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Exploiting electroconvective vortices in electrodialysis with high-frequency asymmetric bipolar pulses for desalination in overlimiting current regimes

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ABSTRACT

Electrodialysis (ED) intensification is introduced by application of asymmetric pulses of reverse polarity. Very short pulses (10 to 100 μ s) at high frequencies (from 100 to 4,000 Hz) were tested, modulating the amplitude of the pulses to adjust energy consumption. Their effect in Limiting Current Density (LCD) and resulting desalination performance were investigated under various operation modes. To fully exploit electroconvective vortices, oscilloscopic profiles were used to optimize the pulsed operation. Under such conditions, the LCD increased by up to 1.6 times compared to conventional ED. The results demonstrate an effective intensification of the desalination process using pulsed electrodialysis reversal (pEDR), with a significantly reduced time in overlimiting regimes (~43% less time compared with sub-limiting conditions), while maintaining a stable pH during the operation. The energy consumed under such overlimiting current conditions, however, increased by ~56% or 14% compared to conventional ED at sub-limiting or overlimiting current regimes, respectively. This new strategy for desalination is expected to decrease the capital costs of ED plants given the prospects of operation under reduced equipment sizes.

Keywords: Pulsed electrodialysis reversal; ED intensification; asymmetric bipolar switch; asymmetrically pulsed electrodialysis.

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1. Introduction

Electrodialysis (ED) is a widespread technique for desalination to produce, effectively and sustainably, fresh water, easing the concerns about its ever-increasing demand. ED has been used for more than five decades in the industry, for the treatment of brackish and residual water streams and to produce drinking water [1]. An upgraded version of ED uses self-cleaning by reversing the electrical and hydraulic polarity of the systems, the so-called Electrodialysis Reversal (EDR). This operation can release colloidal material and re-dissolve minerals that otherwise occur by fouling and scaling onto the surface of ED membranes. Thus, EDR can minimize the demand for cleaning chemicals and chelators [2]. EDR with a typical reversal period of 15-30 min is widely used to prolong the lifetime of systems used for desalination of brackish water [3]. Although periods shorter than

15 minutes could improve the performance of the process, this is not practical given the possibility of product mixing and the waster production time required to reverse the hydraulics of the whole system [3].

Other ED intensification method is the application of a Pulsed Electric Field (PEF) [4]. Here, alternated pauses (pulse-relaxation) are performed to control concentration polarization phenomenon and to decrease fouling [5], [6]. A constant current is applied during a prescribed time, followed by a pause under no current is applied at all [5]. Despite its simplicity and flexibility, as far as a special anode requirement compared to EDR, PEF is no as intensive for self-cleaning. Moreover, the working time is reduced when pausing the system, increasing the membrane area (and number of cells) needed to run a specific process. Such drawback has not been considered yet in literature, which is a critical factor in desalination. The operation time directly affects the economy of processes at industrial scale. On the other hand, an extension of PEF involves the application of pulses of reverse polarity [7]. Despite the reduction of fouling and lower demand for membrane maintenance, reversal polarity (applied in the order of seconds) is disadvantageous given back migration of ions, which increases desalination time [8] and energy consumption [7], limiting its adoption in industry.

Recently, the scientific community has gained a better understanding of the phenomena involved during the pauses in PEF electrodialysis. After pausing the system, a low electrical resistance is achieved because of the restitution of ions in the depleted layer beside membranes, in the diluate compartment. The re-application of a voltage after each pulse cycle promotes electroconvective vortices (ECVs) that translates into current surges [9]. The electroconvection affects turbulence, even at low Reynolds numbers [10]. ECVs promote the transfer of ions onto the surface of the membranes [11], making it possible to work in overlimiting current conditions under negligible water dissociation [12]. It is therefore reasonable to expect that by exploiting this phenomenon it is possible to effectively improve electrodialysis [11] and consequently desalination operations.

