



Review

Mitigating electro dialysis membrane fouling in seawater desalination

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ABSTRACT

Seawater electro dialysis with ion exchange membranes provides superior ion selectivity, bypassing the limitations of methods like reverse osmosis. However, fouling poses significant challenges to their efficiency and lifespan. Fouling, emerging from organic accumulation, inorganic scaling, biofouling, and more, disrupts salt rejection, escalates energy consumption, and abbreviates membrane lifespan. This review provides a holistic examination of fouling mechanisms in seawater desalination via ion exchange membranes, delineating types of fouling, their repercussions on membrane performance, and an array of mitigation strategies. These include feedwater pre-treatment, chemical cleaning, membrane surface modifications, and the exploration of emerging technologies like pulsed electro dialysis reversal. Through innovative approaches, the potential of ion exchange membranes can be fully harnessed effectively.

1. Introduction

Electro dialysis (ED), with its distinctive mechanism, allows for the demineralization of saline water by driving ions through selective permeable membranes under the influence of an electric field. This technique offers advantages over other desalination methods, such as operating at lower pressures, thereby not being subjected to the limitations imposed by osmotic pressures that are typical in processes like reverse osmosis [1–4]. It has the potential to be scaled down efficiently for use in small, economically viable plants situated in residential areas or communities facing water scarcity, hence broadening the reach and application of water treatment technologies [5].

Ion-exchange membranes, fundamental to ED, possess the admirable ability to discriminate between ions, permitting desirable ions to pass while blocking others. These membranes are crucial for the function of various technologies including ED, shock ED, membrane capacitive deionization, and microbial desalination cells [1–4]. However, despite these advantages, the persistent challenge of membrane fouling significantly undermines the efficiency and longevity of ion-exchange membranes in ED applications for seawater desalination. Fouling is the undesirable accumulation of contaminants and impurities on the membrane surface, thereby impeding the membranes' operational efficiency and salt rejection capacity [6,7].

Fouling not only disrupts the optimal ion transport but also necessitates higher operational inputs, such as increased pressures or voltages, to maintain desired water flow and salt rejection rates. This increase in operational demands invariably leads to elevated energy consumption and operational costs [8]. Moreover, the chronic issue of fouling accelerates the wear and tear on ion-exchange membranes, resulting in damage, shortened lifespan, and frequent need for replacement or maintenance [8].

To counteract the detrimental effects of fouling, various mitigation strategies have been explored. Surface modification of membranes is one approach that enhances their resistance to fouling [9]. In addition, established procedures like backwashing and employing specialized cleaning agents have shown effectiveness in removing foulants from the membrane surface [7,9,10]. Optimizing the design of membrane modules and implementing efficient feedwater pretreatment processes further aids in preventing fouling, thus preserving the integrity and prolonging the life of ion-exchange membranes in ED systems [9].

Since the 1960 s, there has been a notable growth in literature on both ion exchange membrane fouling and seawater ED (Fig. 1 a). The ion exchange membrane fouling study observed steady increases in publications from 1966 until a significant uptick in the 2000 s, culminating in a peak in 2021 with 75 publications. This burgeoning interest underscores the crucial role of addressing membrane fouling challenges in

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ion exchange systems, providing a robust foundation for understanding fouling mechanisms, prevention, and mitigation. Concurrently, literature on seawater ED has also expanded, particularly from 2000 onwards, with 2021 again being a standout year with 75 publications. This growing body of work reflects the escalating demand for efficient desalination technologies amidst intensifying global water scarcity issues.

Fig. 1 b reveals extensive interdisciplinary research in fouling ion exchange membranes and seawater ED. For both topics, predominant contributions are in Chemical Engineering, Chemistry, and Environmental Science, highlighting their relevance in water treatment and environmental protection. Publications in Materials Science and Engineering across both domains underscore the focus on innovation and application in desalination technologies, while the Energy sector

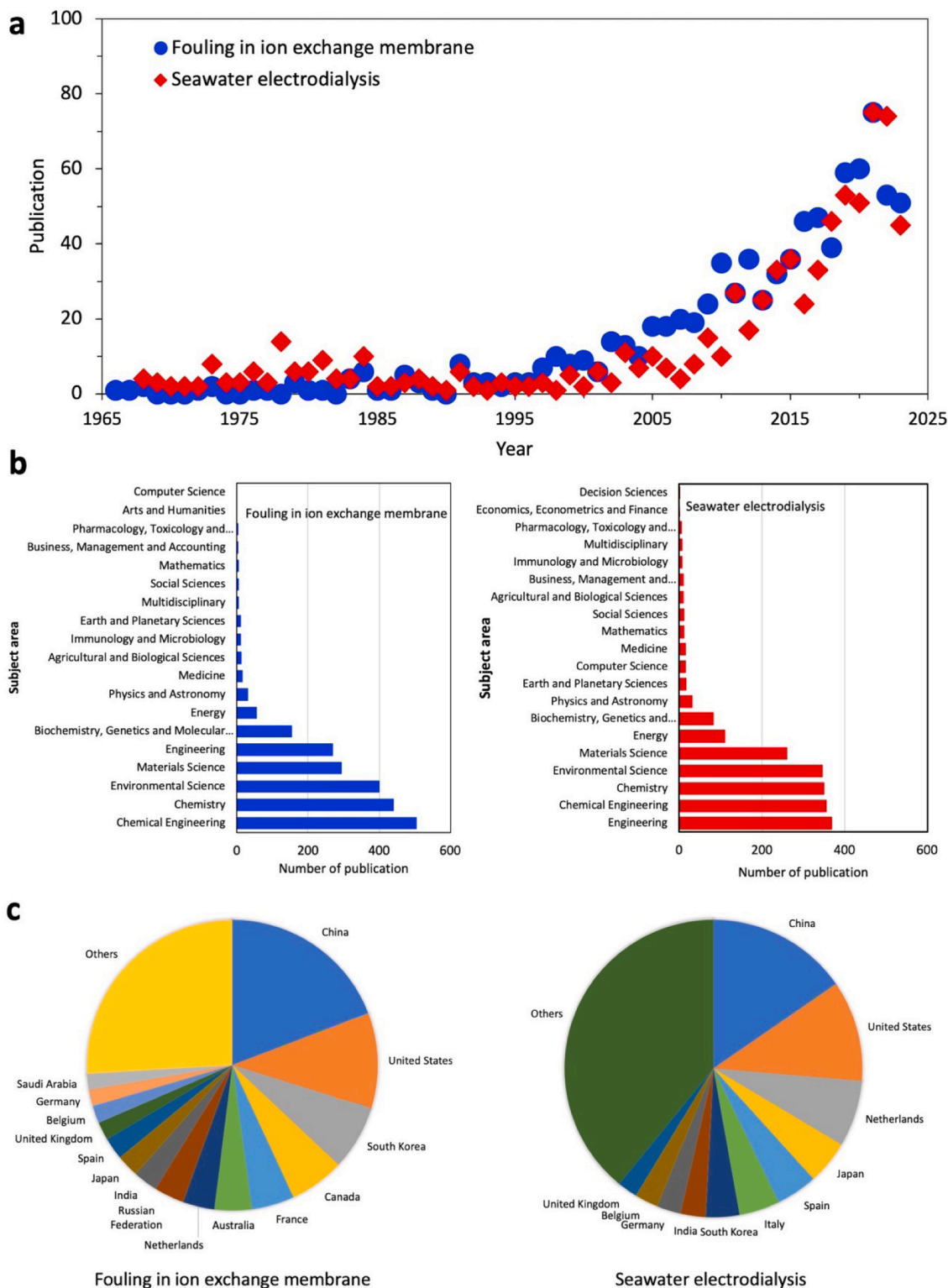


Fig. 1. (a) Number of publication related to ion exchange membrane fouling and seawater desalination by electro dialysis (retrieved from SCOPUS database, October 4th, 2023). (b) publications by subject. (c) Publications by country/territory.

explores their sustainability and efficiency. The diverse engagement from fields like Biochemistry, Physics, and Social Sciences in these areas indicates the technologies' wide applications and implications for addressing global water and sustainability challenges. Fig. 1 c illustrates a robust global research effort in seawater ED and ion exchange membrane fouling, with China and the United States as leading contributors. Significant publications also originate from the Netherlands, Japan, Spain, Italy, South Korea, Canada, France, and Australia, highlighting the global recognition and collaborative research in these vital desalination and water treatment technologies. This international engagement aims to innovate and optimize solutions for efficient and sustainable water treatment, addressing urgent global water scarcity and treatment challenges across various contexts and regions.

Fig. 2 a and 2b provide valuable insights into the research landscape surrounding fouling in ion exchange and seawater ED. Fig. 2 a reveals that fouling in desalination processes has become a focal point for researchers. There is a growing interest in developing ion exchange membranes with anti-fouling properties to address this challenge. These membranes aim to prevent or reduce fouling, thereby improving desalination systems' overall performance and longevity. Fig. 2 b highlights the significance of seawater desalination as a primary application of ED technology. This field has witnessed extensive research efforts, with a recent emphasis on ion-exchange membranes. Researchers are exploring novel materials and designs for these membranes to enhance the efficiency and sustainability of seawater desalination processes. By focusing

on ion-exchange membranes, scientists aim to optimize ion transport and selectivity, ultimately improving the overall effectiveness of ED for producing fresh water from seawater. This research addresses the pressing global issues of water scarcity and the increasing demand for sustainable desalination solutions.

The body of literature on membrane fouling in electro dialysis has been greatly enriched by previous studies [1,9,11], which have collectively advanced our understanding of the complex fouling mechanisms, identified their negative effects on membrane performance, and investigated various strategies for prevention. The comprehensive analysis provided by ref. [9] highlights the critical importance of comprehending the different types of fouling, their consequences, and the methods used for characterization in the context of ion-exchange membrane fouling in the food industry. Ref. [11] focuses on the exploration of fouling challenges in electro dialysis reversal technology, specifically the interactions between natural organic matter and metal ions. Additionally, ref. [1] provides a thorough examination of the fouling mechanisms that are relevant to seawater desalination, emphasizing the significant challenges posed by the accumulation of organic matter, scaling from inorganic substances, and biofouling.

The present review paper focuses specifically on strategies for mitigating membrane fouling in seawater desalination in order to define its scope. It aims to provide a comprehensive analysis of various fouling phenomena, evaluate their effects, and examine innovative methods for mitigating fouling. By synthesizing insights from existing literature, this

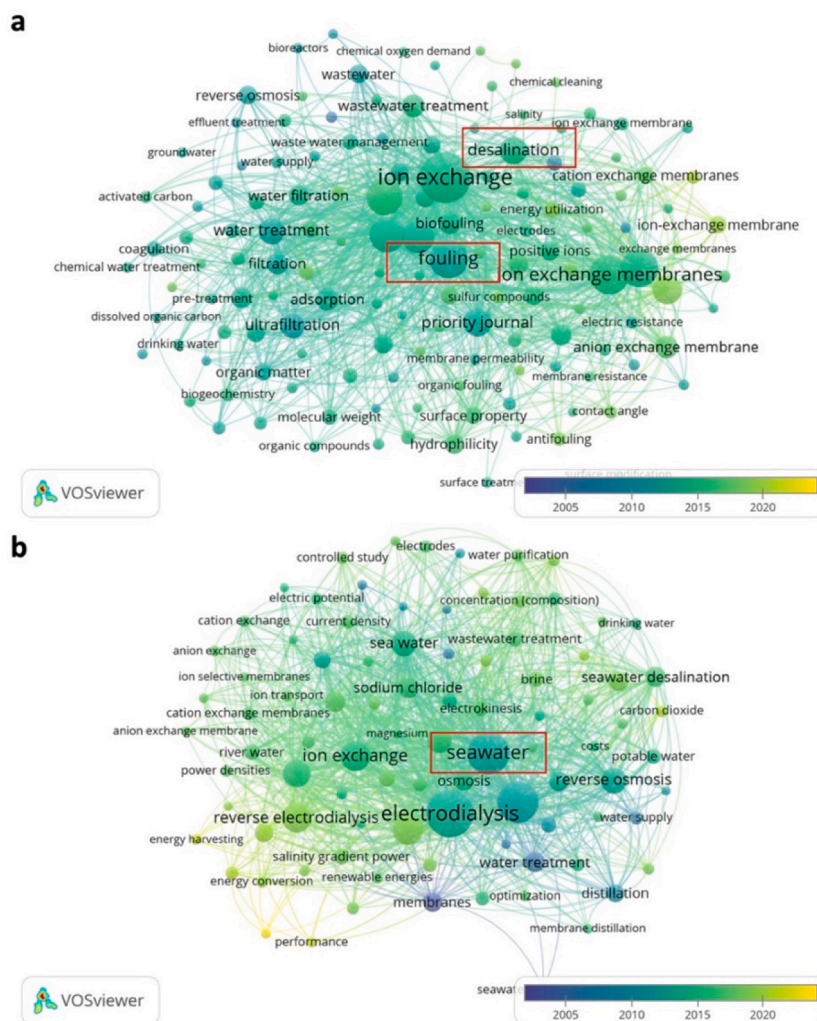


Fig. 2. Overlay visualization of keyword from publications related to (a) fouling in ion exchange membrane and (b) seawater desalination by electro dialysis (generated by VOSviewer).

paper proposes novel approaches, such as the utilization of pulsed electrodialysis reversal, to tackle these challenges. However, it maintains a critical standpoint throughout, acknowledging the limitations of current knowledge and the need for further empirical research to determine the effectiveness of these strategies. This approach not only contributes to the scholarly discussion in the field, but also aims to guide future research efforts, improve operational efficiency, and prolong the lifespan of electrodialysis membranes in seawater desalination applications, while recognizing the ongoing challenges and uncertainties in this area of study.

2. Seawater electrodialysis

2.1. Brackish water and seawater electrodialysis

ED is an electro-membrane process used to transport ions through ion-exchange membranes selectively. It applies an electric field across alternating cation-exchange and anion-exchange membranes, creating separate compartments for the anions and cations in a solution. As a result, positively charged ions migrate toward the cathode, while negatively charged ions move toward the anode, effectively separating the ions based on their charge. ED finds applications in various fields, including seawater and brackish water desalination, food and beverage, and pharmaceutical industries, where it is used for ion exchange, concentration, and purification processes [5,12]. Its ability to efficiently remove ions from solutions makes it a valuable technique for addressing water purification and resource recovery challenges.

