New insights into the definition of membrane cleaning strategies to diminish the fouling impact in ion exchange membrane separation processes

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Abstract

Ion exchange membranes represent the main core of a number of separation processes such as electrodialysis, diffusion dialysis and Donnan dialysis, among others, at which the key role of these membranes is to control the transport of ionic species and their selective separation simultaneously. However, the ion exchange capacity, selective separation, stability and durability of ion exchange membranes in separation processes are especially limited under the use of natural feedwaters due to their heterogeneous and multivalent ionic composition, which leads to several fouling issues. This effect provokes a clear undesirable evolution with time in the initial membrane properties and characteristics, thus significantly decreasing the overall process performance in several applications. As a consequence, not only a further understanding of the fouling mechanisms and the interactions between foulant(s) and membrane(s) is crucial, but also development of adequate membrane cleaning protocols to alleviate the fouling impact after prolonged operations. Therefore, the aim of the present review is to define efficient membrane cleaning strategies to control and mitigate the impacts of fouling phenomena on ion exchange membranes in separation processes, paying special attention to the type of membrane, its characterization (before and after cleaning) and the target application. Herein, promising membrane cleaning approaches reported in the recent years are summarized and discussed. Alternative physical, chemical and mechanical cleanings (or their combination) can be considered, even though the control of the number of cleaning cycles, cleaning conditions and combination of cleaning approaches seem to be essential to achieve an optimum global cleaning efficiency. To sum up, although further research in understanding the role of fouling in material stability and degradation after cleaning is still needed, this review provides novel insights into the definition of the most appropriate membrane cleaning strategy in different ion exchange membrane separation processes.

Keywords: ion exchange membranes; separation processes; fouling impact; membrane cleaning; electrodialysis.

1. Background

The current worldwide water, energy, materials, food and environmental issues has made evident that the main challenge of the XXI century is to secure human health and social welfare through sustainable perspectives [1]. For instance, one of the most important issues affecting human health is not only the accessibility of safe drinking water, but also its quality, which is responsible for different life-threatening diseases [2]. Furthermore, the continuous increase of the worldwide energetic demand as well as the uninterrupted burning of fossil fuels to produce energy has led to the investigation and development of alternative environmentally friendly and renewable power sources [3]. In this respect, the high energy demand can be satisfied, and the impact of global warming due to the continuous increase of CO_2 levels in the atmosphere might be decreased simultaneously [4]. Therefore, the study of deeper comprehensive analyses about water, energy, materials and food nexus is essential to find opportunities and solutions in order to reach synergetic beneficial objectives for sustainable development [5,6].

In this context, ion exchange membrane separation processes (IEMSPs) represent sustainable approaches to provide effective alternatives in several interesting application contexts. According to Strathmann [7], seven different IEMSPs can be identified, namely i) electrodialysis (ED), ii) ED with bipolar membranes (EDBM), iii) continuous electrodeionization; iv) electrolytic processes (*i.e.,* chemical synthesis such as the chlor-alkali electrolysis), v) diffusion dialysis, vi) Donnan dialysis, and vii) energy conversion and storage systems (*e.g.,* fuel cells). The first four IEMSPs are externally electrically driven approaches (i-iv), whereas the last three are not (v-vii), as represented in Fig. 1. The process driving force in both diffusion dialysis and Donnan dialysis is a concentration gradient between two aqueous solutions separated by an ion exchange membrane (IEM). In fuel cell-based systems, a fuel (mainly hydrogen gas) and an oxidizing agent (usually oxygen) are used as external chemical inputs. Furthermore, although Reverse Electrodialysis (RED) does not represent a separation process, since its experimental setup is comparable to that of ED systems [8], this technology has also been considered in the discussion of the present review. The dominant factor affecting IEM fouling in separation processes is the feeding solution composition (highlighted in Fig. 1), whose effect on fouling tendency is much larger compared to that of the IEMSP itself. For example, food containing solutions (*e.g.,* wine or juice making industries) would tend to foul much more compared to drinking water stream, whatever the ion-exchange membrane assisted process is. In this context, similar feed solution compositions can also be used in different IEMSPs for the same application, such as the recovery of organic acids. In this framework, ED and Donnan dialysis are both used [9], but ED will be much more prone to fouling due to the presence of electrodes. In this light, electrodialysis reversal (EDR) mode is often considered.

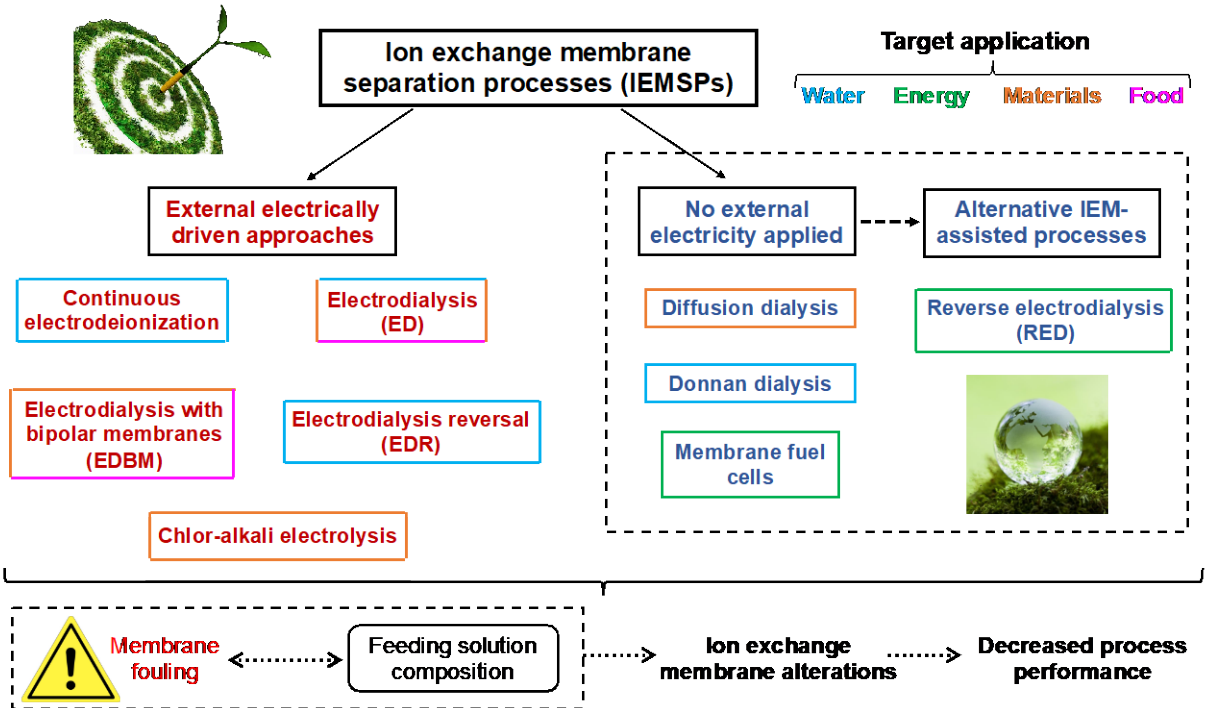

Fig. 1. Overall scheme of IEMSPs and alternative IEM-assisted processes: classification, main applications and fouling issues. Colourful boxes indicate the main application(s) of each IEMSP: water (blue), energy (green), materials (orange) and food (pink).

The main key elements of the above-mentioned processes are the IEMs, whose main role is to control the transport of ionic species, including their selective separation. In general, the most desired properties of IEMs in separation processes are: a) high permselectivity, b) low electrical resistance, and c) remarkable mechanical, form, chemical and thermal stability [7,10]. As a result, several IEMs of different nature have been developed and investigated since the early 1900s, as schematically shown in Fig. 2. It is worth mentioning here that the first IEMSP (at industrial operation) was developed in the late 1950s and early 1960s, when an ED setup was proposed as an economic method for the desalination of brackish water [7]. Nevertheless, the principle of ED desalination was firstly presented in 1890 by Maigrot and Sabates [11]. Since the year 2000, innovative and sustainable IEMs have continuously been under development for industrial applications [12].

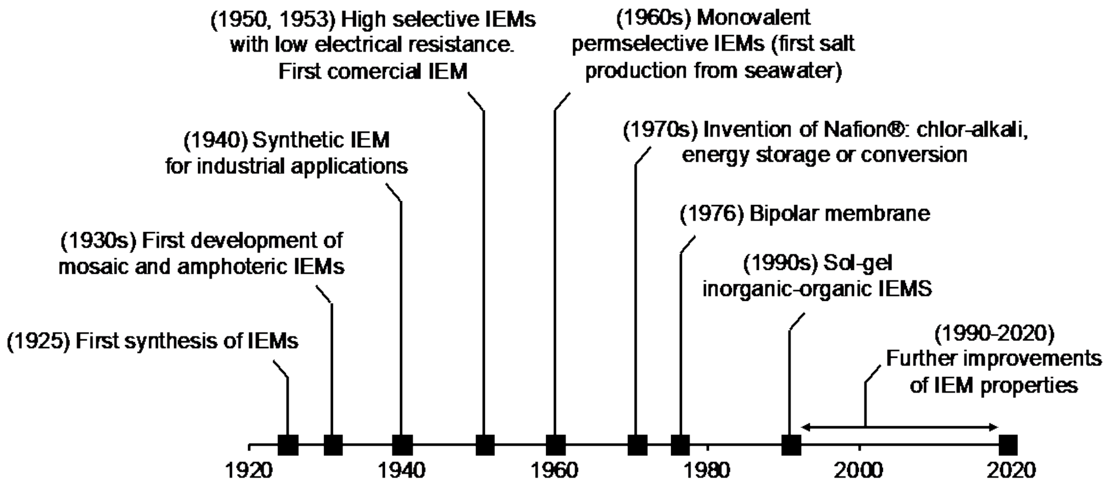

Fig. 2. Development of IEMs over the years. Adapted from [12].

With respect to the applications derived from IEMSPs, the environmentally friendly production of clean water represents one of the main objectives of 2030 Agenda for Sustainable Development [3,13]. Thus, the use of monovalent IEMs in ED configurations has been considered for the removal of fluoride and arsenic from water streams [14,15]. Although ED is mainly used to generate drinking water [16], the treatment of polymer flooding produced water derived from oil industry has also been investigated [17]. Water-energy hybrid systems have also been proposed as a cost-effective and sustainable strategy for water desalination with simultaneous wastewater treatment and energy harvesting through bio-electrochemical devices [18]. Moreover, electrolytic processes such as the chlor-alkali technology (commercially proposed in 1975 [19]) represents one of the most important applications of IEMSPs [20], at which IEMs based on Nafion® are mainly utilized [12]. By contrast, the costly Nafion® membranes, the low chlorine quality reached, and the high thermal energy consumption symbolize the main handicap of this separation process [21,22]. On the other hand, diffusion dialysis strategies are used to purify and recover acids and bases through the application of anion exchange membranes (AEMs) and cation exchange membranes (CEMs), respectively [7,23]. The recovery of valuable toxic heavy metal ions from industrial effluents is, by contrast, the main application of Donnan dialysis experiments, even though the investigation and monitoring of (bio)fouling on the surface of IEMs has also been proposed through Donnan dialysis studies [24,25]. Furthermore, among the available energy conversion and storage separation processes, PEM (Polymer Electrolyte Membrane) fuel cell technologies seem to be attractive options for power generation due to their high efficiencies and low emissions [26]. However, the high cost of Nafion® membranes has led to the development of alternative approaches such as alkaline anion exchange membrane fuel cell (AAEMFC) configurations [27–29]. Carbon dioxide electro-conversion methods, however, have been investigated to store intermittent renewable energy, otherwise wasted, in chemical bonds [30–32]. In this approach, a CEM is mainly required to assure an efficient transport of protons.