Taking into consideration the recent reports on ECVs, and given the challenges still present in PEF electrodialysis, we propose a new strategy by the application of asymmetric bipolar (reverse polarity) pulses. The following work considers the electrodialysis operation by the application of asymmetric bipolar pulses (in the order of μs) at very high frequencies. Different operation modes are tested in sub-limiting and overlimiting current regimes for desalination of a brackish solution. To the best of our knowledge, this strategy has not been attempted before. The results indicate a great promise in intensification of electrodialysis for its industrial implementation.

2. Asymmetric Bipolar Switch (ABS) device and experimental setup

2.1. Asymmetric Bipolar Switch

A custom-made Asymmetric Bipolar Switch (ABS) allows alternating polarity in a fast and controlled way. Associated design, construction and integration is reported elsewhere [13]. Our device is based on an H-Bridge configuration with some differences compared with conventional electronic architectures. Firstly, two power supplies feed electrically the system; the first one is employed to drive desalination, and the second one is used to apply pulses of reverse polarity, being possible to finely adjust the amplitude of the pulses with the second power supply. Secondly, an integrated circuit timer is used to re-fill a bootstrap capacitor, in order to work under constant DC mode (without pause/pulses) [13].

2.2. Electrodialysis (ED) Operation

Our ED system includes two power supplies, pumps, automatic valves, sensors, and an electrodialysis cell (ED64), all packed in a laboratory-scale unit available from PCCell GmbH, Germany. Ten pairs of ion exchange membranes provided a total surface area of 640 cm² (individual membrane area of 64 cm²). The flow rate was fixed at 0.33 l/min. A solution of 0.25 M Na₂SO₄ (flowrate of 1.6 l/min) was recirculated in the compartment used for electrode rinsing [14]. The solutions were kept at 20°C with a water jacket.

The ABS device was connected to the power supplies for the application of pauses, and reverse polarity pulses, with varying times and amplitudes in a process called Asymmetrically Pulsed Electrodialysis (APED) or Pulsed Electrodialysis Reversal (pEDR). Henceforth, a subscript is used to indicate the amplitude of the pulses. For instance, pEDR_{2.0} means a reverse polarity pulse with an amplitude two times higher than the power used in desalination (voltage in potentiostatic mode or current in galvanostatic mode). The potentiostatic mode (constant voltage) was used in the experiments; in this case, the amplitude was controlled by adjusting the voltage applied using the second power supply. When working in galvanostatic mode (constant current), the amplitude represented reverse current pulses in the electrodialysis cell. For measuring the current after the re-application of voltage, an oscilloscope (Instek GDS-1052U, Good Will Instrument Co., Taiwan) was utilized using a non-invasive clamp probe in the cathode wire (Fig. 1).

Fig. 1. System configuration for the application of asymmetric pulses of reverse polarity with different amplitudes. A second (adjustable) power supply is used to tune the amplitude of the bipolar pulses.

2.3. Demineralization Rate and Energy Consumption

A brackish solution (1,000 ppm NaCl) was used to determine LCD using Cowan and Brown method [15] (raw data and full details are given in the Supplementary material), and to study the desalination performance at 80% and 140% of the determined LCD. A calibration curve was constructed by measuring the conductivity at different NaCl concentrations in solution at 20°C. The measured conductivity was utilized to determine the amount of salt necessary for the calculation of the demineralization rate (%) in the electrodialysis experiments [12], [16]:

$$DR_{ion}(\%) = \left(1 - \frac{C_t}{C_0}\right) \times 100 \quad (1)$$

where C_t and C_0 (mol/L) are the concentrations of NaCl at time t and 0, respectively. The change in volume was neglected during operation. For each determination of DR, a fixed volume of 1 liter and a flowrate of 20 l/h (lineal velocity of 1.39 cm/s, considering a spacer thickness of 0.5 mm) were used in both diluate and concentrate compartments. Volume variation throughout the experiment was neglected. Finally, energy consumption was calculated using Eq. (2) [17], and normalized by volumetric unit of treated water (kWh/m³):

$$E = \int \frac{UI dt}{V} \quad (2)$$

where U (V) is the voltage drop across the ED cell (constant in potentiostatic mode); I (A) is the current utilization, and V is the volume of treated water (m^3). The time was defined as that needed to reach a 50% of desalination rate.