Understanding feed water characteristics is crucial for optimizing performance and mitigating fouling in ED. Brackish water exhibits lower salinity and ion concentrations compared to seawater, which can have TDS levels as high as 42,420 mg/l (Table 1). This significant difference in salinity affects ED performance by influencing ion transport rates and membrane selectivity. Brackish water typically requires less energy for desalination and poses a lower risk of membrane fouling due to its lower concentrations of scaling ions such as calcium and magnesium. However, the presence of high levels of sulphate, as observed in refs. [13] and [14], can still pose a risk for scaling, highlighting the need for tailored fouling mitigation strategies.

Seawater desalination, on the other hand, challenges ED systems with its high ionic strength and diverse ion composition, including high concentrations of sodium, magnesium, and chloride (Table 1). The high salinity increases the likelihood of concentration polarization and scaling, necessitating more robust anti-fouling measures. Additionally, the characteristics of seawater desalination brine, with extremely high TDS (e.g., 58 g/l) and ion concentrations [15], exemplify the concentrated waste streams generated by ED, which require careful management to minimize environmental impact.

Fig. 3 a illustrates a relationship between the salinity of the feedwater and the energy demand of electrochemical desalination processes, including ED. As the salt concentration in the feedwater increases—moving from deionized water to brackish water and finally to seawater—the energy required for electrochemical desalination methods also rises. Notably, in the lower salinity range, electrochemical methods are less energy-efficient compared to reverse osmosis, which remains relatively constant as indicated by the blue line. However, as salinity approaches that of seawater, the energy consumption of electrochemical methods increases more gradually. Fig. 3 b shows the specific energy consumption (SEC) profiles of ED relative to the degree of salt extraction across a spectrum of saline feedwaters. The feedwater salinities examined include 1 g/L (represented in orange), 3 g/L (in red), 5 g/L (in blue), and 10 g/L (in purple), effectively spanning the typical salinity range encountered in brackish water environments. With water recovery and productivity constants set at 80 % and 20 L/m²/h, the SEC for ED is observed to rise in conjunction with increasing salt removal and feedwater salinity. Compared to reverse osmosis, ED is not limited by osmotic pressure constraints, allowing it to concentrate salts to

Table 1

Characteristics of brackish water and seawater used in electrodialysis studies.

Water type	Characteristics	Ref.
Brackish water	TDS = 1100 mg/l. pH = 8.9. Calcium = 11 mg/l. Magnesium = 18 mg/l. Sodium = 348 mg/l. Potassium = 3 mg/l. Total hardness as CaCO ₃ = 104 mg/l.	[18]
Brackish water	Electrical conductivity = 0.78 mS/cm. pH = 7.8. Turbidity = 3.2 NTU. Calcium = 108 mg/l. Chloride = 13.3 mg/l. Sulphate = 181.7 mg/l. Total organic carbon = 1.8 mg/l. Total Fe = 648 mg/l. As = 25.6 µg/l. Se = <1.0 µg/l.	[19]
Brackish water (after 0.45 µm filter)	Electrical conductivity = 0.59 mS/cm. pH = 8.2. Turbidity = 0.7 NTU. Calcium = 140 mg/l. Chloride = 51.6 mg/l. Sulphate = 87.6 mg/l. Total organic carbon = 3.9 mg/l. Total Fe = 78.4 mg/l. As = <1.0 µg/l. Se = 32 µg/l.	[19]
Brackish water	Electrical conductivity = 2.98 mS/cm. TDS = 1972 mg/l. Calcium = 12.9 mg/l. Chloride = 1092 mg/l. Magnesium = 15.3 mg/l. Sodium = 661.3 mg/l. Potassium = 30.1 mg/l. Sulphate = 161.4 mg/l.	[20]
Brackish water	Electrical conductivity = 2.48 mS/cm. TDS = 1490 mg/l. Calcium = 230 mg/l. Chloride = 382 mg/l. Magnesium = 66.8 mg/l. Sodium = 142 mg/l. Sulphate = 72.4 mg/l. Alkalinity (HCO ₃ ⁻) as CaCO ₃ = 648 mg/l.	[13]
Brackish water	TDS = 2736 mg/l. Electrical conductivity = 4.6 mS/cm. Sodium = 721 mg/l. Calcium = 168 mg/l. Magnesium = 40 mg/l. Potassium = 18 mg/l. Chloride = 1370 mg/l. Sulphate = 297 mg/l. SiO ₂ = 28 mg/l.	[14]
Seawater (Red seawater)	TDS = 42,420 mg/l. Electrical conductivity = 67.8 mS/cm.	[21]
Seawater	TDS = 34.2 g/l. Sodium = 10.6 g/l. Calcium = 0.4 g/l. Magnesium = 1.26 g/l. Potassium = 0.38 g/l. Chloride = 19.1 g/l. Sulphate = 2.65 g/l.	[22]
Seawater	Sodium = 6770 mg/l. Calcium = 626 mg/l. Magnesium = 753 mg/l. Chloride = 12,449 mg/l. Bicarbonate = 168 mg/l. Sulphate = 1620 mg/l.	[23]
Seawater (synthetic)	TDS = 37,685 mg/l. Sodium = 11,178 mg/l. Calcium = 700 mg/l. Magnesium = 1332 mg/l. Potassium = 822 mg/l. Chloride = 21,674 mg/l. Sulphate = 1980 mg/l.	[17]
Seawater desalination brine (synthetic, and after nanofiltration)	TDS = 58,708 mg/l. Sodium = 22,163 mg/l. Calcium = 392 mg/l. Magnesium = 303 mg/l. Chloride = 35,622 mg/l. Carbonate = 145 mg/l.	[15]

substantially higher levels [16]. Additionally, ED operates at lower pressures, thus eliminating the need for specialized piping and instrumentation. Its modular nature also facilitates easy scaling, making it particularly suitable for small-scale applications [17], which is advantageous for decentralized desalination facilities.

2.2. Operational parameters

Ion-exchange membranes are indispensable elements, offering selective permeation pathways for ions. These membranes are meticulously designed to either facilitate cation (positive ions) or anion (negative ions) passage. Usually constructed from polymers imbued with specific ionic functional groups, the membranes exhibit selective permeability. The ionic functional groups are tailored to interact preferentially with cations or anions, effectively allowing for their selective transport through the membrane under the influence of an externally applied electric field [1,25]. The electric field application is a critical

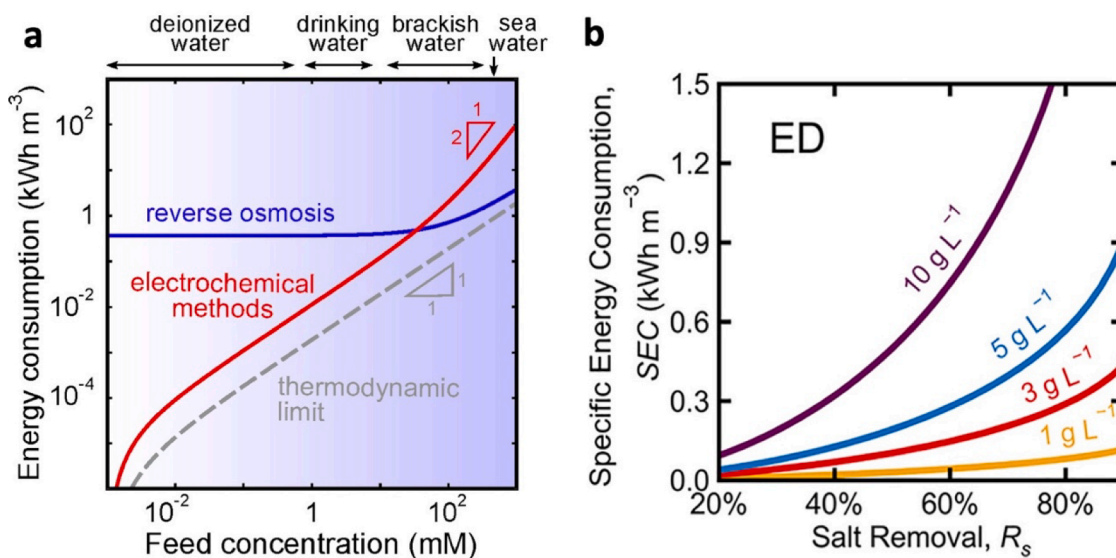


Fig. 3. Energy consumption for ED in desalination process. (a) Energy consumption reverse osmosis and electrochemical methods as function of feed concentration [5]. Copyright © 2022. The Authors. Published by American Chemical Society. (b) Specific energy consumption of ED as function of feed concentration and salt removal [24]. Copyright © 2021. The Authors. Published by American Chemical Society.

aspect, serving as the driving force propelling ions through the ion-exchange membranes. This directed movement under the electrical potential results in ions migrating towards their respective electrodes; with cations moving through cation-exchange membranes towards the cathode, and anions through anion-exchange membranes towards the anode. This systematic and selective ion movement orchestrates the separation of salts from water. A nuanced understanding of the compartment configuration within ED units is crucial. Here, a calculated alternation of cation and anion exchange membranes is deployed, creating a lattice of diluate (desalted water) and concentrate (salt-enriched water) compartments. Seawater introduced into the system flows through the concentrate compartments, and as ED process unfolds, desalted water is progressively accumulated within the diluate compartments [23,26,27].

Operational parameters wield substantial influence over the process efficacy and efficiency in ED [28–30]. For instance, the applied voltage and current density are paramount factors determining the rate and degree of desalination, as well as the overall energy efficiency of the system. An increment in applied voltage might amplify the desalination effect but concurrently heightens the risk of membrane fouling, underscoring the need for meticulous optimization of these parameters. Flow rates constitute another vital operational facet, influencing both the desalination rate and the likelihood of membrane fouling [28–30]. Optimal flow rates necessitate careful calibration to ensure efficient ion removal while minimizing fouling potential, striking a delicate operational balance that maximizes system longevity and performance.

Fig. 4 a underscores the energy efficiency of ED in desalination processes investigated in ref. [31]. It reveals that to desalinate seawater from 500 mM to 0.01 mM freshwater with a 50 % water recovery, approximately 0.95 kWh/m³ of reversible energy is required. In comparison, contemporary SWRO (Seawater Reverse Osmosis) installations, which typically operate with water recoveries between 35 % and 45 %, consume an average energy of around 3.4 kWh/m³. This stark difference highlights that a substantial portion, approximately 75 %, of the energy in current SWRO plants is lost irreversibly. While it may seem advantageous to have low water recovery based on Fig. 4 a, it is essential to consider the broader picture. Low water recovery necessitates increased water intake, additional pretreatment, storage capacity, pumping, and concentrate discharge per unit of product water, offsetting energy savings. Therefore, due to these factors, an optimal water recovery rate may lean toward higher values. Additionally, Fig. 4 b demonstrates the

relationship between current density, membrane stack voltage, and dilute conductivity, illustrating the impact of current and resistance on the specific desalination energy, which is a critical parameter for assessing desalination efficiency.

Fig. 4 c-e elucidates key factors influencing mass transfer in ED reported by [27]. Fig. 4 c reveals that increasing brine concentration boosts mass transfer flux due to deionized water as the drawing fluid, maintaining a concentration gradient that drives ion migration. Conversely, Fig. 4 d shows that simultaneous feed and draw liquid flow rate increases and decreases mass transfer flux, mainly by reducing the diffusion boundary layer thickness through heightened turbulence in the freshwater chamber. Fig. 4 e illustrates that higher electrolyte concentrations enhance mass transfer flux throughout the ED system, driven by the dual conductivity nature of ED units. Additionally, increased draw fluid flow rates elevate solution resistance within the concentration chamber and the overall system's total resistance, as they reduce the solution's interaction time with the ion exchange membrane's surface, affecting ion adsorption and desorption. These findings offer insights into the complex dynamics governing mass transfer in ED.

The performance of multistage ED systems presents a compelling subject of study [23], as illustrated in Fig. 4 f, which depicts the energy consumption dynamics within such systems. Initially, stage 1 dominates the energy consumption, but as the limiting current density (LCD) of stage 1 decreases, its energy consumption also decreases. In response, stages 2 and 3 compensate for the reduced performance of stage 1, highlighting the system's adaptability and ability to maintain a relatively constant outflow total dissolved solids (TDS) concentration of 1.9 g/l. It is worth noting that the World Health Organization (WHO) guidelines recommend a TDS concentration below 0.6 g/l for drinking water quality. The energy consumption required to desalinate the water until it reaches 1.9 g/l stands at approximately 3 kWh/m³. This observation underscores the intricate interplay between different stages in multistage ED systems, emphasizing their potential to achieve desired water quality standards while optimizing energy efficiency.

2.3. ED performances in seawater desalination

Several recent studies have explored the performance of electroanalysis (ED) in seawater desalination, revealing critical insights into its applicability, efficiency, and potential challenges (Table 2 and Table 3). In an endeavor to address acute water scarcity, exacerbated by natural