To sum up, since the main core of IEMSPs is the membrane/s, an efficient and stable performance of IEMs is crucial to achieve an optimum continuous process operation. However, the behavior of IEMs is still strongly limited by different fouling and scaling phenomena, which represents the attachment of specific substances to the surface and/or in the interior of the membrane structure [33]. This phenomenon therefore leads to a significant decrease in the process efficiency and to increased overall costs [33,34]. In this context, membrane cleaning protocols must be defined to decrease the negative fouling impact on the behavior of IEMs in separation processes to allow for their prolonged (re)use.

Hence, the aim of the present review is to identify and present appropriate and prospective membrane cleaning protocols to control and mitigate the undesirable impacts of fouling on IEMs, which is required to move forward into the implementation of several IEMSPs at a larger scale. This review focuses mainly on the cleaning of IEMs used in ED, which represents the most important IEMSP, although prospective cleaning strategies applied in other ion-exchange membrane assisted processes are also considered. The available effective cleaning strategies reported so far are discussed as a function of the membrane type and target application, paying special attention to membranes characterization and process performance before and after cleaning.

In this respect, the fundamental knowledge about membrane types and characteristics, fouling mechanisms and the foulant(s)-membrane(s) interactions is indispensable to define cleaning decision criteria for an improved IEM durability in separation processes.

2. Ion exchange membranes in separation processes and fouling-derived issues

IEMs can be firstly classified into homogeneous or heterogeneous materials, depending on their physical structure and fabrication method [35]. The usage of homogeneous membranes is often limited by their high cost compared to that of heterogeneous IEMs [24,36]. As a consequence, since the up-to-date high cost of commercial homogeneous IEMs is hampering the large-scale implementation of IEMSPs [37], trade-offs between membrane properties and costs must be taken into account. Secondly, according to the charge and distribution of fixed ionic groups, IEMs can also be classified into five different categories [38], namely AEMs, CEMs, bipolar membranes [39], amphoteric samples [40] and mosaic membranes [41], even though the first three membrane types are the most commonly structures applied in IEMSPs.

Depending on the target application, different membrane properties are sought by research community to improve process performance. For example, membranes with effective separation of cations from anions are required in ED systems [42], whereas IEMs with lower voltage drop and decreased electrical resistance are needed to reduce the overall electricity consumption of electrolytic approaches (*e.g.,* chlor-alkali) [43]. In alternative IEMSPs such as diffusion dialysis and Donnan dialysis, high selectivity between ions of the same electrical charge represents a key aspect to achieve an optimum process performance, even though IEMs with low thicknesses are also preferrable to obtain moderate fluxes [7]. On the other hand, high chemical and stable proton conductive polymers is essential for PEM fuel cell applications [44], while AEMs with extraordinary thermal stability and excellent alkaline resistance are required to improve the performance of AAEMFC [28]. In CO_2 conversion processes, high proton conductive membranes with low water transmission rates are necessary for improved gas-phase CO_2 electroreduction performance [45,46]. By contrast, IEMs with monovalent permselective, hydrophilic and ion conductive properties are required to maximize the obtainable net power density in RED techniques [47–49].

As already stressed above, the main limitation of IEMSPs is related to fouling issues. In general, the different types of membrane fouling can be classified into the following four categories [50]: i) particulate/colloidal fouling (physical interaction), causing pore blocking and/or a fouling surface layer; ii) organic fouling, such as dissolved organic substances that can be attached to the membrane via adsorption; iii) inorganic fouling/scaling or, in other words, precipitation of dissolved components due to pH alterations or oxidation; and iv) biofouling, in which different microorganisms might be joined to the membrane surface forming a biofilm. These negative phenomena lead to significant alterations in specific essential characteristics of IEMs. In particular, decreased membrane durability/stability and raised pressure drops in the systems used are commonly observed. Besides, important membrane properties in IEMSPs such as hydrophilicity, ion exchange capacity, counter-ion membrane permselectivity and electrical resistance are also significantly influence by (bio)fouling and scaling conditions [33,51]. With respect to the relation between the type of membrane and fouling behavior, AEMs are generally more prone to organic fouling in comparison with CEMs owing to the negatively charged nature of natural organic matter (NOM) presented in real water streams [52]. As a consequence, different strategies, especially surface modification techniques [53–58] have been applied to reduce the impact of fouling on AEMs in applications involving such feedwaters.

Although more comprehensive and dedicated studies on both fouling mechanisms and the interactions between different foulants and IEMs after prolonged operations are still needed, different methods have been proposed to follow and study the effect of fouling on IEMs in a simple and economic way, such as the two-dimensional fluorescence spectroscopy technique [59] and electrochemical impedance spectroscopy measurements [60]. Also, both approaches can be used to study the degree of recovery of the initial membrane properties after cleaning.

The correct selection of the membrane cleaning strategy is, therefore, crucial to reduce (in an effective way) the fouling impact in IEMSPs. In this context, physical and chemical cleaning methods have been mainly proposed in literature to mitigate IEM fouling [61]. However, although the development of efficient and prospective IEM cleaning protocols may also involve a significant decrease in the overall process cost (that is essential in terms of process implementation at a large scale), its clear definition is still missing in literature. In this respect, the membrane requirements for each specific application should be taken into account to develop dedicated and prospective cleaning methods.

Thus, the following section of this review focuses on the discussion of several IEM cleaning strategies reported so far as a function of membrane characteristics and target application. Special emphasis is also paid to membrane characterization and process performance before and after cleaning, in an attempt to better understand the chemical behavior of fouling on IEMs in different separation processes.

3. Available ion exchange membrane cleaning strategies in separation processes

The cleaning of IEMs affected by fouling, scaling or degradation phenomena represents an essential step that must be taken into consideration in different separation processes, especially after long-term operations. The main purpose of the cleaning step is to restore the initial membrane properties and characteristics (*e.g.,* permselectivity, ion exchange capacity, electrical resistance or hydrophilicity) to improve membrane durability and its re-use [16]. The available membrane cleaning methods can be classified into the following two main groups [61]: a) physical/mechanical procedures and b) chemical approaches. The first group involves physical processes, such as hydraulic, sonication, pneumatic, or mechanical steps, among others. By contrast, the chemical strategies involve the use of different chemical agents depending on their nature, such as alkaline/acid approaches and enzymatic strategies, as shown in Table 1. For instance, the combination of air sparging and hydraulic backflush is commonly utilized as a physical approach to alleviate and reduce the biofouling, while the clean-in-place (CIP) approach represents the most suitable chemical method to combat or avoid fouling issues [61]. However, although chemical methods are most frequently considered for IEM(s) cleaning than physical techniques, their application must be controlled due to the possibility of membrane damage (usage of large quantities of chemicals) and waste generation, among others [62]. Besides, it is essential to understand how the selected cleaning agent may affect the foulants presented on the membrane surface according to the following key questions: i) can the foulants be removed? ii) can the membrane morphology be modified (*e.g.,* swelling)? and/or iii) can the surface chemistry (hydrophobicity or charge) of the foulant(s) be altered? [63].

Table 1. Classification of agents used for IEM chemical cleaning

Chemical cleaning type	**Main chemical agent used**
Acid	HCl, HNO_3, H_2SO_4
Alkaline	NaOH
Surfactant	sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS)
Enzymatic	Combination of enzyme-based solutions (*e.g.,* Corolase and Tyrosinase in a potassium phosphate buffer solution)
Other alternatives	NaCl (saline), O_3 (disinfectant), H_2O_2 and $KMnO_4$ (oxidants), EDTA (sequestration agent), and metal chelating agents

The importance of the membrane nature in the ion-exchange sample deterioration using oxidant agents has been clearly demonstrated [64,65]. For instance, the response of homogeneous (Neosepta CMX-SB and AMX-SB, Astom, Japan) and heterogeneous (cationic MK-40 and anionic MA-41, Shchekinoazot, Russia) IEMs under strong oxidizing conditions was studied using sodium hypochlorite (NaClO) [65]. The ageing protocol consisted of soaking the samples in 400 ml of the ageing solution (pH adjusted from 11 to 8 using HCl) for 20, 60, 100, 200, 300, and 700 h. The membranes were afterwards rinsed with ultrapure water and immersed in three different solutions (1 M NaCl, 0.5 M NaCl and 0.1 M NaCl for 24 h in each solution) and kept in 0.1 M NaCl solution before analysis. The authors concluded that the ageing mechanisms are different as a function of membrane nature (*i.e.,* AEMs and CEMs). In this respect, the oxidizing agent provoked a degradation of the quaternary ammonium sites of AEMs (while sulfonate sites of CEMs were not degraded) and chain scission of the poly(styrene-co-divinylbenzene) backbone of both AEM and CEM through chain radical oxidation. However, similar findings were reached in the degradation of homogeneous and heterogeneous membranes of the same nature (AEM or CEM). The differences in their physicochemical membrane properties were not significant. Besides, both type of polymer binders (*i.e.,* polyvinyl chloride (PVC) and polyethylene for homogeneous and heterogeneous IEMs, respectively) were observed to be resistant under NaClO environments.

In the following lines, different available IEM cleaning methods reported so far are presented and discussed, paying special attention to the cleaning protocol adopted as well as to the operating conditions, membrane characterization and target application, including the polymer stability and degradation after cleaning. The discussion is mainly focused on IEMs applied in ED systems, since this technology represents the most important separation process with the involvement of IEMs. However, IEM cleaning studies in alternative IEMSPs and electro-membrane processes are also included.

3.1. Cleaning of IEMs in electrodialysis-based applications

The importance of IEM cleaning in ED applications has been continuously shown to be essential in terms of membrane durability and process performance. For example, the effect of the type of membrane in different cleaning strategies was investigated through the application of a traditional chemical cleaning approach (using 2 M HCl and 2 M NaOH solutions) on homogeneous (Neosepta AMX-SB, Astom, Japan) and heterogeneous (MA-41, Shchekinoazot, Russia) AEMs for 50, 100, 200, 300 and 700 h at room temperature. Besides, cleaning cycles of HCl-NaOH (0.1 M each for 30 min from 100 to 400 h) were also analyzed in order to simulate the chemical CIP method commonly used in industrial ED processes [66]. The heterogeneous AEM suffered severe degradation in strong acid conditions, while the homogeneous AEM did not. However, the heterogeneous AEM was more resistant than the homogeneous AEM in strong alkaline conditions. In this regard, the authors observed transformation of the binder of homogeneous samples (*i.e.,* PVC) into polyene structure owing to dehydrochlorination. In addition, although the HCl-NaOH cleaning cycles involved changes in both membranes, strong modifications in the polymer network of the homogeneous structure were observed due to the constant change of cleaning solution nature, which led to decreased membrane toughness. This work, therefore, clearly demonstrates that the effect of OH^- is not the only cause of AEMs ageing in industrial ED configurations. The following membrane cleaning discussion is classified as a function of the target application in ED-based approaches.