3. Results and discussion

3.1. Effective Duty Cycle

Duty cycle is defined as the fraction of time when a system is active. The term is widely used in PWM (Pulse Width Modulation, a technique that allows to control the delivery of power into devices), and it depends on the frequency and pulse width. When applying PWM, the system turns on and off to modulate the delivered power. For instance, a duty cycle of 70% means that the system is off 30% of the time. The definition of duty cycle changes in electrodialysis when using pulses of reverse polarity. The system is active when the energy is consumed in desalination. Nevertheless, in reverse polarity mode the ions migrate back into the demineralized compartment, counteracting the work done in desalination. The amplitude of these bipolar pulses determines the velocity of back migration, influencing the calculation of duty cycle. To include this term, T_{OFF} (pausing time) or T_{REV} (time in reverse polarity) was multiplied by a ratio between reverse and forward voltage. Thus, effective duty cycle (eDC) is formulated, defined by Eq. (3) as:

$$eDC (\%) = \frac{T_{\text{ON}} - T_{\text{REV}} \times \left(\frac{A'}{A}\right)}{T_{\text{ON}} + T_{\text{REV}}} \times 100 \quad (3)$$

where A is the amplitude of the working voltage in forward mode, and A' is the amplitude of reverse voltage. T_{ON} is the time in the forward mode. Then, if the amplitude of the bipolar pulses is increased, the effective duty cycle will consequently decrease (Fig. 2). However, if pauses are applied instead of reverse polarity pulses, the duty cycle will conserve its original definition used in PWM. If the effective duty cycle turns negative, it means that the system is running backwards, and no work (or desalination in the case of electrodialysis) will occur.

Fig. 2. Effective duty cycle in the operation of (a) PEF electrodes reported in previous work. (b) PEF electrodes at medium frequency, pEDR₀. (c) pEDR_{2.0} electrodes at medium frequencies. (d) PEF electrodes at high frequencies. (e) pEDR_{1.0} electrodes at high frequencies. When comparing a, b, c and d, clear differences are shown in the operational window. Frequency, pulse duration and amplitude directly affects the effective duty cycle. (f) Schematic representation of application of pauses (PEF operation). (g) Schematic representation of asymmetric bipolar pulses with an amplitude of A' .

Non-stationary regimes of electric fields (PEF electrodes) could reduce the concentration polarization phenomenon, leading to intensification of the electrodes process, increasing the limiting current density and decreasing the occurrence of water splitting [18]–[20]. The pauses in PEF should be short, otherwise back diffusion would occur, counteracting the desalination processes [18]. Nevertheless, the pauses are usually reported in the order of tens of seconds and even minutes, and duty cycles ranging between 20 to 90% have been extensively used in literature, calculated by the utilization of the reported T_{ON} and T_{OFF} (Table 1). Using such long pauses times, only low frequencies, in the order of mHz, can be applied (Fig. 2a).