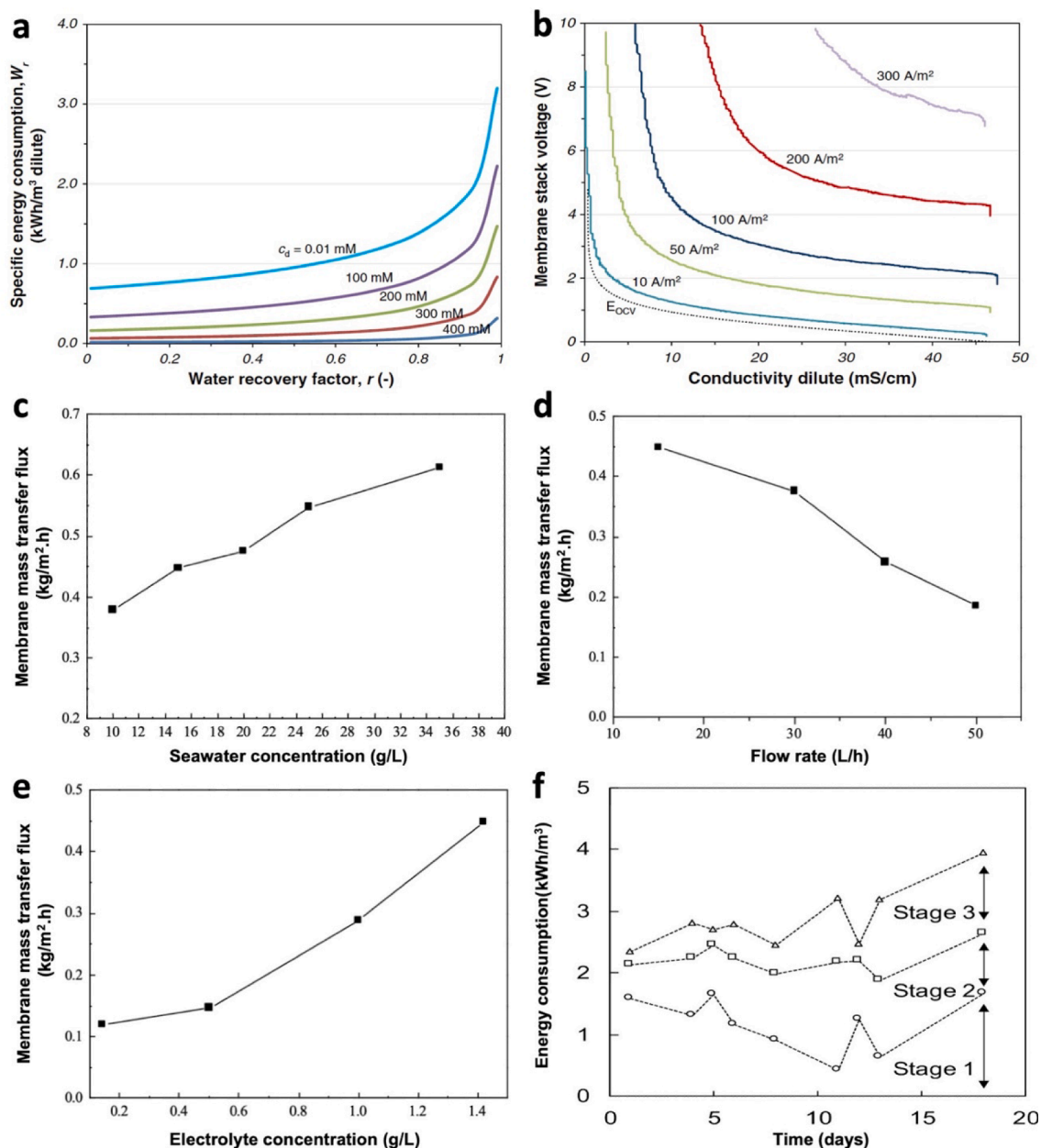


Fig. 4. Impact of ED Operating Parameters. (a) Energy consumption plotted against water recovery. (b) Variation in cell voltage with different current densities. In panels a and b, the seawater conditions are represented by a 0.50 M NaCl solution at 293 K. Reprinted with permission from [31]. (c) Impact of seawater concentration, (d) flowrate, and (e) electrolyte concentration on ions flux in ED. Panels c-e are reprinted from [27]. Copyright © 2022. The Authors. Published by MDPI. (f) Effect of multi-stage ED on energy consumption [23] Copyright © 2021. The Authors. Published Elsevier B.V.

phenomena in northern Peru, which contaminate freshwater sources and impede distribution networks, a study posits a resolution via seawater desalination employing ED [32]. The research meticulously predicts system behavior, desalination timelines, and energy consumption through intricate simulation and mathematical modeling of the desalination process. Noteworthy results demonstrate the potent desalination of high-salinity solutions, adhering to rigorous legal standards for potable water, with sodium chloride (NaCl) being effectively extracted.

Conversely, pivoting towards enhancing efficiency and economic viability in seawater desalination for irrigation purposes, another study juxtaposes monovalent selective ED with reverse osmosis (RO) [22]. RO, while adept at removing both monovalent and divalent ions, necessitates nutrient supplementation due to its indiscriminate ion removal. On the other hand, selective ED strategically extracts monovalent ions while

retaining beneficial divalent ions. A thorough characterization of membrane selectivity, limiting current, and resistance, amalgamated with a comprehensive cost model, implies that although monovalent selective ED may present slightly elevated costs compared to RO, it can potentially become a competitive alternative, especially in scenarios with reduced electricity costs or the incorporation of solar power.

Exploring innovative approaches to seawater brine treatment, an additional study unveils a hybrid selective ED (HSED) system, accentuating resource recovery and the high-value utilization of mixed salts [34]. The HSED process concurrently extracts major divalent cations and anions, notably NaCl, from seawater brine. The resulting concentrated NaCl-rich stream amalgamates effortlessly into a selective bipolar membrane ED (SBMED) process, facilitating acid/base preparation devoid of necessitating additional purification steps. The optimization of unit voltage within the HSED process bolsters the removal ratio of

Table 2
Selected studies of ED in seawater desalination.

Ref.	Research focus	Important findings
[21]	Comparison of ED and RO in terms of removal efficiency, recovery, and energy usage.	ED exhibited 97 % removal efficiency, 83.33 % recovery, and 2.03 Wh/L energy usage.
[32]	The application, simulation, and modeling of ED for seawater desalination.	Successfully desalinated water from 36,500.00 ppm to 145.37 ppm, adhering to legal limits for drinking water.
[27]	Influence of voltage gradient, concentration, and flux on ED desalination performance.	Optimized operating conditions identified: 24 V, 35 g/L feed concentration, 1.42 g/L electrolyte concentration, and 15L/h flow rate.
[33]	Integration of bipolar-membrane ED with a single-pass RO scheme for seawater desalination.	Integration led to a decreased seawater desalination footprint.
[22]	Economic and efficiency analysis of monovalent selective ED versus RO, considering solar power utilization.	Selective ED costs 30 % more than RO but may be economically viable with reduced capital/solar power usage.
[23]	Investigation into the influence of multivalent ions on the performance of ED in seawater desalination.	The removal of calcium and magnesium was higher than sodium in a multistage ED system.

divalent ions, thereby offering potential for enhanced utility. Moreover, the SBMED stack displays exceptional stability over numerous cycles, signaling a robust resistance to scaling challenges. This avant-garde approach furnishes a sustainable methodology for managing seawater brine, ensuring resource recovery and mitigating environmental impact.

Membrane fouling represents a significant operational hurdle, manifesting in various forms including colloidal, organic, inorganic scaling, and biofouling [28,35,36]. Each fouling variant presents distinct challenges and necessitates specific countermeasures and mitigation strategies. Developing effective fouling mitigation strategies requires a deep dive into understanding the specific mechanisms at play, ranging from particle deposition, organic materials adsorption, inorganic salts precipitation, to microbial activity on the membrane surfaces. Understanding these mechanisms provides a roadmap for the development and implementation of strategies aimed at preventing and controlling fouling, a critical endeavor for maintaining system efficiency and longevity. Furthermore, it provides a framework for future research aimed at not only addressing the current challenges but also innovating new materials and operational strategies to further enhance the performance and reliability of seawater ED systems.

3. Fouling mechanisms in ion exchange membrane

3.1. Inorganic fouling

Inorganic fouling, particularly from multivalent ions like Ca^{2+} and Mg^{2+} , significantly impacts ion exchange membranes during electrodiagnosis, leading to membrane deterioration and reduced performance [40]. Scaling experiments [41] have shown that at higher current densities (9 and 12 mA/cm²), anion-exchange membranes experience a marked flux decline, while at a lower density of 6 mA/cm², suggesting minimal impact on calcium migration. Notably, scaled heterogeneous membrane (MK-40 membranes) at 6 mA/cm² shows a flux slightly lower than in non-scaled membrane. SEM analysis reveals extensive scaling at 12 mA/cm², correlating with a rapid flux decline. Moreover, the onset of scaling—and consequently, performance degradation—occurs earlier at higher current densities, with heterogeneous membrane (MK-40) more susceptible than homogeneous membrane (CMV membrane). Membrane potential difference measurements, influenced by CaSO_4 precipitation, indicate an increase in ion transport resistance, more sharply and earlier in heterogeneous membrane (MK-40) than in homogeneous membrane (CMV.) This effect is linked to varying degrees of water splitting and pH changes across different current densities [41]. The increase in stack

Table 3
ED performances in seawater desalination.

ED Unit	Feed Water	Operating conditions	Performances	Ref.
Membranes: Penton-AEM-72-05-5 % crosslinking, Ralex® Membrane Membrane CMHPP – Mega-EU. Membrane area: 0.04 m ² in each compartment. Electrode: Stainless steel 316. Compartments: 2 diluate, 2 concentrate, 2 electrode.	Red seawater. TDS: 42420 mg/L.	Optimal conditions: 20 V applied voltage, 200 ml/min of flow rate.	Salt removal: 97 %. Water recovery: 83.33 %. Energy consumption: 2.03 Wh/L.	[21]
Membranes: MA-7500 and MC-3475. Membrane area: 25 cm x 45 cm in each compartment. Compartments: 1 diluate, 2 concentrate, 2 electrode. Electrodes: graphite plate, a stainless steel plate.	NaCl solution. TDS: 35000 mg/L.	Voltage gradient: 2 V/cm. Flow rate: 15 L/h	Salt removal: >27 %.	[27]
Membranes: (i) Neosepta ACS and Neosepta CMS. (ii) Fujifilm Type 16 membranes. Membrane area: 0.43 m ² (total active area) Compartments: 10 compartments.	Simulated seawater composition. TDS: 34.2 g/l and 45.4 g/l.	Flowrate: 95 L/h. Water recovery: 86 %. Current density: 300 to 600 A/m ²	Salt removal: ~77 % (for 45 min., for Fujifilm membranes) Desalination cost: ~4 \$/m ³ Energy: 7.0 kWh/m ³	[22]
Three stages of ED. Cells: 100 cells in stage 1, 50 cells in stage 2, 25 cells in stage 3. Membranes: Fujifilm Type 10 AEMs and Type T1 CEMs in stage 1. Fujifilm Type 10 CEMs in stage 2. Fujifilm Type 2 AEMs and Type 2 CEMs in stage 3. Membrane area: 220 × 220 mm ² per compartment. Electrodes: titanium.	Simulated seawater. TDS: 25 – 30 g/l.	Current density: 90 % of limiting current density.	Salt removal: >90 %. Final salt concentration: 1.9 g/l. Energy: ~3 kWh/m ³ .	[23]
Four stages of commercial ED (REDstack). Membranes: Fujifilm AEM type 10; Fujifilm CEM type 10; Fujifilm AEM	NaCl solution. Salt concentration: 510 mM NaCl.	Flow rate: 2.2 L/h. Current density: 95 % of limiting current density.	Final salt concentration: 6.3 mM NaCl. Energy: 2.2 kWh/m ³ .	[37]

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Table 3 (continued)

ED Unit	Feed Water	Operating conditions	Performances	Ref.
Type 2; Fujifilm CEM Type 2; Fumasep AEM FAB-PK-130.				
Two pass Shock ED. Nafion N115. Membrane area: 1 cm x 2 cm each. Compartment was filled with porous borosilicate frit. Electrodes: platinum.	Artificial seawater. TDS: 37,685 mg/l.	Flow rate: 0.021 ml/min. Applied voltage: 1 – 10 V.	Salt removal: 99.8 %. Water recovery: 70 %. Energy: 500 – 600 kWh/m ³ .	[17]
Four stages of commercial ED (REDstack). Membranes: Fujifilm AEM type 10; Fujifilm CEM type 10; Fumatech AEM FAB-PK-130. Membrane area: 2.15 m ² (total of four stages).	Synthetic seawater. Salt concentration: 510 mM NaCl.	Flow velocity: 5 – 15 mm/s. Current density: 95 % of limiting current density.	Final salt concentration: 11.4 mM. Energy: 3.6 kWh/m ³ .	[38]
Membranes: cation exchange membrane CR67, MKIII; anion exchange membrane AR204SXR412. Membrane area: 60 x 65 mm ² of each membrane. Electrode: platinum. Compartment: one cell pair.	NaCl solution. NaCl concentration: 30,000 mg/l.	Applied voltage: 6 V. Flow rate: 0.3 ml/s.	Final salt concentration: <500 mg/l.	[39]

resistance in ED systems, which is caused by the formation of scale, particularly the deposition of insoluble compounds like Ca(OH)₂ and Mg(OH)₂ on and inside the membranes and spacers, has also been reported in ref.. This occurrence is particularly noticeable at higher current densities (9 and 12 mA/cm²).

Scaling, characterized by the attachment of salt crystals to the spacer mesh, leads to blockages in the flow path, consequently increasing the pressure drop within the channels of ED [42]. This phenomenon is evidenced by the progressive rise in daily-averaged pressure drops in the concentrate compartment observed over nine days of desalination batches. Microscopic analysis of the dried concentrate channel spacer, specifically after nine days of batch experiments using pulsed electro-dialysis (PED) at a frequency of 5 Hz, revealed salt particles adhering to the spacer screen. While spacers in other operational conditions also experienced partial clogging, notably higher daily-averaged pressures in PED at a frequency of 0.5 Hz were indicative of more severe spacer clogging, likely due to increased bulk crystallization within the concentrate channel under this specific operational condition. In contrast, diluate spacers remained clean across all operational conditions, underscoring the localized nature of the scaling impact on module pressure drop [42].

Scaling of multivalent ions on or within the membrane can occur due to solution polarization or supersaturated precipitation [43]. Furthermore, minerals such as Ca²⁺ and Mg²⁺ can react with dissociated OH⁻ ions in water, resulting in precipitation on the membrane surface and contributing to fouling [44]. The formation and characteristics of membrane fouling are influenced by variables such as electric current, coexisting components, temperature, pH, and operation time [43].

These factors collectively shape the nature and extent of fouling on ion exchange membranes.

Mechanisms of mineral membrane fouling growth in ED were investigated [45]. As depicted in Fig. 5 a, water splitting generates OH⁻ ions at the membrane interface, leading to alkalization due to OH⁻ leakage from the alkaline concentrate stream. Pulsed current modes disrupt proton barriers formed by ion-exchange membranes, intensifying OH⁻ leakage. The resulting pH elevation causes a shift in species equilibrium and an upsurge in CO₃²⁻ concentration in the diluate. Consequently, calcium carbonate (CaCO₃) precipitates on both sides of cation-exchange membranes (CEMs). Moreover, OH⁻ leakage coupled with water splitting triggers magnesium hydroxide (Mg(OH)₂) formation on both sides of the CEM. Notably, fouling predominantly occurs on the CEM-concentrate side, with the impact of current pulsation varying at each membrane interface. Calcium sulfate can also precipitate and give rise to deposits on the surface of the CEM membrane, as exemplified in Fig. 5 b.

Iron is another type of foulant that can deposit on ion exchange membranes and affect membrane performance. A study has investigated the fouling behavior of Fe(III) species on a Nafion film at different pH values [46]. The results showed that Nafion interacted strongly with Fe (iii). Adsorption of Fe(III) on Nafion followed pseudo-first-order growth with limited surface site availability. During rinsing with neutral water, a transient decrease in adsorbed Fe(III) was observed on the Nafion film, followed by a notable jump and subsequent decline. Acidic elution of Fe (iii)-bound Nafion resulted in a rapid mass loss and pseudo-first-order decay. The study proposed heterogeneous fouling pathways, including loosely bound Fe(III) on the surface, iron exchange with sulfonic groups, and Fe(III) species trapping in the cluster channel. Release of Fe(III) from the Nafion surface exhibited pH-dependent behavior, with hydrolysis under neutral conditions and stronger interaction with sulfonic groups under acidic conditions. Over time, a decline in the amount of adsorbed Fe(III) was observed on Nafion under neutral conditions, possibly due to the leaching of precipitates or fretting of the Nafion film.

