixture was stirred for 45 min using the Platypus 4G Jar Tester. Samples were then allowed to settle for 1–2 h before applying MF under vacuum (Nylon, 0.45 μ m, Sterlitech) on the supernatant.

2.3.3. Stripping

Removal of NH_4^+ and HCO_3^- was achieved via pH adjustment followed by stripping using nitrogen (N_2) gas (Nitrogen Gas Generators, LNI). Removal of excess HCO_3^- was applied to eliminate scale formation contributors and consequently prevent RO membrane fouling. Although NH_4^+ salts are quite small and less likely to cause RO membrane scaling, their levels in treated effluents are strictly monitored and regulated for specific reuse applications [69]. RO NH_4^+ rejections are pH dependent. At high pH, ammonia gas (NH_3) is prevalent, and being a gas, will not be rejected by the RO. At low pH, the prevalent ion is NH_4^+ , which is then rejected by the RO [69]. Based on that, it is also of vital importance to evaluate the NH_4^+ removal efficiency and associated effects on RO performance. Effluent PW from the softening-MF step would be at high pH (\sim 11.5). At these alkaline conditions, NH_4^+ will deprotonate to volatile NH_3 gas, which can be then stripped by bubbling N_2 gas [70]. N_2 gas bubbling was applied at high intensity for 24 h, which was determined based on the achieved removal efficiency from multiple experimental trials. Removal efficiencies were measured via analyzing treated samples for NH_4^+ content. Similarly, close to neutral pH, HCO_3^- ions will be present in the water, while at low pH (i.e., < 6) HCO_3^- ions will be in the form of carbon dioxide (CO_2) [71]. Therefore, the PW pH was then lowered to \sim 5 using a 6 N HCl solution. The samples were purged again using N_2 gas for 1–2 h. HCO_3^- removal efficacy was verified via inorganic carbon analysis. An indication of CO_2 removal was also evident via an increase in pH to \sim 7–8. In terms of DOC, as the solubility of some organics is pH dependent, this treatment step is expected to contribute to partial DOC removal, which may include volatile organics and/or other insoluble organic species at low pH conditions [70].

2.3.4. Adsorption

Organic fouling is a major concern limiting RO performance. While inorganic and biological fouling can be typically managed using chemicals, organic fouling on the other hand is managed by pretreatment [72]. The industry-standard absorbent granular activated carbon (GAC) was applied targeting the removal of organics from PW. Attributed to its surface hydrophobic properties, GAC treatment is expected to mostly target the hydrophobic-type organic species present in the PW [73–75]. Minimal impact on the hydrophilic organic fraction, such as organic acids, is anticipated. A fixed-bed column setup was built consisting of three main parts: feed pump and tank, column, effluent collection. To prevent corrosion issues, Perfluoro alkoxy (PFA) tubing and fittings were used. The column (PFA, Parker, diameter: 1.6 cm) height was fixed at \sim 40 cm. Feed PW was pumped through the column using a positive displacement pump (KNF, Switzerland) at a flowrate of 2 mL/min in a bottom to top flow direction. The adapted design and/or operating conditions will then allow for operating an empty bed contact time (EBCT) of 40 min, which is within typical EBCT ranges applied for GAC [73,75,76]. First, weighed amounts of glass wool (\sim 80 mg) were placed at the bottom and top column fitting parts to hold the media in place. For GAC preparation, the media was initially sonicated in deionized (DI) water for 0.5 h (Basis: 5–6 cycles for every 10 g media/250 mL DI water) and then dried at 105 $^\circ\text{C}$ for 4 h. Media sieving (USA standard test sieve, Cole Parmer) was performed to obtain a specific size range and prevent pressure build up in the bed by fine particles. A mixture of 14 mesh (40 %) and 16 mesh (60 %) sizes was used [75]. GAC was then loaded to the

column. The bed was first flushed with DI water for 24–48 h to dissolve air bubbles/gaps within the bed and confirm minimal release of residual organics from the GAC bed (i.e., effluent DOC < 1 mg/L). After that, the operation was switched to PW treatment mode. Effluent samples were collected automatically at different time intervals to assess DOC removal and column breakthrough. The sampling at specific time intervals was accomplished via Open Manipulator P from Robotis. (ROS, Open-Source Robotics Foundation, USA) controlled with a custom-made C++ code [75,77].

2.4. RO testing for membrane fouling evaluation

An RO test protocol was developed to assess the efficiency of PW pretreatment and the expected product water quality. In Fig. 3, a typical staged OARO system, crossflow reverse osmosis (CFRO) with brine reflux [13,39,42], for concentrating PW from \sim 100 to \sim 200 g/L is shown. This mode involves applying three CFRO stages and one RO stage. The integration of an RO stage is crucial to help increase process efficiency/viability and allow for generating clean water for reuse applications. Initially, the 2nd CFRO stage will receive the feed PW coming at \sim 100 g/L and the sweep PW at 150 g/L (from 3rd CFRO stage). The feed will be concentrated, and the sweep will be diluted. Similarly, the 3rd CFRO stage will use a 150 g/L feed coming from stage 2 with a recycled 200 g/L PW sweep. The 1st stage will take the 100 g/L sweep from stage 2 and a 60 g/L RO brine as the feed. Finally, the sweep solution exiting the 1st CFRO stage will be at \sim 40 g/L, which is within the operable salinity range of a conventional RO. The objectives of this study involve assessing the saline PW pretreatment efficiency, the membrane fouling tendency, and the generated product water quality. Thus, mimicking the RO stage will provide initial understanding on the minimum PW pretreatment requirements as well as generate product water quality data while operating at moderate pressures. It will also aid in identifying fatal flaws related to RO membrane fouling and operation. Therefore, a test setup and procedure were designed targeting the RO stage in the CFRO system under relevant industrial conditions.

2.4.1. RO bench scale setup

A custom-built bench set-up was used for this evaluation (Fig. 4). The unit consists of a high-pressure pump (Hydracell, USA), membrane cell (Sterlitech, USA), water bath (Julabo, Germany) and feed tanks (Sterlitech, USA) connected in a closed loop. All the wet parts under pressure (pump, membrane cell, heat exchanger) are made of Hastelloy (alloy C-276) to prevent corrosion due to the high salinity of the feed stream. Commercial thin-film composite RO membranes (SWC5, Hydranautics)

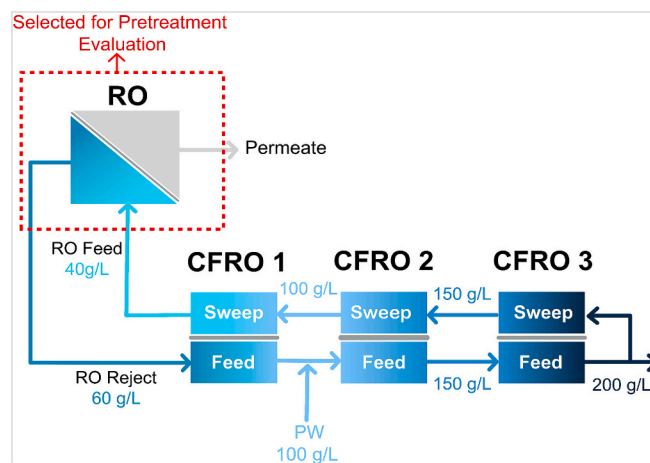


Fig. 3. A schematic of a typical OARO configuration, a staged CFRO system. The figure highlights the RO stage being targeted in the study for pretreatment, membrane fouling, and product water quality evaluation.

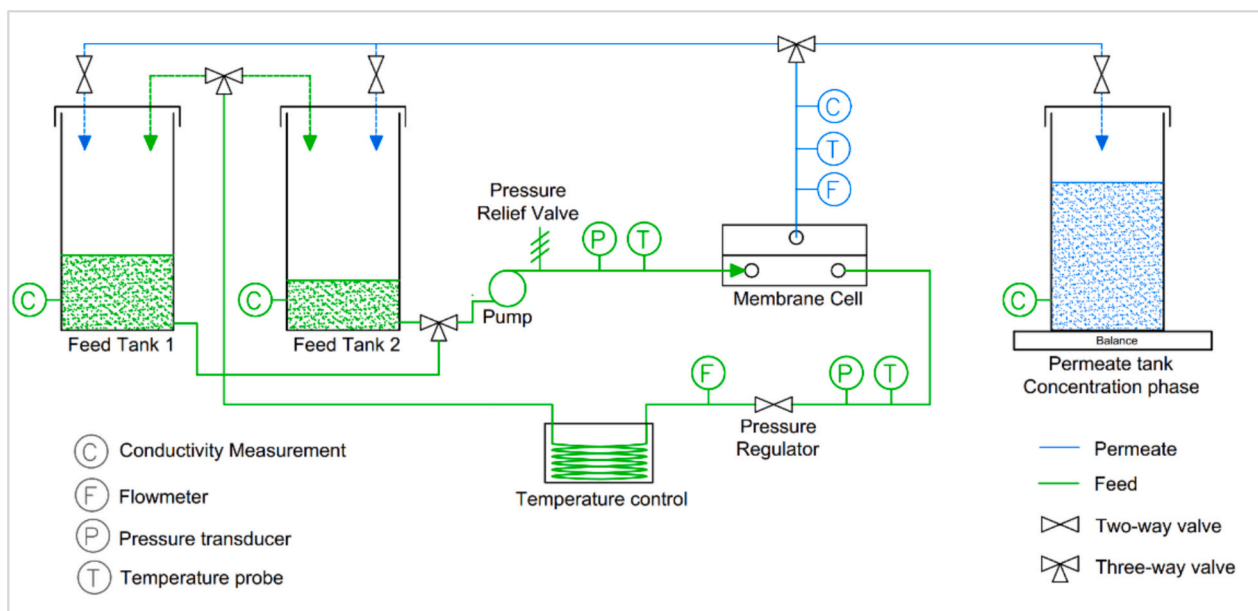


Fig. 4. RO bench scale test setup diagram.

were applied for testing. In terms of piping material, Hastelloy pipes were deployed for the high salinity pressurized feed side, and PFA tubing were used for the low salinity and pressure permeate side. The unit is controlled through a LabVIEW Compact RIO system (NI, USA) which can maintain the feed flowrate constant using a proportional-integral-derivative (PID) controller. The PID reads the flowmeter data and adjusts the revolution per minute (RPM) of the pump to reach the target flowrate. For pressure control, a second PID controller is used; this PID gets feedback from the pressure sensors to automatically adjust a back pressure regulator using a Dynamixel actuator (Robotis, South Korea). The unit can run on two operating modes: recirculation and concentration. During recirculation mode, the permeate is sent back to the feed tank. During concentration mode, the permeate is collected in a separate tank and the cumulative weight is monitored using an analytical balance (Mettler Toledo) to determine the feed concentration factor. For both operating modes, the permeate flow is measured through a liquid flowmeter (Sensirion, Switzerland) installed at the outlet of the cell. To avoid depressurizing the system while changing between the baseline and feed solutions, two inline feed tanks were installed with isolation valves to allow switching of the solutions. During operation, key operational parameters, feed and permeate conductivity, temperatures, pressures, and water flux were recorded as function of time.

2.4.2. RO test procedure

Fig. 5 depicts the developed RO test protocol steps. To mimic the RO operation within the CFRO staged system (Fig. 3), the pretreated PW samples were diluted with DI water to a target salinity of ~ 40 g/L (within RO operable salinity limit). Accordingly, PW 1, with TDS of ~ 85 g/L, was diluted by $\sim 50\%$, while PW 2, with TDS of ~ 112 g/L, was diluted by $\sim 65\%$. The dilution using DI water is consistent with the CFRO system operation (Fig. 3) at which only pure water permeates through the membrane causing the dilution of the sweep solution (feed to RO). First, the RO membrane was compacted for 24 h using DI water at ~ 52 bar until stable water flux is achieved. Dosages of antiscalant (5.5 mg/L) and biocide (3.7 mg/L) chemicals were used throughout testing for scaling and biological fouling inhibition, respectively [72]. The test protocol, applied for both the synthetic and real solutions, involved six steps operated at a pressure of ~ 52 bar:

- Step 1: an initial baseline test was conducted using a NaCl solution at 40 g/L in recirculation mode until stable flux was achieved.