Table 1

Tested conditions of PEF electrodialysis

Reported values		Calculated		Ref
T _{ON} (s)	T _{OFF} (s)	eDC (%)	Frequency (Hz)	
1-30	1-30	50.0	0.02-0.50	[5]
10	10-40	20-50	0.02-0.05	[6]
10	10-33.3	50-23	0.02-0.05	[21]
5-20	5-20	33-67	0.03-0.10	[20]
1-3	0.33-1	50-90	0.25-0.75	[22]
2	0.5-0.67	75-80	0.37-0.40	[23]
2	0.2*	82-91	0.45	[7]
50-25	10-25	50-83	0.02	[24]
0.1-100	0.1-10	50-99	0.01-5.00	[12]
180-30	3-5*	71-97	0.01-0.03	[8]

* Includes polarity reversal

As mentioned before, back migration occurs when working with polarity reversal instead of pauses, affecting directly the electrodialysis operation [8]. Consequently, an Asymmetric Bipolar Switch was designed and constructed to work in an operational window comprising very short reverse polarity pulses, in the order of milli- and micro-seconds, frequencies up to 4,000 Hz, and varied amplitude of bipolar pulses [13]. Under these conditions, the effective duty cycle can be adjusted to values that exceed 90%, in contrast to literature values, in order to control back migration in an acceptable fashion.

3.2. Current surge in overlimiting regimes

When running electrodialysis, the concentration profile can be divided in two parts. (1) A bulk solution, where the concentration remains in steady-state, and (2) the solution close to the membrane depleted of ions, which concentration is oscillating in PEF mode as a result of ion restoration. After each pause or bipolar pulse, the concentration polarization is reduced significantly due to diffusion (PEF) and migration (pEDR). Therefore, at the beginning of each pulsing cycle the electrical resistance is very low; as a result, high current densities are achieved when re-applying a voltage, defined as a current surge, which triggers the formation of electroconvective vortices [12] (Fig. 3c). Consequently, it is recommended to increase the frequency in order to take advantage of this initial current surge, promoting mass-transfer [19].

Fig. 3. Demineralization mechanism at overlimiting current regimes. (a) Concentration polarization and water splitting in overlimiting current in electrodialysis. The ion-depleted layer is near the membrane surface in the diluate compartment, while a high concentration of ions is in the other side of the membrane, prone to scale in the presence of OH^- . (b) Disturbance of the polarization by reversion of electrical polarity. Counterions migrate back into the ion-depleted zone, and co-ions reload the depleted layer, coming from the bulk. (c) Electroconvective vortices promoted when re-applying voltage, promoting turbulence and mass transfer.

It is well known that PEF electrodialysis is effective for desalination, especially after the re-application of power, due to the low electrical resistance caused by the restoration of ions [25]. Such high voltage (in constant current mode), at the beginning of each cycle, induces the formation of ECVs [19]. As demonstrated, operation at 5 Hz was effective for avoiding ECVs to completely disappear, e.g., remaining throughout a desalination process [19]. The ECVs increase the availability of ions by supplying fresh solution from the bulk onto the membrane surface, and by removing the ion-depleted solution. These phenomena are the main mechanisms for desalination in overlimiting current regimes [25]. They improve mass transfer and limit pH swings, making it possible to work above the Limiting Current Density (LCD) at the beginning of each pause cycle, with negligible water splitting [19].

After re-application of voltage in every new cycle, a current surge is expected due to the low electrical resistance of the membrane stack. This current surge and its decay were measured with an oscilloscope, and found to be depend on the pause/pulse duration, bipolar pulse amplitude, and frequency (Fig. 4). In general, the current surge (peak) increased with the pause/pulse duration and amplitude, showing a faster decay when decreasing the duration and amplitude of the same pulses. This is explained by the direct correlation between the pause duration and restoration of the ion-depleted layer by diffusion from the bulk, which has a higher concentration of ions compared with the near-surface in the diluate compartment [12]. Under shorter pauses, partial restoration occurs and the surface of the membrane is depleted faster, after re-application of power. The amplitude

Fig. 4. Current surge determination. (a) Voltage applied in the electrodialysis cell, varying pauses/bipolar pulses duration, amplitude of bipolar pulses, and frequency. (b) Current response obtained from the oscilloscope (voltage in yellow and current in light blue). (c-e) Oscilloscope profiles with a pause of 1s, 100ms, and 10ms respectively. Every square represents 500ms. (f) Zoomed record of profile e, with a division of 500 μ s per square. A small current surge signal is observed with a decay in 2ms. (g-h) Measured current surge after the application of PEF/pEDR_{1.0} at different frequencies. It is observed that even in the order of microseconds there is an increment of the current surge, especially at high frequencies.