3.2. Nature and impact of organic accumulation

Organic fouling involves the accumulation of organic substances, such as proteins, humate, surfactants, or other large organic molecules, on membrane surfaces. This accumulation hampers the transport of ions, leading to decreased system efficiency [43,47]. According to a study [47], Ca²⁺ ions have a significant drop in flux when organics are present, however Cl⁻ and K⁺ ions show migration fluxes that are comparable to those in control tests without organics, suggesting that organics have little effect on their migration. In addition, the presence of organics has negligible effects on water flux, attributed to the dominant form of water migration as hydrated ions, with water flux substantially exceeding ion flux [47]. Anion exchange membrane desalination performance is greatly impacted by the presence of organics in the diluted compartment during ED because they alter solution conductivity changes over time [48]. The addition of organics such as sodium methane sulfonate, sodium benzene sulfonate, and sodium 6-hydroxynaphthalene-2-sulfonate resulted in only modest increases in final solution conductivity, indicating a negligible effect on anion exchange membrane performance. In contrast, the absence of organics caused solution conductivity to drop from 10.72 to 6.84 mS/cm. On the other hand, the presence of sodium dodecyl sulfate and sodium dodecyl benzene sulfonate reduced solution conductivity less, to 8.48 mS/cm and 9.71 mS/cm, respectively. This suggests that the formation of dense fouling layers on the anion exchange membrane is a major hindrance to desalination performance [48]. A study uses the potential difference (ΔE) as a fouling indicator to further clarify the various effects of organic fouling on anion exchange membranes during ED [49]. For example, after 180 min of exposure to sodium dodecyl sulfate, AMX membranes showed a rapid increase in ΔE to approximately 1.25 V, indicating serious fouling. On the other hand, HAEM's ΔE changed very little while AMA's ΔE increased more

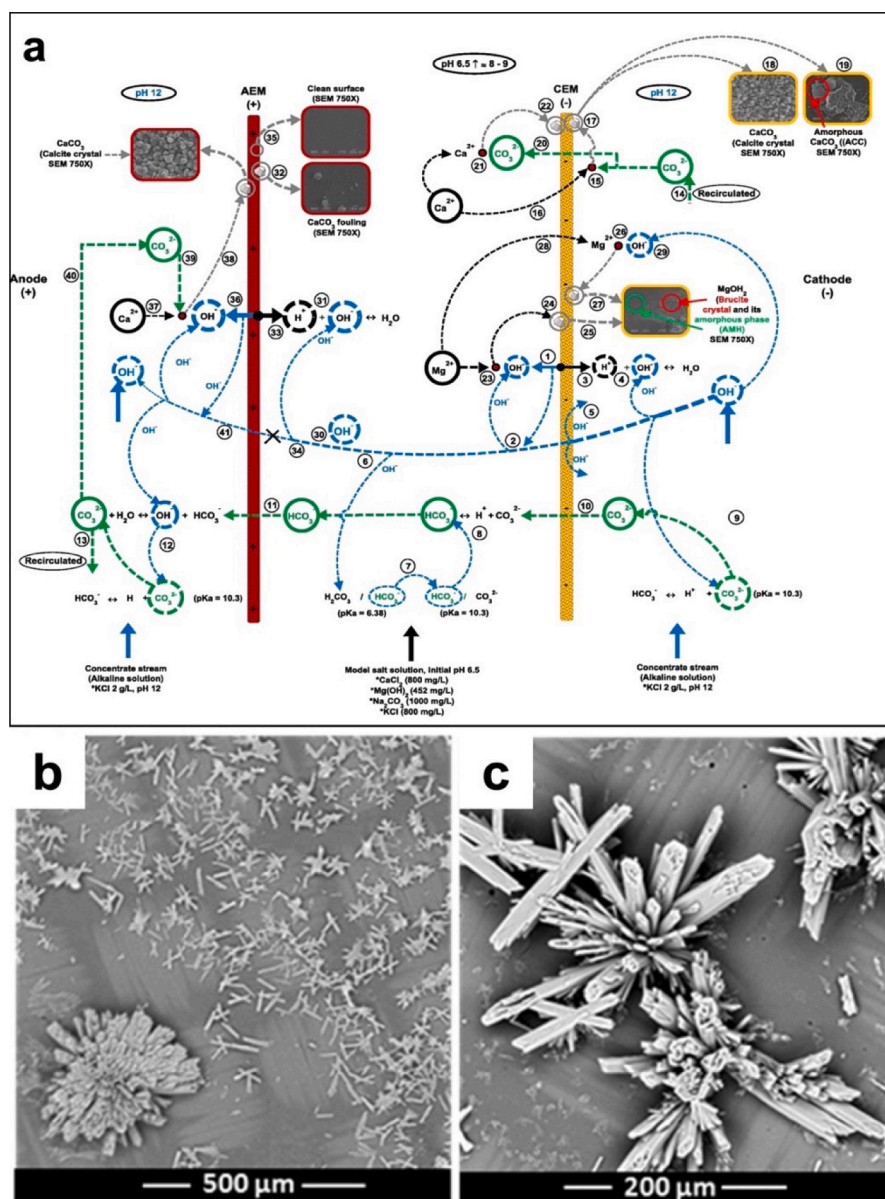


Fig. 5. Inorganic fouling on cation-exchange membrane. (a) Mineral fouling formation. Reprinted with permission from [45]. Copyright © 2014. Elsevier Inc. (b) and (c) CMV membrane fouled by CaSO_4 . Reprinted with permission from [41]. Copyright © 2018. Elsevier B.V.

gradually to roughly 0.5 V, suggesting that different AEM types are more or less susceptible to fouling. In particular, the presence of sodium dodecyl sulfate reduced the desalination rate for AMX by 42.3 %, whereas the decreases for AMA and HAEM were 15.3 % and 9.2 %, respectively. This emphasizes how sodium dodecyl sulfate effect on anion exchange membrane performance varies significantly and is mostly determined by the intrinsic characteristics of the membranes.

Various factors contribute to organic fouling, including the presence of organic matter in the feed water, water pH, and operational conditions [43]. The consequences of organic fouling encompass reduced efficiency, lowered ion flux, increased energy consumption, and decreased membrane lifespan. The fouling process occurs through the adsorption of organic matter onto the membrane surface, facilitated by hydrophobic interactions, hydrogen bonding, electrostatic attractions, or a combination of these mechanisms [9,43].

Researchers have investigated the mechanisms of organic fouling on different ion exchange membranes, aiming to understand how these membranes interact with organic foulants [50]. The study findings revealed that anion exchange membranes (AEMs) are more prone to

fouling by negatively charged organic molecules compared to cation exchange membranes (CEMs). Fouling stems from a combination of electrostatic, affinity, and geometric interactions between the foulants and the membranes. Rapid fouling induced by sodium dodecylbenzenesulfonate (SDBS) notably elevated electrical resistance, particularly in dense and aromatic AEMs. Aromatic organic fouling arises due to π - π interactions with aromatic AEMs, whereas hydrophobic organic fouling is more prevalent with hydrophobic AEMs [50].

A systematic study delved into the mechanism of AEM fouling caused by natural organic matter (NOM), with a focus on the influence of calcium ions [51]. The presence of calcium ions exacerbated NOM fouling on AEMs due to the formation of Ca-NOM complexes. Using the extended Derjaguin–Landau–Verwey–Overbeek (xDLVO) approach, researchers analyzed the interaction energy between the membrane surface and foulants. Short-range acid-base interactions emerged as the primary contributor to membrane fouling, whereas electrostatic interactions had minimal impact. The study demonstrated that calcium ions prompted the formation of ionic bridges between NOM components, resulting in the creation of a compact gel layer that worsened

AEM fouling [51].

A similar investigation was detailed in ref. [52], proposing a fouling mechanism for membrane fouling by humic acid (HA) and HA-Ca^{2+} . Fig. 6a illustrates the mechanism. Vibrational spectroscopic data confirmed the role of electrostatic double-layer interactions between HA or HA-Ca^{2+} and AEM surfaces. The presence of Ca^{2+} reduced HA's negative charge by complexing with COO^- sites, impacting the formation of membrane- HA-Ca^{2+} ternary complexes. Free Ca^{2+} in synthetic waters created intermolecular bridges and cation- π complexes, enhancing HA accumulation and the stability of HA-derived foulants on AEMs. HA fouling behavior changed notably in the presence of Ca^{2+} , exhibiting irreversible hydrophobic interactions with the membrane. Common interactions, such as hydrogen bonding, $\text{CH}-\pi$ interactions, van der Waals forces, polar- π interactions, and salt bridges, persisted regardless of Ca^{2+} presence.

The effects of calcium ions (Ca^{2+}) on the fouling of heterogeneous ion-exchange membranes by anionic polyacrylamide (APAM) were investigated during the treatment of polymer-flooding wastewater in the oil production industry using ED [53]. The study delved into fouling mechanisms, examining desalination performance, physicochemical and electrochemical characteristics, electrostatic interactions, and interfacial free energy. APAM fouling primarily affected anion-exchange membranes (AEMs) due to electrostatic attraction, with higher molecular weight (MW) APAM leading to more severe membrane fouling. Interestingly, heterogeneous ion exchange membranes exhibited lower susceptibility to APAM fouling compared to homogeneous membranes. The introduction of Ca^{2+} into the APAM solution complexed with APAM's carboxylate ions, weakening electrostatic attraction between APAM and AEMs.

Fig. 6b shows bovine serum albumin (BSA) deposits on anion exchange membrane. ED experiments with FITC-BSA confirmed the migration of BSA across the membrane, as green-colored FITC-BSA was observed on the membrane's surface and throughout its thickness [54]. This finding suggested that BSA could penetrate the membrane despite its initially considered homogeneous and dense nature, possibly due to gaps between matrix reinforcing fibers, enabling the charged solute passage.

Fouling behavior of homogeneous and heterogeneous ion-exchange membranes in the presence of hydrolyzed polyacrylamide (HPAM) as an organic foulant was also explored [55]. Heterogeneous ion exchange membranes experienced greater desalination efficiency reduction and higher energy consumption due to HPAM fouling than homogeneous IEMs. Transmembrane potential measurements revealed that HPAM adsorption led to more severe fouling on the membrane surface of heterogeneous IEMs. Membrane resistance increased with higher MWs of HPAM, particularly pronounced in heterogeneous IEMs. Intriguingly, the presence of oil in the feed water had a lesser impact on membrane fouling compared to HPAM.

3.3. Biofouling formation in ion exchange membrane

Biofouling involves the colonization of ion exchange membranes by microorganisms like bacteria, algae, and fungi, leading to the formation of biofilms. Fig. 7 illustrates the bacterial (*P. Putida* dan *Aeromonas*) deposition on the anion exchange membrane. Microorganisms initially attach to the membrane through electrostatic interactions, surface hydrophobicity, or specific binding sites [56,57]. This attachment reduces the membrane's ion exchange capacity (IEC) and maximum current achievable by cyclic voltammetry (CV) [56]. Intriguingly, biofouling can also create a bipolar structure on the membrane surface, positively affecting water splitting and resulting in enhanced t^+ values [58].

Once attached, microorganisms secrete extracellular polymeric substances (EPS), forming a protective matrix that establishes and stabilizes the biofilm [59,60]. EPS comprises a complex mix of polysaccharides, proteins, lipids, and other organic compounds. The biofilm serves as a reservoir for nutrients and organic matter, fostering

microorganism growth. A study observed that a biofouled Nafion membrane exhibited a higher t^+ of 0.94 compared to the fresh Nafion membrane's t^+ of 0.91, both analyzed in a nutrient mineral buffer solution [61]. This result's exact cause remains unclear but could be attributed to negatively charged biofoulants actively pulling cations through the solution.

The operational effectiveness of pristine and biofouling-resistant modified membranes has been the main focus of a thorough evaluation of the effect of biofouling on ED performance [62]. The study reports marginal increases in average energy consumption for modified membranes (E-Lys at 2.94 kWh/kg and E-Lys@Thps at 2.88 kWh/kg) compared to the pristine membrane (2.77 kWh/kg), using a 0.5 M NaCl solution and a constant current density of 15.29 mA/cm². Modified membranes also saw a little decrease in current efficiency. Desalination ratios continued to be high in spite of these modifications, with the E-Lys@Thps membrane in particular demonstrating considerable promise for desalination applications with a 98.02 % ratio attained after 240 min [62].

The decline in flux due to biofouling is influenced by membrane structure and functional charge [63]. Heterogeneous ion exchange membranes experience a more significant flux reduction than homogeneous ones. Furthermore, anion exchange membranes show a more pronounced flux decline compared to cation exchange membranes upon biofouling. The larger biovolumes observed on heterogeneous membrane surfaces are attributed to increased concentration polarization. Despite anion exchange membranes supporting biofilm formation to a lesser extent, their ion flux decline is more prominent due to preferential binding of negatively charged extracellular polymeric substances to positively charged ionic groups on the membrane surface, obstructing ion exchange.

3.4. Colloids and particulate fouling

An important component of membrane interactions, colloidal fouling, mainly caused by negatively charged silica sol adsorption on anion exchange membranes in ED systems, results in noticeable modifications to the membrane's characteristics [65]. The ED performance is not negatively impacted by silica sol fouling, despite early worries about its possible negative effects on several AEMs. Rather, this interaction causes a reversible cake layer to form on the membrane surface (see Fig. 8a), which increases the hydrophilicity of the membrane in experimental settings without lowering the efficacy of electrodialysis. It's interesting to note that during the ED process, the presence of this silica sol cake layer has been shown to enhance cell resistances, NaCl flux, and current efficiency in addition to maintaining the ionic transport rate in certain cases. The less fouling seen in AEMs with lower water content despite the presence of a loosely packed silica sol cake layer is evidence that colloids may actually improve ED performance rather than hinder it. This improvement is attributed to the increased hydrophilic properties induced by silica sol adsorption [65].