3.1.1. ED: wastewater treatment

Different chemical cleaning strategies have been reported in wastewater treatment-based applications. For instance, a three-stage chemical cleaning protocol was developed and applied to commercial heterogeneous CEMs (HDX200, Hidrodex, Brazil) and AEMs (HDX100, Hidrodex, Brazil), which were used in the treatment of electroplating industry effluents through ED [16]. The cleaning steps were as follows: i) rinsing step with deionized water and immersion in 0.1 M NaOH solution for 72 h; ii) rinsing with water to remove traces of the first cleaning solution, and immersion in the effluent for 24 h; and iii) immersion (72 h each) in 0.5 M and 1 M NaOH alkaline solutions. The membrane integrity as well as its performance recovery after cleaning were investigated by chronopotentiometric measurements (limiting current density), current-voltage curves (ohmic resistance), Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR), and Scanning Electron Microscopy (SEM) equipped with Energy Dispersive x-ray Spectroscopy (EDS). The SEM images of the AEM and the CEM before and after cleaning are represented in Fig. 3 and Fig. 4, respectively, at which a color sorting has been considered to show interesting regions, characteristics and agglomerates. The SEM images of the AEMs show non-conductive regions (yellow) before and after cleaning, whereas conductive sites with functional groups (blue) are displayed in Fig. 3a. Conductive regions with species agglomerated on the fixed charges (green) can also be seen in Fig. 3b. In this respect, the SEM picture with higher magnification (Fig. 3c) clearly shows the agglomerates (green), which are mainly composed of Zn (as an oxide or complexed with EDTA). This fact therefore denotes the inefficacy of the selected cleaning method for the removal of scaling on AEMs, in accordance with the ATR-FTIR observations. Furthermore, the SEM images of the CEMs also display non-conductive (yellow) and conductive (blue) regions, due to their heterogeneous structure. The agglomeration of species at the fixed charges (orange) is clearly shown in the high-magnification SEM image of the CEM (Fig. 4c), in which high density regions of the element Na can be observed. This finding is explained by the authors through the attraction of Na to the fixed charges of the membrane, since an alkaline cleaning was conducted. Finally, the cavities observed in Fig. 3b and Fig. 4b (shown in black) clearly demonstrate the polymer degradation of both membranes under severely alkaline cleaning treatments, which involves a decrease in the conductive area of the membranes. As a result, high alkaline concentrations (up to 1 M NaOH) are not recommended for the cleaning of IEMs used in ED stacks for the above-mentioned application, whereas mild alkaline conditions (0.1 M NaOH) seem to provide the best trade-off in terms of performance recovery and polymer degradation.

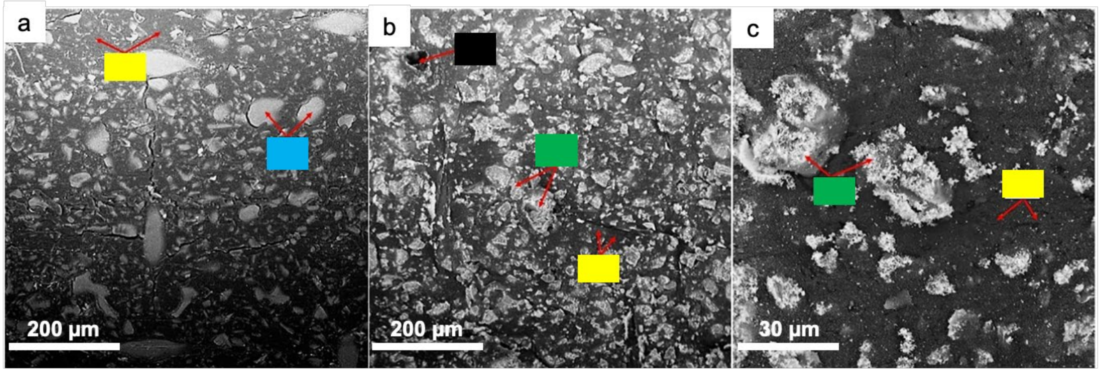

Fig 3. SEM images of: a) pristine AEM; b) AEM after 344 h of electrodialysis + three cleaning steps; c) higher magnification of used and cleaned AEM. Color sorting: non-conductive regions (yellow), conductive sites with functional groups (blue), conductive regions with species agglomerated on the fixed charges (green), cavities (black). Adapted from [16].

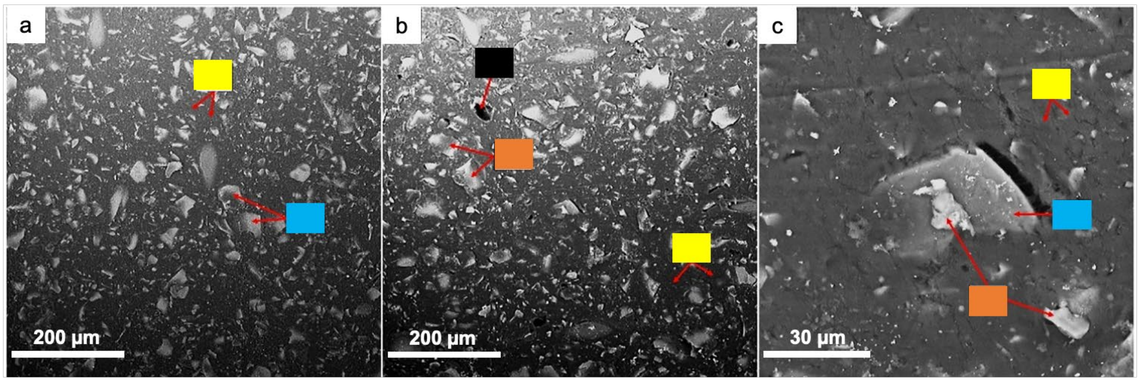

Fig. 4. SEM images of: a) pristine CEM; b) CEM after 344 h of electrodialysis + three cleaning steps; c) magnification of used and cleaned CEM. Color sorting: non-conductive regions (yellow), conductive sites with functional groups (blue), conductive regions with species agglomerated on the fixed charges (orange), cavities (black). Adapted from [16].

The development of IEM cleaning protocols is also crucial on the treatment of oily wastewater streams via ED due to the undesirable effect of fouling phenomena on membrane performace, which deteriorates the membranes lifetime as well as their initial properties. Although studies on the cleaning of IEMs fouled by oily wastewaters have scarcely been reported yet, the chemical cleaning effect (and its mechanisms) on heterogeneous CEMs and AEMs has been assessed at plant-scale in 2015

[67]. The desalination performance was evaluated in an ED stack consisting of 400 cell pairs that operated at 280 V. Before starting the cleaning protocol, the fouled IEMs were rinsed with deionized water to remove the loosely bonded foulants on membrane surface. The chemical cleaning was carried out by soaking the samples into alkaline (0.1 M NaOH) or acidic (0.1 M HCl) solutions at room temperature for 24 h. Finally, the cleaned IEMs were rinsed with deionized water to eliminate possible residual cleaning agents and stored in a 0.5 M NaCl solution. The authors clearly demonstrated that the acidic cleaning was much more effective for both membranes than the alkaline cleaning procedure in terms of global cleaning efficiency. However, NaOH solutions were preferred for the removal of APAM fouling on the CEMs, while the removal of these compounds on AEMs was improved by acidic cleaning. This fact denotes that the deprotonation effect of NaOH enhanced the electrostatic APAM-CEM repulsion, whereas the protonation of HCl involved the reduce of the electrostatic APAM-AEM attraction. With respect to the treatment of oil-based fouling, NaOH cleaning was preferable. Besides, ATR-FTIR and SEM-EDX measurements (performed before and after cleaning) suggested possible inorganic fouling aggravations under alkaline cleaning conditions, thus denoting than acidic cleanings are preferrable to alleviate the effect of inorganic foulants. Therefore, this study clearly highlights the importance of identifying the governing fouling and cleaning mechanisms in order to determine the optimal cleaning protocols for long-term IEMs based operations in separation process using natural feedwaters.

3.1.2. ED: food industry

The importance of membrane cleaning in food industry ED-based applications has been recently reported in literature. For example, an interesting cleaning approach was investigated on CEMs (confidential characteristics, but based on polystyrene-co-divinylbenzene copolymer, with sulfonic functional sites) used in ED for the above-mentioned application [68]. Two different chemical solutions were considered as an *ex-situ* and non-aggressive cleaning strategy: a) low-cost saline solutions such as 35 g L^{-1} NaCl or reconstituted seawater); and b) water-ethanol mixtures (12 %v ethanol acidified with sulfuric acid). The cleaning procedure was based on immersing the CEMs in 200 ml of the selected cleaning solution during 120 h, followed by 30 min in deionized water and finally, 24 h in 0.1 M NaOH solution. The effect of the cleaning protocol was evaluated by several membrane characterization measurements such as IEC, thickness, conductivity, water contact angle, water content, FTIR, SEM and tensile strength. The saline-based treatments were only effective for surface cleaning (water contact angle decreased by 12 %), even though part of the active sites were unavailable for cation exchange due to irreversible interactions between free functional sulfonic sites, the polyphenol (contained in the food industry effluent) and divalent ions of the reconstituted seawater. On the other hand, the behavior of the CEMs treated with the acid hydro-alcoholic mixtures as the cleaning agent was improved in terms of membrane electrical conductivity, IEC and volume fraction of the “inter-gel” solution. However, from economic and environmental viewpoints, the ethanol should be recovered (*e.g.,* by distillation) and then re-used in alternative treatments.

The same authors have also studied the cleaning and characterization of AEMs in the same application framework for the sake of comparison [69]. The confidential anion-exchange samples were based on polystyrene-co-divinylbenzene copolymer with quaternary ammonium functional sites, and provided by industrial ED units used in food processing. Since the authors were interested in applying chemical agents with environmentally friendly, low-cost and non-aggressive characteristics, the same cleaning solutions used in the previous work were herein applied. The same cleaning protocol (shown above) was adopted, even though the effect of the immersion time into the cleaning solution (as the first cleaning step) was also evaluated from 3 h up to 120 h. The physicochemical characterization of the samples after cleaning showed that the AEMs were more easily fouled with organic acids and aromatic polyphenol compounds in comparison with CEMs. The saline solutions were only efficient for surface cleaning (decreased contact angle). Nevertheless, neither the NaCl solution nor the reconstituted seawater (RSW) were able to remove colloid nanoparticles from the membrane pores. On the other hand, the acidified water-ethanol mixture (EtOH) allows a significant recovery of the IEC (up to 33 %), including a significant increase in the membrane conductivity after 120 h of treatment. The recovery of the conductivity was more significant in AEMs because of the higher expansion of the pores of these structures. The evolution of the IEC of the AEMs under study (including the comparison with a CEM) as a function of the chemical cleaning duration is represented in Fig. 5, which clearly shows that the use of acidified water-ethanol strategies represents the most suitable method for both external and internal membrane cleaning. Therefore, this strategy can be recommended for industrial *in-situ* cleaning processes, even though the total duration of the treatment can be reduced up to 12 or 24 h in dynamic cleaning operations. The ethanol recovery, however, should also be taken into account for its further reuse.