of bipolar pulses could boost the replenishment of ions in the depleted layer and simultaneously bring co-ions from the bulk to the surface of the membrane (Fig. 3b). A different case applies to the frequency. At high frequencies, the length of the pause/pulse is reduced, affecting ion replenishment and the subsequent generation of ECVs. It seems counterproductive, however, at high frequencies and by continuously applying new pulses, it is possible to keep the surface of the membrane replenished, before reaching the complete decay of the current surge. In other words, if frequency is increased, there is no time for depletion of ions, and ECVs will pump constantly new ions from the bulk solution.

The duration and amplitude of bipolar pulses are limited because of the effective duty cycle and back migration. To overcome these drawbacks, we moved into the high frequency range, up to 4,000 Hz, using pulses of very short duration (in the order of micro-seconds) and amplitudes of 0-2 times compared with the employed working voltage. The high frequency should allow a constant replenishment of ions onto the depleted surface, while the amplitude of the pulses should compensate the short duration of the reverse polarity pulses at these tested high frequencies.

3.3. Pauses and bipolar pulses at high frequencies

Pulse Current and Pulse Reverse Current is widely studied in electroplating. It is possible to finely control the deposition of metals by regulating the frequency and length of the pauses or bipolar pulses. Frequencies up to 500 Hz have been successfully used to improve the rate of mass transfer. Nevertheless, an electric double layer could dominate at higher frequencies, decreasing the efficiency of the process [26]. Although, even much higher frequencies can be applied, depending on the working conditions. Thus, in practice, PRC allows the production of ultra-thin layers of nickel, free of voids, using 90% of duty cycle at 400 kHz [27].

PEF experiments, at a relatively high frequency, e.g. 5 Hz, showed an improved electrodialysis performance, increasing demineralization rate by 81% and decreasing energy consumption by 16%, compared with a conventional DC mode. Although PEF at this frequency improves the process, compared to the DC mode, the demineralization time is increased two times due to the low duty cycle employed (50%). In other terms, the system is OFF half of the time (0.1s-0.1s cycles) of each period [19]. An improved electrodialysis performance at high frequencies has been observed, with optimal values around 100 Hz. Indeed, it seems that the mass transfer is reduced at frequencies > 100 Hz using pauses [20]. This can be explained by the short pauses at such high frequencies, leaving no time for diffusion and subsequent replenishment of the membrane surface with fresh ions. To address this, asymmetric bipolar pulses can be employed, accelerating the transfer of counter and co-ions onto the depleted layer by electrochemical migration, and thus decreasing ohmic resistance when re-applying the working/forward voltage, even when using very short pulses in the order of micro-seconds (Table 2).

Table 2

Set of different tested ABS operation in the high frequency range

Test	Experimental setting			Results			
	Reversal time (μ s)	Frequency (Hz)	pEDR amplitude	Current surge peak (A)	LCD (mA/cm^2)	Increased times of LCD	eDC (%)
T ₀	---	---	---	---	5.53 ± 0.29	---	---
T ₁	50	100	0.0	1.11	6.14 ± 0.09	1.11	99.5
T ₂	50	100	1.0	1.21	6.46 ± 0.10	1.17	99.0
T ₃	50	1,000	0.0	1.12	6.23 ± 0.08	1.13	95.0
T ₄	50	1,000	1.0	1.28	7.69 ± 0.38	1.39	90.0
T ₅	50	2,000	0.0	1.13	6.26 ± 0.15	1.13	90.0
T ₆	50	2,000	1.0	1.32	8.48 ± 0.20	1.53	80.0
T ₇	100	500	0.0	1.15	6.69 ± 0.17	1.19	95.0
T ₈	100	500	1.0	1.30	7.43 ± 0.15	1.34	90.0
T ₉	10	4,000	0.2	1.09	8.30 ± 0.26	1.50	95.2
T ₁₀	10	4,000	1.0	1.12	8.65 ± 0.27	1.56	92.0
T ₁₁	10	4,000	2.0	1.29	8.88 ± 0.07	1.61	88.0