The impact of negatively charged silica sol on anion exchange membranes in ED was studied by Lee and Moon [66]. Their findings demonstrated the importance of silica sol's colloidal stability, which is determined by the electrochemical properties of the sols and electrolyte solutions, in fouling processes. Depending on the circumstances, a layer formed by silica sol deposition on the membrane surface may either promote or obstruct ion transport. In particular, even with 0.4 wt% silica sol, NaCl transport rates improved marginally in the presence of CaCl_2 concentrations below the critical coagulation concentration (CCC) of 0.008 M in a 0.1 M NaCl solution (Fig. 8b). This is because the membrane has a loosely packed layer that facilitates ion mobility. However, because of silica sol coagulation, NaCl transport rates dramatically dropped at concentrations higher than the CCC (0.01 M). Furthermore, cell resistance rose in the early stages up to 200 min when divalent cations such as CaCl_2 were present, but it dropped after 500 min when more divalent ions were present, aiding in ion mobility. The delicate

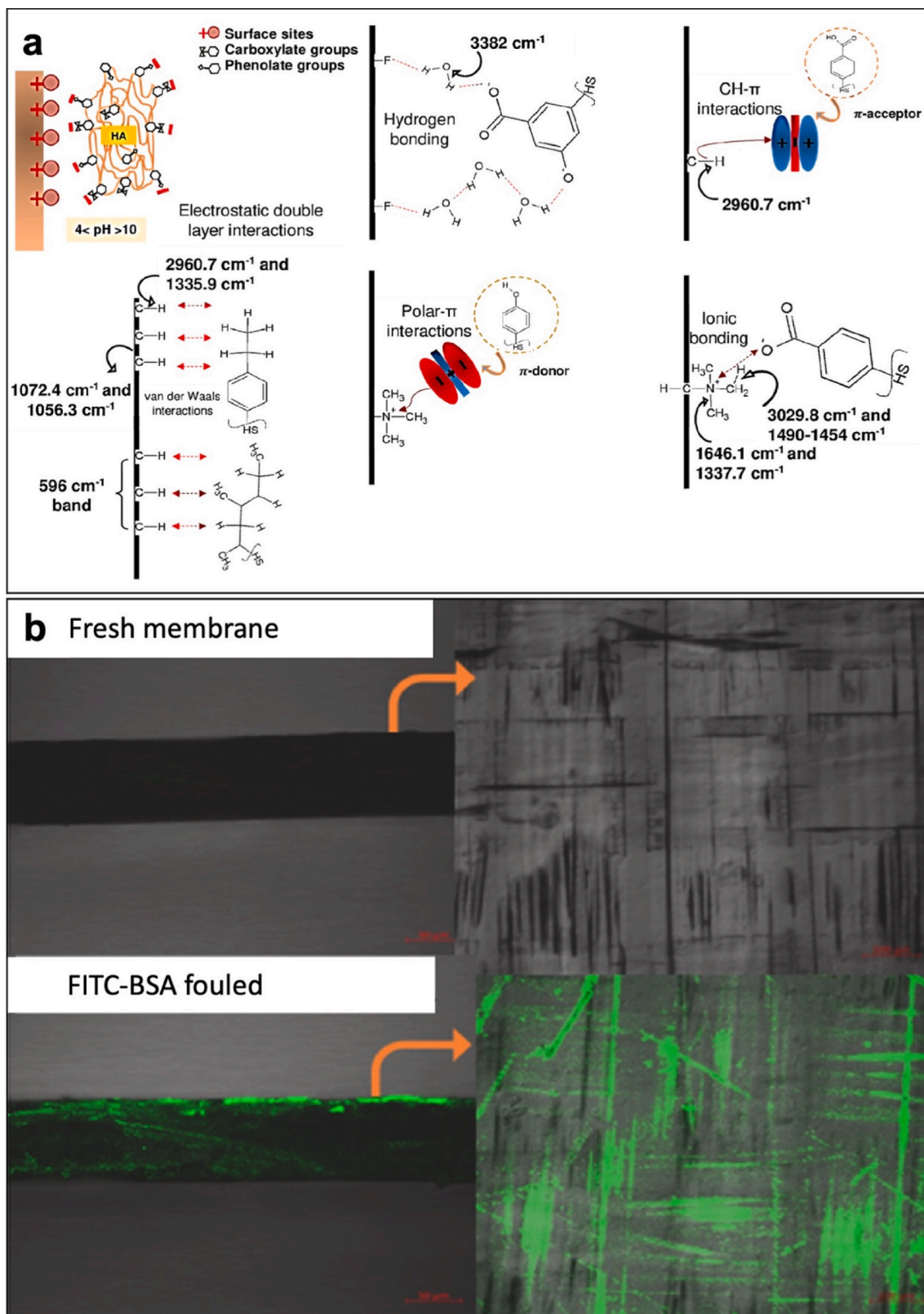


Fig. 6. Organic fouling on ion-exchange membrane. (a) Humic acid fouling formation by through membrane-humic acid complex. Reprinted with permission from [52]. Copyright © 2021. Elsevier B.V. (b) Fluorescence images displaying the surface and cross-section of a fresh membrane (top) contrasted with a fouled membrane (bottom), exposed to 50 mg/L fluorescein isothiocyanate-labeled bovine serum albumin (FITC-BSA) in the presence of 0.1 M NaCl. Reprinted with permission from [54]. Copyright © 2022. Elsevier B.V.

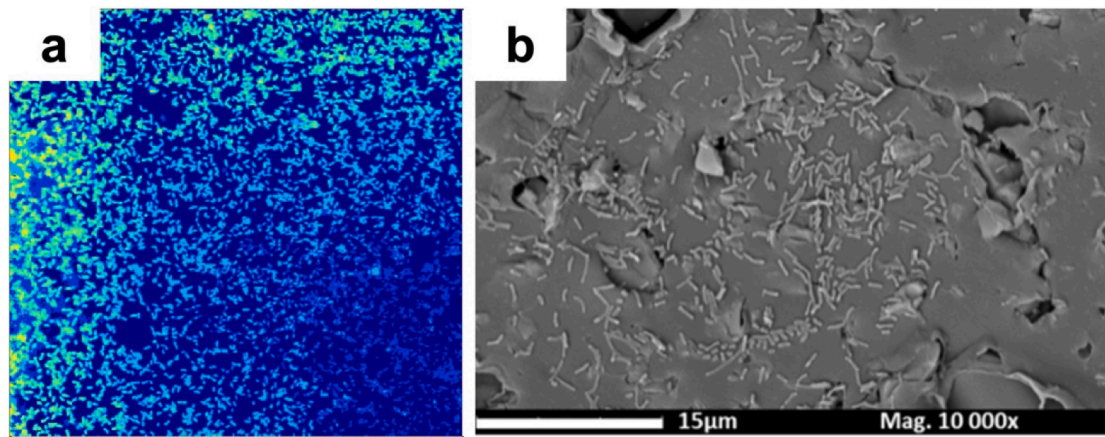


Fig. 7. Biofouling on anion-exchange membrane. (a) Confocal Laser Scanning Microscopy image of AMX membrane surface and deposited *P. putida* suspension. The membrane surface is depicted in blue, while the yellow speckles represent viable cells that have been stained. Reprinted from [64] with permission. Copyright © 2016. Elsevier B.V. (b) Scanning electron microscopy image of Ralex heterogeneous membrane fouled by *Aeromonas*. Reprinted from [56]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

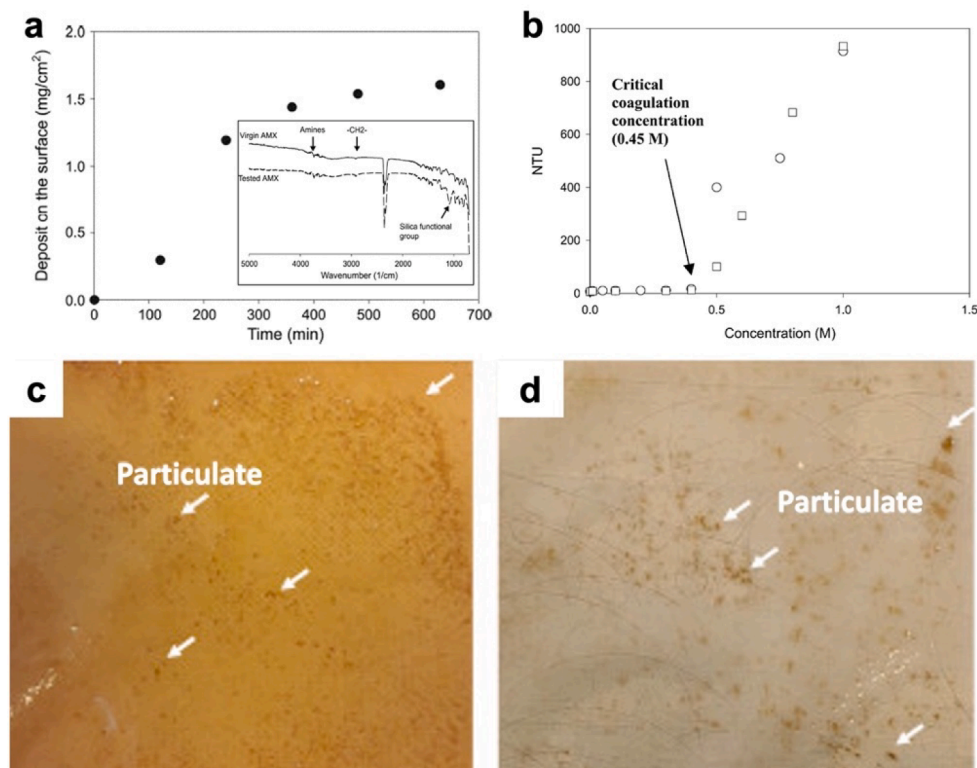


Fig. 8. Colloidal (silica) and particulate depositions on ion exchange membrane. (a) Si deposits on AMX membrane (silica sol: 0.4 wt% in 0.1 M NaCl). Reprinted with permission from [65]. Copyright © 2003. Springer Nature. (b) Critical coagulation concentration of silica. Reprinted with permission from [66]. Copyright © 2003. Elsevier Inc. (c) Particulate matter deposited on (c) anion and (d) cation exchange membranes [67]. Copyright © The Authors. Published Elsevier B.V.

balance between colloidal fouling, ion concentration, and ED efficiency is demonstrated by the declining performances with CaCl_2 concentrations above the CCC. Below the CCC, NaCl flux and current efficiency were maintained high, at roughly 2.14–2.18 mol/m²h and above 89 %, respectively.

Another type of fouling originates from particulate matter, consisting of micrometer-sized inorganic or organic suspended particles and aggregates [67]. Examples include silt, clay, iron and aluminum oxide precipitates, silicates, organic aggregates, and cellular debris [67]. These particles can obstruct the membrane surface, reducing efficiency in water treatment processes. Vital et al. [67] highlighted the occurrence

of particulate fouling in ion exchange membranes utilized in reverse electro dialysis of river and seawater. By day 54, distinctive differences were observed between AEM and CEM samples. Notably, AEMs presented a brownish layer (Fig. 8c and 8d), linked to humic acids — a characteristic absent in CEMs. The inherent negative charge of humic acids prompts their adherence to the positively charged AEMs. Both membrane types showed evidence of particulate fouling. Interestingly, microfiltration resulted in less fouling than dual media filtration, suggesting the latter's superior efficacy in particle accumulation. Notably, particles with an average size of 10 μm emerged as key culprits, leading to a significant 25 % decline in stack performance across the 54-day span

without any cleaning interventions.

4. Pre-treatment strategies for fouling mitigation

To combat fouling and maintain the performance of ion exchange membranes, various fouling mitigation strategies can be implemented. These strategies aim to minimize fouling deposition, facilitate fouling removal, and improve the overall operational efficiency of the membrane system. Pre-treatment processes play a crucial role in minimizing fouling potential by removing or reducing foulant precursors before they reach the ion exchange membranes. These processes are typically implemented upstream of the membrane system and aim to improve the feedwater quality.

Water softening is often employed as a pre-treatment technique to remove hardness-causing ions, particularly calcium and magnesium ions, from the feedwater [68]. Hardness in the water can lead to scaling and fouling on ion exchange membranes. Softening processes, such as ion exchange or precipitation, involve the removal or transformation of these ions into insoluble forms, thus reducing their fouling potential [69]. Adjusting the pH of the feedwater can help minimize fouling by controlling the solubility and precipitation of certain foulants [70]. Depending on the specific water chemistry and foulant composition, increasing or decreasing the pH can enhance the removal of specific ions or prevent their precipitation. pH adjustment can be achieved through the addition of acids or bases, or through the selection of appropriate current density aiming to optimize the water chemistry and reduce fouling potential [70].

Oxidation processes involve the use of oxidizing agents, such as chlorine or ozone, to degrade and remove organic foulants present in the feedwater. Oxidation reactions break down organic compounds into smaller, less foulant-prone substances, making them more susceptible to removal by subsequent treatment processes. Additionally, oxidation can disinfect the feedwater by inactivating or killing microorganisms, reducing the potential for biofouling [71,72].

Coagulation and flocculation processes are used to destabilize and aggregate fine colloidal particles present in the feedwater, making them easier to remove through subsequent filtration steps. Chemical coagulants, such as aluminum sulfate (alum) or ferric chloride, are added to the feedwater to neutralize the surface charges of colloidal particles and promote their aggregation into larger particles called flocs [73]. Flocculation is the gentle mixing or stirring of the feedwater to allow the formation of larger flocs. The formed flocs can be effectively removed by filtration processes, thus reducing fouling potential [74–76].

Filtration processes, such as microfiltration (MF) and ultrafiltration (UF), are commonly employed as pre-treatment steps to remove suspended solids, colloidal particles, and larger foulants from the feedwater [77]. These physical filtration methods use porous membranes with

specific pore sizes to retain and separate particles based on their size. Filtration not only removes foulants that can cause physical fouling but also reduces the concentration of particulate matter that could act as nucleation sites for scaling [78]. For instance, the effective control of fouling on ion-exchange membranes caused by particulate matter has been successfully achieved by employing dual media filtration and microfiltration techniques [67]. The performance of ED reversal in desalination, with filtration used as a pre-treatment, is illustrated in Fig. 9a and 9b.

5. Surface Engineering and membrane modification

Surface modification techniques offer a potent avenue to bolster the fouling resistance of ion exchange membranes, yielding improved performance by altering their surface properties [25]. These modifications aim to diminish fouling adhesion, simplify fouling removal, and enhance overall membrane functionality (Table 4).

5.1. Scaling control

A study explored the modification of ion-exchange membrane charge using a polyquaternium-22 polymer [81]. This enhancement led to intensified electroconvection through electro-osmosis, which diminished water splitting rates and fostered vortex structures near the membrane surface (Fig. 10 a). Consequently, scaling resistance improved, as evidenced by long-term stability experiments showcasing superior anti-scaling performance in the modified membranes compared to unmodified ones. Architectural strategies, such as depositing zeolitic imidazolate framework-8 (ZIF-8) on commercial membranes, have been employed to develop monovalent permselective cation exchange membranes, effectively hindering scaling in seawater desalination processes [82]. The ZIF-8 layer acts as an ion-selective filter, enhancing ion transport and limiting the formation of scale on the membrane surface.