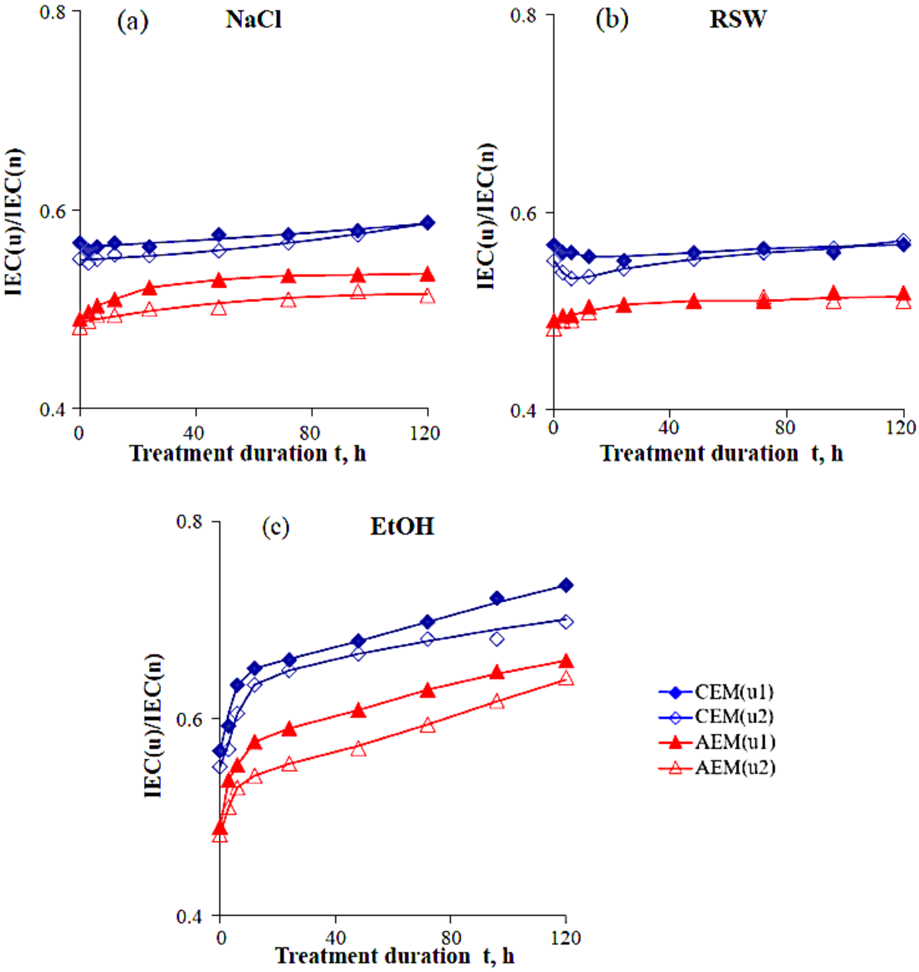

Fig. 5. Evolution of the IEC of different IEMs as a function of chemical cleaning duration: a) 35 g L^{-1} NaCl; b) reconstituted seawater (RSW), and c) hydro-alcoholic solution (12 %v ethanol, pH = 3.5). The script “u” represents used membranes, while “n” is referred to new samples. Reproduced with permission from [69].

The application of enzymatic cleaning agents has also been considered in ED configurations for the treatment of red wine as a promising and innovative procedure, which demonstrates the experimental applicability of enzymes for the cleaning of IEMs [70]. In this respect, homogeneous CEMs (CMX-Sb, Astom, Japan) were evaluated after 2738 h of operation, and three different enzymatic agents were considered according to their properties, namely Rohalase® BXL (beta-glucanase), Corolase® 7089 (neutral protease) and Tyrosinase® (polyphenol oxidase). The authors highlighted that the optimum pH in terms of specific enzymatic activity and temperature (30-50 ºC) must be maintained to avoid activity losses. Firstly, two different concentrations of each enzyme were considered (0.1 and 1 g L^{-1}) to prepare, separately, one component-based enzymatic solutions. Thus, the membranes were soaked into 10 ml of each enzymatic solution to determine the optimal cleaning operation conditions. Besides, 10 ml of a mixture of two or three enzymes in a potassium phosphate buffer at pH 6.8 was also considered as the cleaning solution. The optimal enzyme concentration was found to be 0.1 g L^{-1}, whereas the most appropriate temperature was observed to be 50 ºC. Higher enzyme concentration levels (*i.e.,* 1 g L^{-1}), however, may imply that enzymes and proteins act as foulants. The membrane characterization results after cleaning show effective internal and external membrane cleanings with recoveries of 25 %, 14 % and 12 % in the electrical conductivity, IEC and contact angle values, respectively. The authors finally demonstrated a possible improvement of the global cleaning efficiency by combining different enzyme-based solutions while reducing cleaning durations simultaneously.

Due to the high importance of the cleaning agent nature and concentration, the American Water Works Association (AWWA) has recommended an optimum concentration range (Table 2) for acid, alkaline and chlorine chemical cleanings on IEMs in typical separation processes such as ED and EDR, which are commonly considered in several industrial applications.

Table 2. American Water Works Association (AWWA) recommendations for the chemical cleaning of IEMs in ED and EDR [71]

Chemical cleaning type	**Chemical agent**	**Recommended concentration**
Acid	HCl	2-5 %
Alkaline	NaCl	3-5 % (adjusted to pH 8-10 using NaOH)
Chlorine	Chlorine solution	10-50 mg L^{-1}

In this context, Talebi et al. studied the fouling and *in-situ* cleaning of IEMs during the ED operation of fresh acidic and sweet whey with the aim of partially removing lactic acid (LA) and minerals from feedstreams received from a dairy plant in Australia containing LA, proteins, K, Na, Ca, Mg and P [72]. With the purpose of evaluating the efficiency of applying the AWWA recommendations, the authors investigated the effect of the proposed cleaning agents (Table 2) on Neosepta CMB CEMs and Neosepta AHA AEMs (Astom, Japan). The membrane cleaning protocol began with a <2 % HCl solution (with pH 1.0 ± 0.2) for two days. Although an HCl concentration between 2-5 % is recommended, a less concentrated solution was utilized to ensure the membrane pH tolerance provided by the manufacturer. Subsequently, the samples were soaked in 3 % NaCl solution first at pH 9.2 ± 0.2 and then at 5.5 ± 0.5 (adjusted using NaOH) for two days each. The results displayed that the acid cleaning was effective for *in-situ* removal of mineral deposits. In this regard, increasing the solution flowrate and reducing the current density during the ED experiments may be helpful to reduce the mineral fouling. By contrast, the recommended alkaline cleaning method (3 % NaCl at pH 9.2) was ineffective in removing the strongly bound protein deposits. As a consequence, the authors propose to operate with a concentrate stream at an acidic pH to avoid calcium phosphate precipitation and to achieve strong removal of lactate ions, which is essential in industrial applications. Besides, the combination of the proposed ED system with EDR or pulsed electric field approaches should be considered in future perspectives in order to diminish the protein fouling at the same time.

Overall, acid-base cleaning cycles seem to be effective in ED-food industry applications. Nevertheless, prolonged chemical contacts with the membranes might involve significant structural and mechanical membrane matrix alterations, which has led to the use of enzymatic cleaning approaches in order to decrease the high number of required chemical cleaning cycles. In this approach, the enzymes must be carefully chosen taken into account foulants and membranes material natures [73].

3.1.3. ED: desalination

The desalination capacity in different applications has also been significantly affected by fouling and/or scaling of IEMs after long operation periods in ED systems, which denotes the requirements of developing efficient cleaning methods to increase the lifespan of the membranes involved.

One of the first works related to the cleaning of IEMs in water desalination applications was carried out in 1977, when Kishi et al. developed an electrodialyser composed of heterogeneous IEMs to desalinate the river water of Shatt Al Arab in Iraq [74]. The prepared membranes consisted of powdered ion-exchange resin dispersed in polypropylene matrix. The effects of a wide variety of cleaning procedures were investigated every 200 – 300 h. Among the chemical strategies, alkaline solutions (NaOH) were firstly evaluated as a function of cleaning temperature and agent concentration, followed by HCl rinses (time and concentration effect). Besides, sulfuric acid (5 %) solutions were also considered as acid cleaning. Finally, physical/mechanical approaches such as air bubbling or back wash flushing with water were also studied, including polarity reversal approaches. The best results were achieved under chemical cleaning conditions with NaOH (3 %) at 40 ºC for 1 h and HCl rinse (30 min). Under this cleaning protocol, the membranes were completely cleaned and their performance capacities were fully recovered and maintained during 6000 h of operation. By contrast, different agent concentrations and cleaning temperatures, as well as alternative acid cleaning (H_2SO_4) and physical approaches led to decreased desalination ratio recoveries.

More recently, seven different *in-situ* cleaning procedures were investigated in the treatment of polymer flooding produced water with homogeneous IEMs made from polyphenylene (Shandong Tianwei Membrane Technology Co., Ltd., China) in order to ensure the desalination capacity of the IEMs during ED [17]. Different feed solutions were prepared in order to evaluate the effect of a wide variety of foulants (and their combination) such as hydrolyzed polyacrylamide (HPAM) as organic fouling, $CaCl_2$ + $NaHCO_3$ as inorganic fouling, HPAM + inorganic fouling, oil emulsions, and oil + HPAM + inorganic fouling. The following cleaning methods were studied for 30 min: 1) distilled water; 2) acid cleaning (0.1 M HCl); 3) base cleaning (0.1 M NaOH); 4) surfactant sodium dodecyl benzene sulfonate (SDBS, 0.3 wt%); 5) acid-base cleaning (0.1 M HCl, followed by 0.1 M NaOH); 6) base-acid (0.1 M NaOH, followed by 0.1 M HCl); and 7) acid-base-SDBS. The indicators utilized to follow the behavior of the fouled and cleaned IEMs were the desalination rate, the membrane electrical resistance and the water contact angle. The authors demonstrated higher membrane resistance values and lower desalination rates when inorganic components were combined with HPAM to foul the IEMs (intensified fouling with oil emulsion), in comparison with individual inorganic and HPAM fouling. With respect to the cleaning investigations, the removal of the HPAM-inorganic fouling was effective with acid-base strategies. Moreover, the use of SDBS was efficient to recover the figures of merit against oil emulsion, whereas the acid-base-SDBS cleaning method was clearly beneficial for oil-HPAM-inorganic fouling, thus increasing the desalination performance by 36.45 % in terms of desalination rate. By contrast, the AEMs were more severely affected by organic fouling (*i.e.,* oil and/or HPAM) and, therefore, the application of chemical cleaning was not straightforward. Finally, the authors proposed the fouling routes as well as the cleaning mechanisms, as displayed in Fig. 6, showing that the AEMs were commonly fouled by HPAM and oil emulsion at the ED dilute side due to electrostatic interactions. On contrary, the CEMs were more prone to inorganic scaling, even though the oil emulsion also had a negative effect on the concentrate side of these membranes.