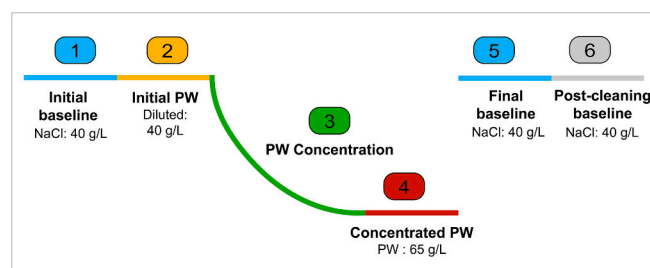


Fig. 5. RO bench scale test protocol steps, presented in terms of membrane permeability. All test steps were operated at ~52 bar in presence of biocide (3.7 mg/L) and antiscalant (5.5 mg/L). Pretreated PW is treated by RO: first an initial baseline test (NaCl, TDS:40 g/L). Then in Step 2, the initial PW test (TDS:40 g/L) is performed. This is followed by the PW concentration test in Step 3 (TDS: 40 to 65 g/L). Step 4 is the concentrated PW test (TDS:65 g/L) (showing lower permeability due to increased salinity). The final baseline test is performed in Step 5. After recirculating the cleaning solutions (citric acid followed by SDS + EDTA), a post-cleaning baseline test is performed in Step 6 (NaCl, TDS:40 g/L).

- Step 2: depending on their salinity (i.e., PW 1 or PW 2), the pretreated PW was first diluted using DI water to mimic the RO stage in the CFRO system, and then subjected to the membrane in recirculation mode. This step, performed using only the diluted conditions, was utilized for assessing possible immediate fouling scenarios (i.e., fatal flaw).
- Step 3: the pretreated PW was then concentrated to ~ 65 g/L via operating in concentration mode. This step was employed to study membrane fouling at concentrated conditions, mimicking the RO performance in the CFRO system.
- Step 4: the membrane was then subjected to the concentrated PW quality at ~ 65 g/L at recirculation mode until stable flux was achieved.
- Step 5: a final baseline test was performed and compared to the initial baseline. Differences between the initial and final baseline tests were exploited as indicators of membrane fouling.
- Step 6: a post-cleaning baseline was conducted to determine the total membrane flux recovery due to chemical cleaning. Standard RO chemical cleaning protocols, recommended by membrane vendors

[78], were applied for membrane cleaning and flux recovery under no pressure. The standard RO protocol included two chemical cleaning stages. First, a low pH stage targeting inorganic fouling using a 2 % citric acid solution recirculated for 30 min. After an NaCl baseline (like step 1), the second cleaning step was applied at high pH targeting organic fouling by recirculating a 0.025 % sodium dodecyl sulfate (SDS) and 0.8 % ethylenediaminetetraacetic acid (EDTA) solution at pH of 11 for 30 min. Although this is a commercially applied standard procedure, it is merely effective for certain types of foulants at specific operating conditions [79].

The RO test results, obtained as water permeability/flux in L/m².h (LMH), were normalized by driving force and reported as LMH/bar. The driving force (bar) reflected the difference between the applied hydraulic pressure and the osmotic pressure. Osmotic pressures were estimated using OLI Systems [66] based on measured conductivity. Additionally, mass balance calculations, using concentrations and volumes of the RO feed, permeate, and reject, were carried out to elucidate the fouling mechanism.

3. Results and discussion

3.1. Pretreatment evaluation

3.1.1. Pretreatment schemes

As shown in Fig. 6, three PW pretreatment levels were developed: level I, level II, and level III. Each level targeted the removal of specific contaminants, generating different pretreated water qualities for subsequent membrane fouling assessment. Level I involved bulk removal of oils, suspended solids, and hardness (i.e., Ca and Mg) achieved via application of chemical coagulation, softening, and MF. The removal of hardness is key for RO operation and membrane performance to prevent inorganic fouling caused by scale formation. Level II included an additional two-stage N₂ stripping, first at high pH for NH₄⁺ removal, and then at low pH for HCO₃⁻ removal. The removal of HCO₃⁻ will further reduce risks of membrane fouling due to scale formation. Significant levels of NH₄⁺ were detected in the PW samples. Evaluating NH₄⁺ removal under pretreatment will allow for assessing its removal efficiency and impact on final RO permeate quality (i.e., for reuse applications). Additionally, as the solubility of some organics is pH dependent, the pH adjustment/stripping step is expected to contribute in partial DOC removal, which may include volatile organics and/or other insoluble organic species at low pH conditions [70]. Finally, level III targeted enhanced removal of organics, particularly hydrophobic organic carbon (HOC), via application of GAC adsorption. HOC compounds are usually considered a major concern impacting RO operation and membrane lifespan. With GAC targeting HOC, performance data obtained from level II and level III pretreatment will allow for assessing the fouling propensity attributed to HOC. Pretreatment and RO evaluations were initially carried out on PW 1, possessing higher DOC content than PW 2, while PW 2 was later tested

for validation purposes.

3.1.2. Pretreatment efficiency results

3.1.2.1. Inorganics. The assessment of efficiency for the three developed pretreatment levels was divided into two categories: inorganics, and organics. Table 2 summarizes the removal efficiencies achieved for selected inorganic constituents in PW 1. All pretreatment levels realized >99 % removal of turbidity and other high fouling potential species like Ca, Mg, Fe, and Mn. Also, ~99 % removal was achieved for Sr, and Ba, and ~84 % for Si. Lower removals of ~19 % were obtained for B. Although high pH conditions were provided, effective boron removal requires applying other treatment technologies such as ion exchange or RO at high pH conditions [80,81]. level II pretreatment, involving stripping at high followed by low pH conditions, exhibited improved removals of NH₄⁺ up to 99 % and HCO₃⁻ up to 97 %. Similar inorganic removal performances were obtained for level II and level III pretreatments since they only differed in terms of organics removal (i.e., due to GAC adsorption). As expected, removals of <5 % were realized for Na, Cl, K, SO₄²⁻, and Li since they were not targeted by applied treatment technologies.

3.1.2.2. Organics. The second category for the assessment of pretreatment efficiency included organics removal. In this study, different strategies were adapted to manage membrane fouling. While inorganic fouling was controlled by using antiscalants, biofouling was managed by

Table 2

Summary of the removal efficiencies for different pretreatment levels obtained for selected inorganics in PW 1.

Parameter	Unit	Feed (PW 1)	Pretreatment Removal %		
			Level I	Level II	Level III
Turbidity	NTU	240 ± 7	>99 %	>99 %	>99 %
Ca	mg/L	2615 ± 136	>99 %	>99 %	>99 %
Mg	mg/L	324 ± 16	>99 %	>99 %	>99 %
Fe	mg/L	17 ± 1	>99 %	>99 %	>99 %
Mn	mg/L	0.4 ± 0.2	>99 %	>99 %	>99 %
Sr	mg/L	527 ± 15	99 %	99 %	99 %
Ba	mg/L	2.2 ± 0.3	99 %	99 %	99 %
NH ₄ ⁺	mg/L	514 ± 23	17 %	99 %	99 %
HCO ₃ ⁻	mg/L	163 ± 1	N. a. ¹	97 %	97 %
Si	mg/L	22 ± 5	84 %	84 %	84 %
B	mg/L	104 ± 0.5	19 %	19 %	19 %
Cl	mg/L	52,319 ± 437	<2 %	<2 %	<2 %
Na	mg/L	28,745 ± 210	<2 %	<2 %	<2 %
K	mg/L	517 ± 15	<2 %	<2 %	<2 %
Br	mg/L	459 ± 3.4	<2 %	<2 %	<2 %
SO ₄ ²⁻	mg/L	370 ± 3	<2 %	<2 %	<2 %
Li	mg/L	22 ± 1	<2 %	<2 %	<2 %

N.a.: Not applicable. Excess bicarbonate was added to the PW to enhance softening. Removal of bicarbonate was achieved by stripping (Levels II and III).



Fig. 6. Pretreatment levels tested in the study: level I, level II, and level III.

using biocides, in addition to the PW high salinity which can to some extent limit bio-growth. Managing organic fouling, however, can only be achieved via adequate pretreatment [72]. Water quality is a key component in the process of developing optimum pretreatment strategies. Fig. 7 shows a graphical representation of the organics in PW 1, in terms of DOC, prior to pretreatment. With a total DOC of 127 mg/L, the HPIC results on PW 1 confirmed the presence of considerable concentrations of acetic acid (~65 % of total DOC) and some propionic acid (~3.7 % of total DOC). In the figure, this DOC fraction, representing organic carbon from acetic and propionic acids, was referred to as “Organic acids”. The remaining DOC was considered as “unidentified DOC”. The unidentified DOC comprised of other fractions including but not limited to HOC and other hydrophilic components (e.g., neutrals, humics, and others), as elaborated by Dr. Huber [74,82,83]. Previous studies have investigated the fouling propensities of organic acids, specifically acetic acid, and other neutral species. Due to factors involving their hydrophilicity, charge, or size, these compounds were found to exhibit low RO membrane fouling tendencies as compared to HOC [15,84–86]. The HOC compounds are considered a major concern for RO operation as they tend to adsorb and foul the membrane [87]. Therefore, the pretreatment evaluation in this investigation targeted reducing the “unidentified” fraction, containing HOC and exhibiting higher fouling potential, while simultaneously tracking the organic acids content.

Fig. 7 also compares test results for pretreatment level I, level II, and level III applied on PW 1. Focusing on the unidentified DOC fraction, from a total DOC of 42 mg/L in PW 1 (before pretreatment), level I achieved ~17 % removal down to 35 mg/L. For all pretreatment levels, analyses revealed negligible impact on the concentrations of organic acids (~85 mg/L). The data also showed that stripping, applied vigorously for extended durations at adjusted pH conditions, has contributed

to removing some organics. The DOC distribution for PW 1 after level II pretreatment showed a decrease in the unidentified DOC fraction down to 26 mg/L (~38 % removal). As highlighted earlier, these may represent volatiles and/or other insoluble organics under certain pH conditions. For level III, attributed to its inherited surface hydrophobic properties, GAC treatment further reduced the unidentified DOC fraction down to ~16 mg/L, predominantly targeting HOC species. Level III achieved the maximum unidentified DOC fraction removal efficiency at ~62 %. RO tests were then conducted to assess the three pretreated PW 1 qualities and compare their fouling propensities.