Moreover, one strategy to combat scaling formation involves the use of monovalent permselective membranes, which inhibit the permeation of bivalent or multivalent ions towards the concentrate side, thereby preventing their precipitation or scaling on the membrane surface [83]. Monovalent permselective cation exchange membranes showed higher current density and desalination efficiency in seawater desalination studies [83]. They demonstrated a separation efficiency for $\text{Na}^+:\text{Ca}^{2+}$ and $\text{Na}^+:\text{Mg}^{2+}$ that effectively prevented Ca^{2+} and Mg^{2+} precipitation in the membrane and cathode. Monovalent permselective anion exchange membranes also exhibited excellent permselectivity [61]. A polyvinyl alcohol-based monovalent anion selective membrane demonstrated long-term operational stability and superior permselectivity for $\text{Cl}^-/\text{SO}_4^{2-}$ compared to commercial alternatives [84]. These advancements offer promising solutions to address fouling and scaling challenges in

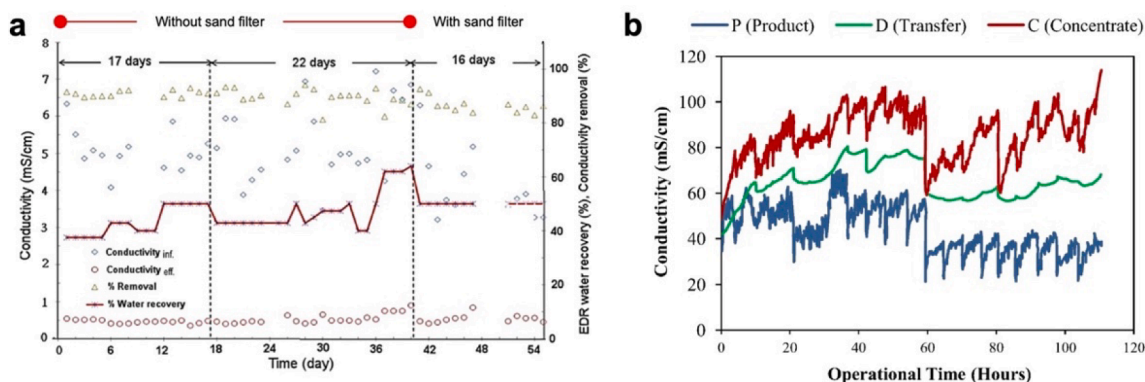


Fig. 9. Stability of ED performance with filtration as pre-treatment. (a) Performance of ED reversal during the treatment of industrial wastewater. The pre-treatment was sand filter. Reprinted from [79] with permission. Copyright © 2016. Elsevier Ltd. (b) ED reversal was used to treat basal water with microfiltration and ultrafiltration as pre-treatment. Reprinted with permission from [80]. Copyright © 2015. Elsevier B.V.

Table 4
Modified membranes with improved anti-fouling properties.

Ref.	Modified Membrane	Modifier or Method	Significant Findings
[99]	AEM	Polyphenol-polyamine co-deposition and Graphene oxide	Enhanced antifouling ability, improved negative charge density, and alkaline stability.
[87]	AEM	TiO ₂ coating	Improved antifouling properties and good fouling reversibility in AEMs
[100]	AEM	Mussel-inspired deposition (PDA/DSA complexes)	Enhanced antifouling performance against organic foulants.
[101]	AEM	Polydopamine and Poly (sodium 4-styrenesulfonate) (PDA@PSS-M)	Improved antifouling properties.
[102]	AEM	Sulfonated polydopamine coating (SDA)	Improved permselectivity and superior anti-fouling properties
[103]	AEM	Surface-sulfonated graft modification	AEMs with monovalent ion selectivity and antifouling properties.
[104]	AEM	Partially hydrolyzed polyacrylamide (HPAM)	Severe fouling effects of HPAM on AEMs, influenced by solution composition.
[91]	AEM	PEG400	Enhanced resistance to organic fouling.
[105]	CEM	Conductive polymers and nanomaterials	Improved anti-biofouling properties and energy efficiency.
[106]	CEM	Polyethyleneimine (PEI), TiO ₂ nanoparticles, and Graphene oxide (GO) nanosheets	Enhanced anti-organic fouling and desalination performance.

AEM – anion exchange membrane; CEM – cation exchange membrane.

various membrane processes. Monovalent permselective cation exchange membranes were synthesized by coating a quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO) layer on the surface of the SPPO-PVA (SPVA) composite membrane [85]. The influence of the selective barrier (thickness) resulted in high perm-selectivity up to 12.7 for the Li⁺/Mg²⁺ system. The prepared membranes demonstrated low electrical resistance and high limiting current density and exhibited stable behavior for eight consecutive ED cycles without fouling/scaling. The observed high perm-selectivity was attributed to the electrostatic repulsion between divalent ions and the cross-linked nature of the base membrane (Fig. 10 b).

Wang et al. [86] introduced a method of modifying membranes by creating a Janus-charged monovalent cation-exchange membrane (M–CEM). This particular membrane has a unique design consisting of two distinct structures (Fig. 10 c). On one side, there is a thin layer with a positively-charged surface made of trimesic acid/polyethyleneimine. Simultaneously, the other side integrates a conventional, negatively charged CEM. This Janus-charged structure effectively prevents the unwanted migration of anions, a common issue with porous CEM. As a result, the membrane's perm-selectivity and total cation flux are enhanced. Comparing it to existing M–CEMs, this innovative Janus-charged M–CEM displayed remarkable perm-selectivities, with values of 145.77 for Na⁺/Mg²⁺ and 14.11 for Li⁺/Mg²⁺. These values exceed the established “Upper Bound” standards for the separation of monovalent-bivalent ions (Fig. 11b).

5.2. Organic fouling and biofouling prevention

One approach involves applying hydrophilic coatings to the membrane surface, thus augmenting its hydrophilicity and reducing fouling susceptibility. Hydrophilic coatings like polyethylene glycol, polydopamine, zwitterionic materials, or nanoparticles exhibit superior water

affinity and low surface energy, rendering them resistant to fouling [87–91]. These coatings deter foulants from adhering firmly to the membrane surface, simplifying their removal during cleaning. For instance, ion-exchange membranes with a TiO₂ coating, such as the PDA-PSS/TiO₂ modified AEMs, demonstrate exceptional anti-fouling properties [87]. The TiO₂ modification fosters super-hydrophilicity on the membrane surface, diminishing interactions between organic foulants and the membrane and allowing easy washing during rinsing. The robust adhesion capability of PDA to TiO₂ further bolsters anti-fouling performance during long-term experiments (Fig. 11 a). Compared to pristine AEMs, the modified counterparts show notably lower cross-membrane voltages, attesting to their superior anti-fouling efficacy. Furthermore, these modified AEMs can be efficiently cleaned with a simple one-hour water rinse, eliminating the need for UV irradiation. In cases of severe fouling, UV irradiation can be employed to activate the photocatalytic effect of TiO₂, decomposing foulants and rejuvenating membrane performance.

Another example of surface-modified ion exchange membranes is the composite-modified poly (sodium 4-styrene sulfonate)/polydopamine membrane (PSS&PDA-M) [89]. It comprises an electrodeposited poly (sodium 4-styrene sulfonate) (PSS) modified layer that boosts surface hydrophilicity and negative charge density, coupled with a polydopamine (PDA) self-polymerization modified layer that enhances stability and diminishes surface roughness. The PSS&PDA-M delivers exceptional fouling resistance against sodium dodecyl sulfonate while maintaining effective desalination performance. Even after a rigorous 120-hour rinsing test, its superior anti-fouling capabilities remain intact. Research also shows that PDA coating on the membrane surface influences bacterial adhesion and growth [64]. In Fig. 11 b, it is evident that live bacteria accumulate on the membrane surface, with no dead bacteria or significant extracellular polymeric substance (EPS) formation observed. The number of bacteria adhering to the membrane surface decreases with PDA coating and then increases with dopamine concentration. Colony heights and total cell volumes attached to the membrane surface, as shown in Fig. 10b1 and Fig. 10b2 using CLSM images and COMSTAT software, confirm that total cell volumes and bacterial coverage decrease with increasing dopamine concentration in the modification solution, followed by an increase after reaching a minimum at around 0.1 kg/m³ dopamine concentration. PDA coating effectively suppresses bacterial attachment and growth on the membrane surface by increasing hydrophilicity and introducing negative surface charges. Another promising example is a multi-cationic cross-linked anion-exchange membrane, where functionalization of polyimide with dianhydride and grafting multi-cationic groups offers excellent antibacterial properties against waterborne *E. coli* [92]. The architectural design of cross-linking and side chain grafting of multi-cationic groups affords fine control over properties, stabilities, hydrophilic-hydrophobic attributes, anti-fouling, and antibacterial characteristics.

Surface charge modification can similarly exert a notable influence on fouling behavior. By adjusting the surface charge through chemical treatments or functionalization, interactions between the membrane surface and foulants can be altered [93]. For example, modified anion exchange membranes were developed by self-polymerizing L-dopa on the surface of commercial AEM (Fuji I type) and grafting 4-amino-benzenesulfonic acid monosodium salt (ABS) onto the L-polydopamine layer [94]. These modified AEMs showcased negatively charged functional layers that induced an electrostatic repulsion effect, preventing negatively charged bacteria like *E. coli* and *S. aureus* from adhering to the membrane surface. As a result, L-PDA@ABS-Cl displayed remarkable fouling resistance and effective inhibition against these bacteria.

Additionally, controlling the surface roughness of ion exchange membranes can influence fouling behavior [95]. Smoother surfaces with reduced roughness provide fewer adhesion sites for foulants, making it challenging for them to adhere strongly [96]. Techniques like plasma treatment or surface coating can be employed to smoothen the membrane surface and reduce fouling [49]. Another method involves

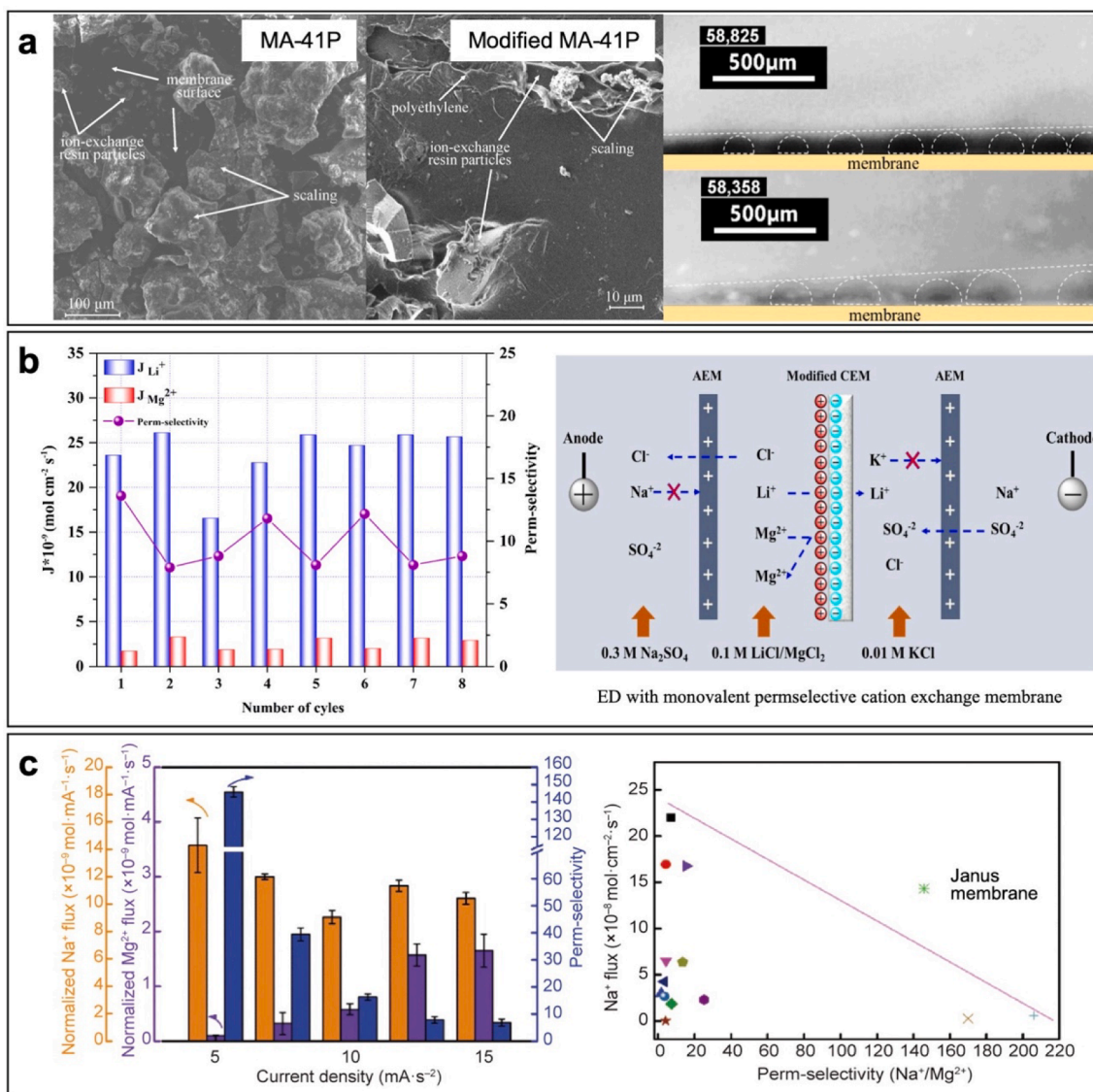


Fig. 10. Membrane modification for increasing monovalent permselectivity and scaling prevention. (a) AEM modified by polyquaternium-22 shows less scaling formation and more vortices by electroconvection [81]. Copyright © 2022. The Authors. Published by MDPI. (b) Monovalent permselective CEM has a stable performance (cation flux) and no scaling formation after 8 desalination cycles. Reprinted with permission from [85]. Copyright © 2019. Elsevier B.V. (c) Janus membrane with high monovalent permselectivity exceeding standards for the separation of monovalent-bivalent ions [86]. Copyright © 2022. The Authors. Published by Elsevier Ltd.

depositing a graphene oxide (GO) layer and a thin polydopamine (PDA) coating on an anion exchange membrane, resulting in a highly hydrophilic and negatively charged surface that exhibits enhanced anti-fouling performance without compromising desalination efficiency [97]. In brackish water desalination, cation exchange membranes prepared from polysulfone, polyvinylpyrrolidone (PVP), and sodium dodecylbenzene sulfonate (SDBS) demonstrated improved performance attributed to higher hydrophilicity and lower surface roughness [98].