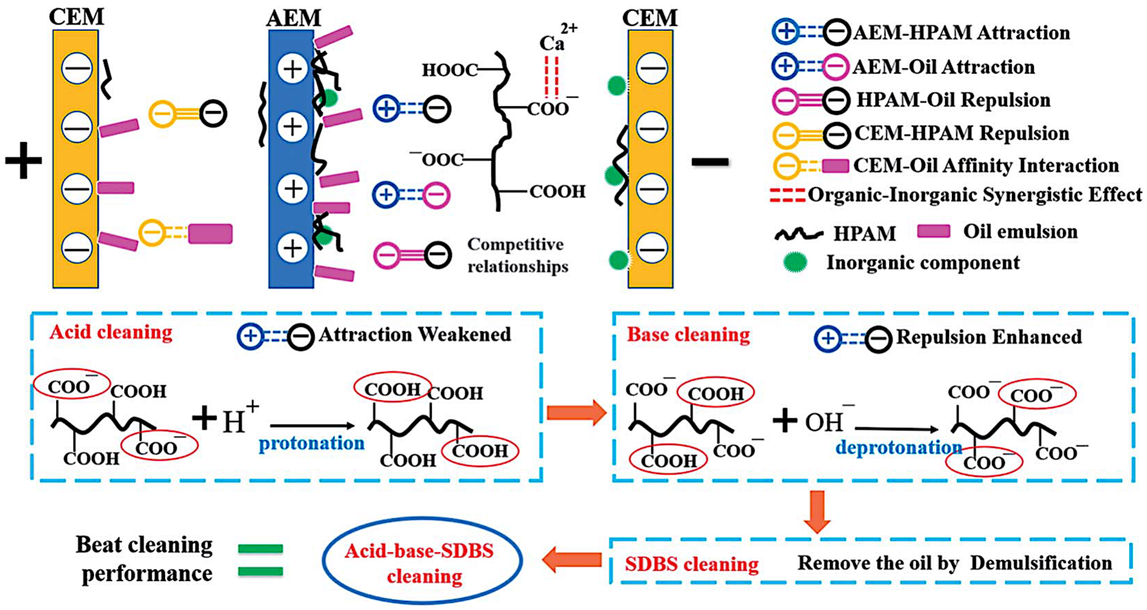

Fig. 6. Proposed fouling route and cleaning mechanisms of IEMs used in the treatment of polymer flooding produced water. Reproduced with permission from [17].

Besides, in order to understand better the effects of long-term alkaline cleanings in the desalination rate recovery of IEMs, Xia et al. investigated the behavior (after cleaning) of commercial homogeneous IEMs based on polyphenylene oxide polymer backbones (Shandong Tianwei Membrane Technology Co., Ltd., China) in a six-cell ED-based configuration under anion polyacrylamide (APAM) foulant conditions [75]. In this context, 0.1 M NaOH solutions were used for 1, 3, 6, 20, 40 and 60 days at room temperature. In addition, in some experiments the membranes after the alkaline cleaning step were immersed in a 0.1 M HCl solution for 6 h. The authors reported minor alterations in CEMs after aging them in the alkaline solution, whereas a significant degradation was observed in AEMs in terms of lower IEC, higher membrane electric resistance, hydrophilicity losses, weak mechanical strength and lower desalination performance, among others, which might be associated with degradation of the quaternary ammonium functional groups of the AEMs into tertiary amines (ylide-formation route) in alkaline solution, as represented in Fig. 7 (pink box) as one of the possible degradation routes of the tested AEM. However, the desalination rates were restored by using the acid solution as the last step of the cleaning procedure for the AEMs, because the generated tertiary amine groups were transformed from OH^- into a Cl^- form (see Fig. 7 – blue box). The authors suggested that this alteration led to an improved anion-exchange capacity and, thus, to a significant desalination performance recovery. Therefore, it can be clearly concluded that alkaline cleanings are only effective for CEMs, while an additional acid-cleaning solution is required for the efficient cleaning of AEMs in the presence of polyacrylamide-based foulants.

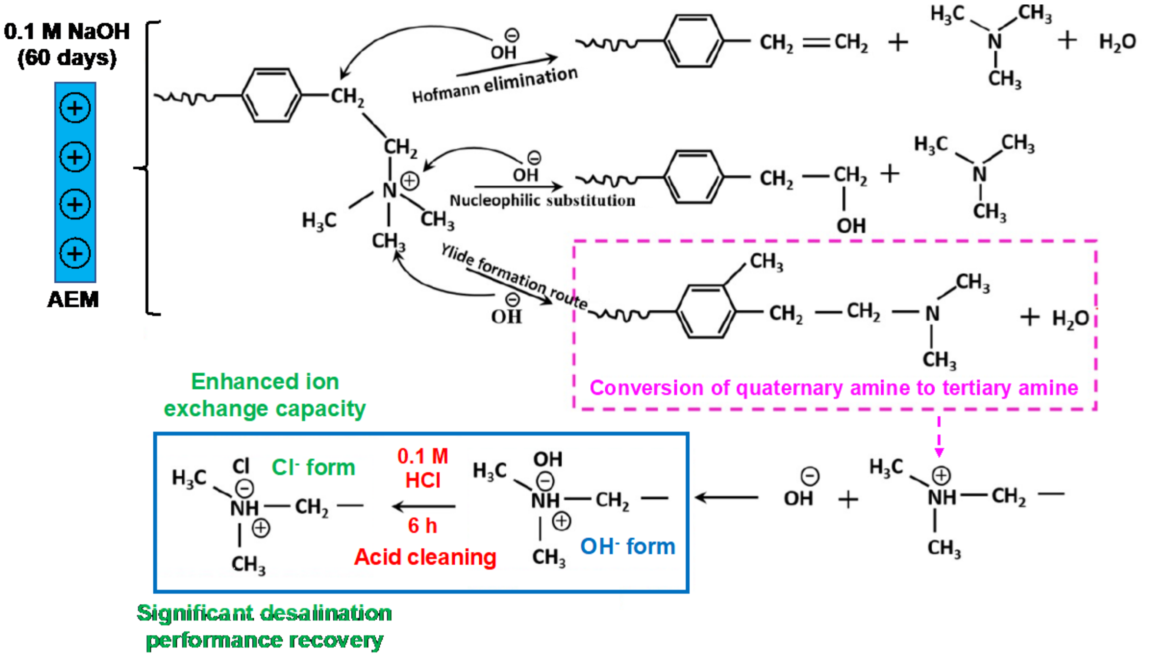

Fig. 7. Schematic representation of AEM degradation and transformation of functional groups under alkaline and acid (as a final step) cleaning strategies. Adapted from [75].

Powerful characterization techniques, such as electrochemical impedance spectroscopy (EIS), have also been proposed to study and monitor the fouling and cleaning efficiency (*in-situ*) of IEMs in electro-membrane desalting ED applications. For instance, the performance recovery of a homogeneous AEM with quaternary ammonium fixed groups and a CEM with fixed sulfonate groups (both provided by Beijing Tingrun Membrane Technology Development Co., Ltd., China) was investigated by different cleaning approaches [76]. Two different cleaning strategies were proposed for the treatment of the IEMs after being fouled with sodium dodecyl sulfate (SDS), SDBS and bovine serum albumin (BSA) in a home-made ED device. The polarity of the electrical potential applied on the electrodes was inverted for 30 min at the same voltage of that applied in the fouling experiments, and, on the other hand, a low-cost and harmless chemical cleaning based on the use of ultrapure water solutions at room temperature for 48 h (the solution was substituted every 12 h by fresh ultrapure feedwaters) was also evaluated. The results showed that the chemical cleaning strategy was clearly superior to the polarity inversion of the applied electrical potential approach in terms of ion flux recovery.

Interestingly, the effect of ultrapure water as the cleaning agent has been previously proved to be similar to that of HCl-based solutions for the cleaning of AEMs in desalination applications [77]. In this study, a commercial Neosepta AMX AEM (Astom, Japan) was fouled with SDS (50-200 ppm) and cleaned through three different methods. The fouled AEM was soaked into ultrapure water, 0.28 M HCl or 0.25 M NaOH solutions at room temperature. The cleaning efficiency of the SDS fouling layer was comparable for ultrapure water and acid cleaning solutions, while the use of NaOH involved a lower cleaning efficacy. In all cases, the effect of the cleaning time analyses showed that the electrical resistance (measured by EIS) of the AEMs decreased gradually as the cleaning time increases. However, this value was still larger than the pristine membrane resistance after considering a cleaning operation time of seven days, which denotes that part of the SDS fouling layer was irreversible. In addition, higher SDS concentrations (> 100 ppm) led to a severe restriction of the counter ion migration through the membrane, as well as to desalination performance decreases. As a result, controlling the cleaning time seems to be essential to improve the cleaning efficiency in terms of ion transport through the membranes and the desalination performance in IEM-based water desalting processes, even though high foulant concentrations may negatively affect the cleaning effectiveness. As a consequence, pretreatment of the feedstreams is highly recommended to ensure an optimum membrane operation.

3.1.4. ED and EDBM: value-added products recovery

An adequate long-term membrane operational performance is also vital in the recovery and concentration of important value-added products through ED configurations. Thus, membrane cleaning represents an attractive option to increase the lifespan of the IEMs involved. As an example, the restoration of the initial properties of homogeneous Neosepta AMX and Neosepta CMB membranes (Astom, Japan) used for the recovery/concentration of ammonia from swine manure via ED, have been investigated by developing two-step cleaning protocols under agitation [78], since processing ten batches of swine manure involved a clear decrease in both the electrical conductivity and the IEC of the membranes. The first cleaning step consisted of immersing membrane samples into NaOH (0.5 %) for 20 min, followed by rinsing with water. Then, the samples were immersed into 1 % HCl solution for 20 min, including a final water rinsing step. After the two-step cleaning protocol, the CEM conductivity and IEC were almost completely restored; however, although the deposit visually observed on the AEM surface was successfully removed, its electrical conductivity was only partially recovered, as shown in Table 3. The authors attributed this finding to partial irreversible organic fouling, manifested by the dark coloration of the AEM surface observed after cleaning.

Table 3. IEM conductivity alterations before and after a two-step cleaning protocol in an ED system for the recovery and concentration of ammonia from swine manure. Results based on data presented in [78]

Neosepta IEMs (Astom, Japan)	**Loss of electrical conductivity related to the initial value (%)**
AMX fouled	-31.2 ± 0.5
AMX cleaned once	-20.0 ± 0.0
AMX cleaned twice	-19.1 ± 0.9
CMB fouled	-6.9 ± 1.2
CMB cleaned once	-3.3 ± 1.0
CMB cleaned twice	+0.6 ± 1.6

Another more recent example is the extraction of lignin from the electrochemical acidification of kraft black liquor through EDBM [79]. In this specific system, a series of five CEMs and four bipolar membranes (BPMs) were utilized. Four commercial CEMs capable of working at severe alkaline conditions were evaluated, namely FKB (FuMA-Tech GmbH, Germany), Neosepta CMB (Astom, Japan), Ralex CM(H)-PES (Mega a.s., Czech Republic), and Nafion^{TM} 324 (DuPont, USA). However, due to the limited availability of commercial BPMs, only a FBM BPM (FuMA-Tech GmbH, Germany) was tested. The effect of a dynamic chemical cleaning protocol on the IEMs integrity was therefore studied by using NaOH (2.5 wt%, pH 12.5) and fresh diluted black liquor (BL, total dissolved solids = 10 % and pH 12.5) as the cleaning agents, which were introduced through the EDBM setup for 30 min after disconnecting the power supply. The colloidal fouling was successfully suppressed after cleaning, either with caustic soda or fresh diluted BL solutions. The CMB and Nafion 324 CEMs were the most chemically stable membranes under alkaline conditions. The initial properties of CMB, Nafion 324 and BPM samples, were recovered after the cleaning cycle. Finally, although the use of NaOH involved better results in terms of property reestablishments and surface cleaning, the authors finally suggested the utilization of *in-situ* BL solutions taken into account sustainability and eco-efficiency perspectives.

