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Evaluation of chemical free cleaning techniques for reverse electrodialysis stacks fed with natural waters

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ABSTRACT

Reverse electrodialysis (RED) is a promising technology to harvest salinity gradient power (SGP) that is available where fresh and sea water mix, using anion (AEM) and cation exchange membranes (CEM) in a stack. Fouling of the membranes is one of the main challenges for RED, since it leads to a reduction in attainable net power output. In this study, we combined the use of profiled ion-exchange membranes (200 μm thick compartments) with a pre-treatment by a dual media filter for both natural water streams (Lake Ijssel and Wadden Sea), with four different cleaning procedures: (i) increased flow, (ii) reverse and increased flow, (iii) reverse flow and feed switch, and (iv) air sparging. Cleaning with air sparging was the most effective technique, limiting the pumping losses and not influencing the power generation capacity. The cleaning with reverse flow and feed switch also showed to be suitable, keeping the pressure drop losses lower than 100 mbar for both water streams. Post experiment membrane autopsy showed that CEMs were more subjected to particulate fouling than AEMs, and that a lower accumulation of fouling by particulate resulted in a higher concentration of humic acids and biofouling on the membrane surface.

1. Introduction

Reverse electrodialysis (RED) is a promising technology that can be used to harvest the salinity gradient power (SGP), also known as Blue Energy, that is naturally available where fresh and sea water mix [1,2]. SGP is a renewable energy source that can be used in combination with other sustainable energy sources, such as solar and wind, as the SGP is a continuous source of energy and does not suffer from high fluctuations of yield due to weather conditions or day and night cycles [3]. The RED principle is based on exploiting the chemical potential difference from the controlled mixing of low and high salinity streams separated by ion-exchange membranes converting it into an electrochemical potential difference [1,2,4]. Electrical energy can be harvested by alternating anion exchange membranes (AEM) and cation exchange membranes (CEM), which direct anions to the anode and cations to the cathode of the RED stack, and through redox reactions in the end compartments, using electrodes and an electrolyte solution [1].

Fouling of the ion exchange membranes is one of the main challenges hindering the viability of this technology, since it leads to a reduction of the exploitable net power [5,6]. Prevention and management of fouling is of utmost need for this technology to reach the market [5,7,8]. Fouling formation can be slower when using an effective pre-treatment of the inlet waters (sea and fresh), that removes a large amount of foulants even when the daily and seasonal variations in weather and climate result in a varying inflow of foulants. Many pre-treatment methods have been tested on inlet water for RED in the past, such as a drum filter, cartridge filter, river bank filtration, coagulation with polyaluminum chloride (PAC) and sand filter [6,9,10]. The desired pre-treatment should be robust, durable, with simple operation and maintenance and, most importantly, with a low energy demand [11]. In previous studies we showed that a dual media filter, using anthracite and sand as media, could fulfill many of these requirements, being effective for both seawater and fresh water pre-treatment [12]. In our work, it was also shown that the formation of a fouling layer composed by particulate matter was the main contributor to pumping power losses in the process, but at the same time, its formation could also limit attachment and

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growth of microorganisms and thus biofouling [12,13]. Thus, the presence of small amounts of particulate matter can be beneficial, and fouling management through cleaning should consider this aspect.

Together with a robust pre-treatment, fouling management with cleaning techniques is necessary to avoid a loss in performance during long-term RED operation [7,8,14]. This can be achieved by applying certain operational techniques, such as increased flow, or a proper cleaning procedure that includes the use of a cleaning agent such as compressed gas or chemical solution [7,14]. A combination of frequently applied operational techniques and less frequent cleaning with a cleaning agent could be considered to tackle different types of fouling at low energy expenditure. To make RED a viable and sustainable technology, the desirable cleaning procedure should require low amounts of energy, be effective, not use harsh chemicals, and not produce toxic by-products since it is likely that cleaning residues will be disposed of in the sea. In addition, it should not hamper RED stack performance and membrane properties or demand a long downtime in operation [8]. Previous research on this matter included the work of Post et al. [15], who proposed switching of feed waters in the compartments' regularly to promote an osmotic shock of microorganisms and prevent biofouling development. Vermaas et al. [16] compared the periodic feed water switching with air sparging, with both techniques being applied every 30 min, and air sparging was shown to be more effective in long-term operation. Moreno et al. [17] investigated the best configuration of operation for air and CO_2 sparging, implementing the use of short pulses of compressed gas. The main conclusion was that applying CO_2 was more effective since less stagnant bubbles were trapped on the spacers mesh, allowing for more constant performance of stacks [17]. Finally, when using a basic solution as a cleaning agent, Chon et al. showed that both organic and inorganic foulants were more effectively desorbed from the membrane surface in fresh and sea water in comparison to an acid solution, but no details on the potential by-products formed were presented [18].

In (reverse) electro-dialysis, it is common to use spacers to create the compartments for feed waters, but recent studies showed that the use of spacers could hinder stack performance, due to the spacer shadow effect and by enhancing the surface available for fouling attachment [8,19–21]. In addition, the spacers can have a negative effect when applying cleaning techniques, such as air sparging, by trapping bubbles and increasing the resistance of the cell [16,17]. Thus, an alternative for spacers was designed by imprinting channels on the membrane surface to make the compartments, the so-called profiled membranes [21–23]. Profiled membranes have been shown to yield better power output when using natural waters and allow for more customization of desired flow distribution inside the cell [16,19,23].

Despite the above-mentioned benefits, profiled membranes are not yet commercially available due to the difficulties of profiling surfaces at a large scale and low demand for this type of membrane.

In this study, we combined the use of thermo-pressed profiled ion-exchange membranes, that created water compartments of 200 μm thickness, with dual media filter pre-treatment of both inlet waters and four different (new and more established) cleaning procedures, namely increased flow (IF), reverse and increased flow (RIF), reverse flow and feed switch (RFFS), and air sparging (AS). The selection of the techniques was based on results from previous research [16,17,19] and the above-mentioned needs for RED to be a viable and sustainable technology. The use of a combination of chemical-free techniques with long intervals in between cleanings, with some of the cleaning techniques targeting different types of fouling, is studied for the first time in RED.

The cleaning procedures were compared for their impact on stack performance and fouling removal potential. The applied cleaning techniques had different impacts on the fouling build-up and performance loss over long-term operation (67 days) under realistic operation conditions with natural waters. In addition, fouling removal and membrane autopsy analysis were carried out to investigate fouling layers' formation in time and the effects of each of the cleaning techniques on different kinds of fouling.

2. Materials and methods

2.1. Experimental set-up

Fig. 1 presents a schematic representation of the set-up used in the experiment, built in the pilot plant installation at the REDstack BV facility (Breezanddijk, the Netherlands) located on de Afsluitdijk, a flood defense dike spanning between the provinces of North Holland and Friesland. Five RED stacks were operated in parallel and fed with equally pre-treated fresh and sea water. First, both waters were filtered with a drum filter with a pore mesh of 40 μm, immediately followed by rapid dual media filtration, and stored in 30 m^3 storage tanks. The rapid dual media filter consisted of two distinct layers: first an anthracite layer (1.2 mm – 2.0 mm) followed by a sand layer (0.5 mm – 1.0 mm). Operation of the filters was automated, and backwashing was done with treated water and compressed air.

All RED stacks were constructed identically and operated equally, with the only difference being the cleaning procedure applied. 10 × 10 cm cross-flow stacks were supplied by REDstack BV (The Netherlands), and 5 cell pairs were used, totalizing a membrane area of 0.1 m^2. The stacks were run with a flow velocity of 1 cm/s, and operated continuously for 67 days.