3.1.3. Performance comparison

In Table 3, the pretreatment removal efficiencies obtained were compared to other recently reported relevant pretreatment evaluations targeting membrane desalination. With focus on saline PW (i.e., TDS ~ > 100 g/L), the selected pretreatment train in this investigation, applied with few modifications for purposes of technology qualification for the targeted PW quality/application and improvement of removal efficiency for specific contaminants of concern, was found to be comparable to other studies while showing improved performances in few areas. In terms of inorganics, DAF or coagulation/flocculation were mainly considered. The current study showed enhanced removals (i.e., >99 %) for high fouling potential metals like Fe and Mn. Also, the applied pretreatment in this study involved softening which better reduced inorganic fouling risks via removing Ca, Mg, Si, Sr, and Ba. The study also assessed stripping for NH_4^+ removal to provide insights on treatment efficiency as well as achievable product water quality for reuse. >99 % removal for NH_4^+ was achieved via high pH stripping. For organics, the tested pretreatment uniquely targeted the removal of high molecular weight and/or HOC species, which are known to exhibit high RO membrane fouling tendency. Although a few studies investigated the

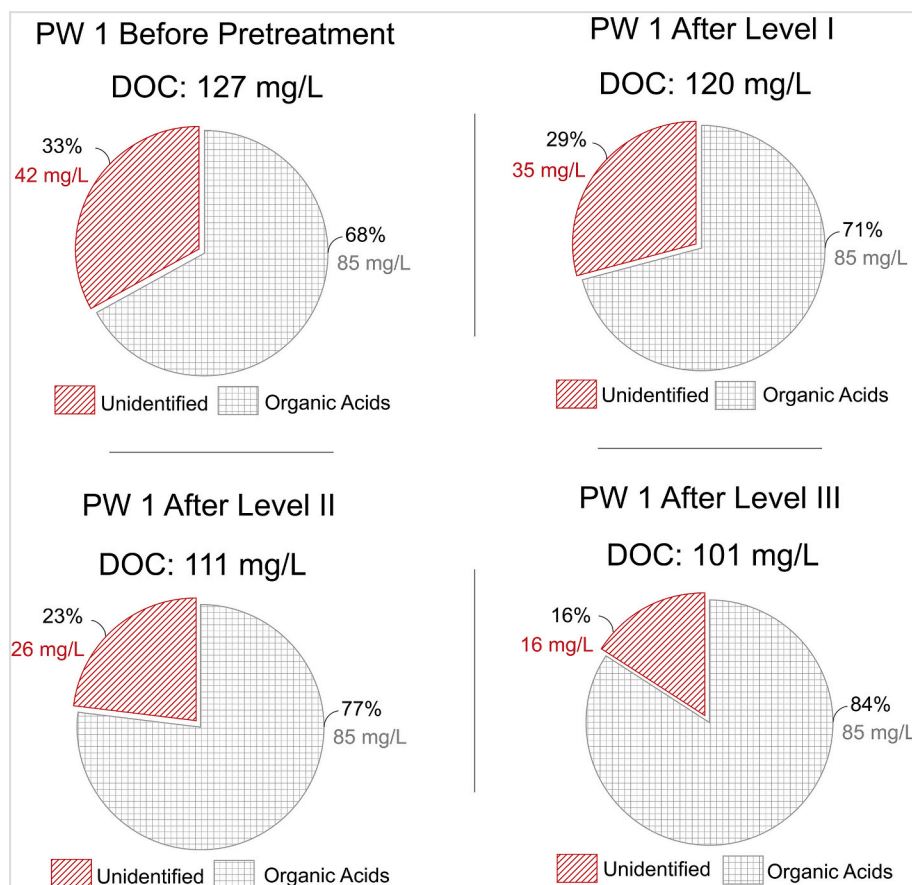


Fig. 7. PW1 DOC distribution before and after application of level I, Level II, and level III pretreatments.

Table 3

A comparison of pretreatment performance efficiency with published studies on saline PW samples.

Ref.	Wastewater	Pretreatment	Removal efficiency
This study	PW from the Permian Basin (TDS: 80–120 g/L)	<ul style="list-style-type: none"> – Coagulation – Caustic-soda ash softening – MF – N₂ Stripping – GAC adsorption 	Inorganics: maximum removals achieved > 99 % for turbidity, Ca, Mg, Fe, Mn ~ 99 % for Sr, Ba, and NH ₄ ⁺ ~ 84 % for Si ~ 19 % for B < 2 % for Li, Cl, Na, K, Br, and SO ₄ ²⁻ Organics: initial DOC = 127 mg/L ~ 17 % for coagulation + softening + MF ~ 38 % for coagulation + softening + MF + N ₂ stripping ~ 62 % for coagulation + softening + MF + N ₂ stripping + GAC Inorganics: maximum removals achieved > 99 % for Fe > 56 % for Zn > 36 % for P ~ 21 % for K < 15 % for B, Br, Na, Cl, S, Mg, Ba, Li, Ca, Ba, Mn, Sr, NH ₄ ⁺ Organics: initial DOC = 649 mg/L ~ 4 % for DAF ~ 8 % for DAF + ozonation ~ 36 % for DAF + ozonation + GAC ~ 95 % for DAF + ozonation + GAC+ aerobic degradation
[88]	Shale gas flowback water (TDS: 103 g/L)	<ul style="list-style-type: none"> – DAF – Ozonation – GAC adsorption – Aerobic degradation 	Inorganics: maximum removals achieved ~ 10–15 % for B, Ca, Mg, K, SO ₄ ²⁻ , and Sr < 10 % for Cl, Br, Na, and Mn Organics: initial DOC = 41 mg/L ~ 48 % for Coagulation/Flocculation ~ 83 % for Coagulation/Flocculation+ MBR ~ 91 % for Coagulation/Flocculation+ MBR + GAC + IX
[89]	PW from the Permian Basin (TDS: ~119 g/L)	<ul style="list-style-type: none"> – Coagulation/Flocculation – MBR – GAC adsorption – IX 	Inorganics: maximum removals achieved > 99 % for turbidity Organics: initial DOC = 100 mg/L ~ 73 % for DAF + Cartridge filter + PAC+ MF
[64]	PW from unconventional operations in the United States (TDS: ~314 g/L)	<ul style="list-style-type: none"> – DAF – Cartridge filtration (1 µm) – Powdered activated carbon (PAC) – MF 	

application of biological processes such as membrane bioreactors (MBR) for the removal of DOC, yet challenges associated with salinity impacting the microorganism viability and/or efficiency still require further optimization. It is worth mentioning that the applied biological treatment in the reported studies primarily targeted the removal of low molecular weight organics (known to possess low membrane fouling tendency).

3.2. RO membrane fouling evaluation

3.2.1. Benchmark tests

Selected preliminary RO tests were systematically performed using synthetic solutions to establish proper performance benchmarks for the organic fouling evaluation. To start with, a benchmark test using a synthetic NaCl feed solution (40 g/L), antiscalant, and biocide was conducted to condition and assess the stability of the developed test setup and experimental protocol. As shown in Fig. 8A, generated water flux data were plotted against experiment time for each of the test steps. Obtained membrane water fluxes were stable at ~12 LMH throughout the initial baseline and the initial feed conditions (operated at constant salinity – recirculation mode). Upon concentration (RO protocol: Step 3), the membrane permeability gradually decreased due to the increase in feed salinity, before stabilizing at ~4 LMH at the final feed salinity of 65 g/L. The difference between the initial and final baseline tests was used to assess membrane fouling. As expected, when compared to the initial baseline, the final baseline test showed a negligible drop in membrane flux (i.e., <1 %) upon the concentration of the NaCl solution. SEM images comparing the membrane surface morphology before and after testing are shown in Fig. 8B and Fig. 8C, respectively. The images show that the membrane surface morphology before and after testing is comparable, which is confirmation of maintained membrane integrity.

Two more benchmark tests using SPW solutions were conducted. While the study focused on assessing the fouling behavior of organics, it is of equal importance to initially establish a benchmark for the fouling

tendency of inorganics. The first test involved using SPW 1 solution at 40 g/L consisting of a multi-element composition mimicking level II or III pretreated PW 1. Level II or III were considered to account for all inorganics targeted by the applied pretreatment, including NH₄⁺ and HCO₃⁻. Consistent with the systematic benchmark testing approach, the second test used SPW 2 which targeted the organic acids fraction. SPW 2 comprised of multi-inorganics, like SPW 1, along with acetic acid which represented majority of the organic acids in PW 1. Likewise, the difference between the initial and final baseline tests was used to assess membrane fouling as compared in Fig. 9. Upon comparing the normalized baseline fluxes from the three benchmarks tests, NaCl, SPW 1 and SPW 2, comparable flux losses ranging between ~1–2 % were realized. These results confirm efficiency of the applied pretreatment in reducing fouling concerns associated with the inorganics. They also verify the minimal RO fouling contribution by organic acids, which allows focusing the real PW evaluation on the behavior of the unidentified DOC.

3.2.2. Organic fouling

3.2.2.1. Pretreatment screening. RO organic membrane fouling assessments were split into three parts. The first part involved performing a quick RO test including steps 1 & 2 only from the developed RO evaluation protocol. The test was conducted to determine the minimum PW pretreatment requirement and assess potential instant fouling scenarios. Fig. 10 compares the resulted RO membrane permeabilities, in LMH/bar, from applying level I (Fig. 10A) level II (Fig. 10B) and level III (Fig. 10C) on PW 1. As shown in Fig. 10 A, although the pretreated PW 1 quality was diluted by ~50 % (i.e., to lower the salinity to 40 g/L), the subjection of level I quality to the RO membrane resulted in immediate decline in permeability (~20 %). On the contrary, Fig. 10 B and Fig. 10 C show negligible decline (<1 %) in membrane permeability upon testing either level II or level III pretreated PW 1 qualities. Based on this, it was confirmed that at least level II pretreatment quality is required to

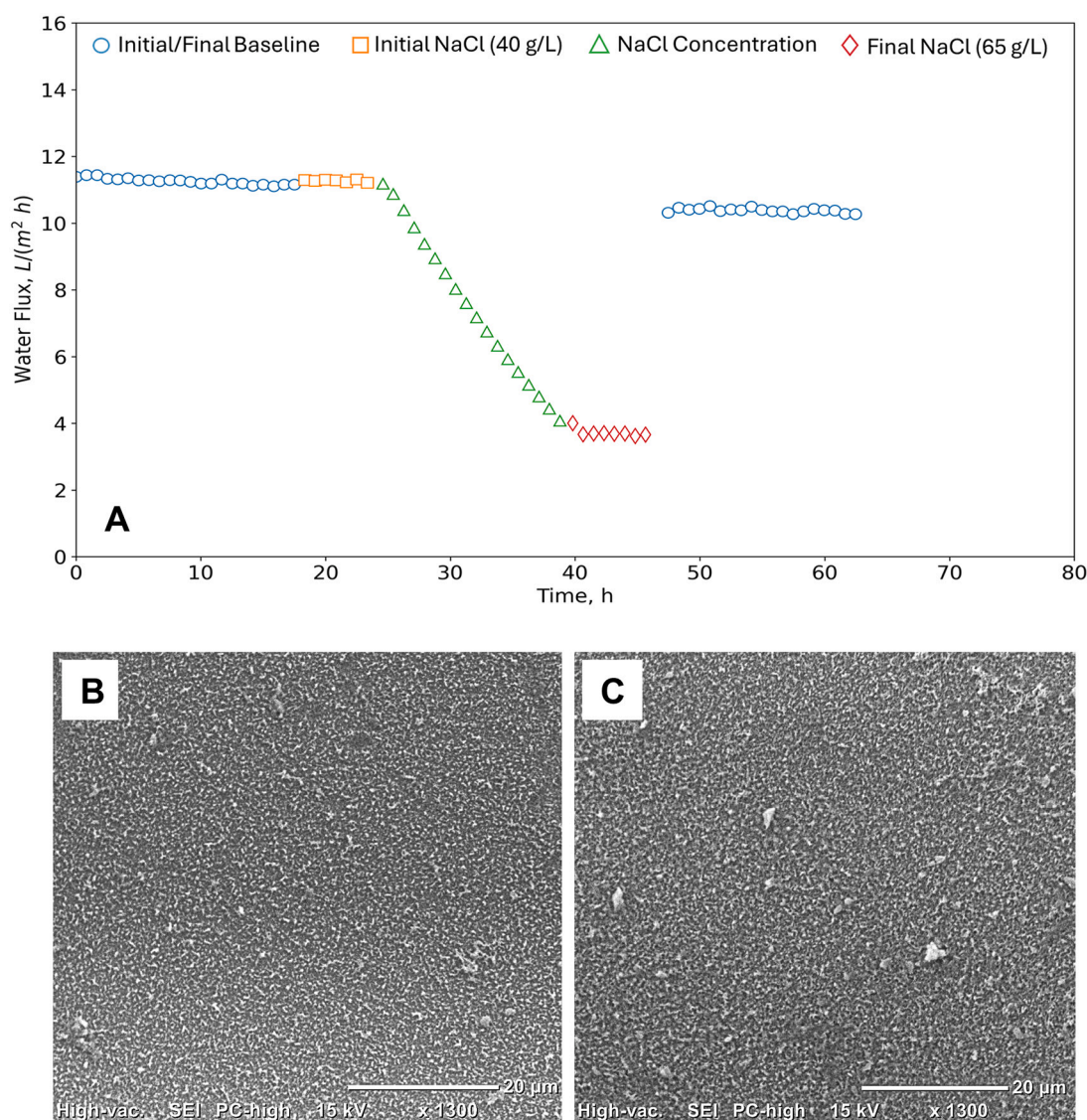


Fig. 8. A: Real-time flux data (LMH) for the NaCl synthetic solution test using the developed RO protocol (operated at ~ 52 bar), B: SEM image showing the surface morphology of the clean RO membrane (before testing), and C: SEM image showing the surface morphology of the RO membrane after testing.

prevent extreme scenarios of membrane fouling. The following full RO tests, involving the concentrated conditions of pretreated PW 1, were then conducted to compare the performance efficiency of pretreatment level II and level III.