Similarly, Wang et al. also studied the EDBM process to regenerate ammonium and sulfuric acid from industrial glutamate production stream containing ammonium, sulfate, LA, protein, calcium, magnesium, etc. (previously filtered by ceramic membrane to remove the bacteria) [80]. The EDMB process was carried out in five consecutive batches using four JCM-15 CEMs (Huanyu Lida Co., Ltd., China), four RMAX-7 AEMs (Guangya Co., Ltd., China) and five Neosepta BP-1 BPMs (Astom, Japan). Different fouling deposits (calcium hydroxide, calcium carbonate and magnesium hydroxide) were observed by SEM and elemental analysis mapping. Due to the fact that the presence of precipitates of Ca and Mg salts may cause significant CEM fouling, the authors focused on evaluating the foulant removal efficiency by physical and chemical methods (or their combination), such as ultrasonic application, deionized water solution, acid cleaning approach (1 wt% HCl for 3 h under agitation at 20 ºC), and ultrasonic-acid cleaning. This last cleaning strategy was found to be the best method to remove both the internal and the external (surface) fouling. Thus, after sonicating the sample in a beaker containing HCl (1 wt%) at 50 KHz, 0.25 W cm^{-2} and 20 ºC for 1 min, the initial physical and chemical properties of the cleaned CEM were almost completely restored. Additionally, a plane and clean surface of the cleaned sample was clearly observed by SEM, denoting the efficiency of the acid-ultrasonic cleaning approach.

3.1.5. EDR strategies

The use of EDR approaches as a membrane self-cleaning operation mode can also be considered since ED-based separation processes are expected to be more prone to fouling because of the presence of electrodes [81]. However, the foulants are not only present on the surface of IEMs, but also in the channels and spacers used in the EDR setup [82]. As a consequence, *ex-situ* and *in-situ* membrane cleaning procedures are needed to maintain stable process performance. The *ex-situ* chemical cleaning should be considered when irreversible internal fouling is observed, even though the dismantling of the EDR stack to carry out manual cleaning is a time-consuming and costly procedure. On the other hand, the *in-situ* CIP cleaning strategies did not involve dismantling steps to remove foulants [83]. In particular, the application of CIP methods are widely considered to overcome reversible fouling issues, in which the foulants are physically adsorbed onto the IEM surfaces [84]. In this context, acidic solutions mainly based on HCl are often used to eliminate precipitated salts such as $CaCO_3$, $CaSO_4$, and $MgSO_4$, whereas alkaline agents (most often NaOH) are usually applied to remove organic foulants, such as different proteins. Strong oxidants (NaClO and Cl_2), by contrast, are used to prevent biological growth via degradation of protein functional groups present in bacteria

[81]. Besides, salt-based solutions (*e.g.,* NaCl) may be helpful to destabilize the foulant-membrane electrostatic interactions. The combination of the above-shown cleaning protocols could also be considered in EDR applications. For example, a two-step cleaning method based on salt (5 wt% NaCl at pH from 8 to 10.5) and acid (5 wt% HCl, pH<1.2) solutions was found to be effective in the removal of organic foulants, while ensuring an optimal EDR performance in desalting a brackish water stream [82].

3.2. Cleaning of IEMs in Donnan dialysis and diffusion dialysis-based applications

The effect of IEM cleaning in Donnan dialysis approaches has also been studied with the purpose of improving the membrane(s) lifespan, thus reducing the operating cost of the IEMSP simultaneously. For instance, as shown in some AEMs used in ED experiments, AEM surface coloration was also observed in our previous Donnan dialysis studies [25], in which a biofouled Ralex-AMH-polyester (PES) AEM (Mega a.s., Czech Republic) was cleaned by 1 % NaOH aqueous solutions for 30 min in order to alleviate the membrane biofouling effect in an IEM bioreactor for the treatment of drinking water contaminated with nitrate and perchlorate. It was demonstrated that the original membrane properties, such as the membrane density and the IEC were completely restored after applying the above-mentioned chemical cleaning strategy. In this respect, the initial properties of the Ralex AEMs were shown to be unaffected for, at least, 10 consecutive alkaline washing cycles. This idea was further supported by evaluating the membrane surface coloration before and after cleaning, as represented in Fig. 8. A significant surface coloration alteration was observed, which denotes the effectiveness of the alkaline cleaning strategy to reduce the biofouling effect on Ralex-PES AEMs. Thus, it has become evident that defining IEM cleaning protocols is required in Donnan dialysis operations to improve the performance of the process, especially after prolonged experiments.

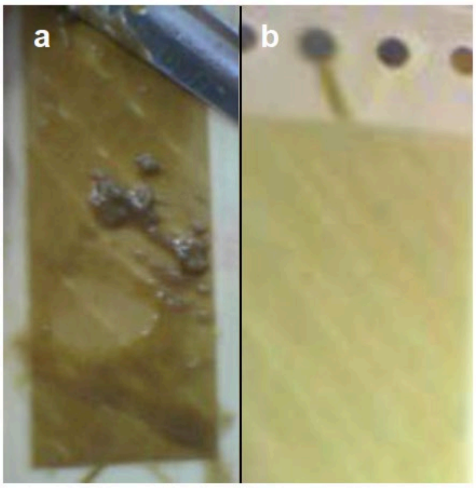

Fig. 8. Membrane surface coloration in an IEM bioreactor for the treatment of drinking water, a) before cleaning, and b) after alkaline cleaning. Adapted from [25].

The microbial biofouling formation was also investigated in several commercial CEMs and AEMs of homogeneous and heterogeneous nature in order to analyze the undesirable effect of biofouling on IEMs as a function of their membrane type and characteristics, using a *Pseoudomonas aeruginosa* PAO1 Gram-negative bacterium in a FC 821-PC transmission flow cell [85]. The microbial biofilm formation was observed to be higher on CEMs in comparison with AEMs, due to the antimicrobial properties of the AEM surfaces associated with the presence of quaternary ammonium moieties. The authors also highlight the importance of the IEM surface roughness effect on the interactions between the bacteria and the samples, thus demonstrating that this interaction is strong on heterogeneous IEMs than on homogeneous structures. Besides, the effect of biofouling on the transport properties of the pristine and biofouled membranes was also studied through Donnan dialysis analyses in terms of sulfate and potassium passage through the IEMs. The counter-ion transport was clearly decreased with time due to microbial biofouling, especially in heterogeneous samples. This effect was also more pronounced for AEMs than for CEMs, owing to the adsorption of the negatively charge extracellular polymeric substances to the positively charged surfaces of the AEMs, which led to a reduced counter-ions passage. Consequently, this novel study evidences the strong interest of developing IEM cleaning protocols to diminish the biofouling impact on the behavior and performance of IEMs in Donnan dialysis approaches.

Furthermore, the inorganic scaling has been demonstrated to represent a key factor in the performance of IEMs during Donnan dialysis applications in terms of counter-ion flux decline and changes in the potential difference across the scaled-membrane [86,87]. Initially, homogeneous

(AMV, Asahi Glass, Japan) and heterogeneous (MA-40, Shchekinoazot, Russia) AEMs were evaluated under scaling conditions in a Donnan cell with optical characteristics for in-situ analysis, using a receiving $CaCl_2$ solution (Na_2SO_4 aqueous solution as the feed), which leads to the formation of gypsum ($CaSO_4{\cdot}2H_2O$) scaling, since sulfate ions move from the feed to the receiver, thus interacting with calcium ions to cause the inorganic scaling [86]. On the one hand, surface scaling deposits were observed in the homogeneous IEMs, which involves a moderate decrease in the counter-ion flux during Donnan dialysis. However, a more severe flux decline was observed in heterogeneous IEMs, owing to internal precipitation that leads to complete membrane clogging. This fact, on the other hand, involved an increase in the membrane potential after operating under scaling conditions, whereas the potential difference in the case of the homogeneous AMV membrane was not significantly increased.

Moreover, the same authors investigated the effect of gypsum scaling on homogeneous (CMV, Asahi Glass, Japan) and heterogeneous (MK-40, Shchekinoazot, Russia) CEMs during Donnan dialysis for the sake of comparison [87]. As observed in the behavior of AEMs under scaling conditions, surface precipitation was identified in the homogeneous CEMs, while membrane interior scaling was predominant in the heterogeneous CEMs, as confirmed by SEM analyses (Fig. 9). The internal gypsum inorganic crystals on the heterogeneous surfaces can be seen in Fig. 9b and Fig. 9c, whereas the preferential crystal growth on the surface of the homogeneous membranes can be clearly identified in Fig. 9e and Fig. 9f. The effect of internal inorganic scaling (MK-40 CEMs) was clearly larger than the surface scaling phenomenon (CMV CEMs), since earlier flux declines as well as larger potential differences were observed in the heterogeneous structure. Finally, this investigation shows that the studied CEMs are less prone to inorganic scaling in comparison with the behavior of AEMs (previous study) under similar Donnan dialysis conditions, which evidences the key role of the membrane matrix composition (chemical nature and structure) in the undesirable inorganic scaling formation with time on IEMs.

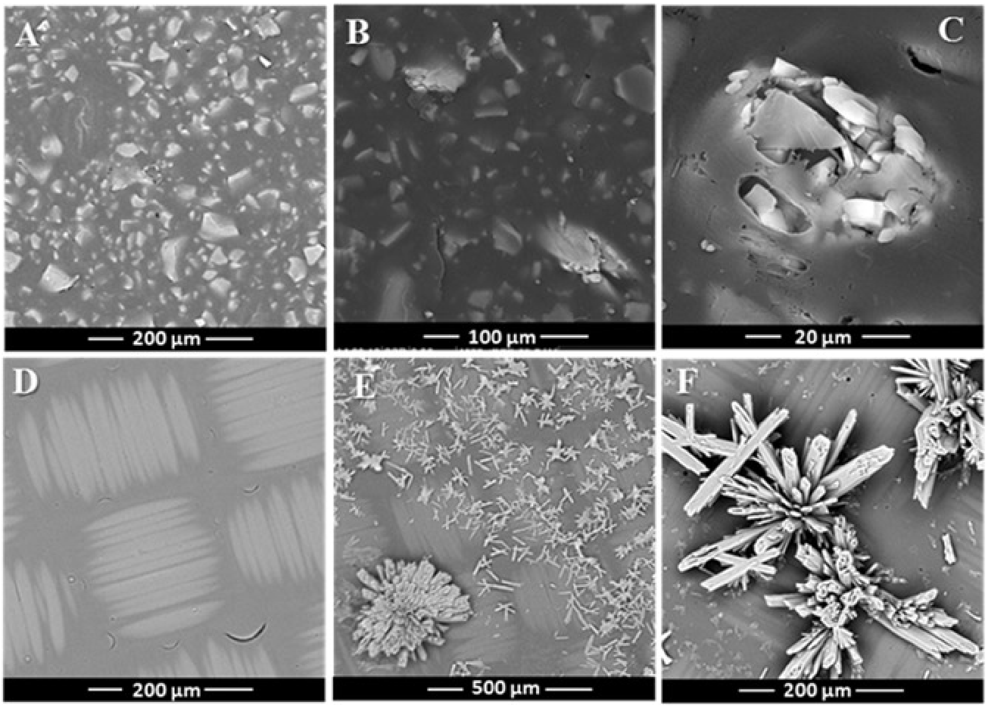

Fig. 9. SEM images of: A) Pristine heterogeneous MK-40 CEM; B and C) $CaSO_4$ scaling in MK-40 CEM; D) Pristine homogeneous CMV; E and F) $CaSO_4$ scaling in CMV CEM after scaling experiments under Donnan dialysis conditions. Reproduced with permission from [87].