2.2. Profiled membranes and stack operation

The membranes used in the experiment were supplied by Ralex (Mega, Czech Republic), more specifically CMH-PES and AMH-PES, and the characteristics can be found in [21]. These membranes were chosen due to their suitability to make profiles with the thermo-pressing method, which employs heterogeneous membranes that can withstand temperatures up to 140 °C [21,22,24].

CEM membranes were profiled on both sides, with perpendicular direction, to maintain a cross flow pattern in the stack. Profiling was done as in [21] by applying 140 °C for 10 min with 200 bar of pressure after pre-heating the moulds for 2 min. The pressure was kept until the cooling of the membranes was completed to approximately 45 °C. A picture of a freshly prepared profiled CEM is shown in Fig. 2, together with a cross-section picture of a profile, showing the height of the channels of around 200 μm. AEMs were used flat, without any modifications. All membranes were stored and conditioned as recommended by the supplier.

The anode and the cathode of the stack consisted of titanium electrodes mesh with a galvanic platinum coating of 2.5 μm and with an active area of 10 × 10 cm (Magneto Special Anodes B.V., The Netherlands). The electrolyte solution was recirculated in the electrode compartments and kept at an overpressure of 0.3 bar, and composed of 0.05 M $K_3Fe(CN)_6$, 0.05 M $K_4Fe(CN)_6$ and 0.25 M NaCl (VWR, USA). A pressure difference transmitter (Yokogawa, Japan) continuously measured pressure drop over the outlet and inlet of the stacks. A sensor connected to a data logger (Yokogawa, Japan) recorded temperature and conductivity of the feed waters after treatment every 60 s.

The voltage of the stacks was measured using a potentiostat (Iviumstat, Ivium Technologies, The Netherlands) connected via a peripheral differential amplifier. Chrono potentiometric series were applied allowing for calculation of the open circuit voltage and gross power density based on obtained I-V curves. The net power density was calculated by subtracting the pumping power required to pump the feed waters to the stacks from the gross power density, as done in [25]. The chronopotentiometry series consisted of constant current density steps of 2 A/m^2, 3 A/m^2, 4 A/m^2, 5 A/m^2 and 6 A/m^2 applied for 80 s each to allow the stack voltage to reach a constant value. The current steps were separated with 80 s without applied current when the open cell voltage (OCV) could be measured. The results are shown as a day average of four measurements per day, which were done with 6 h intervals. The rest of

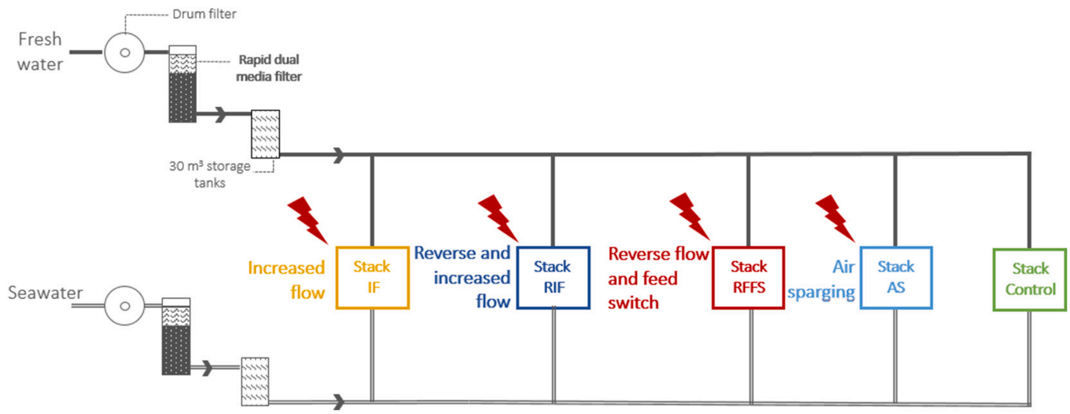

Fig. 1. Schematic representation of the experimental set-up used for the experiments presented in this work. Five stacks were operated in parallel with equally pre-treated feed waters (via a drum sieve and a dual media filter) while a different cleaning technique was applied on each stack throughout the experiment. In stack control, no cleaning technique was applied.

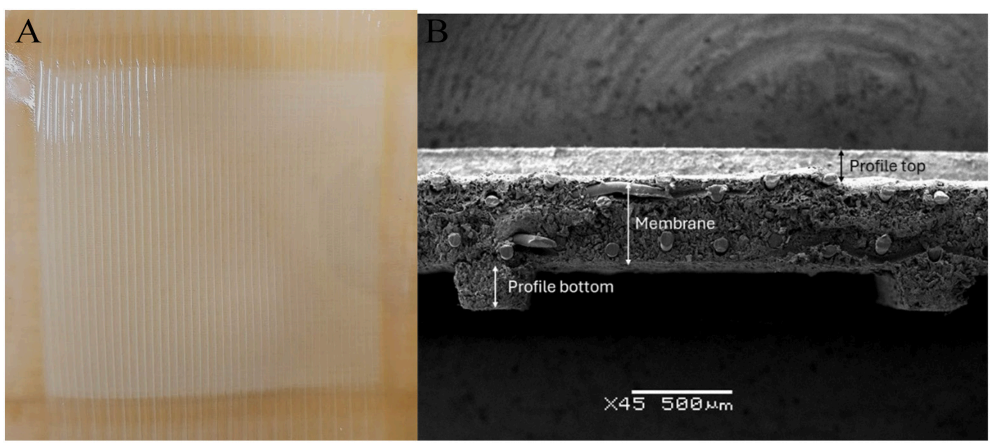

Fig. 2. Image of a clean profiled CEM (A) and the SEM image (B) showing a detail of the profiles generated by thermos-pressing method, in cross-flow configuration (transversal profiles). The profile/ridge height is around 200 µm. Scale bar is 500 µm.

the time the stacks were operated at constant current density to simulate the RED process.

2.3. Cleaning techniques

The four applied cleaning procedures were selected for their suitability and potential for fouling removal, looking as well at how easily they can be implemented and performed.

- *Increase of flow to three times the original flow for 5* min *(IF).* This technique aims to cause fouling detachment and release simply by increasing the shear forces along the membrane surface [26].
- *Reverse inlet and outlet of the stack coupled with flow increase to three times the original flow for 5 min (RIF).* This procedure was chosen due to fouling starting to accumulate at the inlet of the stack, and by increasing the flow foulants are pushed out [13,19].
- *Reverse inlet and outlet of the stack coupled with switching the feed waters compartment's (RFFS).* With this procedure, the compartment that was receiving fresh water in the inlet, now receives seawater from the outlet (new inlet). By switching water compartments, the difference in salinity of the feed water streams causes an osmotic shock, which can lead to detachment of the fouling layer and to adverse conditions for organic and biofouling. This happens mostly when the previous freshwater compartment receives seawater, which acts as a draw solution to desorb the foulants that were absorbed or attached to the surface [15].
- *Air sparging (AS).* In this procedure, compressed air is used as a cleaning agent and flown inside the stack along with the feed water, causing a disturbance in the water compartment due to the high pressure of the air bubbles. This leads to fouling detaching from the membrane and be washed out by the water flow [16,17,27].

2.3.1. Combination of cleaning techniques

A combination of techniques is expected to be required for fouling management in RED. Thus, an additional chemical cleaning was introduced and a concentrated salt solution was chosen instead of acid and base solutions that can damage the membrane surface [8,28]. For this purpose, a brine of 90 g/L of sodium chloride was prepared and recirculated for 1 h 30 min in all stack compartments on day 54, except in the control stack [28].

In addition, the frequency of treatment of all stacks was increased from day 60 until 64 to daily, to evaluate if more frequent cleaning could be beneficial. On day 64, after the normal cleaning of each stack, air sparging was performed in the four stacks receiving cleaning treatments, to test the possibility of combining the mechanical cleanings with a more intensive procedure with a cleaning agent (compressed air). The effluent water collected after the cleaning procedure was analysed for quantification of the removed fouling, with the same techniques as described in section 2.4.