From Table 2 it is concluded that compared with $pEDR_{1.0}$, $pEDR_0$ (PEF) is not significantly influenced by the frequency, especially when using short pulses (Fig. 4h). Among all the tested operation modes, T_{11} showed the highest LCD, while conserving a high effective duty cycle of 88%. Moreover, at very high frequencies (2,000 - 4,000 Hz) current surge did not completely decay at the end of each pulsing cycle, using an amplitude of 0.2 to 2.0 in reverse polarity mode (Fig. 5). A full decay is related to pH variations owing to the depletion of ions on the surface layer. To keep a high current and to avoid a full decay of current surge, higher frequencies are needed. The peak current surge correlates to the increased LCD (Table 2). Thus, under dynamic conditions and in real applications, an easy way to achieve optimal values of pulse time, frequency, and amplitude, is by signal monitoring (oscilloscope profiles) by using different samples and operational parameters, including temperature of the treated water, pH, flowrate, and conductivity. In general, a stable and incomplete current decay is preferred, using an effective duty cycle above 90%.

Fig. 5. Current surge peak and fading after re-application of voltage in overlimiting condition, by pausing the electrodialysis system (T_1 , T_3 and T_5), by reversing the electrical polarity for 50 microseconds (T_2 , T_4 , and T_6), and by reversing the polarity for 10 microseconds (T_9 and T_{11}), at different frequencies.

LCD directly relates to a low concentration of counter-ions on the surface of the membranes facing the diluate compartment. For maintaining electroneutrality, co-ions are reduced as well. If current density (or potential) is increased to accelerate desalination, the ions will be pushed further, moved by the electrical field, up to their depletion on the membrane surface in the diluate compartment (ion-depleted layer, Fig. 3a), reaching the limit of the system or LCD. At this point, water splitting is promoted, transporting H^+ and OH^- through the ion exchange membranes, and triggering fouling and scaling in the same membranes [28]. LCD is empirically determined by measuring the electrical resistance of the membrane stack using Ohm's law, and plotting this value against the reciprocal current measured in the same cell (Supplementary material). The crossing point between the negative and positive slopes in the graph is defined as the LCD of the system, under specific conditions [15]. Thus, when determining LCD, the voltage is increased stepwise and the current density is measured. The data obtained from LCD determination could shed some light for further experiments on desalination.

Fig. 6. Desalination and pH evolution through the limiting current density determination experiments. Demineralization rate is demarked as blue circles and pH value is represented as yellow triangles. These tests from Table 2 showed a defined behavior, depending on the frequency, pulse width, and amplitude of the reverse polarity pulses.

As observed in Fig. 6, demineralization rate and pH are influenced by the current density and the reached LCD. pH quickly shifts after reaching the limiting current density. This change in pH is delayed, especially when using asymmetric bipolar pulses. On the other hand, the demineralization rate in one single pass through the electrodialysis cell displayed an increment at high current densities; this is enhanced in PEF and reduced in pEDR at high frequencies. Even PEF experiments (T₁, T₃, and T₅) using short pauses of 50 μ s showed an increased LCD. However, the PEF mode is not significantly influenced by frequency (Table 2). As expected, the higher the frequency and amplitude of the asymmetric bipolar pulses, the higher the attained LCD. The most remarkable results were at 4,000 Hz and 10 μ s of reverse polarity pulses, using an amplitude of 0.2 to 2.0 (T₉, T₁₀ and T₁₁). The short reversal time was enough for migration and restitution of the ion-depleted layer, increasing LCD while conserving demineralization rate and pH. Thus, based on these results, desalination experiments were effectuated, using the LCD of conventional ED as reference to work in sub-limiting and overlimiting current regimes.