Finally, it is essential to point out here that fouling/scaling phenomena is not a quite important issue in diffusion dialysis-derived applications, due to the use of strong acids or bases [23], which can be considered as the cleaning agents themselves.

3.3. Cleaning of IEMs in alternative IEM-assisted processes

In this section, different IEM cleaning approaches reported in literature in alternative electro-membrane processes are summarized and discussed. The sustainable and eco-friendly production of clean water through the membrane capacity deionization (MCDI) technology, initially proposed in 2006 [88], has also been continuously studied for the desalination of (mainly) brackish water by means of selective IEMs, thus allowing the transport of counter-ions toward carbon electrodes. However, fouling and scaling phenomena usually hamper the efficiency of this process and increase its operating costs at the same time [3]. Therefore, the development of dedicated membrane cleaning strategies are clearly needed for the practical implementation of this emerging energy efficient technology [62]. In this context, physical cleaning methods, such as air sparing or vibration, have been demonstrated to be effective in pressure-driven process, but not in the case of dense nonporous IEMs like those applied in MCDI systems [80]. As a result, chemical cleaning is considerably preferred in MCDI applications in order to weaken the bonds between the foulants and the membrane surface [89]. It is important to emphasize here that the type of chemical approach should be selected based on the nature of the foulant, the compatibility of the chemical with the processing equipment, chemical availability, cost, and safety [79,89]. Thus, alkaline cleaning should be applied to remove organic foulants, such as peptides and proteins, whereas acidic solutions and chlorinating agents are likely to reduce mineral deposits and biofouling, respectively. The use of sequestrating agents such as EDTA; however, might involve a loss of charged ions from the membrane structure [62]. The membrane type under investigation also represents a key factor to be taken into consideration. In this regard, Langevin and Bazinet demonstrated that CEMs were doubly more prone to peptide fouling in comparison with AEMs [90]. The authors showed that 2 % and 5 % aqueous NaCl solutions were effective to remove larger foulants (with molecular mass > 900 Da) on CEMs, whereas the elimination of smaller particles was significantly less efficient under these cleaning conditions. Finally, pretreatment strategies must be applied to the brackish water inlet stream in order to decrease the amount of dissolved organic matter with the purpose of reducing the electrode fouling owing to the blocking of the activated carbon pores. Besides, the presence of Fe seems to have a significantly higher effect on this type of fouling in comparison with that observed for Ca or Mg [91].

Moreover, the presence of charged foulants in river water streams represents the worst IEM fouling scenario in RED systems for energy harvesting in terms of process performance (*i.e.,* power density) [8]. Accordingly, cleaning strategies must be explored to diminish the fouling impact in RED approaches, especially in the river water compartments. In this context, two-phase cleaning approaches have also been demonstrated to be efficient to mitigate fouling in RED configurations, whose IEMs arrangement is similar to that of ED stacks. Relatively cheap liquid-gas combinations can be applied to reduce IEM fouling, which is essential to improve the obtainable net power density, as shown Moreno et al. [92]. In this study, two different cleaning approaches (water/air sparging and CO_2 saturated water injection) were investigated. Natural seawater and river water were the feedstreams of a RED stack located in the Netherlands operated for 60 days, and the homogeneous CEMs and AEMs utilized were Neosepta CMX and Neosepta AMX (Astom, Japan), respectively. The generated power density was decreased by up to 50 % due to fouling phenomena during the operation of the system before cleaning. The comparison of the two cleaning strategies results showed a significant improvement in terms of obtained net power density (0.18 W m^{-2}) when using

CO_2 saturated water, whereas the stacks equipped with air sparging could only produce an average net power density of 0.04 W m^{-2}. These findings were associated with an increased stack resistance (measured by an EIS technique) due to the presence of bubbles during air sparging. On the contrary, the use of CO_2/water strategies decreased the solution pH, thus introducing an additional cleaning effect to the stack, which is appealing in order to avoid the continuous use of environmentally unwanted cleaning agents. To support this hypothesis, several representative SEM images of different RED stack elements in contact with the seawater compartment were obtained, as displayed in Fig. 10. This compartment was selected because fouling issues were strongly observed in that place of the stack. Less fouling deposits were clearly observed on the CEMs (Fig. 10a) with respect to those presented on the AEMs (Fig. 10c and Fig. 10d), denoting that the AEMs are much more prone to fouling than the CEMs, which can be attributed to the adsorption of humic acids on AEM surfaces. Besides, Fig. 10a clearly shows the location of the foulants in the spacer filaments, as further demonstrated in Fig. 10b. With respect to foulant-cleaning interactions, $CaCO_3$ and $MgCO_3$ (detected by EDX analyses) were only observed with water/air sparging treatments (Fig. 10d). However, a precipitation of Ca or Mg carbonate crystals was not observed for the CO_2 saturated water cleaning approach (Fig. 10c), which demonstrates that the carbonates are successfully dissolved due to the pH drop in the feed after applying this strategy.

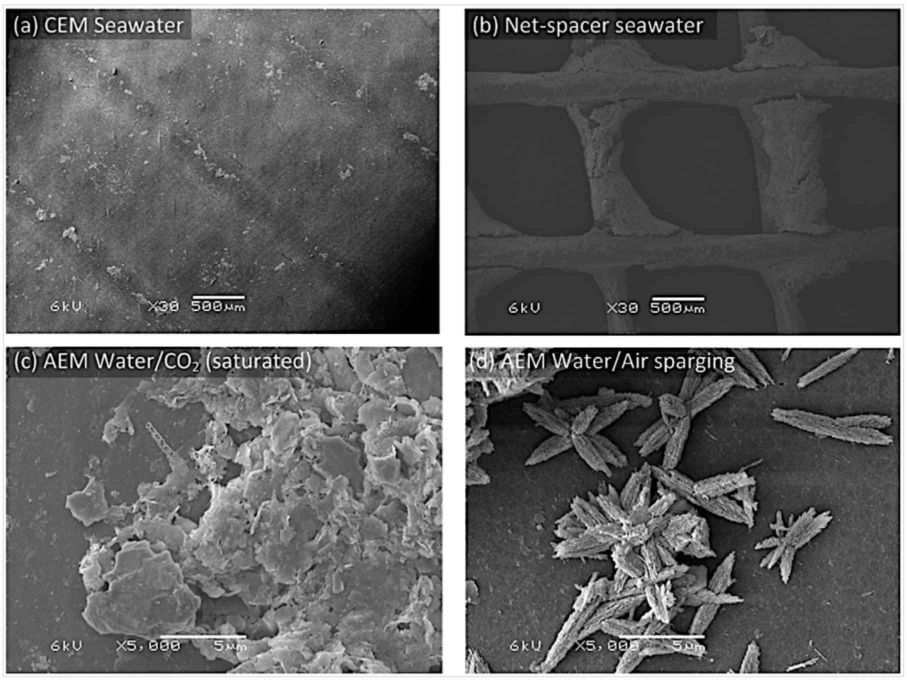

Fig. 10. SEM images of different elements of the RED stack in contact with seawater after 60 days of operation: a) CEM - CO_2 saturated water; b) Net spacer – water/air sparging; c) AEM - CO_2 saturated water; d) AEM – water/air sparing. Reproduced with permission from [92].

Interestingly, the combination of surface modification and cleaning approaches during RED operation represents an interesting strategy to improve the performance of IEMs in RED stacks with the purpose of controlling fouling phenomena, and thus the obtainable gross power density, as proposed by Pintossi *et al.* [93]. Since fouling of AEMs is more critical than fouling of CEMs due to the negative charge of most foulants, the authors chemically modified the surface of commercial Fujifilm AEMs type I (Fujifilm Manufacturing Europe BV, The Netherlands) with zwitterionic monomers or zwitterionic brushes, which led to increased membrane hydrophilicities. The fouling analyses were carried out in a cross-flow RED stack as a function of AEM type (*i.e.,* pristine and modified samples) using artificial seawater (30 g L^{-1} NaCl) and river water (1 g L^{-1} NaCl) feedwaters, including 100 ppm of SDBS as the model foulant in the river water feedstream. Firstly, both feedstreams were used without foulant content for 8 h, followed by clean seawater and river water (containing the foulant) solutions for 16 h. Finally, new clean NaCl-based feedstreams (without SDBS) were employed as the cleaning agents (fouling recovery) for 3 h to evaluate the membrane fouling reversibility. Although the modified AEMs with zwitterionic monomers were able to delay the fouling onset, the zwitterionic brushes-based AEMs also decreased the fouling layer growth simultaneously, which can be associated with their more hydrophilic nature. Consequently, the zwitterionic brushes-based modification approach is efficient in decreasing the power density losses during fouling, while the cleaning approach has been demonstrated to be useful on the recovery of the gross power density, especially for the modified membranes. Therefore, combining membrane modification and cleaning strategies represents an interesting tool to enhance the performance of AEMs in RED applications, even though validation tests under real conditions are required. In addition, recent fouling propensity studies of IEMs (Fujifilm Manufacturing Europe B.V., The Netherlands) in RED apparatus operated with seawater and hypersaline brine have also revealed a higher sensitivity of CEMs to scaling (through $CaCO_3$ precipitation tests), which denotes that IEM fouling (both on AEMs and CEMs) represents the bottleneck of the process in RED applications for blue energy generation from salinity gradients [94].

3.4. Ion exchange membrane cleaning overview

Overall, several studies about IEM cleaning in several separation processes have been widely reviewed and discussed. Among the available possibilities, the authors of the present review would like to recommend the most appropriate cleaning procedures as a function of the membrane type (including its nature and characteristics) and the final target application, as shown in Table 4. Up to date, the use of chemical cleanings seems to be the most effective strategy to diminish the negative fouling impact on different IEMs. Thus, their initial properties will be restored at the same time, and the membrane lifetime would be considerably increased. However, further research is still required in order to optimize the membrane cleaning protocols in different applications. As a consequence, different cleaning parameters must be further studied, such as the number of cleaning cycles, the dosage of the cleaning agents, their environmentally friendly properties, the contact time, the volume (immersion), pH, temperature and the optimal combination of approaches, among others, taken into account the foulant nature and its interaction with the membrane surface under investigation. To sum up, the selection of the most efficient chemical cleaning procedure is not always simple, as a number of factors are usually involved in the determination of the global cleaning efficiency. Therefore, a deeper understanding on the interaction between the foulants (including fouling mechanism analyses) and the IEM surface are highly required to move forward into the development of more efficient membrane cleaning strategies.

It is also worth noting that different physical procedures such as sonication, hydraulic flushing, pneumatic and mechanical approaches (effectively proven in membrane pressure-driven processes) could also be adopted and considered to be applied over several IEMs used in separation processes. In this regard, efficient hybrid physico-chemical cleaning methods might improve the current state-of-the-art on IEM cleaning efficiencies.