2.4. Fouling removal water analysis and membrane autopsy

Samples of the outlet fresh and sea water from the stacks were taken during the cleaning procedures and analysed to quantify the fouling removal by means of organic carbon quantification via TOC analysis and LC-OCD, suspended solids concentration, particle size distribution (PSD), with the same procedures as described in [13].

At the end of the experiments, a membrane autopsy was performed in all stacks to visually evaluate the effect of the cleaning procedures. Fouling appearance was visualized by naked eye and is presented with camera photos. Membrane pieces were cut in duplicate for microscopy investigation via optical and scanning electron microscopy (SEM). To visualize the carbohydrate fraction of the extracellular polymeric substance (EPS) characterizing biofilms and thus biofouling, membrane samples were stained with Alcian Blue 8 GX 0.1 % solution (Sigma Aldrich, USA) for 30 min and washed with MilliQ water to remove excess dye [29,30]. For SEM analysis, membrane pieces were first fixed with 2.5 % glutaraldehyde solution overnight and dehydrated with graded series (30, 50, 70, 90 and two times 100 %) of ethanol for 20 min each step and finally dried for 30 min at 55 °C oven. The SEM analysis was performed with a JEOL JSM-6480LV (JEOL, Japan) at an acceleration voltage of 6 kV and magnifications up to 15,000×.

Finally, to study residual fouling on the membrane surface in more detail, membrane pieces of 2 × 5 cm were cut and placed in 30 mL of 90 g/L NaCl brine to extract as much foulants as possible from the membrane surface to a solution. The samples were placed for 30 min on a shaker, followed by 30 min on the ultrasonic bath and left overnight at 4 °C. The next morning, the samples were shaken for 30 min again, before the analysis was done. With the foulants in the brine solution, suspended solids and humic acids analysis were performed in the same way as for the outlet water collected during the cleaning procedures, described earlier in this section.

3. Results and discussion

The effect of the different cleaning strategies was evaluated by monitoring stack performance in time and by analysis of the effluent water after cleaning to get insights on the type and the amount of foulants removed. Moreover, at the end of the experiment, a membrane autopsy was performed to identify different types of fouling on the membrane surface.

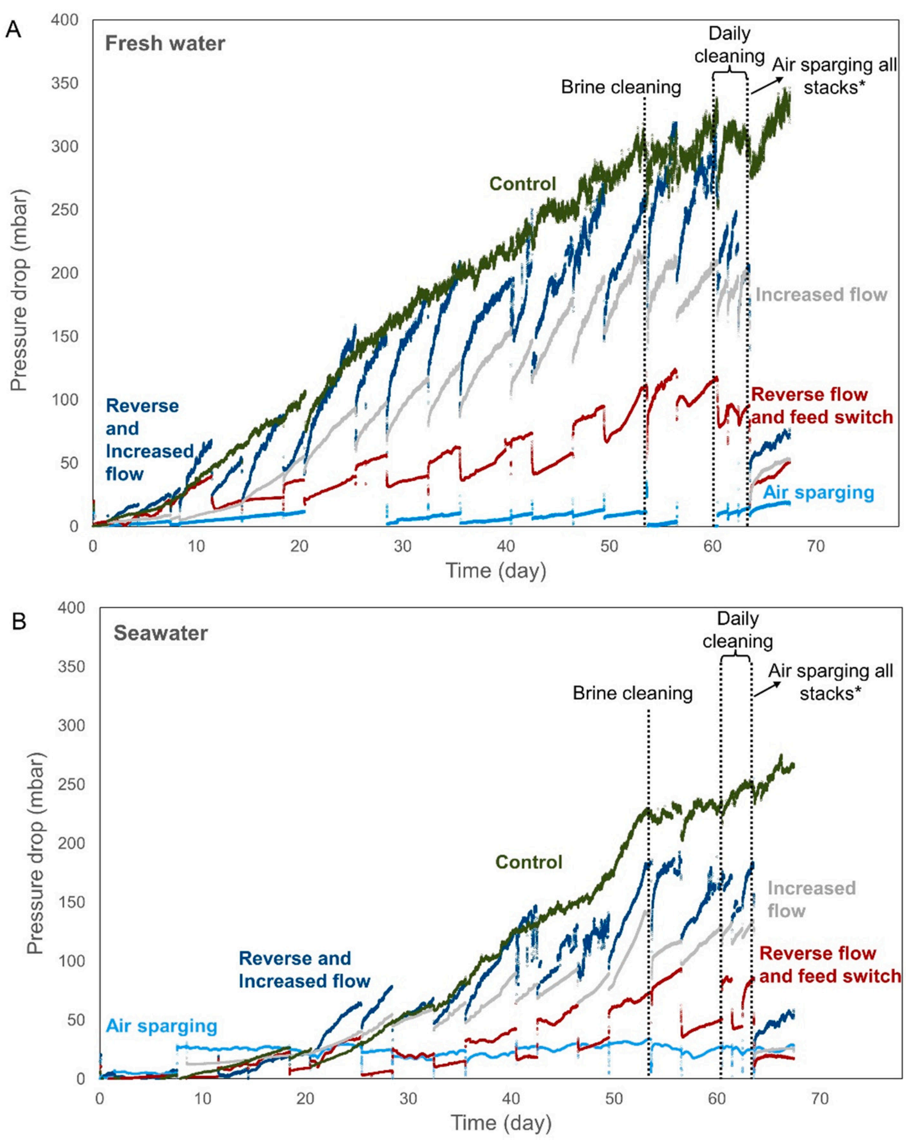

Fig. 3. Pressure drop over the inlet and outlet of fresh water (A) and seawater (B) compartment of the five stacks in operation. The type of cleaning of each stack is positioned next to its curve in the graph. (*) Air sparging was performed on day 64 in all stacks receiving cleaning throughout the experiment.

3.1. Stack performance

The experiment was carried out for 67 days and evaluated over time by monitoring the pressure drop (Fig. 3) and by measuring the electrochemical performance via OCV and gross power density measurements (Fig. 4). Finally, these parameters can be combined in the net power density (Fig. 4), revealing the overall performance.

The use of dual media filtration as pre-treatment showed to be effective in keeping the pressure drop at low values throughout the experiment, with a maximum pressure drop of 350 mbar for the stack Control (Fig. 3). This is about half of the values reported by Vermaas et al. [16] in an experiment using similar profiled membranes and natural waters, but a different pre-treatment (a 10 μm cartridge filter). These results show that the pre-treatment with a dual media filter is reliable and performs better than a cartridge filter, which has a lower specific pore size and needs to be replaced frequently. The results achieved by cleaning techniques, such as Air sparging and Reversed flow and feed switch are remarkable, keeping the pressure drop values below 100 mbar for more than 2 months of operation. In the study of Vermaas [16], the pressure drop values reached more than 400 mbar over a similar long period of operation when only a feed switch was performed. This underlines that the combination of a pre-treatment with a cleaning technique could achieve better results.

As shown in Fig. 3, the pressure drop constantly increased over time in both fresh water and seawater compartments due to fouling accumulation in the compartments. In all the stacks where a cleaning strategy was applied, the pressure drop was kept lower than the pressure drop in the control stack (Fig. 3). The lowest pressure drop in both seawater and fresh water compartments was observed in stack AS, highlighting a minimal fouling build-up (Fig. 3). This underlines the efficacy of the air sparging as a cleaning technique, which reduced the fouling to initial levels and that allows for longer intervals in between cleaning.