Since it is not possible to have pulses shorter than 10 μ s, due to hardware limitations, no higher frequencies were tested, otherwise, the effective duty cycle turns too low. It is likely that by working in the order of nanoseconds (at higher frequencies) better results could be obtained, as long as the reverse polarity pulses disturb concentration polarization and promote electroconvective vortices. The idea is to apply just the right amount of energy (by adjusting the amplitude) to restore back the ion-depleted layer, and at this very short duration in the order of nanoseconds, asymmetric bipolar pulses could effectively accelerate migration in a controllable way.

3.3. Desalination performance and stability under overlimiting current regime

Compared to conventional electrodialysis, the application of PEF and polarity reversal in overlimiting current regimes is more advantageous for the desalination performance [7]. However, desalination time is wasted due to OFF periods using duty cycles of 20-90% reported in literature. To address this, very short pauses are employed at high frequencies, with effective duty cycle above

90%. To compensate the insufficient time for diffusion, polarity reversal is used instead of pauses, accelerating the migration of ions into the depleted layer. Accordingly, desalination experiments were performed using 80% of T_0 LCD (conventional electrodesalination) or sub-limiting current regime, and 90% of T_6 LCD, which represents 140% of T_0 LCD, defined as overlimiting current regime (Fig. 7).

As expected, under sub-limiting current regime, the desalination takes a longer time for T_5 (PEF at 90% eDC) and T_6 (pEDR at 80% eDC), compared with conventional electrodesalination, due to back diffusion and back migration respectively. When comparing overlimiting vs sub-limiting conditions, the most remarkable change is the desalination time to reach 50% of demineralization rate. It takes longer for T_6 than T_5 or T_0 in sub-limiting conditions, due to the low eDC of T_6 , although less pronounced the differences between them in the overlimiting current regime (Fig. 7b). The pH was stable during the whole operation, up to reaching 50% desalination in sub-limiting conditions, equivalent to one stage of electrodesalination. Nonetheless, in overlimiting conditions, T_6 was the only operation where pH was stable during the whole desalination experiment (Fig. 7d). The reversing of polarity for 50 μ s effectively limits water splitting, or the generated OH^- and H^+ ions under this conditions are immediately returned back after their generation, neutralizing themselves although spending energy in the process. Thus, it is technically feasible to work with T_6 in overlimiting current conditions, while T_0 and T_5 would present problems related to pH instabilities; hence, it is not possible to work under these operational modes, even though T_0 and T_5 are faster and require less energy to desalinate the same amount of water (Table 3).

Fig. 7. Desalination of 1,000 ppm NaCl at different current regimes (80% and 140% LCD) of T_0 , T_5 , T_6 and T_9 . (a-b) Time needed to demineralize 50% of the brackish solution. (c-d) pH evolution throughout the desalination experiments. (e-f) Electrical resistance of the electrodesalination stack while desalting the brackish solution.