3.2.2.2. Fouling evaluation on PW 1. The second part of the RO organic fouling assessment involved applying the six-step test procedure to evaluate the efficiency of pretreatment level II and level III. Different from the first part, in these tests the membrane will be subjected to both the initial and concentrated PW 1 qualities. Fig. 11 compares the obtained normalized water fluxes (LMH/bar) for the initial, final, and post-cleaning baseline tests. Results showed reductions of 8 % and 4 % in membrane permeability from operating level II and level III pretreated PW 1 qualities, respectively. Since fouling by inorganics and/or organic acids was ruled out via benchmark tests, the obtained data, specifically for level II scheme, confirm organic membrane fouling attributed to the “unidentified” DOC fraction. However, the PW fouling tendency was reduced with the application of level III pretreatment, involving enhanced DOC removal by GAC. Chemical cleaning for flux recovery was conducted on the tested membranes as shown in Fig. 11. Flux recovery was not achieved (i.e., irreversible organic fouling) as both

baseline fluxes, final and post-cleaning, were comparable. Fig. 12 shows results from FTIR analysis performed to inspect organic deposits/residual on the membrane surface after testing different pretreated PW 1 qualities. Obtained spectra for the clean/fresh, after level II, and after level III membrane samples were compared. With a focus on the C—H stretching represented by wavelengths ranging between 2850 and 3100 cm^{-1} , increased deposition of organics was detected on the membrane surface subjected to level II pretreated quality. Consistent with the RO test results, lowered C—H stretching intensities were observed for the membrane tested with level III pretreated quality. The data herein demonstrates the crucial role of pretreatment in minimizing organic membrane fouling as well as the need for developing alternative chemical cleaning procedures to improve flux recovery.

3.2.2.3. Fouling evaluation on PW 2. As shown in Fig. 13A, PW 2 possesses a lower DOC concentration, specifically for the unidentified fraction. Data generated on PW 1 quality showed that at least extensive levels of pretreatment (i.e., level III) are required to minimize RO fouling tendencies. Therefore, for data validation, PW 2 was used to assess the impact of initial water quality, specifically the unidentified DOC, on both the pretreatment efficiency and RO fouling propensity. Fig. 13B

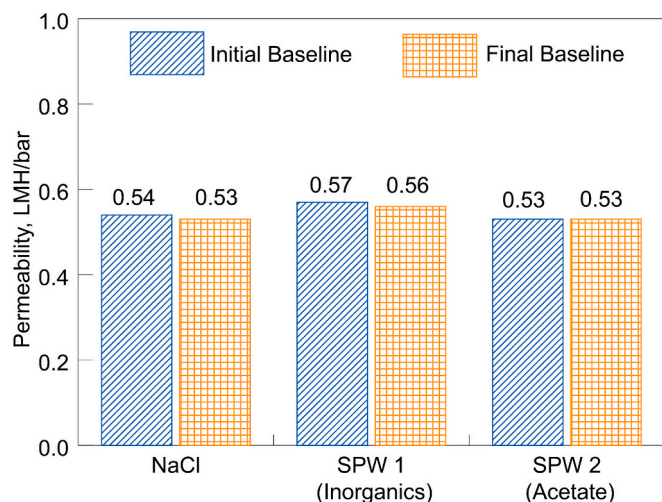


Fig. 9. Benchmark RO test results using synthetic solutions. SPW 1 mimicked the inorganic fraction of PW 1 (no organics), to test fouling by inorganics. SPW 2 mimicked the inorganic fraction of PW 1 along with acetate, to test fouling by organic acids.

presents PW 2 DOC distribution before and after application of level III pretreatment. Focusing on the unidentified DOC fraction, ~85 % removal was achieved down to a concentration of ~3 mg/L. Fig. 13C compares the obtained RO test results for level III pretreated PW 1 and PW 2. The lower DOC content of PW 2 allowed for assessing the impact of the unidentified DOC concentration on membrane fouling. The comparison between the initial and final baseline results for PW 2 showed a lower total flux loss of ~2 %, as compared to PW 1 at ~4 %.

The results emphasize the vital role of pretreatment in removing problematic organic species, like HOC, from the PW to sustain RO operation.

3.2.3. Organics fouling mechanism

Based on water quality results obtained from the pretreatment and RO testing, a fouling mechanism describing the behavior of the different DOC fractions present in the PW samples was elucidated. Table 4 shows the PW 1 RO water quality and mass balance summary comparing the pretreatment level II and level III. The mass balance results confirm the higher fouling tendency of level II PW quality, exhibiting a higher DOC

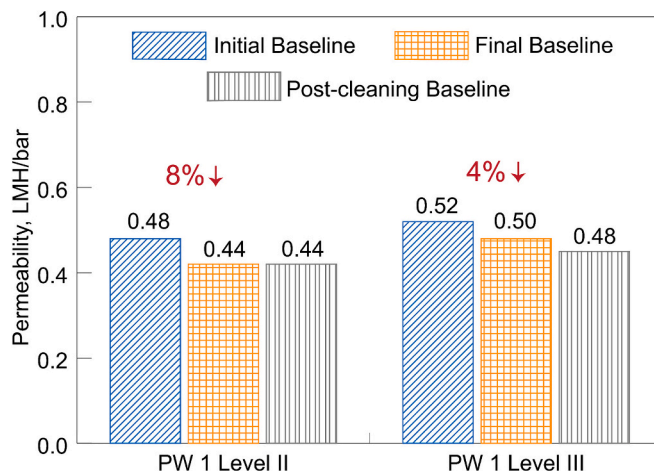


Fig. 11. RO organic fouling evaluation for pretreatment level II and level III using PW 1.

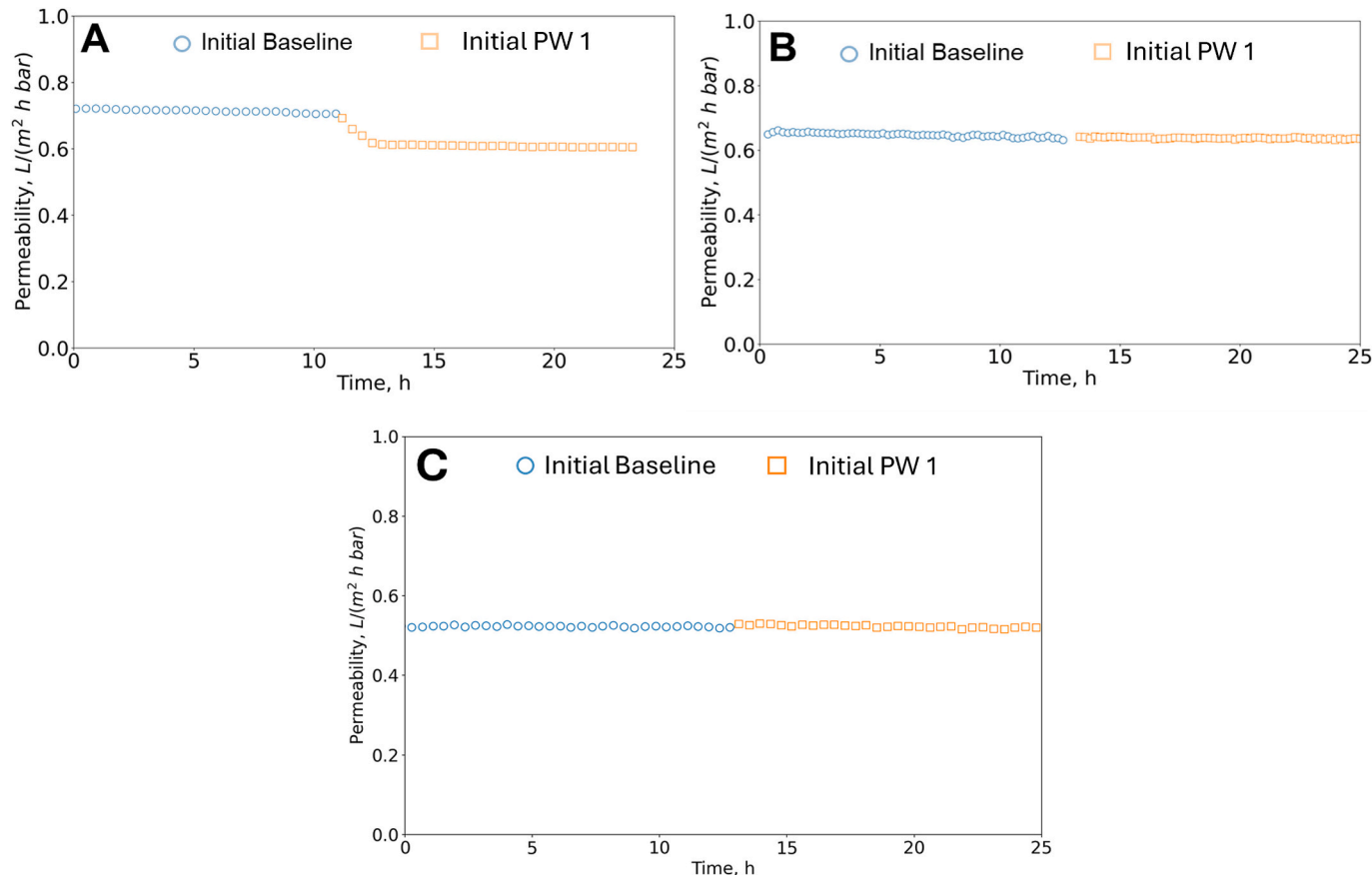


Fig. 10. Organic fouling evaluation: quick RO assessment to screen the pretreatment requirement using PW 1, A: Level I, B: level II, and C: Level III.