The reversed flow and feed switch (stack RFFS) cleaning technique was also shown to be effective, keeping pressures drop in the stack below 100 mbar for 67 days (Fig. 3). With this simple technique, we cannot assume that fouling was completely removed from the stack, but it was mitigated, due to changing of the nature of the waters in the compartments and by flushing foulants partially out.

The treatment with RIF and IF was not effective in keeping a low pressure drop, as the pressure drop quickly increased again after the cleaning procedure was applied (Fig. 3). These simple cleaning techniques were not able to decrease fouling to its initial levels, and thus new fouling layers can build-up fast, possibly leading to irreversible fouling [31,32].

In terms of electrochemical performance, the biggest impact is seen at the beginning of the experiments (from day 0 to day 1) (Fig. 4), when divalent ions poisoned the membrane and reduced OCV and consequently gross power density [33] (Fig. 4A and B). This decrease was observed in all stacks and can be attributed to the chemistry of the polymeric membranes. From day 2 until the end of the experiment, the gross power density of all stacks reduces similarly over time; with stack

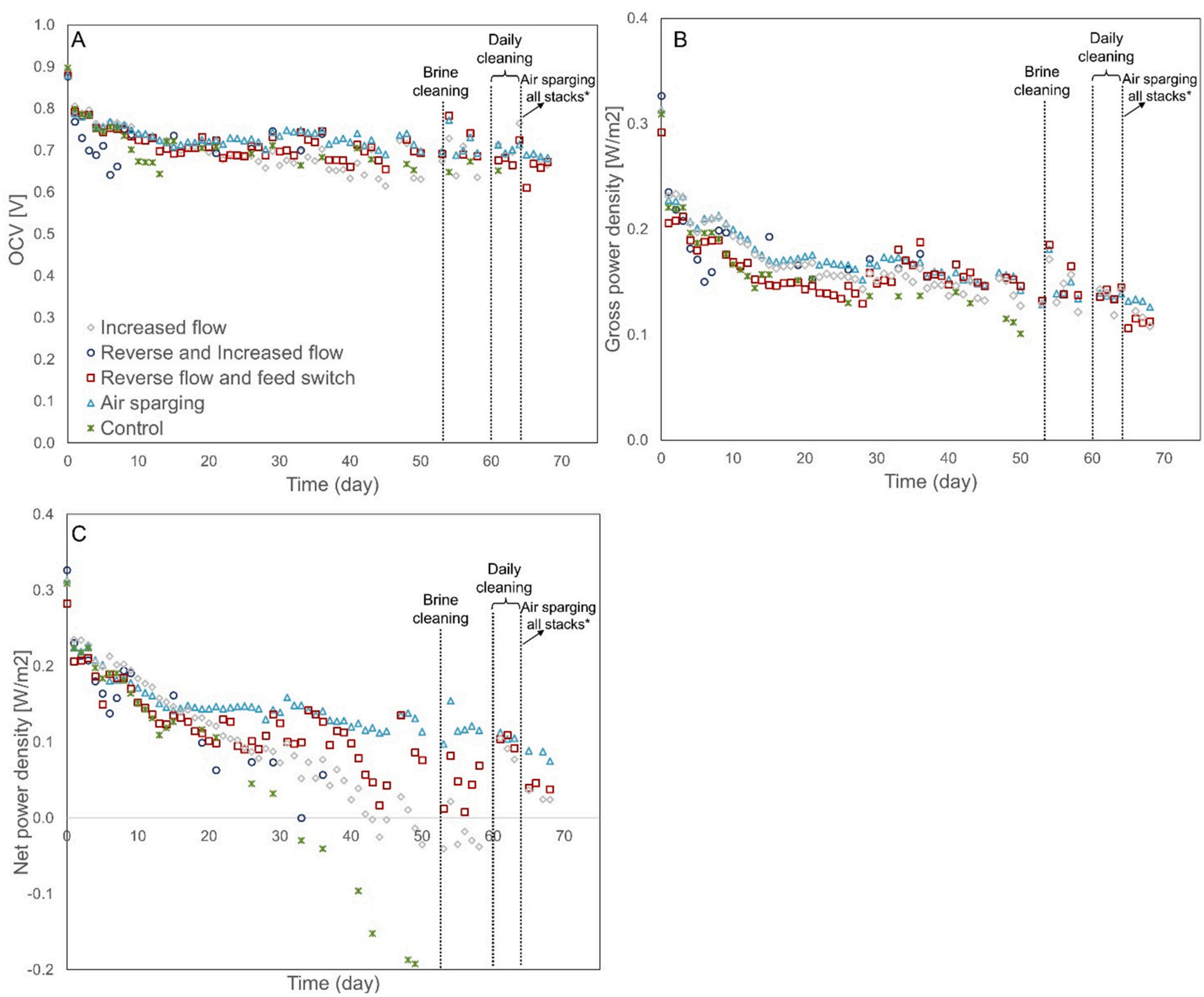

Fig. 4. Electrical performance of the five stacks operated during the experiment, reported as OCV (A), gross power density (B), and net power density (C). (*) Air sparging was performed on day 64 in all stacks receiving cleaning throughout the experiment. Additional data is given on Fig. S7.

Control having a bit sharper and faster decrease than other stacks (Fig. 4B). This overall decrease in performance is due to a reduction in the temperature of waters and variations of the salinity gradient (conductivity), as shown in Fig. S1, but also due to the different types of fouling accumulation in the membrane surface varying with the inlet water quality (Table S1). The temperature of both feed waters decreased around 6 °C and reached about 10 °C, which can impact the power density to a great extent [3]. The temperature decrease could also impact OCV, which dropped around 0.1 V per stack (Fig. 4) [3,16]. In addition, fouling by organics, such as humic acids present in natural waters, can get trapped inside the membrane and results in a loss of ion-exchange capacity of the membrane [18,32]. After day 37, stack RIF, and at day 50, stack Control started to fail electrochemically (Fig. 4) and could not be evaluated at the end of the experiment. These two stacks were also the ones with the highest pressure drops and most affected by fouling, which could have led to the power failure.

At the end of the experiment all the stacks produced a similar gross power density, except for the control and RIF stacks (Fig. 4B). That means that the fouling removal by the other three cleaning procedures had little effect on the electrical performance of the stacks, possibly due to the applied cleanings not affecting the kind of foulants that would influence the ion transfer through the membranes and, consequently, the electrical performance of the stack.

In conclusion, based on the pressure drop and the net power density air sparging showed the best cleaning performance.

It is important to highlight that three out of these four cleaning strategies did not use a cleaning agent and can be seen as an operational practice that can delay fouling formation and recover performance, at least partially, for some time. Cleaning with air sparging is seen as a greater intervention in the stack operation, but still, a simple technique since it uses only compressed air as a cleaning agent. Compared to previous cleaning strategies applied in RED (16,17,18), this work shows that operational costs can be reduced, as the frequency of cleaning required to keep the performance is much less than the previous 30 min frequency. The use of air and feed streams as cleaning agents prevents the need for additional investment costs for the construction of chemical lines and reduces the operational costs compared to other cleaning products. Most importantly, the formation of possible toxic by-products that will need to be disposed of is prevented, which will also have an impact on the financial model of an operating power plant.

3.1.1. *Analysis of foulants removed with cleaning*

The cleaning techniques were evaluated in their potential to remove foulants from the stacks, by analysing the effluent water collected during the application of each technique. The removal of suspended solids (Fig. 5), confirmed that air sparging was most effective to remove foulants originating from both feed waters, which are known to cause an increase of pressure drop [26]. The removal was clearly larger in the freshwater compartments and that could be attributed to a higher content of suspended solids in this inlet water (~ 6 mg/L). The treatment with the dual media filter provides inlet seawater with a low content of suspended solids (~2 mg/L), but for fresh water the treatment is less effective, and over time, this slightly higher concentration of solids entering the stacks accumulates in a fouling layer. The fouling build-up in the freshwater compartments is then tackled by the cleaning techniques, resulting in higher removals than from seawater compartments. It is worth noticing that the fouling from the freshwater feed is mostly of organic nature, as seen in the higher fraction of volatile suspended solids (Fig. 5), and that high amounts could be removed with the cleaning techniques.