Last but not least, it is of outmost importance to remark that fouling phenomena is not necessarily an undesirable effect, even though is always thought to be a disadvantage aspect in the performance of membranes during different IEMSPs. In this context, the fouling deposition concept has also been proposed as an efficient approach for the surface modification of IEMs with the purpose of improving the monovalent permselectivity of the membranes [95]. In this novel strategy, a Neosepta AMX AEM was modified by fouling deposition of sulfonated poly(2,6-di-methyl-1,4-phenylene oxide) (SPPO) through an ED setup under different supplied current densities. The highest permselective coefficient ($P\ Cl^-/SO_4^{2-}$ = 52.44) was reached at 10 $mAcm^{-2}$, which was larger than the unmodified membrane, as well as to commercial permselective ACS membranes. In a similar approach, the surface of commercial heterogeneous Ralex AEMs (Mega a.s., Czech Republic) were modified by direct contact with poly(acrylic acid), previously considered as a model foulant [96], for enhanced monovalent permselectivity [24]. Significantly improved sulfate rejection and hydrophilicity results were reported without compromising the electrical resistance of the modified IEMs.

4. Conclusions and future prospects

The presence of foulants in natural feedstreams is leading to a significant decrease in the performance of ion exchange membranes in separation processes, especially after prolonged uses. Consequently, the definition of cheap, efficient and sustainable membrane cleaning protocols is crucial to increase membrane durability and stability in the long term. Hence, this review summarizes the wide variety of ion exchange membrane cleaning methods available so far, paying special attention to electrodialysis-based approaches, which represent the most important ion exchange membrane separation process. However, alternative ion exchange membrane separation processes (*e.g.,* Donnan dialysis) and different electro-membrane process (*e.g.,* reverse electrodialysis) are also discussed. In this respect, the use of chemical cleaning procedures (both *ex-situ* and *in-situ*) represents the best strategy for the cleaning of IEMs, even though the type of membrane, foulants nature and target application must be taken into consideration for the selection of the most appropriate cleaning agents. Alternatively, enzymatic approaches have been shown to be promising to remove foulants in food industry applications through electrodialysis configurations. Lately, physical strategies such as sonication in combination with chemical procedures represent hybrid alternatives that could also be considered to increase membrane durability. After summarizing and discussing the up-to-date membrane cleaning research, we present here for the first time several cleaning recommendations as a function of the membrane type, target application and foulants nature, among others. Therefore, this study represents a step forward into providing dedicated novel cleaning perspectives about one of the most important challenges in the membrane fouling field. It is also worth noting the requirement to carry out a pretreatment step of the natural feedstreams in those cases where the concentration of foulants is extremely high, which might be particularly helpful for improving the overall membrane cleaning efficiency.

However, further investigations are still required to optimize the global cleaning efficiency in different ion exchange membrane separation processes, which is essential to improve the process performance and to reduce several operating costs. Accordingly, the authors would also like to recommend the study of the following remaining key challenges with the aim of enhancing membrane cleaning decision criteria: i) a more comprehensive understanding of the fouling mechanisms is extremely necessary to understand the effect of different foulants (as a function of their nature, concentration, etc.) on the external and internal surfaces of different ion exchange membranes; ii) the interactions between the foulants and the ion exchange membranes should also be studied to determine the optimum cleaning agent to remove/alleviate fouling phenomena; iii) in-depth investigations are required to evaluate the effect of several cleaning parameters (*i.e.,* the concentration of the cleaning agent, the amount of cleaning cycles, the pH, the temperature and the contact time) on the global cleaning efficiency to determine the optimum cleaning protocol in each case; iv) the use of real feedstreams rather than mimicking natural streams is required, in order to examinate the membrane behavior and its performance under real conditions; v) the combination of cleaning and surface modification strategies must be further considered in natural streams that contain a wide variety of foulant types in order to provide an useful tool to reduce the global fouling impact; vi) environmental impact analyses about membrane cleaning from cost and eco-friendly perspectives are clearly missing and should be therefore developed to analyze the most effective cleaning possibility.

All in all, this review provides help and support into the definition of the optimum membrane cleaning strategy as a function of the ion exchange membrane separation process, membrane type and target application, while deepening the knowledge about the removal of the negative fouling effect in ion-exchange surfaces with different properties and characteristics at the same time.

Table 4. Summary of prospective ion exchange membrane cleaning strategies proposed in the literature

IEM-assisted process	Target application	Model solutions	Membrane type	Membrane role	Membrane cleaning recommendation	Cleaning alternatives	Referen
ED	Membrane ageing (whey demineralization)	-	Homogeneous AEMs (AXM-SB, Astom, Japan)	Efficient counter-ions mobility	Acid conditions (< 2 M HCl)	Controlled acid-base cycles (0.1 M)	[66]
			Heterogeneous AEMs (MA-41, Shchekinoazot, Russia)		Alkaline cleaning (< 2 M NaOH)		
ED	Wastewater treatment (electroplating industry)	Synthetic wastewater effluent: $CuSO_4{\cdot}5H_2O$, $ZnSO_4{\cdot}7H_2O$, EDTA disodium salt, NaOH	Heterogeneous AEMs (HDX200, Hidrodex, Brazil)	Permselective properties	Mild alkaline conditions (0.1 M NaOH)	Strong conditions (< 1 M NaOH)	[16]
			Heterogeneous CEMs (HDX100, Hidrodex, Brazil)				
ED	Wastewater treatment	Oily wastewater feed solution in plant-scale ED	Heterogeneous CEMs	Desalination rate	APAM fouling: alkaline	NaOH (oil fouling)	[67]
			Heterogeneous AEMs		APAM fouling: acid		
ED	Food industry	Confidential industrial ED modules	CEMs (confidential)	Ion exchange capacity and permselectivity	Water-ethanol (12 %v) mixtures[1]	Saline solutions (NaCl): surface cleaning	[68,69
			AEMs (confidential)		Water-ethanol (12 %v) mixtures[2]		
ED	Food industry (red wine production)	Treated red wine, brine solution (KCl or KNO_3, etc) in ED stack	Homogeneous CEMs (CMX-Sb, Astom, Japan)	To reduce the concentration of potassium hydrogen tartrate (KHT) in wine	Enzymatic cleaning (0.1 g L^{-1}) at 50 ºC	Combining enzymatic solutions[3]	[70]
ED	Food industry (removal of LA and minerals in dairy industries)	Real streams received from a dairy plant containing LA, proteins, K, Na, Ca, Mg and P	Homogeneous IEMs (Neosepta AHA and CMB, Astom, Japan)	To remove (partially) LA and minerals	Acid cleaning + alkaline cleaning (pH importance). Higher alkaline pH (9.2) is ineffective for proteins removal	-	[72]

ED	Desalination	River water of Shatt Al Arab (Irak)	Heterogeneous IEMs (home-made; polypropylene matrix)	Resistance against organic pollutants	Alkaline-acid strategy: NaOH (3 %) at 40 ºC and HCl rinse	-	[74]
ED	Desalination	Artificial solutions (NaCl + inorganic compounds, HPAM and oil emulsions) mimicking the treatment of polymer flooding produced water	Homogeneous CEMs and AEMs (Shandong Tianwei Membrane Technology Co., Ltd., China)	Desalination rate	Acid-base-SDBS combination[4]	Depending on fouling: acid-base (organic and inorganic fouling); SDBS (oil fouling)	[17]
ED	Desalination	Artificial mixed solution of NaCl (0.01 M) and different foulants (SDS, SDBS and BSA) in a home-made ED device for *in-situ* EIS analyses	Homogeneous AEMs (Beijing Tingrun Membrane Technology Development Co., Ltd.**,** China)	Membrane resistance against different foulants	Chemical cleaning with ultrapure water[5]	Inverted electrodes (less efficient)	[76]
ED	Value-added products recovery	Filtered effluent of swine manure to recover and concentrate ammonia through ED	Homogeneous IEMs[6] (Neosepta AMX and CMB, Astom, Japan)	Membrane fouling characterization after 10 batches and ion-exchange capacity	Alkaline + water rinsing + acid + water rinsing	-	[78]
EDBM	Value-added products recovery	Prefiltered Kfraft BL (Canadian pulp mill) for its acidification and subsequently extraction of lignin	CEMs: Neosepta CMB (Astom, Japan) and Nafion™ 324 (DuPont, USA)	Colloidal fouling effect on membrane integrity	Colloidal fouling: NaOH (2.5 wt%, pH 12.5)	Diluted black liquor solutions	[79]
EDBM	Value-added products recovery	Filtered industrial glutamate production wastewater containing ammonium, sulfate, glutamate, alanine, LA and protein (to regenerate ammonium and sulfuric acid)	JCM-15 CEMs (Huanyu Lida Co., Ltd., China)	Fouling deposits analyses during EDBM process	Acid solution (HCl, 1 wt%) + ultrasounds (50 KHz, 0.25 W cm^{-2}, 20 ºC)	Hydraulic cleaning	[80]

EDR	Desalination (drinking water)	Raw water with, inorganic, biological and organic matter content (EDR treatment)	IEMs (in general)	Efficient permselectivity	Cationic salts: acid (HCl); organic foulants: alkaline (NaOH); biofouling: strong oxidants (NaClO, Cl_2); Destabilization of electrostatic interactions: saline (NaCl)	Combination of approaches (*e.g.,* NaCl-NaOH + HCl)	[81,82
Donnan dialysis	Wastewater treatment (drinking water)	Synthetic polluted water (tap water from Lisbon public network, adding 600 ppm of nitrate and 100 ppb of perchlorate)	Heterogeneous AEMs (Ralex-AMH-PES, Mega a.s., Czech Republic)	Efficient transport of charged anionic micropollutants	Alkaline cleaning (1 % NaOH aqueous solution)[7]	-	[25]
MCDI	Desalination	Mainly brackish water in membrane capacity deionization (MCDI)	IEMs[8] (in general)	Transport of counter-ions toward carbon electrodes	Organic foulants (*i.e.,* peptides): alkaline cleaning. Mineral deposits: acid method. Biofouling: chlorinating agents. Larger foulants (>900 Da) in CEMs: NaCl solutions	Combination of approaches depending on brackish water composition	[62,89,
RED	Energy harvesting	Seawater (Wadden Sea) and river water (Ijsselmeer), The Netherlands	Homogeneous IEMs (Neosepta AMX and CMX, Astom, Japan)	Monovalent permselectivity	Two phase cleaning: CO_2 saturated water	Two-phase water/air sparging approach	[92]
RED	Energy harvesting	Artificial NaCl aqueous solutions mimicking seawater and river water (with SDBS as the model foulant)	Pristine and modified Fujifilm AEMs type I (Fujifilm Manufacturing Europe BV, The Netherlands)	Monovalent permselectivity	NaCl cleaning	-	[93]

Notation: [1] Ethanol should be recovered (*i.e.,* by distillation); [2] Higher membrane conductivity recovery in AEMs due to a larger expansion of the pores in the cleaning solution; [3] The combination of different enzymes in the same solution seems to be appealing to increase the global cleaning efficiency; [4] Highly efficient for the removal of oil, organic and inorganic fouling; [5] Ultrapure water has a similar effect compared to HCl (0.28 M); [6] Irreversible organic fouling in AEMs (conductivity partially recovered); [7] Biofouling treatment; [8] The cleaning type is highly dependent on the foulant nature.

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Conflicts of Interest

The authors declare no conflict of interest.

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