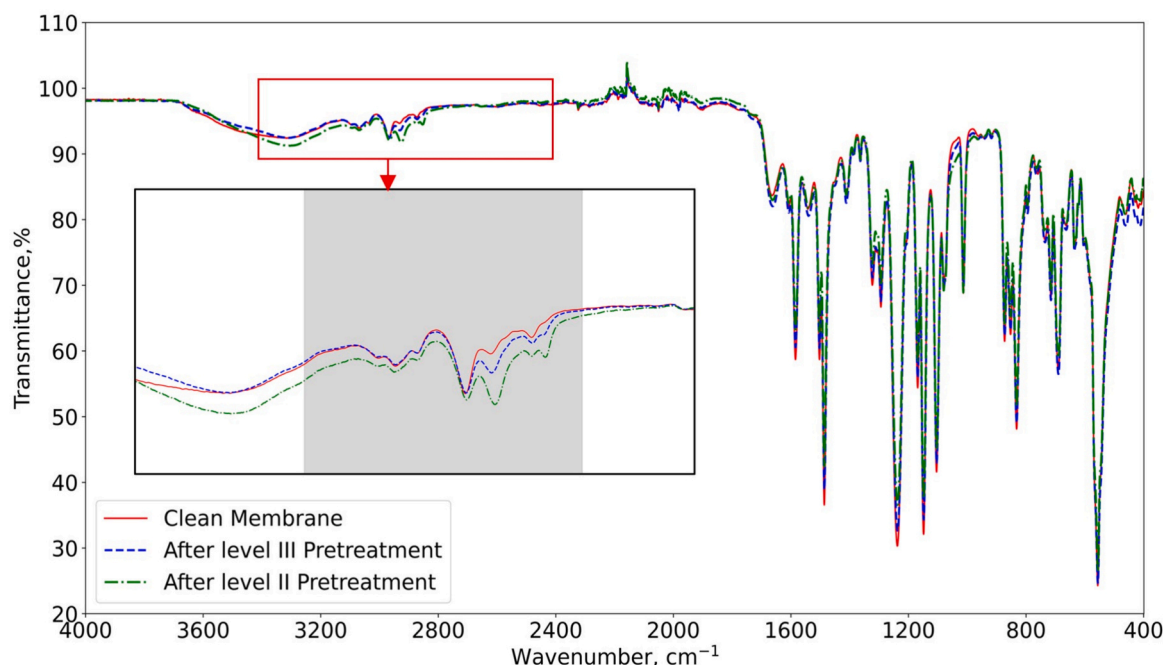


Fig. 12. FTIR analysis showing the impact of organic fouling on the chemical properties of the RO membrane surface for a clean RO membrane against membranes tested with levels II and III pretreated PW 1 quality.

loss percentage ($\sim 10\%$) as compared to level III PW quality ($\sim 1\%$). The mass balance calculations agreed with the obtained RO fouling behaviors demonstrating higher membrane permeability losses for level II against level III PW qualities. Since the tested pretreatment schemes only differed in terms of the application of GAC adsorption, HOC fractions in PW 1, not removed by GAC in level II pretreatment, were likely the primary cause of the RO membrane fouling. Calculations for major inorganics, such as Na and Cl, as well as for acetic acid showed good balance ($\sim < 5\%$). The table also shows that acetic acid was rejected by the RO membrane, which agrees with reported RO rejections of similar compounds in other studies [15]. However, some DOC levels were detected in the RO permeate. The fact that these organic species were not rejected by the RO membrane indicates that these compounds do not possess a hydrophobic nature. HPIC analysis on the RO permeate confirmed absence of acetic acid and/or other charged organic species. This suggests that the measured DOC in the permeate is likely to reflect hydrophilic uncharged-type species passing through the RO membrane. RO rejections of uncharged species (i.e., neutrals) may vary depending on multiple factors including diffusion, n-octanol/water partition coefficient (K_{ow}), and/or molecular size [84,87].

In Fig. 14, experimental findings, including water quality and membrane surface analysis, were used to describe the separation of the different DOC fractions via RO as well as the membrane fouling mechanism. Based on the pretreatment and RO results, the PW (RO feed) consisted of organic acids and an “unidentified fraction” which was found to primarily comprise of HOC and some neutrals. The figure depicts the removal mechanism for different DOC fractions present in the PW. Rejection of organic acids was accomplished by electrostatic interactions with the membrane, which agrees with the achieved RO rejections [90]. The membrane fouling was found to be mainly attributed to the adsorption of HOC compounds on the membrane as verified by FTIR and mitigated via level III pretreatment. For neutrals, once identified, the mechanism will be dependent on the properties/nature of the compound, which will govern the RO membrane rejection [85]. Although preliminary conclusions were presented based on experimental/applied routes, proper identification of the DOC species, especially those contributing to membrane fouling, will allow for optimizing the pretreatment strategies and/or membrane chemical cleaning

procedures targeting fractions of concern.

3.3. Product water quality

Table 5 presents preliminary RO permeate quality generated in this study upon the treatment of PW 1 and PW 2. In terms of rejections, $\sim 97\text{--}98\%$ and $\sim 83\text{--}88\%$ were achieved for TDS and DOC, respectively. The membrane also showed rejections $>99\%$ for SO_4^{2-} , Sr and acetic acid. As expected, lower boron rejections, in the range of $\sim 50\text{--}70\%$, by RO were obtained due to the operating pH. Boron is generally in the form of boric acid at neutral pH and dissociates into negatively charged borate at high pH (i.e., $\sim 10\text{--}11$), which can be then removed via ion exchange and/or membranes processes [80,81]. Removals for other species present in PW 1 and PW 2 were found to range between $\sim 89\text{--}98\%$. Obtained preliminary data can be used, depending on the target application (industrial, irrigation, agriculture, or others) to optimize pretreatment and/or develop fit-for purpose posttreatment strategies to comply with environmental regulations for reuse and/or discharge applications [9,91]. Post-treatment will be needed to bring specific constituents to acceptable reuse levels [92]. For instance, bromide levels in the permeate must be reduced to avoid the formation of toxic brominated disinfection by-products [93]. Subsequent treatment (e.g., IX, zeolites, etc.) may also be required for boron, sulfate, ammonium, DOC, and others as per targeted reuse specifications [92]. Comprehensive water quality analysis, including toxicity tests, is key in optimizing the implemented treatment train to allow for treating the PW to non-toxic levels and remove contaminants of concern.

3.4. OARO research outlook

Multiple research studies have extensively investigated factors governing the commercial applicability of OARO for brine concentration [25,35,42,44,94]. Based on simulations, bench/pilot testing using synthetic and/or real solutions, and technoeconomic assessments, key performance aspects associated with OARO application were studied. These mainly included permeability/flux, rejection, fouling, membrane chemistry and/or availability, concentration polarization, flow and/or membrane configuration, pressure, feed/sweep salinities, recovery and

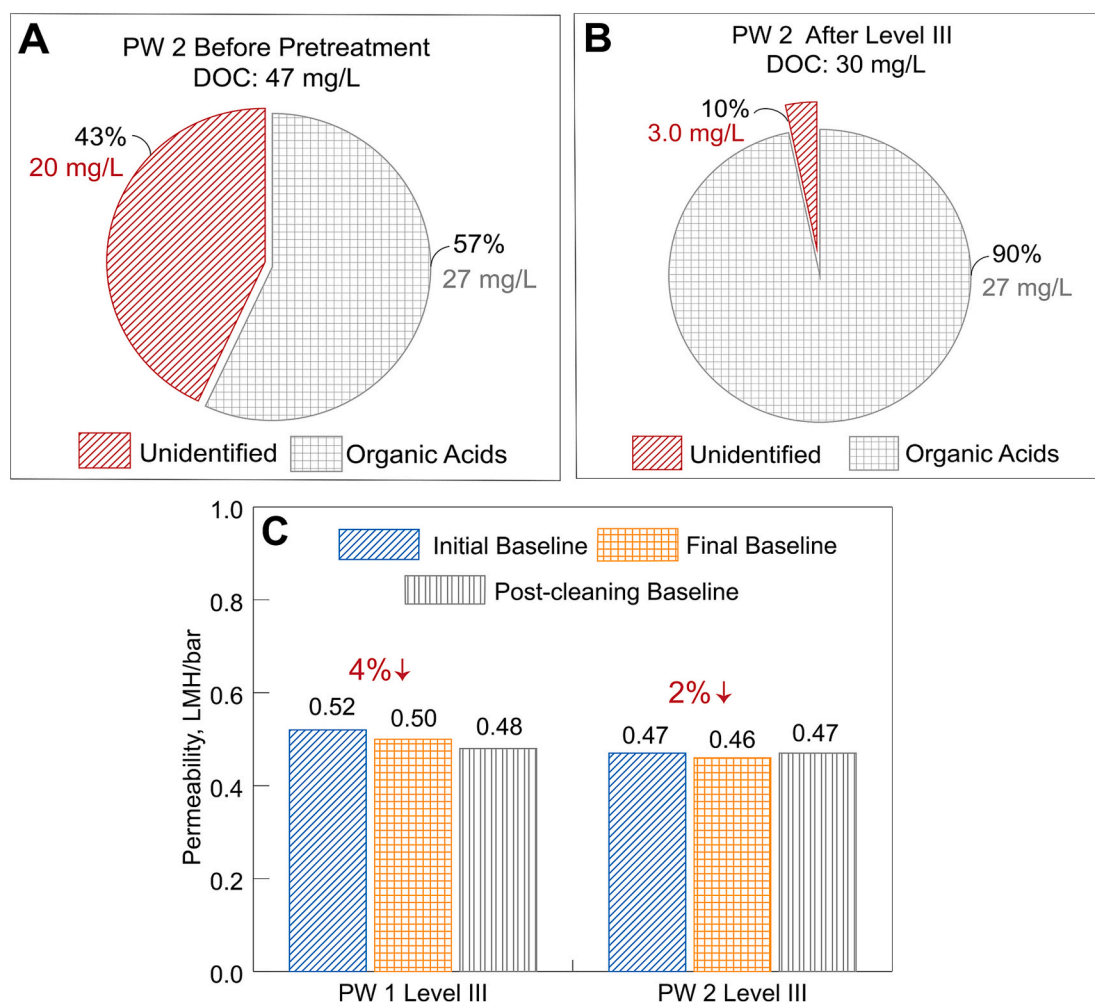


Fig. 13. Pretreatment and organic fouling evaluation on PW 2. A: PW 2 DOC distribution before pretreatment, B: PW 2 DOC distribution after level III pretreatment, and C: membrane fouling comparison for PW 1 and PW 2 pretreated by level III.

Table 4

PW 1 RO mass balance summary: Level II vs Level III levels.

	Na	Cl	DOC	Acetic acid
PW 1 Level II				
RO feed (mg/L)	15,396	23,360	45	88
RO permeate (mg/L)	494	757	5.6	<0.1
RO reject (mg/L)	23,309	35,497	57	125
Mass in (mg)	61,592	93,453	178	352
Mass out (mg)	63,861	97,262	162	341
Deviation (%)	4 %	4 %	−10 %	−3 %
PW 1 Level III				
RO feed (mg/L)	15,287	23,325	41	92
RO permeate (mg/L)	418	636	6.5	<0.1
RO reject (mg/L)	22,705	34,643	58	135
Mass in (mg)	61,155	93,311	164	368
Mass out (mg)	62,025	94,636	165	366
Deviation (%)	1 %	1 %	1 %	−1 %

staging, capital and operating expenditures (CAPEX/OPEX), pretreatment, product water quality, and others. While most of these performance aspects were broadly investigated, some still require further exploration. OARO future research directions should focus on optimized pretreatment strategies integrated with advanced organic characterization, improved membrane materials and/or cleaning protocols, targeted assessment of posttreatment requirements supported by toxicological

evaluations, thorough technoeconomic assessments, and detailed evaluation/review of product water quality and regulatory requirements for beneficial reuse. Additionally, tests should also consider studying the impact of staging on process performance including long-term assessment through pilot testing.