Looking at other fractions of fouling, such as organic carbon and humic acids, little effect could be seen in their removal by the different cleaning techniques (Fig. 6, Fig. S2 and Fig. S3). The exception was the cleaning with reverse flow and feed switch which was the only technique that could remove humic acids from the freshwater compartment (Fig. 6).

When the feed waters were switched in stack RFFS, the fouling accumulated in the previous freshwater compartment was suddenly subjected to an osmotic stress when the compartment is switched to seawater. This caused an osmotic gradient that likely allowed the humic acids to desorb from the fouling layer to the feed water compartment (Fig. 6), with seawater acting as a draw solution for this foulant [15,16].

The lack of removal of humic acids from the seawater compartments (Fig. 6) can be explained by freshwater feed not being able to desorb humic acids from the seawater compartments. Fresh water bodies are known to have high concentration of humic acids, while seawater is less affected by it [18]. Thus, the fouling layer in the seawater compartment has a lower content of humic acids and that possibly allows for a fast equalization of concentration of the humic content, together with a fast reduction of the osmotic gradient between the fouling layer and the feed water.

3.2. *Combination of cleaning strategies*

Besides the previously discussed cleaning procedures, also combinations of cleaning strategies were used to help maintain stack

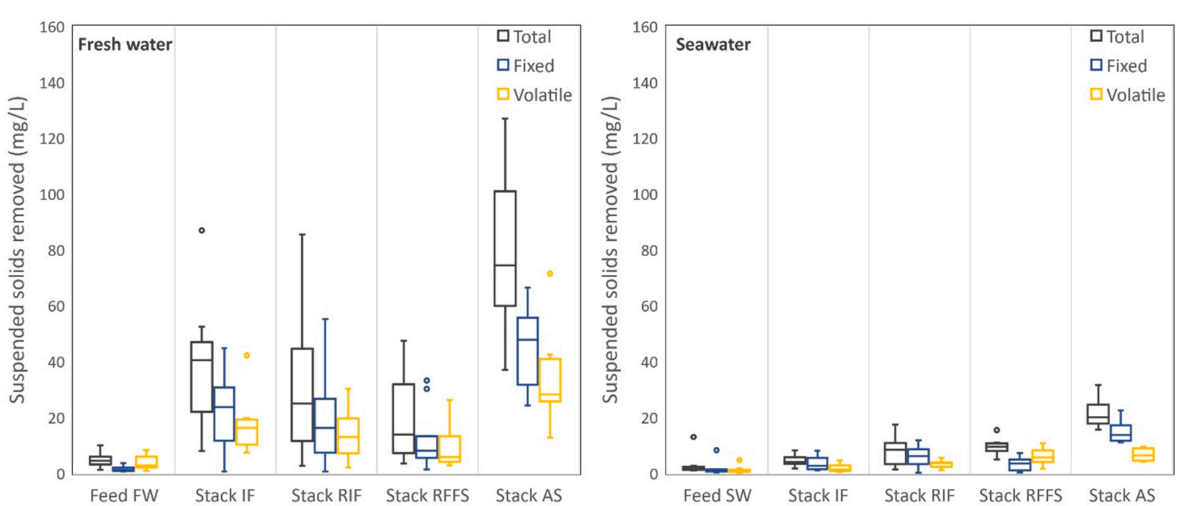

Fig. 5. Box plot distribution of the suspended solids removed in the fresh water and seawater compartment of each stack when a cleaning technique was carried out. For reference, the content of suspended solids on both feed waters is shown. Stack IF received increased flow cleaning, stack RIF was cleaned with reverse and increased flow, stack RFFS received cleaning by reverse flow and feed switch and stack AS with air sparging.

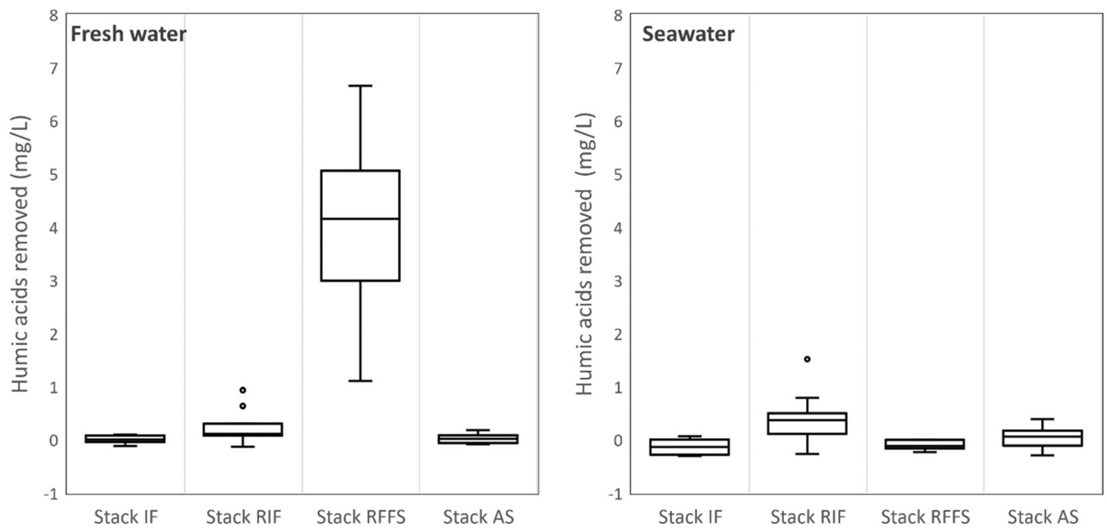

Fig. 6. Box plot distribution of humic acids removal from fresh and sea water compartments for each cleaning procedure performed during the experiment. Stack IF received increased flow cleaning, stack RIF was cleaned with reverse and increased flow, stack RFFS received cleaning by reverse flow and feed switch and stack AS with air sparging.

performance.

A cleaning with brine was performed on day 54 to assess the effect of a chemical technique on fouling and consequent stack performance and the effect was evaluated by the impact on pressure drop (Fig. 3), electrochemical performance (Fig. 4) and suspended solids and COD measurements on the water recovered from the cleaning procedure (Fig. S4).

The pressure drop was not greatly impacted by this technique (Fig. 3), proving that brine cleaning has little effect on particulate fouling, which is the type of fouling mostly responsible for increased pressure drop [26]. When the brine cleaning was applied to both seawater and freshwater compartments, the removal of suspended solids was comparable to or lower than what was achieved with the other cleaning methods already in use (Fig. 5 and Fig. S4).

On the other hand, the gross power density was momentously positively affected by the brine cleaning (Fig. 4B). This can be expected, since the amount of salt present in the stack and membranes after the cleaning could reduce the feed's resistance and increase the power output [16,34]. However, the benefit of this technique was limited to the moment of the cleaning only.

Another attempt to restore the performance was to perform the cleaning procedures more frequently, in this case, every day for 4 days in a row, and the impact on pressure drop (Fig. 3) showed that there was a benefit from more frequent cleaning on decreasing the loss of performance for all stacks. This could be attributed to the cleaning being performed in a shorter time span than needed for fouling build-up. However, this benefit was limited, as shown by the pressure drop reduction; it was only kept at a slightly lower pressure drop during these 4 days but did not return to initial values (Fig. 3). Thus, more frequent cleaning can help to keep a lower pressure drop and limit the effects of fouling build-up. Even with the daily cleaning, the estimated downtime needed is less than 1 % of the full-time operation, considering 24 h of continuous operation.