Compared to conventional ED, the stack resistance was lower in pEDR operation under the described conditions at high frequencies, and slightly higher for PEF operation (Fig. 7). Stack resistance and energy consumption were calculated using the current and voltage throughout the whole desalination process. A high energy consumption was measured for T_6 operation, around 59% higher compared with conventional ED, in overlimiting current regime (Table 3). This high energy consumption is due to the employed 80% of effective duty cycle, where the ions that migrated back into the demineralized compartment must be removed again, spending energy in the process. To overcome this drawback, shorter reverse polarity pulses (10 μ s, the limit of the custom-made ABS) and a frequency of 4,000 Hz was employed, conserving a high effective duty cycle (88 to 95%). The amplitude of the pulses were adjusted to decrease energy consumption (T_9 to T_{11}). Thus, with an optimized amplitude of 0.2 times the working voltage was enough to reach a safe LCD value, to work in the defined overlimiting condition (T_9 , 0.357 kWh/m³), increasing the energy consumption by 14% compared with conventional ED, instead of 54% obtained with the non-optimized condition (T_{11} , 0.421 kWh/m³). Moreover, considering a 1.77 times faster process (214 vs 378 seconds, Table 3), less equipment and membrane area are required to desalinate the same volume of water in sub-limiting current regimes, compensating this extra energy costs. To evaluate this, techno-economic studies should use real samples with more stages and optimized pEDR operations, adjusting frequency, time, and amplitude of the pulses to decrease energy consumption as much as possible, while conserving the benefits of the technique. Furthermore, probably it is not necessary to move so far in the overlimiting region. Sensitivity analysis could determine the ideal operational window to decrease capital and operational costs.

Table 3

Time and energy consumption to demineralize 50% of a 1,000 ppm NaCl brackish solution

	Sub-limiting regime 80% LCD		Overlimiting regime 140% LCD	
	time (s)	EC (kWh/m ³)	time (s)	EC (kWh/m ³)
T_0	378	0.229	180*	0.312
T_5	410	0.231	190*	0.315
T_6	538	0.398	236	0.495
T_9	542	0.312	214	0.357
T_{10}	556	0.352	220	0.421
T_{11}	576	0.404	238	0.481

*unstable pH during operation

be reported in subsequent studies.

The application of pEDR at high frequencies must be used in overlimiting conditions in order to take advantage of this technique. It is not economically feasible to apply pulses in sub-limiting conditions. Actually, with the optimized operation, T_9 , it takes 43% more time and 36% more energy to desalinate the same volume of water, compared with conventional ED in sub-limiting current conditions (Table 3). Although, our trials were carried out by using a model solution of NaCl, the application of pEDR could re-dissolve fresh scale and could release colloids from the surface of the membranes, adding additional benefits to the operation. The effect of scaling and fouling using pEDR at high frequencies will

4. Conclusions

The present work demonstrates the feasibility of electrodialysis intensification by applying adjustable asymmetric bipolar pulses of very short duration, very high frequencies, and low amplitudes. The pulses were optimized to decrease energy consumption by adjusting their amplitude, while preserving pH stability in a fast operation. The incorporation of reverse polarity pulses allow the utilization of very high frequencies, preventing concentration polarization, and inducing the formation of electroconvective vortices. Theoretical explanations and models are required to complement this work, and to find optimal amplitudes, frequencies, and pulse durations for each treated brackish solution.

The limiting current density under asymmetric bipolar pulses is increased, by more than 1.6 times, compared to conventional DC mode. Additionally, the pH was kept stable during the whole desalination process, decreasing the occurrence of detrimental effects caused otherwise by pH swings. Desalination performance under overlimiting conditions exhibited improved mass transfer, while decreasing the demineralization time by 43%. On the other hand, energy consumption increased by 14%, compared with the conventional electrodialysis in overlimiting conditions. Then, there is a trade-off between energy consumption and desalination time, which must be considered if the technology is coupled to ED systems. The higher energy consumption is clearly a drawback of pEDR. However, in certain times where energy is cheap (solar power for instance), small plants could demineralize water in an intensive way.

The transport of ions in PEF mode is dominated by concentration gradients. In pEDR the transport occurs by migration, where transport of counter and co-ions is promoted by an electric field towards the ion-depleted layer, accelerating the refilling process and inducing the formation of electroconvective vortices after re-application of forward voltages. Thus, the proposed new strategy is more technologically feasible as compared to conventional and PEF electrodialysis for ED intensification. Additional studies will be conducted to determine the effect of high-frequency pEDR in the mitigation of fouling and scaling, along with techno-economical evaluations.

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