4. Conclusions

This study evaluated the pretreatment requirement, the membrane fouling potential, and expected product water quality for OARO application to real hypersaline PW collected from O&G operation. Initially, high salinity PW samples were sourced and characterized, with emphasis on dissolved organics (i.e., DOC). After that, a sequence of water treatment processes, including chemical coagulation, softening, microfiltration, stripping, and GAC adsorption; were configured and evaluated as level I, II, and III pretreatment. RO fouling tests were then conducted to assess each pretreatment level on membrane fouling, chemical cleaning efficiency, and product water quality. Key findings from the study include:

- 1- Approximately 60–70 % of organics present in the PW samples originated from organic acids, primarily acetic acid, which exhibited a low membrane fouling potential.
- 2- The remaining DOC (30–40 %), referred to as “unidentified”, composed of other constituents including the high fouling potential

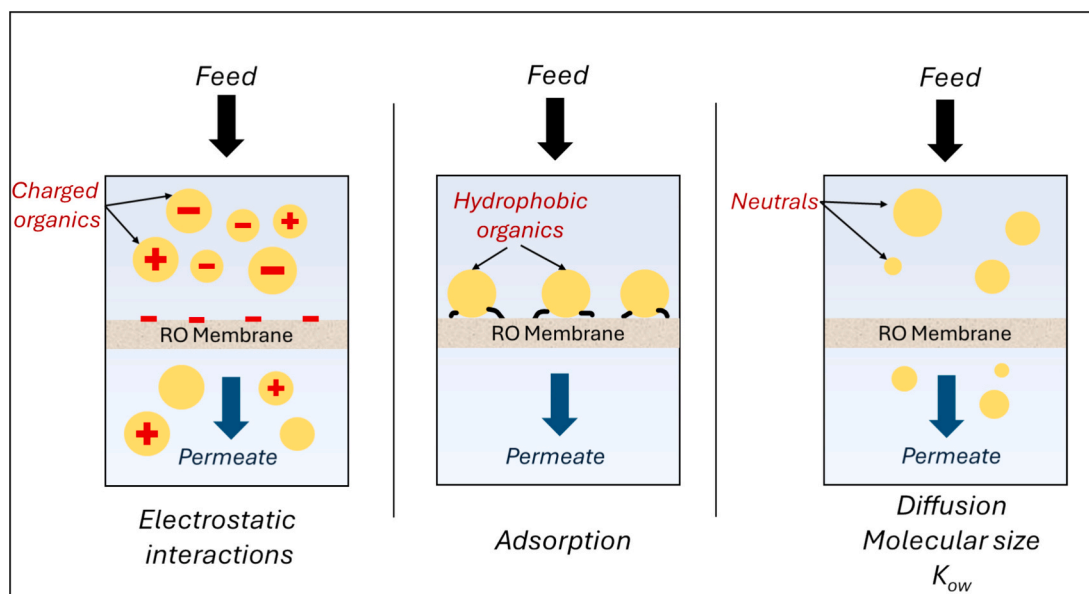


Fig. 14. A depiction of the RO removal mechanism for different organic fractions in the PW including, organic acids (electrostatic), HOC (adsorption), and uncharged/neutrals (diffusion).

Table 5

PW 1 and PW 2 RO product water quality.

Parameter	Unit	PW 1			PW 2		
		RO Feed	RO Permeate	RO Reject	RO Feed	RO Permeate	RO Reject
pH	–	8.1	7.7	7.4	8.1	7.5	7.1
Conductivity	ms/cm	58.6	1.96	82.8	59.5	1.64	85.1
TDS	mg/L	39,205	1080	59,754	38,577	927	60,615
DOC	mg/L	39	6.5	58	9.7	1.2	18.1
Cl [–]	mg/L	23,300	643	35,520	24,082	546	36,057
Na ⁺	mg/L	15,307	421	23,386	13,997	361	23,860
Br [–]	mg/L	208	6.1	298	183	4.3	256
Ca	mg/L	3.1	0.2	4.8	1.7	<0.1	2.9
Mg	mg/L	1.4	<0.1	2.0	0.2	<0.1	0.3
SO ₄ ^{2–}	mg/L	164	1.1	229	23	0.1	32
Si	mg/L	1.6	0.18	2.5	1.9	<0.1	3.6
K ⁺	mg/L	228	8.4	320	251	6.3	353
Acetic acid	mg/L	92	<0.1	135	23	<0.1	30
NH ₄ ⁺	mg/L	2.8	0.13	3.5	7.4	0.46	9.0
Li	mg/L	11	0.23	16	14	0.26	21
B	mg/L	37	16	48	24	8.0	27
Sr	mg/L	6.9	<0.1	9.6	2.7	<0.1	3.3

HOC, were reduced by ~17, ~38 %, ~62 % via applying pretreatment level I, level II, and level III, respectively.

- 3- Level I pretreated PW quality resulted in immediate membrane fouling and flux loss of ~20 %, thus was excluded from subsequent testing.
- 4- Level II pretreated PW quality resulted in ~8 % loss in membrane permeability, which was confirmed unrecoverable by chemical cleaning.
- 5- Level III pretreated PW quality, involving enhanced DOC removal by GAC, exhibited reduced membrane fouling tendency at ~4 % as compared to level II.
- 6- Standard cleaning methods were found ineffective in recovering membrane permeability caused by organic fouling.
- 7- Based on the pretreatment and RO performance results, the fouling mechanism for different DOC fractions including organic acids (electrostatic), HOC (adsorption), and uncharged /neutrals (diffusion) were depicted.
- 8- Preliminary insights into the expected product water quality (i.e., RO permeate) were discussed, which will aid in optimizing pretreatment

and/or evaluating post-treatment strategies for fit-for purpose PW beneficial reuse opportunities.

Findings from the study were utilized to discuss the OARO research outlook including pretreatment optimization, advanced PW organic characterization, development of novel membrane materials and/or cleaning procedures, posttreatment requirements, product water quality and regulatory requirements for reuse, technoeconomic assessments, and finally OARO staging and long-term performance testing.

CRedit authorship contribution statement

Mashaal Al-Maas: Writing – original draft, Formal analysis, Investigation, Methodology. **Joel Minier-Matar:** Writing – review & editing, Methodology, Investigation, Software. **Altaf Hussain:** Writing – review & editing, Investigation, Validation. **Eman AlShamari:** Investigation, Methodology, Validation. **Ramesh Sharma:** Writing – review & editing, Resources. **Samer Adham:** Writing – review & editing, Conceptualization, Project administration, Supervision.

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.

Acknowledgments

The authors would like to acknowledge Gennaro Dicaldo and Nabin Upadhyay for their support in water quality analyses and review of study outcomes. The authors would also like to thank Austin Beam, Luis Baez, Kevin Hinshaw, Jonathan Kiesewetter, and Fadi El Ahmadi, from ConocoPhillips, for their valuable support. The content of this publication is solely the responsibility of the authors and does not necessarily represent the official views of ConocoPhillips.

Open Access funding is provided by Qatar National Library.

Data availability

Data will be made available on request.