Due to the effectiveness of air sparging in reducing pressure drop (Fig. 3), at day 64, this cleaning method was applied to the stacks that were receiving a different cleaning procedure, namely IF, RIF, and RFFS. After the application of air sparging, the amount of suspended solids removed from these stacks was up to 10× higher than what was observed with their initial cleaning procedure, before day 64 (Fig. 5 and Fig. S5), showing that most of the fouling was still present in the stacks was reversible with a more intensive cleaning. This resulted in low values of pressure drop, which were close to the initial ones (Fig. 3). In the case of stack IF, the effect on pressure drop was three times higher than the average reduction observed with the increased flow cleaning alone during the 2 months of operation (Fig. S6). Similar results were achieved with stack RIF, while for stack RFFS the effect was not so evident, but this is due to a previous lower accumulation of foulant (Figs. 3 and S6). The results also showed that a larger fraction of the suspended solids removed is composed of inorganic compounds (non-volatile SS, Fig. S5), highlighting that minerals from sediments constitute a large part of the reversible fouling. Air sparging is a more robust cleaning strategy to remove a large fraction of reversible fouling that is still effective even when applied less frequently.

3.3. Membrane autopsy

By the end of the experiment (day 67), all stacks were opened and subjected to membrane autopsy, and membrane samples were visually analysed. As air sparging was performed in all stacks receiving cleaning at the end of the experiment, almost no fouling could be detected on the membranes by the naked eye, with the exception of stack Control (Fig. S8), used as reference. SEM micrographs (Fig. 7), and optical microscopy images (Fig. S9) confirmed that the control stack had a significant fouling layer in comparison to others. In the profiled CEMs, fouling was mostly found in between membrane ridges, as shown via visual (Fig. S8) and SEM (Fig. 7) analysis. This happens due to the top of the ridges being in contact with the AEM and space for accumulation was limited.

Despite the air sparging step being applied to the stacks by the end of the process, different types of fouling were identified in each stack, highlighting that the different cleaning techniques applied to them during the experiment were selected for a certain type of foulant(s). In stack AS, fouling development involved biological components such as bacterial cells and diatoms (Fig. 7) but not much biofilm, as highlighted by the low amount of EPS detected after applying alcian blue staining (Fig. S9). The diatoms were more commonly found in the CEMs, probably due to favourable charge interactions between the outer 'shell' of the diatom, which is usually negative [35], and the positive ionic charge caused by concentration polarization around the negative charge of the cationic membrane. Vermaas [6] observed an accumulation of diatoms and mineral silica at the AEMs, but in that study both AEM and CEM were profiled and that could interfere with the fouling attachment and formation. As previous studies showed [12,13], when there is less incidence of fouling by particulate matter, there is more available ideal surface area for attachment and growth of bacteria and EPS layer, as

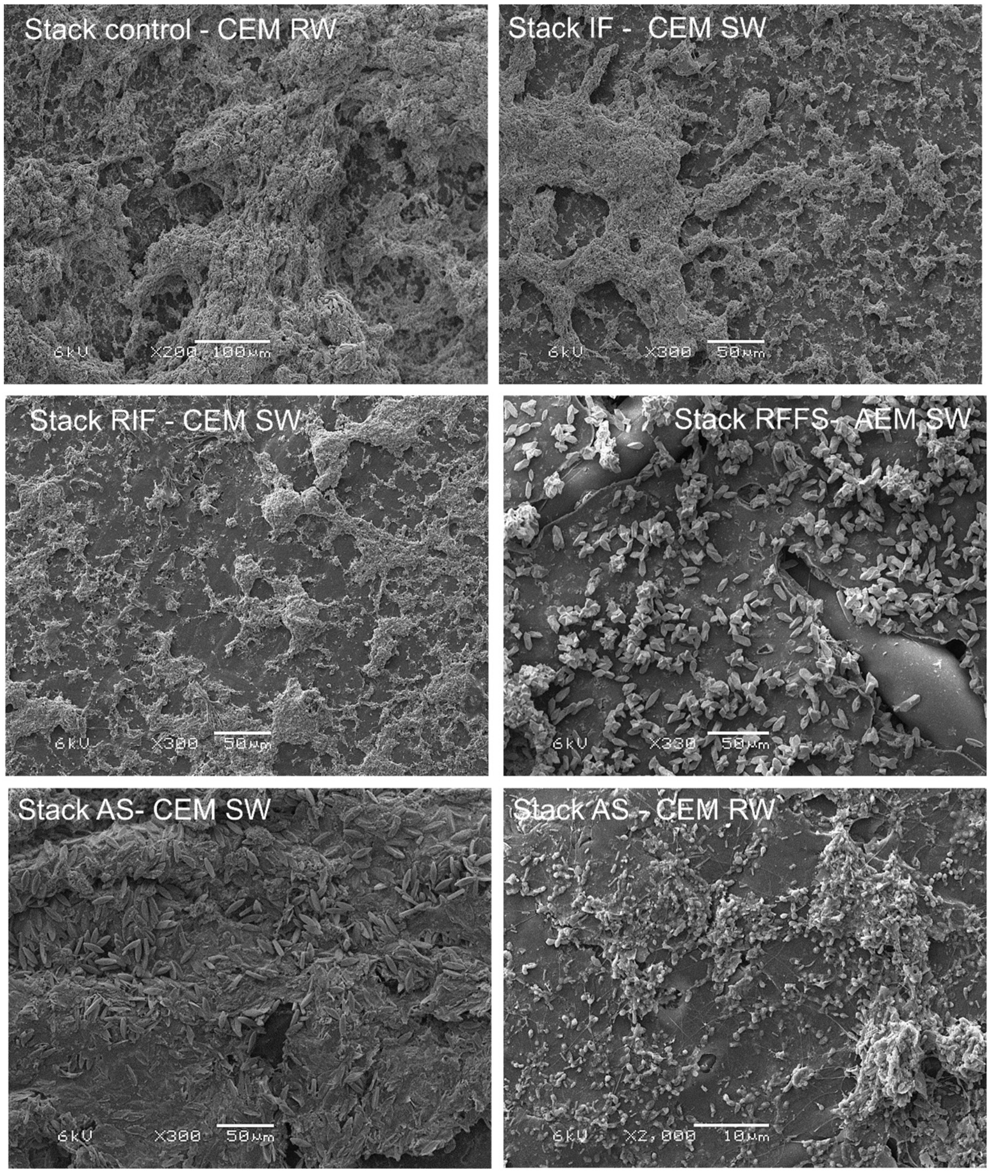

Fig. 7. SEM images of fouling layer of all stacks operated in the experiment. Stack IF received increased flow cleaning, stack RIF was cleaned with reverse and increased flow, stack RFFS received cleaning by reverse flow and feed switch and stack AS with air sparging.

well as diatoms, resulting in pronounced biofouling. Biofouling is more difficult to remove during the cleaning procedure, even when using air sparging [15]. However, despite the presence of low biofouling, the performance of stack AS was not really affected during the experiment, biofouling.

In stack RFFS scaling in the form of calcium precipitates was observed using EDX analysis of the fouling layer (Table S2). The precipitation of salts could have happened due to the switching of feed water compartments, with a sudden osmotic shock and local changes of pH. Additionally, diatoms were found on the CEMs (Fig. S8), highlighting that the presence of biofouling could not be removed with the performed cleanings, similar to the observation of stack AS.

Fouling in stacks IF and RIF was found in similar amounts, and no special type of fouling could be identified with the techniques applied, such as typical traits of biofouling. The two cleaning techniques applied on the two stacks were very similar, with the only difference being the first one includes reversing the flow direction before increasing the flow. The stacks also performed very similarly, as shown in pressure drop measurements for both fresh and seawater (Fig. 3).