To impede the permeation of multivalent ions, ion exchange membranes in electrodesalination often employ opposite charge coatings to enhance their performance. Nevertheless, an equally paramount consideration pertains to the anti-fouling characteristics of these membranes, particularly their capacity to deter the adhesion of proteins and biofilms. This property arises from the heterogeneous charge distribution on the membrane's surface. In the context of marine applications, mitigating biofouling traditionally involves the utilization of hydrophobic, lubricious, or zwitterionic materials, which tend to discourage the settlement of fouling organisms [107–110].

The empirical “Baier curve” highlights the correlation between fouling propensity and contact angles, providing valuable insights, particularly in the context of biofouling (Fig. 12 a). This curve delineates a non-monotonic trend, suggesting that materials like silicone, with a contact angle around $\theta = 105^\circ$, are optimal for anti-fouling purposes. The efficiency of silicone in this context arises from the inherent molecular flexibility and mobility of its backbone and attached organic groups. As reported in [110], silicone oil-infused cross-linked silicone polymers have the potential to be engineered as superior anti-fouling surfaces with slippery attributes. As depicted in Fig. 12 b, the i-PDMS coating exhibited the most impressive performance in the *C. lytica* biofilm retraction assay, displaying the smallest residual biofilm coverage at $7.41 \pm 5.74 \%$. Polytetrafluoroethylene (PTFE), while exhibiting strong anti-fouling attributes, tends to be hydrophobic. In the specific context of ED, it is crucial to prioritize materials that concurrently manifest both anti-fouling and hydrophilic properties. The Baier curve serves as a guiding tool in this endeavor, suggesting polymers such as polyethylene glycol (PEG), polyethylene terephthalate (PET), and

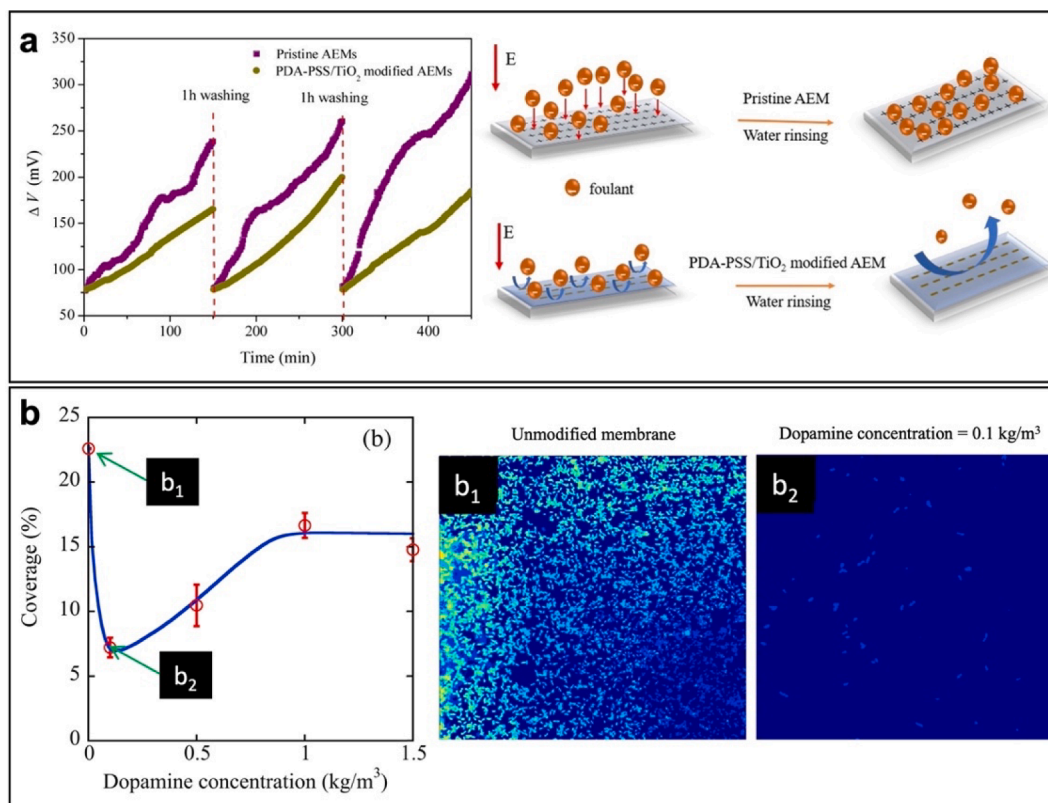


Fig. 11. Membrane modification for fouling control. (a) coating AEM with PDA-PSS/TiO₂ reduces membrane fouling by organic. Reprinted with permission from [87]. Copyright © 2021. Elsevier B.V. (b) PDA modified AEM shows lower biofouling coverage [64]. Copyright © 2016. Elsevier B.V.

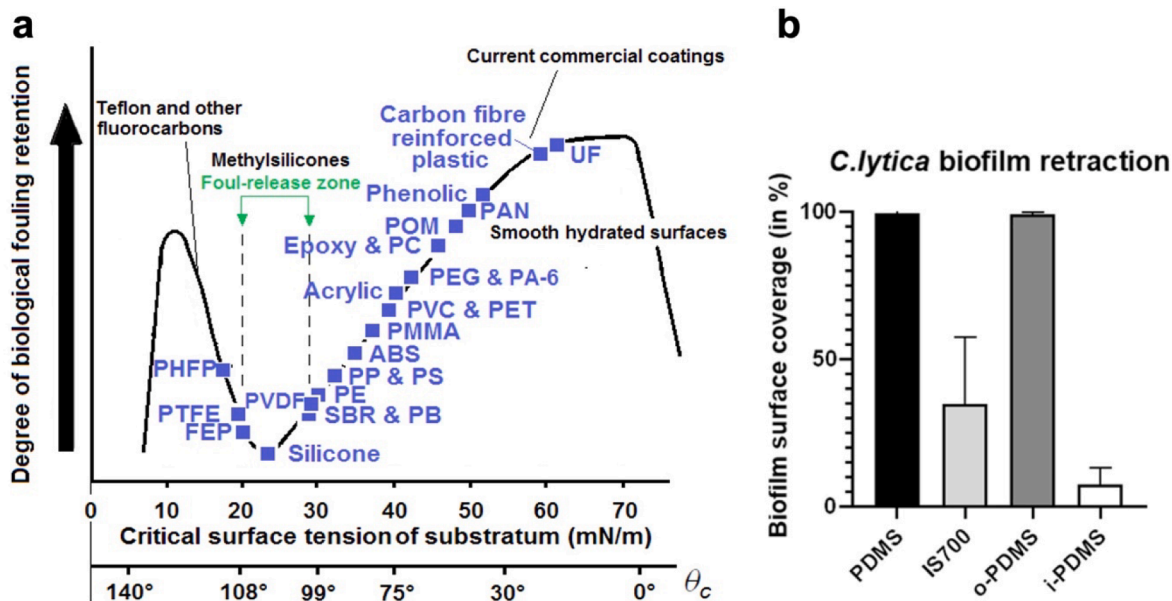


Fig. 12. Coating material and biofouling retention. (a) “Baier curve” of critical surface tension vs biofouling retention [111]. Copyright © 2014. The Authors. Published by JHED. (b) Biofilm surface coverage of oil-containing PDMS. Intersleek 700 (IS700), polydimethylsiloxane (PDMS), one-pot pre-cure oil addition approach (o-PDMS), and post-cure infusion approach (i-PDMS) [110]. Copyright © 2022. The Authors. Published by Springer Nature Ltd.

polymethyl methacrylate (PMMA) as suitable candidates for this purpose.

6. Effective chemical cleaning approaches

Ensuring the long-term functionality of ion exchange membranes

demands regular maintenance procedures to eradicate accumulated fouling deposits. The expenses associated with membrane cleaning and replacement can constitute up to 50 % of the total cost incurred in the production of demineralized water [112]. A variety of techniques are employed to dispel and expunge these foulants that cling either superficially or within the membrane’s pore structures. Chemical cleaning

stands out as one primary method, using specific agents to dissolve or dislodge foulants. The choice of these agents, such as acidic solutions like citric acid or hydrochloric acid, alkaline solutions like sodium hydroxide, or even surfactants, hinges on the type of foulant and membrane compatibility [7]. Notably, while acids can tackle inorganic scales, alkalis prove adept against organic foulants (Fig. 13a). The comprehensive utilization of surfactants also aids in tackling both organic and particulate fouling. However, it is imperative to exercise caution, adhering strictly to manufacturer guidelines and safety protocols while manipulating these cleaning agents.

A comprehensive analysis at the plant-scale level, focused on the treatment of oily wastewater using ED, divulged the superior cleaning efficiency of HCl over other agents [113]. Intriguingly, while NaOH excelled in combating hydrolyzed polyacrylamide fouling on cation-exchange membranes, HCl outperformed it against anionic counterparts on anion-exchange membranes. This distinction is attributed to the deprotonation effect of NaOH, enhancing electrostatic repulsion between anionic polyacrylamide molecules and the CEM, while the protonation effect of HCl reduces electrostatic attraction between anionic polyacrylamide molecules and the anion exchange membrane. Moreover, NaOH demonstrated superior effectiveness in removing oil fouling,

while HCl efficiently eliminated inorganic fouling, including carbonate precipitations of Ca^{2+} and Ba^{2+} and magnesium hydroxide, through double decomposition and neutralization reactions.

However, it is imperative to tread cautiously. Alkaline cleaning environments can instigate the degradation of AEMs [114]. This degradation is evident in the chemical alterations they undergo, culminating in the decline of desalination performance. Although subsequent acid treatments can rejuvenate the membranes to some extent, the initial capacity rarely gets fully restored due to the emergence of non-functional groups on the membranes [114]. Despite the improvement after acid treatment, the desalination capacity of the aged AEMs remained lower than that of the original AEMs due to nucleophilic substitution and elimination reactions, leading to the formation of non-functional groups, such as benzylic alcohol and alkene, on the membranes. These non-functional groups lack ion-exchange capacity and contribute to the overall degradation of the AEMs, as illustrated in Fig. 13b [114].

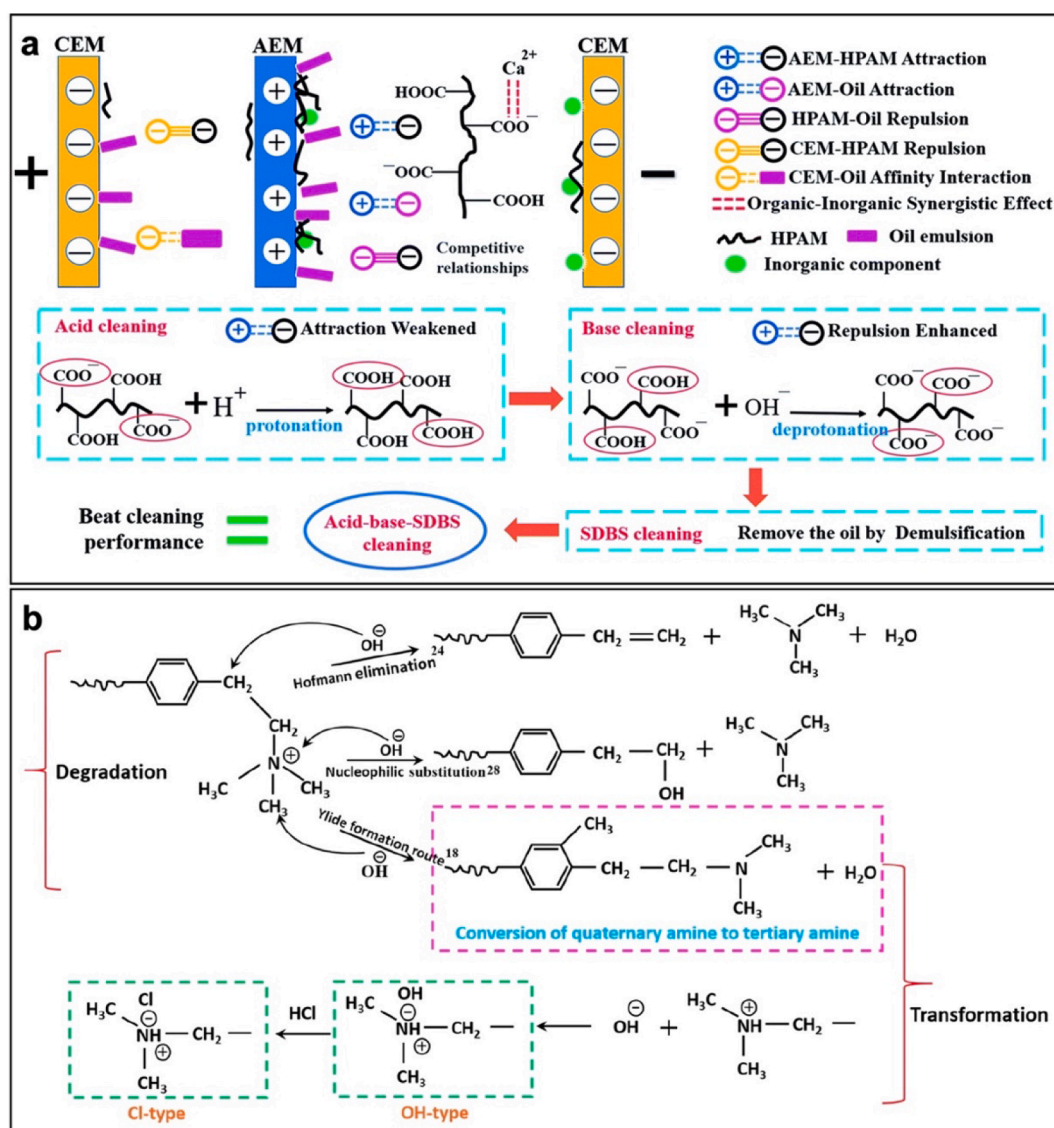


Fig. 13. Membrane cleaning. (a) Fouling route by hydrolyzed polyacrylamide, oil, and inorganic foulants and cleaning theory [7]. (b) Degradation of AEM functional group due to cleaning. Reprinted with permission from [114]. Copyright © 2019. American Chemical Society.