References

- [1] S. Adham, A. Hussain, J. Minier-Matar, A. Janson, R. Sharma, Membrane applications and opportunities for water management in the oil & gas industry, *Desalination* 440 (2018) 2–17, <https://doi.org/10.1016/j.desal.2018.01.030>.
- [2] J. Minier-Matar, M. Al-Maas, D. Dardor, A. Janson, M.S. Nasser, S. Adham, Industrial wastewater volume reduction through osmotic concentration: membrane module selection and process modeling, *J. Water Process Eng.* 40 (2021) 101760, <https://doi.org/10.1016/j.jwpe.2020.101760>.
- [3] R. Dores, A. Hussain, M. Katebah, S.S. Adham, Using advanced water treatment technologies to treat produced water from the petroleum industry, *SPE Int. Prod. Oper. Conf. Exhib.* (2012), <https://doi.org/10.2118/157108-MS>.
- [4] Y. Choi, Y. Kim, Y.C. Woo, I. Hwang, Water management and produced water treatment in oil sand plant: a review, *Desalination* 567 (2023) 116991, <https://doi.org/10.1016/j.desal.2023.116991>.
- [5] G. Campisi, A. Cosenza, F. Giacalone, S. Randazzo, A. Tamburini, G. Micalé, Desalination of oilfield produced waters via reverse electrodialysis: a techno-economical assessment, *Desalination* 548 (2023) 116289, <https://doi.org/10.1016/j.desal.2022.116289>.
- [6] I.-M. Hsieh, M. Malmali, Combined chlorine dioxide-membrane distillation for the treatment of produced water, *Desalination* 551 (2023) 116396, <https://doi.org/10.1016/j.desal.2023.116396>.
- [7] K. Bennett, Permian embraces produced water recycling, *Am. Oil Gas Report*. (2023). <https://www.aogr.com/magazine/frac-facts>.
- [8] S. Joag, J. Kiesewetter, S. Chellam, Electrode corrosion, pH, and dissolved oxygen dynamics, and hardness/silicon removal during aluminum electrocoagulation of hypersaline produced water, *ACS ES T Eng.* (2024), <https://doi.org/10.1021/acsestengg.4c00459>.
- [9] B.R. Scanlon, R.C. Reedy, P. Xu, M. Engle, J.P. Nicot, D. Yoxheimer, Q. Yang, S. Ikonnikova, Can we beneficially reuse produced water from oil and gas extraction in the U.S.? *Sci. Total Environ.* 717 (2020) 137085 <https://doi.org/10.1016/j.scitotenv.2020.137085>.
- [10] H.M.K. Delanka-Pedige, Y. Zhang, R.B. Young, H. Wang, L. Hu, C. Danforth, P. Xu, Safe reuse of treated produced water outside oil and gas fields? A review of current practices, challenges, opportunities, and a risk-based pathway for produced water treatment and fit-for-purpose reuse, *Curr. Opin. Chem. Eng.* 42 (2023) 100973, <https://doi.org/10.1016/j.coche.2023.100973>.
- [11] D.L. Shaffer, L.H. Arias Chavez, M. Ben-Sasson, S. Romero-Vargas Castrillón, N. Y. Yip, M. Elimelech, Desalination and reuse of high-salinity shale gas produced water: drivers, technologies, and future directions, *Environ. Sci. Technol.* 47 (2013) 9569–9583, <https://doi.org/10.1021/es401966e>.
- [12] C.M. Cooper, J. McCall, S.C. Stokes, C. McKay, M.J. Bentley, J.S. Rosenblum, T. A. Blewett, Z. Huang, A. Miara, M. Talmadge, A. Evans, K.A. Sitterley, P. Kurup, J. R. Stokes-Draut, J. Macknick, T. Borch, T.Y. Cath, L.E. Katz, Oil and gas produced water reuse: opportunities, treatment needs, and challenges, *ACS ES T Eng.* 2 (2022) 347–366, <https://doi.org/10.1021/acsestengg.1c00248>.
- [13] X. Chen, N.Y. Yip, Unlocking high-salinity desalination with cascading osmotically mediated reverse osmosis: energy and operating pressure analysis, *Environ. Sci. Technol.* 52 (2018) 2242–2250, <https://doi.org/10.1021/acs.est.7b05774>.
- [14] A.T. Bouma, J.H. Lienhard, Split-feed counterflow reverse osmosis for brine concentration, *Desalination* 445 (2018) 280–291, <https://doi.org/10.1016/j.desal.2018.07.011>.
- [15] H. Wu, L. Valentino, S. Riggio, M. Holtzapfel, M. Urgan-Demirtas, Performance characterization of nanofiltration, reverse osmosis, and ion exchange technologies for acetic acid separation, *Sep. Purif. Technol.* 265 (2021) 118108, <https://doi.org/10.1016/j.seppur.2020.118108>.
- [16] A. Soo, J. Kim, H.K. Shon, Technologies for the wastewater circular economy – a review, *Desalin. Water Treat.* 317 (2024) 100205, <https://doi.org/10.1016/j.dwt.2024.100205>.
- [17] W. Ding, K. Ma, A.E. Childress, Compaction of pressure-driven water treatment membranes: real-time quantification and analysis, *Environ. Sci. Technol.* 58 (2024) 18404–18413, <https://doi.org/10.1021/acs.est.4c05865>.
- [18] X. Wei, K.T. Sanders, A.E. Childress, Reclaiming wastewater with increasing salinity for potable water reuse: water recovery and energy consumption during reverse osmosis desalination, *Desalination* 520 (2021) 115316, <https://doi.org/10.1016/j.desal.2021.115316>.
- [19] Y.J. Lim, Y. Ma, J.W. Chew, R. Wang, Assessing the potential of highly permeable reverse osmosis membranes for desalination: specific energy and footprint analysis, *Desalination* 533 (2022) 115771, <https://doi.org/10.1016/j.desal.2022.115771>.
- [20] M. Tawalbeh, L. Qalyoubi, A. Al-Othman, M. Qasim, M. Shirazi, Insights on the development of enhanced antifouling reverse osmosis membranes: industrial applications and challenges, *Desalination* 553 (2023) 116460, <https://doi.org/10.1016/j.desal.2023.116460>.
- [21] N.A. Shahrim, N.M. Abounahia, A.M.A. El-Sayed, H. Saleem, S.J. Zaidi, An overview on the progress in produced water desalination by membrane-based technology, *J. Water Process Eng.* 51 (2023) 103479, <https://doi.org/10.1016/j.jwpe.2022.103479>.
- [22] L. Ranieri, R.E. Putri, N. Farhat, J.S. Vrouwenvelder, L. Fortunato, Gravity-driven membrane as seawater desalination pretreatment: understanding the role of membrane biofilm on water production and AOC removal, *Desalination* 549 (2023) 116353, <https://doi.org/10.1016/j.desal.2022.116353>.
- [23] N. Martins, Technical and Economical Evaluation of Water Desalination Systems Powered by Fossil and Renewable Energy Sources, 2019.
- [24] A. Politano, R.A. Al-Juboori, S. Alnajdi, A. Alsaati, A. Athanassiou, M. Bar-Sadan, A.N. Beni, D. Campi, A. Cupolillo, G. D'Olimpio, G. D'Andrea, H. Estay, D. Fragouli, L. Gurreri, N. Ghaffour, J. Giron, N. Hilal, J. Occhiazzi, M.R. Carvajal, A. Ronen, S. Santoro, M. Tedesco, R.A. Tufa, M. Ulbricht, D.M. Warsinger, D. Xevgenos, G. Zaragoza, Y.-W. Zhang, M. Zhou, E. Curcio, 2024 Roadmap on membrane desalination technology at the water-energy nexus, *J. Phys. Energy*. 6 (2024) 21502, <https://doi.org/10.1088/2515-7655/ad2cf2>.
- [25] Z. Wang, D. Feng, Y. Chen, D. He, M. Elimelech, Comparison of energy consumption of osmotically assisted reverse osmosis and low-salt-rejection reverse osmosis for brine management, *Environ. Sci. Technol.* 55 (2021) 10714–10723, <https://doi.org/10.1021/acs.est.1c01638>.
- [26] A. Naderi Beni, I. Ghofrani, A. Nouri-Borujerdi, A. Moosavi, D.M. Warsinger, Membrane properties overview in integrated forward osmosis/osmotically assisted reverse osmosis systems, *Desalination* 569 (2024) 117008, <https://doi.org/10.1016/j.desal.2023.117008>.
- [27] E. Ali, J. Orfi, H. AlAnsary, S. Baakeem, A.S. Alsaadi, N. Ghaffour, Concept and analysis of hybrid reverse multi-stage flash and membrane distillation desalination system, *Environ. Technol.* 45 (2024) 5218–5231, <https://doi.org/10.1080/09593330.2023.2284688>.
- [28] K. Harby, M. Emad, M. Benghanem, T.Z. Abolbda, K. Almohammadi, A. Aljabri, A. Alsaiahi, M. Elgendi, Reverse osmosis hybridization with other desalination techniques: an overview and opportunities, *Desalination* 581 (2024) 117600, <https://doi.org/10.1016/j.desal.2024.117600>.
- [29] H. Kariman, A. Shafieian, M. Khiadani, Small scale desalination technologies: A comprehensive review, *Desalination* 567 (2023) 116985, <https://doi.org/10.1016/j.desal.2023.116985>.
- [30] I. Janajreh, H. Zhang, K. El Kadi, N. Ghaffour, Freeze desalination: current research development and future prospects, *Water Res.* 229 (2023) 119389, <https://doi.org/10.1016/j.watres.2022.119389>.
- [31] M. Turetta, A. Bertucco, F. Briani, N. Michelon, J. Vogel, X.T. Nguyen, E. Barbera, Experimental investigation and mathematical modelling of a spiral wound membrane module for osmotically assisted reverse osmosis applications, *J. Water Process Eng.* 68 (2024) 106355, <https://doi.org/10.1016/j.jwpe.2024.106355>.
- [32] A. Naderi Beni, S.M. Alnajdi, J. Garcia-Bravo, D.M. Warsinger, Semi-batch and batch low-salt-rejection reverse osmosis for brine concentration, *Desalination* 583 (2024) 117670, <https://doi.org/10.1016/j.desal.2024.117670>.
- [33] Y.K. Chong, M. Li, D.E. Wiley, D.F. Fletcher, Y.Y. Liang, Review of modeling methodologies and state-of-the-art for osmotically assisted reverse osmosis membrane systems, *Desalination* 587 (2024) 117893, <https://doi.org/10.1016/j.desal.2024.117893>.
- [34] R.R. Gonzales, K. Nakagawa, S. Hasegawa, K. Kumagai, A. Matsuoka, Y. Okamoto, Z. Li, Z. Mai, T. Yoshioka, T. Hori, H. Matsuyama, Treatment of high-strength wastewater with coupled flocculation and membrane filtration prior to ammoniacal nitrogen enrichment by osmotically assisted reverse osmosis, *Sep. Purif. Technol.* 352 (2025) 128159, <https://doi.org/10.1016/j.seppur.2024.128159>.
- [35] B.D. Van Houghton, J.S. Rosenblum, K. Lampi, E. Beaudry, J.J. Herron, M. Cerro, C.T.K. De Finnda, M. Elimelech, J. Giron, T.Y. Cath, Pilot Scale Demonstration of Low-Salt-Rejection Reverse Osmosis (LSRRO) Desalination of High Salinity Brines, 2024, <https://doi.org/10.1021/acsestwater.4c00673>.
- [36] A. Anvari, J. Wu, A. Edalat, N. Voutchkov, A. Al-Ahmoudi, S. Bhattacharjee, E.M. V. Hoek, What will it take to get to 250,000 ppm brine concentration via ultra-high pressure reverse osmosis? And is it worth it? *Desalination* 580 (2024) 117565, <https://doi.org/10.1016/j.desal.2024.117565>.
- [37] K. Nakagawa, N. Togo, R. Takagi, T. Shintani, T. Yoshioka, E. Kamio, H. Matsuyama, Multistage osmotically assisted reverse osmosis process for concentrating solutions using hollow fiber membrane modules, *Chem. Eng. Res. Des.* 162 (2020) 117–124, <https://doi.org/10.1016/j.cherd.2020.07.029>.