Overall, particulate fouling was found in small amounts in the stacks subjected to the cleaning procedures. This was confirmed by the residual fouling found during the autopsy, quantified as suspended solids and humic acids (Fig. 8). As a reference, the amount of residual suspended solids in the control stack was about 7 g/m^2 of membrane area on the CEM membrane (Fig. 8).

In stack AS, the residual suspended solids on the CEM were slightly lower than other stacks receiving cleaning, as expected by the pressure drop values (Fig. 3). It is interesting to notice that more residual suspended solids were found on CEM membranes of all stacks compared to their AEMs counterparts, except for stack AS (Fig. 8). EDX analysis showed that suspended solids were mostly composed of natural organic matter debris and silica and aluminum sediments found in the natural waters that could not be removed in the pre-treatment (Table S2). This type of foulants is usually negatively charged and, surprisingly, is more attracted to the CEM than to the AEM. This could be due to concentration polarization of positively charged species on the membrane surface or because most of the solids are found in fresh water feed (Fig. 5) and due to the electric field are being attracted to the anode and thus the CEMs [32].

For the residual humic acids, AEMs had higher accumulation than

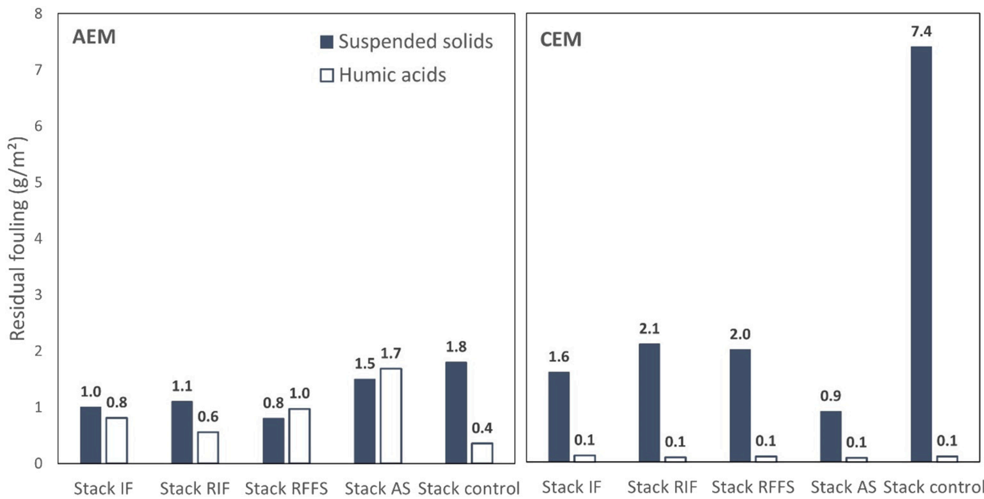

Fig. 8. Estimation of the residual fouling on membrane surfaces on each membrane type (AEM and CEM) of each stack, estimated on the basis of suspended solids and humic acids from the membrane autopsy. Stack IF received increased flow cleaning, stack RIF was cleaned with reverse and increased flow, stack RFFS received cleaning by reverse flow and feed switch and stack AS with air sparging.

CEMs (Fig. 8), which is in accordance with the observed brown colour of the first membranes (Fig. S9) and due to the negative charge interaction of the humic acids with the positive charge of the AEMs, as previously reported in the literature [16,24,36]. In the fresh water compartments, AEMs acquire a very intense brown colour, while the seawater compartment have a faded brown coloration, as shown in Fig. S6, and reported in [24].

Humic acids were found in lower concentrations in the stacks with higher increase in pressure drop, such as Stack RIF and Control (Figs. 3 and 8), and, as observed for biofouling, this could be due to the protection of the membrane surface from being in contact with the larger organic molecules, such as humic acids.

In summary, the cleaning strategies that allowed for maintaining a good performance throughout the experiment were air sparging, reverse flow and feed switch, which in combination with the use of profiled membranes resulted in an overall low-pressure drop. The use of spacers is known to hinder the use of air as a cleaning agent [17]. Thus, the use of profiled membranes is important to achieve the mentioned results. Most cleaning procedures had no effect on chemical parameters associated with fouling, with the exception of reverse flow and feed switch that could combine the effect of low pressure drop and removal of humic acids. In addition, membrane autopsy showed that the presence or absence of a fouling layer of particulate solids can affect the subsequent fouling formation, such as organic and biofouling. This is highly relevant for pre-treatment design and cleaning frequency and should be studied in more detail depending on the feed water sources. Chemical cleaning was not needed to maintain the performance of the stacks during the time frame (67 days) of this experiment.

4. Conclusions

The application of cleaning strategies in stacks operating for more than 2 months gives a good perspective on which cleaning method is preferred to use for different goals and composition of feed water. Air sparging removed particulate fouling well and it seems to be the best strategy to keep a low pressure drop when used in combination with a pre-treatment that allows some particulate matter in the effluent, as the dual media filtration. It was shown that the application of air sparging a few times a week could keep the pumping power losses to a minimum, similar to the initial operation values.

The application of reverse feed and flow switch was shown to be effective in reducing fouling related to humic acids, and is able to keep the pressure drop below 100 mbar. A combination of air sparging and flow switch could be the best method to keep lower amounts of fouling from humic acids and particulate matter and the frequency of cleaning can be adjusted to the desired level of pressure drop. Brine cleaning, which could potentially be suitable for the removal of humic acids, did not show to be particularly effective in this matter and most benefits of this technique could also be achieved by performing flow switch.

Overall, simple and chemical free methods for cleaning can be suitable to maintain the performance of RED stacks, allowing this technology to be considered environmentally friendly and without environmental damage.

The use of profiled membranes is needed for the further development of RED as they give higher power outputs compared to stacks with spacers and allow for more efficient cleaning. Thus, the development of commercial profiled membranes for RED should be the next step to take this technology further.

CRediT authorship contribution statement

Bárbara Vital: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **André M. Baron:** Methodology, Investigation. **Philipp Kuntke:** Writing – review & editing, Supervision, Formal analysis, Data curation, Conceptualization. **M. Cristina Gagliano:** Writing – review & editing, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Hubertus V.M. Hamelers:** Writing – review & editing, Validation, Supervision, Methodology, Funding acquisition, Formal analysis, Conceptualization. **Tom Sleutels:** Writing – review & editing, Supervision, Project administration, Methodology, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: I tried to include the funding we received from the EU horizon Europe program Marie Curie actions. But clicking the option that appeared from the menu resulted in an invalid entry. Must be a hickup in the system, so I mention it here: This work is part of a project that has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Grant Agreement 665,874 This is also mentioned in the manuscript with the acknowledgments If there are other authors, they 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

Evaluation of chemical free cleaning techniques for RED fed with natural waters and stacks with profiled membranes (Original data) (Wageningen University data repository)

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Appendix A. Supplementary data

Additional experimental details, including feed water characterization, additional sample analysis and photographs of membrane and microscopy images are presented in a separate file (DOC). Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2024.105236.