7. Emerging methods for fouling control

7.1. Polarity reversal and pulsed electric field

Lately, periodic polarity reversal (PPR) has captured the attention of researchers, emerging as an efficient strategy to stave off fouling in ion exchange membranes, notably in ED reversal (EDR) operations [115]. This innovative technique involves periodically switching the direction of the applied electric field, resulting in enhanced fouling resilience and optimized operational performance. The magic of PPR lies in its complex electrochemical dynamics. Ordinarily, fouling emerges from the agglomeration of charged species, organics, and particulates on the membrane [116]. PPR instigates localized pH and ion concentration alterations adjacent to membrane surfaces. These modifications foster an ambient conducive to electrochemical purging, allowing electrochemically produced species to dissolve and dispatch fouling agents [117,118]. A highlight of this process is the formation of metal hydroxides at the cathode during the polarity shifts, instrumental in dismantling foulant deposits. The oscillating electric fields intrinsic to PPR have a pronounced impact in weakening the adhesive bonds between foulants and the membrane [119]. This interference renders the foulants' irreversible attachment untenable, streamlining their expulsion in ensuing cleaning cycles. The field's undulations also produce electrokinetic effects that counteract foulant attachment [120–122].

To successfully integrate PPR in EDR processes, a thorough understanding of operational nuances is vital. Elements like feed solution composition, membrane characteristics, and system design influence the frequency and duration of PPR cycles [123]. Systematic optimization studies are pivotal to pinpointing the precise timing and intensity that both prevent fouling and uphold system efficiency [119,123]. While typically, polarity reversals span minutes to hours, shorter durations manifest superior fouling deterrence, albeit at the energy expense [124–126].

Recent studies have contributed significantly to this domain. Alvaro Gonzalez-Vogel et al. unveiled insights into the pulsed ED reversal (pEDR) process [127]. Contrasting with traditional ED, pEDR exhibited remarkable enhancements, notably plummeting production losses and substantially extending the hydraulic reversal duration. Coupled with economic viability and its evident scalability, pEDR stands as a paragon in the realm of process water recirculation, further emphasized by WinGEMS simulation.

Other notable studies include De Jaegher et al., who probed into pulsed electric field (PEF) operations in ED [128], underscoring a delicate balance between current efficiency and fouling restraint. The study revealed reduced fouling susceptibility within the system, partly attributed to alleviating concentration polarization during PEF. Zhao et al. spotlighted the system's prowess of EDR, notably its water recovery efficiency and resilience against fouling, even in extended operations [125]. The lab-scale ED reversal (EDR) system demonstrated remarkable achievements, achieving an impressive water recovery rate of 85 % while simultaneously reducing the volume of industrial reverse osmosis brine by a substantial factor of approximately 6.5 times.

The comparative efficacy of chemical cleaning against inverted electrode cleaning was elaborated in a study [129]. The findings underscored the superior restoration capabilities of chemical cleaning, showcasing nearly complete ion flux recovery. On the other hand, inverted electrode cleaning trailed in efficiency. Specifically, chemical cleaning can restore the ion flux to over 99 %, which demonstrates successful removal of fouling. Conversely, inverted electrode cleaning exhibits less satisfactory outcomes.

7.2. Over-limiting current regime

Operating ED in the over-limiting current regime presents a strategic method for enhancing desalination efficiency while concurrently controlling fouling. Through the application of asymmetric pulses of reverse

polarity, ranging from 10 to 100 μs at frequencies of 100 to 4000 Hz, an improvement in the limiting current density by up to 1.6 times was observed in comparison to conventional ED [130]. This method not only reduced the time spent in over-limiting regimes by approximately 43 % but also maintained a stable pH, albeit at the cost of increased energy consumption by about 56 % or 14 % versus conventional ED in sub-limiting or over-limiting current regimes, respectively [130]. This approach significantly modifies ion transport mechanisms, encouraging the precipitation of substances such as copper hydroxide on membrane surfaces, thereby potentially acting as a proton source to desalting compartments while simultaneously increasing membrane resistance due to hydroxide/oxide formation in large pores [131].

Electroconvection, a primary driver behind over-limiting currents, plays a crucial role in mitigating scaling and fouling, as illustrated by its application in acid whey treatment, resulting in a 40 % higher lactic acid recovery rate [132]. Direct numerical simulations have uncovered phenomena like space-charge breakdown during over-limiting operation, leading to a reduced size and number of EC vortices, thereby diminishing local current density [133]. Such operational conditions also offer a notable decrease in peptide fouling on ion-exchange membranes, significantly extending their lifespan and opening new avenues for ED applications [134]. Additionally, the complex interactions of weak electrolytes under electric fields in over-limiting conditions suggest shifts in chemical equilibria and activation of mass transfer mechanisms such as electroconvection, which influence precipitate formation and reduce system resistance [135].

7.3. Profiled ion-exchange membranes

The advent of profiled ion-exchange membranes represents a significant advancement in the field of electrodialysis, with the aim of optimizing desalination processes and addressing operational challenges directly. These membranes, produced through advanced processing techniques like hot pressing to create distinct surface geometries, have been demonstrated to greatly decrease both pumping power and electrical resistance [136].

The introduction of profiled surfaces on ion-exchange membranes extends beyond mere mechanical improvements; it significantly influences hydrodynamics and ion transport. The elimination of the spacer shadow effect and the induction of advantageous hydrodynamic changes are among the notable benefits, which hinge on the precise geometries of the membrane surfaces. This emphasizes the intricate relationship between the design and dynamics of flow rate and salt concentration in feed streams as crucial factors in realizing performance improvements [137]. The potential of emerging manufacturing techniques, notably 3D printing, to create membranes with unprecedented geometries opens new avenues for enhancing efficiency and expanding application scopes.

For instance, anion-exchange membranes were fabricated using a custom stereolithography setup for 3D-printing with liquid precursors, leading to cross-linked materials through a light-induced photopolymerization reaction [138]. Various membrane designs were tested, including flat membranes and those with micropatterned surfaces using diagonal and tile designs with specific area ratios. The study found that the ionic resistance of these membranes is influenced by both the pattern-to-base area ratio and the membrane thickness, with experimental results indicating that resistance decreases with a decrease in pattern-to-base ratio and equivalent thickness [138]. Specifically, patterns with a 1:2 ratio demonstrated potential for broad applications, with resistance values varying approximately from 1.1 to 1.8 Ω across thicknesses of 300 to 650 μm . Patterns designed for specific applications, such as those generating vortices to enhance mixing, showed that the resistance relationship is independent of the membrane surface pattern design, offering design freedom for optimizing membrane performance for specific applications [138]. The lower resistance of patterned membrane compared to flat membrane was also reported in [139]

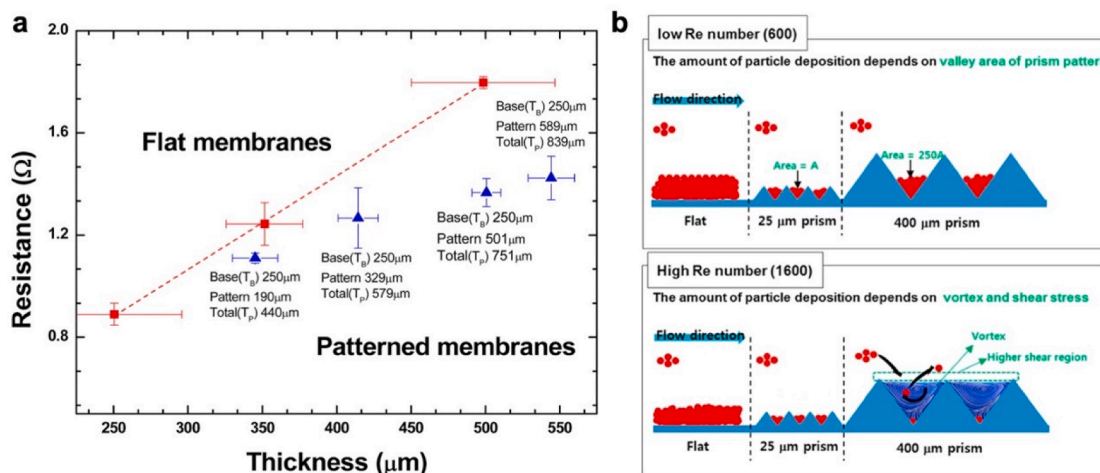


Fig. 14. Profiled or patterned membrane. (a) Resistance of flat and patterned membrane. Reprinted with permission from [139]. Copyright © 2016. American Chemical Society. (b) Effect of vortex and shear of patterned membrane on particle deposition. Reprinted with permission from [142]. Copyright © 2015. Elsevier B.V.

(Fig. 14 a).

Investigations into the electroconvective ion transport at membranes decorated with structured surfaces have provided insight into the profound influence of membrane topology on the movement of ions, as well as their advection and diffusion. This highlights the crucial role that membrane design plays in optimizing the electrokinetic and electrohydrodynamic behaviors, further emphasizing the fact that profiled membranes not only improve the operational parameters of ED, but also contribute to the development of more sustainable and efficient desalination technologies [140]. Specifically, the introduction of surface geometries has been linked to a 50 % reduction in resistance when the structure size aligns with the mixing layer thickness, illustrating a tangible impact on the efficiency of ion transport and the overall performance of the membranes [140].

The emergence of profiled membranes provides potential solutions to challenges such as fouling. The enhanced sorption capacity and the formation of associative structures in external solutions enable innovative methods to mitigate fouling tendencies [141]. Profiled membranes with prism patterns enhance sorption capacity and reduce particle deposition more effectively than non-patterned counterparts. Specifically, smaller patterns are more efficient at low Reynolds numbers, while larger patterns excel at higher Reynolds numbers, such as 1600, due to increased crossflow velocities [142]. Computational fluid dynamics simulations reveal that these patterns create vortices that can redirect particles back to the bulk stream, particularly at higher Reynolds numbers where the interaction between the vortex and the bulk flow is more pronounced (Fig. 14 b).

8. Future directions and challenges

In seawater desalination, electrodialysis stands out for its ability to selectively transport ions, bypassing the challenges faced by methods such as reverse osmosis, especially in relation to osmotic pressure. However, fouling jeopardizes their efficiency and durability. It impacts the salt rejection capabilities, augments energy consumption, and shortens membrane lifespan, underscoring the need for an in-depth understanding of fouling mechanisms to devise efficient mitigation strategies. This review delves deep into the fouling mechanisms in ion exchange membranes used in seawater desalination. It elaborates on the types of fouling, their impact on membrane functionality, and mitigation strategies. In essence, a holistic understanding and innovative strategies are vital for the sustainable and efficient deployment of ion exchange membranes in addressing water scarcity.

Ion exchange membranes face a multitude of fouling challenges.

Organic fouling, for instance, results from the build-up of materials like proteins and large organic molecules, with research indicating that AEMs are particularly vulnerable, especially to negatively charged organic molecules. The presence of calcium ions exacerbates this issue on AEMs, forming Ca-NOM complexes. In the realm of inorganic fouling, multivalent ions such as calcium and magnesium play a prominent role, reacting with dissociated ions in water to cause precipitation on the membrane. Water splitting processes further complicate matters by causing alkalization, leading to the precipitation of compounds like calcium carbonate on CEMs. Biofouling is another challenge, marked by the colonization of microorganisms that establish nutrient-rich biofilms on membrane surfaces. Beyond these, colloids and particulate matter, including silica sol and organic aggregates, introduce additional fouling layers, potentially hindering the membrane's efficiency in water treatment processes.

In the endeavor to counter fouling and enhance ion exchange membrane performance, a myriad of fouling mitigation techniques are in practice. Pre-treatment processes, pivotal in decreasing fouling potential, purify feedwater by eliminating foulant precursors. These processes span coagulation and flocculation, which work collaboratively to aggregate and ease the removal of colloidal particles. Filtration techniques like microfiltration and ultrafiltration are indispensable for eradicating suspended solids and larger foulants, ensuring the curbing of physical fouling and potential nucleation sites for scaling. Oxidation processes take center stage in decomposing organic foulants and disinfecting feedwater, thus abating biofouling risks. Furthermore, water softening methods target hardness-causing ions, crucial in preventing scaling. By adjusting feedwater's pH, the solubility and precipitation of foulants can be controlled, allowing for an optimized water chemistry conducive to minimized fouling. Collectively, these strategies exemplify the comprehensive approach to maintaining the optimal performance of ion-exchange membranes.

Surface modification techniques have emerged as vital tools to enhance fouling resistance of ion exchange membranes. By adjusting surface properties, they reduce adhesion, streamline fouling removal, and boost membrane functionality. Hydrophilic coatings, such as polyethylene glycol (PEG) and polydopamine (PDA), discourage foulant adhesion, while applications like TiO_2 increase hydrophobicity, facilitating easier cleaning. The PDA-PSS/ TiO_2 modified AEMs and PSS&PDA-M membranes are particularly notable for their fouling resistance. PDA coating also effectively curbs bacterial growth by introducing negative surface charges. Surface charge modifications, as seen in L-PDA@ABS-Cl membranes, harness electrostatic repulsion to deter bacterial adhesion. Architectural additions, like the zeolitic

imidazolate framework-8 (ZIF-8), optimize ion transport and reduce scale formation. Techniques addressing surface roughness, using plasma treatment or graphene oxide layers, further reduce adhesion sites. The introduction of monovalent permselective membranes has represented a significant advancement, effectively restricting the migration of multivalent ions and thereby mitigating scaling phenomena. Such advancements, exemplified by the SPPO-PVA composite membrane, offer promising solutions to membrane fouling and scaling challenges. Ion exchange membranes in electro dialysis employ opposite charge coatings to block multivalent ion permeation and deter protein and biofilm adhesion due to their surface's heterogeneous charge profile. The "Baier curve" underscores the appropriateness of materials such as silicone for achieving robust anti-fouling characteristics. This curve serves as a directive in the selection of polymers like PEG, PET, and PMMA, which possess the capacity to blend anti-fouling attributes with essential hydrophilic properties, thereby playing a critical role in the enhancement of electro dialysis membrane performance.

Maintaining ion exchange membranes requires regular procedures to remove fouling deposits. Chemical cleaning, especially using agents like citric acid, sodium hydroxide, or surfactants, is effective based on the type of fouling and membrane compatibility. Recently, Periodic Polarity Reversal (PPR) has emerged as an efficient anti-fouling strategy, particularly in ED reversal operations. By periodically altering the electric field direction, PPR enhances fouling resistance and operational performance. Implementing PPR demands a deep understanding of operational details, considering factors like feed composition and membrane characteristics. Recent advancements like pulsed ED reversal offer better process efficiency, emphasizing the importance of evolving technologies. However, while chemical cleaning exhibits superior restoration capabilities, certain environments, like alkaline, can deteriorate membrane quality. Ensuring optimal cleaning methods is paramount to preserve the membrane's longevity and performance.

CRedit authorship contribution statement

I.G. Wenten: Writing – original draft, Conceptualization. **Martin Z. Bazant:** Writing – review & editing. **K. Khoiruddin:** Writing – original draft.

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.

Data availability

Data will be made available on request.

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