- [38] T. Nakao, S. Goda, Y. Miura, M. Yasukawa, M. Ishibashi, K. Nakagawa, T. Shintani, H. Matsuyama, T. Yoshioka, Development of cellulose triacetate asymmetric hollow fiber membranes with highly enhanced compaction resistance for osmotically assisted reverse osmosis operation applicable to brine concentration, *J. Memb. Sci.* 653 (2022) 120508, <https://doi.org/10.1016/j.memsci.2022.120508>.
- [39] E. Shamlou, R. Vidic, M.M. El-Halwagi, V. Khanna, Optimization-based modeling and analysis of brine reflux osmotically assisted reverse osmosis for application toward zero liquid discharge systems, *Desalination* 539 (2022) 115948, <https://doi.org/10.1016/j.desal.2022.115948>.
- [40] J. Tracy, Long-Term Operating Results of a Membrane Brine Concentration System Integrated with a Seawater Reverse Osmosis Desalination Plant, in: *International Specialty Conference on Ocean Brine Mining*, Al Khobar, Saudi Arabia, 2022.
- [41] R.R. Gonzales, K. Nakagawa, K. Kumagai, S. Hasegawa, A. Matsuo, Z. Li, Z. Mai, T. Yoshioka, T. Hori, H. Matsuyama, Hybrid osmotically assisted reverse osmosis and reverse osmosis (OARO-RO) process for minimal liquid discharge of high strength nitrogenous wastewater and enrichment of ammoniacal nitrogen, *Water Res.* 246 (2023) 120716, <https://doi.org/10.1016/j.watres.2023.120716>.
- [42] T.V. Bartholomew, L. Mey, J.T. Arena, N.S. Siefert, M.S. Mauter, Osmotically assisted reverse osmosis for high salinity brine treatment, *Desalination* 421 (2017) 3–11, <https://doi.org/10.1016/j.desal.2017.04.012>.
- [43] C.D. Peters, N.P. Hankins, Osmotically assisted reverse osmosis (OARO): five approaches to dewatering saline brines using pressure-driven membrane processes, *Desalination* 458 (2019) 1–13, <https://doi.org/10.1016/j.desal.2019.01.025>.
- [44] Z. Zhang, A.A. Atia, J.A. Andrés-Mañas, G. Zaragoza, V. Fthenakis, Comparative techno-economic assessment of osmotically-assisted reverse osmosis and batch-operated vacuum-air-gap membrane distillation for high-salinity water desalination, *Desalination* 532 (2022), <https://doi.org/10.1016/j.desal.2022.115737>.
- [45] G. Bargeman, Creating saturated sodium chloride solutions through osmotically assisted reverse osmosis, *Sep. Purif. Technol.* 293 (2022) 121113, <https://doi.org/10.1016/j.seppur.2022.121113>.
- [46] Z. Mo, C.D. Peters, C. Long, N.P. Hankins, Q. She, How split-feed osmotically assisted reverse osmosis (SF-OARO) can outperform conventional reverse osmosis (CRO) processes under constant and varying electricity tariffs, *Desalination* 530 (2022) 115670, <https://doi.org/10.1016/j.desal.2022.115670>.
- [47] C.D. Peters, N.P. Hankins, The synergy between osmotically assisted reverse osmosis (OARO) and the use of thermo-responsive draw solutions for energy efficient, zero-liquid discharge desalination, *Desalination* 493 (2020) 114630, <https://doi.org/10.1016/j.desal.2020.114630>.
- [48] M. Askari, C.Z. Liang, L.T. (Simon) Choong, T.S. Chung, Optimization of TFC-PES hollow fiber membranes for reverse osmosis (RO) and osmotically assisted reverse osmosis (OARO) applications, *J. Memb. Sci.* 625 (2021), <https://doi.org/10.1016/j.memsci.2021.119156>.
- [49] N. Togo, K. Nakagawa, T. Shintani, T. Yoshioka, T. Takahashi, E. Kamio, H. Matsuyama, Osmotically assisted reverse osmosis utilizing hollow fiber membrane module for concentration process, *Ind. Eng. Chem. Res.* 58 (2019) 6721–6729, <https://doi.org/10.1021/acs.iecr.9b00630>.
- [50] D.M. Davenport, L. Wang, E. Shalusk, M. Elimelech, Design principles and challenges of bench-scale high-pressure reverse osmosis up to 150 bar, *Desalination* 517 (2021) 115237, <https://doi.org/10.1016/j.desal.2021.115237>.
- [51] J. Wu, B. Jung, A. Anvari, S. Im, M. Anderson, X. Zheng, D. Jassby, R.B. Kaner, D. Dlamini, A. Edalat, E.M.V. Hoek, Reverse osmosis membrane compaction and embossing at ultra-high pressure operation, *Desalination* 537 (2022) 115875, <https://doi.org/10.1016/j.desal.2022.115875>.
- [52] M. Turetta, A. Bertucco, F. Briani, E. Barbera, Pilot-scale evaluation of spiral-wound modules in osmotically assisted reverse osmosis, *Chem. Eng. Technol.* (2024) 1–11, <https://doi.org/10.1002/ceat.202300553>.
- [53] K.H. Chu, J.S. Mang, J. Lim, S. Hong, M.H. Hwang, Variation of free volume and thickness by high pressure applied on thin film composite reverse osmosis membrane, *Desalination* 520 (2021) 115365, <https://doi.org/10.1016/j.desal.2021.115365>.
- [54] D.M. Davenport, A. Deshmukh, J.R. Werber, M. Elimelech, High-pressure reverse osmosis for energy-efficient hypersaline brine desalination: current status, design considerations, and research needs, *Environ. Sci. Technol. Lett.* 5 (2018) 467–475, <https://doi.org/10.1021/acs.estlett.8b00274>.
- [55] M.A. Ahmed, S. Amin, A.A. Mohamed, Fouling in reverse osmosis membranes: monitoring, characterization, mitigation strategies and future directions, *Heliyon* 9 (2023) e14908, <https://doi.org/10.1016/j.heliyon.2023.e14908>.
- [56] Q. Li, Z. Xu, I. Pinnau, Fouling of reverse osmosis membranes by biopolymers in wastewater secondary effluent: role of membrane surface properties and initial permeate flux, *J. Memb. Sci.* 290 (2007) 173–181, <https://doi.org/10.1016/j.memsci.2006.12.027>.
- [57] H. Li, H. Xia, Y. Mei, Modeling organic fouling of reverse osmosis membrane: from adsorption to fouling layer formation, *Desalination* 386 (2016) 25–31, <https://doi.org/10.1016/j.desal.2016.02.037>.
- [58] C.D. Peters, D. Li, Z. Mo, N.P. Hankins, Q. She, Exploring the limitations of osmotically assisted reverse osmosis: membrane fouling and the limiting flux, *Environ. Sci. Technol.* 56 (2022) 6678–6688, <https://doi.org/10.1021/acs.est.2c00839>.
- [59] A. Edalat, D. Ph, On gaps and needs for ultrahigh pressure RO (UHPRO) Desalination, in: *Int. Spec. Conf. Ocean Brine Min.*, 2022.
- [60] T. Nakao, Toyobo membrane brine concentration system, in: *Int. Spec. Conf. Ocean Brine Min.*, 2022.
- [61] W.W. Nazaroff, L. Alvarez-Cohen, *Environmental Engineering Science*, Wiley, 2000. <https://books.google.com.qa/books?id=qpf9DwAAQBAJ>.
- [62] S.F. Anis, R. Hashaikh, N. Hilal, Reverse osmosis pretreatment technologies and future trends: a comprehensive review, *Desalination* 452 (2019) 159–195, <https://doi.org/10.1016/j.desal.2018.11.006>.
- [63] K.M. Mousa, A.A. Hassan, Coagulation/ Flocculation Process for Produced Water Treatment View project Electrical engineering and chemical View project. www.solistatetechnology.us, 2020.
- [64] D. Dardor, M. Al Maas, J. Minier-Matar, A. Janson, A. Abdel-Wahab, H.K. Shon, S. Adham, Evaluation of pretreatment and membrane configuration for pressure-retarded osmosis application to produced water from the petroleum industry, *Desalination* 516 (2021) 115219, <https://doi.org/10.1016/j.desal.2021.115219>.
- [65] M. Nadella, R. Sharma, S. Chellam, Fit-for-purpose treatment of produced water with iron and polymeric coagulant for reuse in hydraulic fracturing: temperature effects on aggregation and high-rate sedimentation, *Water Res.* 170 (2020) 115330, <https://doi.org/10.1016/j.watres.2019.115330>.
- [66] OLI Systems, Inc. <https://www.olisystems.com/>, 1971.
- [67] J.T. O'Connor, T. O'Connor, R. Twait, Lime softening, *Water Treat. Plant Perform. Eval. Oper.* (2009) 33–40, <https://doi.org/10.1002/9780470431474.ch3>.
- [68] G.M. Masters, W.P. Ela, *Introduction to Environmental Engineering and Science*, 2014.
- [69] Nitro Group Company HYDRANAUTICS, Reverse Osmosis (RO) Water Chemistry, (n.d.) 1–7.
- [70] N.J. Langenfeld, P. Kusuma, T. Wallentine, C.S. Criddle, L.C. Seefeldt, B. Bugbee, Optimizing nitrogen fixation and recycling for food production in regenerative life support systems, *Front. Astron. Sp. Sci.* 8 (2021) 1–13, <https://doi.org/10.3389/fspas.2021.699688>.
- [71] O. Pedersen, T. Colmer, K. Sand-Jensen, Underwater photosynthesis of submerged plants – recent advances and methods, *Front. Plant Sci.* 4 (2013), <https://doi.org/10.3389/fpls.2013.00140>.
- [72] J. Minier-Matar, E. AlShamari, M. Raja, F. Khan, M. Al-Maas, A. Hussain, S. Adham, Detailed organic characterization of process water to evaluate reverse osmosis membrane fouling in industrial wastewater treatment, *Desalination* 572 (2024) 117128, <https://doi.org/10.1016/j.desal.2023.117128>.
- [73] J.C. Crittenden, P.S. Reddy, H. Arora, J. Trynoski, D.W. Hand, D.L. Perram, R. S. Summers, Predicting GAC performance with rapid small-scale column tests, *J. AWWA* 83 (1991) 77–87, <https://doi.org/10.1002/j.1551-8833.1991.tb07088.x>.
- [74] A. Butkovskiy, A.H. Faber, Y. Wang, K. Grolle, R. Hofman-Caris, H. Bruning, A. P. Van Wezel, H.H.M. Rijnaarts, Removal of organic compounds from shale gas flowback water, *Water Res.* 138 (2018) 47–55, <https://doi.org/10.1016/j.watres.2018.03.041>.
- [75] M. Al-Maas, J. Minier-Matar, I. Krupa, M.A.A. Al-Maadeed, S. Adham, Evaluation of polymeric adsorbents via fixed-bed columns for emulsified oil removal from industrial wastewater, *J. Water Process Eng.* 49 (2022) 102962, <https://doi.org/10.1016/j.jwpe.2022.102962>.
- [76] T. Fundneider, V. Acevedo Alonso, G. Abbt-Braun, A. Wick, D. Albrecht, S. Lackner, Empty bed contact time: the key for micropollutant removal in activated carbon filters, *Water Res.* 191 (2021) 116765, <https://doi.org/10.1016/j.watres.2020.116765>.
- [77] M. Al-Maas, A. Hussain, J. Minier-Matar, M.K. Hassan, M.A.A. Al-Maadeed, K. Alamgir, S. Adham, Performance evaluation of emerging block copolymer membranes for oil-water separation, *Green Technol. Resilience, Sustain.* 2 (2022) 0–10, <https://doi.org/10.1007/s44173-022-00004-0>.
- [78] HYDRANAUTICS, Fouling and Cleaning Procedures for Composite Polyamide RO/NF Membrane Elements, 2020.
- [79] T. Yu, L. Meng, Q.-B. Zhao, Y. Shi, H.-Y. Hu, Y. Lu, Effects of chemical cleaning on RO membrane inorganic, organic and microbial foulant removal in a full-scale plant for municipal wastewater reclamation, *Water Res.* 113 (2017) 1–10, <https://doi.org/10.1016/j.watres.2017.01.068>.
- [80] A. Hussain, R. Sharma, J. Minier-Matar, Z. Hirani, S. Adham, Application of emerging ion exchange resin for boron removal from saline groundwater, *J. Water Process Eng.* 32 (2019) 100906, <https://doi.org/10.1016/j.jwpe.2019.100906>.
- [81] Y. Cengeloglu, G. Arslan, A. Tor, I. Kocak, N. Dursun, Removal of boron from water by using reverse osmosis, *Sep. Purif. Technol.* 64 (2008) 141–146, <https://doi.org/10.1016/j.seppur.2008.09.006>.
- [82] S.A. Huber, A. Balz, M. Abert, W. Pronk, Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-OND), *Water Res.* 45 (2011) 879–885, <https://doi.org/10.1016/j.watres.2010.09.023>.
- [83] S.G.S. Rodriguez, *Particulate and Organic Matter Fouling of Seawater Reverse Osmosis Systems: Characterization, Modelling and Applications*, UNESCO-IHE PhD Thesis, CRC Press, 2011.
- [84] A. Abushaban, S.G. Salinas-Rodriguez, M. Philibert, L. Le Bouille, M.C. Necibi, A. Chehbouni, Biofouling potential indicators to assess pretreatment and mitigate biofouling in SWRO membranes: a short review, *Desalination* 527 (2022), <https://doi.org/10.1016/j.desal.2021.115543>.
- [85] L.N. Breitner, K.J. Howe, D. Minakata, Effect of functional chemistry on the rejection of low-molecular weight neutral organics through reverse osmosis membranes for potable reuse, *Environ. Sci. Technol.* (2019) 11401–11409, <https://doi.org/10.1021/acs.est.9b03856>.
- [86] F. Zhou, C. Wang, J. Wei, Simultaneous acetic acid separation and monosaccharide concentration by reverse osmosis, *Bioresour. Technol.* 131 (2013) 349–356, <https://doi.org/10.1016/j.biortech.2012.12.145>.
- [87] E.R. Cornelissen, D.J.H. Harmsen, B. Blankert, L.P. Wessels, W.G.J. van der Meer, Effect of minimal pre-treatment on reverse osmosis using surface water as a source, *Desalination* 509 (2021) 115056, <https://doi.org/10.1016/j.desal.2021.115056>.

- [88] A. Butkovskiy, A.-H. Faber, Y. Wang, K. Grolle, R. Hofman-Caris, H. Bruning, A. P. Van Wezel, H.H.M. Rijnaarts, Removal of organic compounds from shale gas flowback water, *Water Res.* 138 (2018) 47–55, <https://doi.org/10.1016/j.watres.2018.03.041>.
- [89] B.D. Van Houghton, J. Liu, M.J. Strynar, T. Bailey, P.R. Pfeiffer, D. Jassby, J. C. Corton, J. Rosenblum, T.Y. Cath, Performance evaluation of a high salinity produced water treatment train: chemical analysis and aryl hydrocarbon activation, *ACS ES&T Water.* 4 (2024) 1293–1302, <https://doi.org/10.1021/acsestwater.3c00407>.
- [90] O. Ojajuni, D. Saroj, G. Cavalli, Removal of organic micropollutants using membrane-assisted processes: a review of recent progress, *Environ. Technol. Rev.* 4 (2015) 17–37, <https://doi.org/10.1080/21622515.2015.1036788>.
- [91] E.P. Nancy Stoner, Lek Kadel, EPA Guidelines for water reuse U.S. Environmental Protection Agency, *Guidel. Water Reuse.* (2012) 643.
- [92] Y. Tarazona, H.B. Wang, M. Hightower, P. Xu, Y. Zhang, Benchmarking produced water treatment strategies for non-toxic effluents: integrating thermal distillation with granular activated carbon and zeolite post-treatment, *J. Hazard. Mater.* 478 (2024) 135549, <https://doi.org/10.1016/j.jhazmat.2024.135549>.
- [93] J. Criquet, S. Allard, Chapter Five - Influence of bromide and iodide on the formation of disinfection by-products in drinking water treatment, in: T. Manasfi, J.-L.B.T.-C.A.C. Boudenne (Eds.), *Anal. Form. Disinfect. Byprod. Drink. Water*, Elsevier, 2021, pp. 117–138, <https://doi.org/10.1016/bs.coac.2021.01.004>.
- [94] A.T. Bouma, J.H. Lienhard, Split-feed counterflow reverse osmosis for brine concentration, *Desalination* 445 (2018) 280–291, <https://doi.org/10.1016/j.desal.2018.07.011>.