References

[1] J.W. Post, J. Veerman, H.V.M. Hamelers, G.J. Euverink, S.J. Metz, K. Nymeijer, C. J. Buisman, Salinity-gradient power: evaluation of pressure-retarded osmosis and reverse electrodialysis, J. Membr. Sci. 288 (2007) 218–230.
[2] R.E. Pattle, Production of electric power by mixing fresh and salt water in the hydroelectric pile, Nature 174 (1954) 660.
[3] E.H. Hossen, Z.E. Gobetz, R.S. Kingsbury, F. Liu, H.C. Palko, L.L. Dubbs, O. Coronell, D.F. Call, Temporal variation of power production via reverse electrodialysis using coastal North Carolina waters and its correlation to temperature and conductivity, Desalination 491 (2020) 114562.
[4] R.E. Lacey, Energy by reverse electrodialysis, Ocean Eng. 7 (1980) 1–47.
[5] S. Pawlowski, R.M. Huertas, C.F. Galinha, J.G. Crespo, S. Velizarov, On operation of reverse electrodialysis (RED) and membrane capacitive deioni- sation (MCDI) with natural saline streams: a critical review, Desalination 476 (2020) 114183.
[6] D.A. Vermaas, D. Kunteng, M. Saakes, K. Nijmeijer, Fouling in reverse electrodialysis under natural conditions, Water Res. 47 (2013) 1289–1298.
[7] I. Merino-Garcia, S. Velizarov, New insights into the definition of membrane cleaning strategies to diminish the fouling impact in ion exchange membrane separation processes, Sep. Purif. Technol. 277 (2021) 119445.
[8] A. Nazif, H. Karkhanechi, E. Saljoughi, S.M. Mousavi, H. Matsuyama, Recent progress in membrane development, affecting parameters, and applications of reverse electrodialysis: a review, Journal of Water Process Engineering 47 (2022) 102706.
[9] S. Mehdizadeh, M. Yasukawa, T. Suzuki, M. Higa, Reverse electrodialysis for power generation using seawater/municipal wastewater: effect of coagulation pretreatment, Desalination 481 (2020) 114356.
[10] M. Vanoppen, T. van Vooren, L. Gutierrez, M. Roman, L.J.-P. Croué, K. Verbeken, J. Philips, A. Verliefde, Secondary treated domestic wastewater in reverse electrodialysis: what is the best pre-treatment? Sep. Purif. Technol. 218 (2019) 25–42.
[11] J. Ju, Y. Choi, S. Lee, C.-G. Park, T. Hwang, N. Jung, Comparison of pretreatment methods for salinity gradient power generation using reverse electrodialysis (RED) systems, Membranes 12 (2022).
[12] B. Vital, E.V. Torres, T. Sleutels, M.C. Gagliano, M. Saakes, H.V.M. Hamelers, Fouling fractionation in reverse electrodialysis with natural feed waters demonstrates dual media rapid filtration as an effective pre-treatment for fresh water, Desalination 518 (2021) 115277.
[13] B. Vital, T. Sleutels, M.C. Gagliano, H.V.M. Hamelers, Reversible fouling by particulate matter from natural seawater reduces RED performance while limiting biofouling, Desalination 548 (2023) 116262.
[14] S. Mikhaylin, L. Bazinet, Fouling on ion-exchange membranes: classification, characterization and strategies of prevention and control, Adv. Colloid Interface Sci. 229 (2016) 34–56.
[15] J.W. Post, Blue Energy: Electricity Production from Salinity Gradients by Reverse Electrodialysis. Wageningen, Univ., Diss., 2009, 2009.
[16] D.A. Vermaas, D. Kunteng, J. Veerman, M. Saakes, K. Nijmeijer, Periodic feedwater reversal and air sparging as antifouling strategies in reverse electrodialysis, Environ. Sci. Technol. 48 (2014) 3065–3073.
[17] J. Moreno, N. de Hart, M. Saakes, K. Nijmeijer, CO2 saturated water as two-phase flow for fouling control in reverse electrodialysis, Water Res. 125 (2017) 23–31.
[18] K. Chon, N. Jeong, H. Rho, J.-Y. Nam, E. Jwa, J. Cho, Fouling characteristics of dissolved organic matter in fresh water and seawater compartments of reverse electrodialysis under natural water conditions, Desalination 496 (2020) 114478.
[19] J. Choi, W.-S. Kim, H.K. Kim, S.C. Yang, J.-H. Han, Y.C. Jeung, N.J. Jeong, Fouling behavior of wavy-patterned pore-filling membranes in reverse electro- dialysis under natural seawater and sewage effluents, npj Clean Water 5 (2022).
[20] E. Güler, R. Elizen, M. Saakes, K. Nijmeijer, Micro-structured membranes for electricity generation by reverse electrodialysis, J. Membr. Sci. 458 (2014) 136–148.
[21] D.A. Vermaas, M. Saakes, K. Nijmeijer, Power generation using profiled membranes in reverse electrodialysis, J. Membr. Sci. 385-386 (2011) 234–242.
[22] S. Pawlowski, J.G. Crespo, S. Velizarov, Profiled ion exchange membranes: a comprehensible review, Int. J. Mol. Sci. 20 (2019).
[23] S. Pawlowski, V. Geraldes, J.G. Crespo, S. Velizarov, Computational fluid dynamics (CFD) assisted analysis of profiled membranes performance in reverse electrodialysis, J. Membr. Sci. 502 (2016) 179–190.
[24] S. Pawlowski, C.F. Galinha, J.G. Crespo, S. Velizarov, 2D fluorescence spectroscopy for monitoring ion-exchange membrane based technologies - reverse electrodialysis (RED), Water Res. 88 (2016) 184–198.
[25] J. Moreno, E. Slouwerhof, D.A. Vermaas, M. Saakes, K. Nijmeijer, The breathing cell: cyclic intermembrane distance variation in reverse electrodialysis, Environ. Sci. Technol. 50 (2016) 11386–11393.
[26] J. Di Luque Salvo, A. Cosenza, A. Tamburini, G. Micale, A. Cipollina, Long-run operation of a reverse electrodialysis system fed with wastewaters, J. Environ. Manage. 217 (2018) 871–887.
[27] E.R. Cornelissen, J.S. Vrouwenvelder, S.G.J. Heijman, D. Van der Kooij, X. D. Viallefont, L.P. Wessles, Periodic air/water cleaning for control of biofouling in spiral wound membrane elements, J. Membr. Sci. 287 (2007) 94–101.
[28] M.-E. Langevin, L. Bazinet, Ion-exchange membrane fouling by peptides: a phenomenon governed by electrostatic interactions, J. Membr. Sci. 369 (2011) 359–366.
[29] G.A. O'Toole, L.A. Pratt, P.I. Watnick, D.K. Newman, V.B. Weaver, R. Kolter, Genetic approaches to study of biofilms, Methods Enzymol. 310 (1999) 91–109.
[30] J. Ramus, Alcian blue: a quantitative aqueous assay for algal acid and sulfated polysaccharides, J. Phycol. 13 (4) (1977) 345–348.
[31] U. Metzger, P. Le-Clech, R.M. Stuetz, F.H. Frimmel, V. Chen, Characterisation of polymeric fouling in membrane bioreactors and the effect of different filtration modes, J. Membr. Sci. 301 (2007) 180–189.
[32] D. Pintossi, M. Saakes, Z. Borneman, K. Nijmeijer, Electrochemical impedance spectroscopy of a reverse electrodialysis stack: a new approach to monitoring fouling and cleaning, J. Power Sources 444 (2019) 227302.
[33] J. Moreno, V. Díez, M. Saakes, K. Nijmeijer, Mitigation of the effects of multivalent ion transport in reverse electrodialysis, J. Membr. Sci. 550 (2018) 155–162.
[34] M. Tedesco, A. Cipollina, A. Tamburini, G. Micale, Towards 1 kW power production in a reverse electrodialysis pilot plant with saline waters and concentrated brines, J. Membr. Sci. 522 (2017) 226–236.
[35] N. Poulsen, M. Sumper, N. Kröger, Biosilica formation in diatoms: characterization of native silaffin-2 and its role in silica morphogenesis, Proc. Natl. Acad. Sci. 100 (2003) 12075–12080.
[36] M. Grzegorzek, K. Majewska-Nowak, The influence of humic acids on desali- nation process with the use of electrodialysis, E3S Web Conf. 17 (2017) 27.