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High frequency pulsed electrodialysis of acidic filtrate in Kraft pulping

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Abstract

We introduce high frequency pulsed electrodialysis (*hf*-pED) to process the acidic filtrate of a wood pulp bleaching stage in a Kraft pulping mill pilot. Compared with conventional electrodialysis, *hf*-pED at 2,000 Hz allows a reduction in operational cost by 12%, estimated as 0.54 USD/m^3, while simultaneously preventing membrane fouling. The proposed sectorial stream treatment is demonstrated to significantly improve the quality of the final effluent, according to mass balances, making it more suitable for irrigation applications, considering requirements of irrigation norms. Thus, we estimate a reduction of 59, 21, and 20% in the concentration of chloride, sodium, and sulfate, respectively, in the final effluent of a conventional Kraft pulping mill. This strategy is presented as a sustainable and economic solution compared with the desalinization of the whole final effluent.

Keywords: Pulsed Electrodialysis Reversal; Non-Process Elements Separation; Electrodialysis Kraft Pulping, Irrigation Effluent; High Frequency Pulsed Electrodialysis

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1. Introduction

Kraft pulping is the most popular processes for the production of chemical cellulose pulp (Pokhrel & Viraraghavan, 2004). Related industrial plants consume at least 10 m^3 of water per air dry ton (ADt) of cellulose pulp (Bajpai, 2018), which is a large volume of water when considering the production of cellulose in a typical mill, >1,000 ADt/day. Therefore, there is a major need for recycling and reusing water streams but such system closure and effluent flow reduction induce the accumulation of undesirable species, known as non-process elements (NPE) such as Fe, Mn, Cu, Cl, Si, Al, Mg and Ca (de Almeida Batista et al., 2020). The accumulation of NPE’s promotes clogging of pipes, corrosion in boilers and scales in kilns and heaters; it also reduces the final quality of the produced cellulose pulp (de Almeida Batista et al., 2020; Doldán et al., 2011). Thus, it is still necessary to purge wastewater and ingress fresh makeup or clean water, which would represent a prohibitive cost while posing an uncertain environmental pressure.

It is less expensive to treat sectorial streams inside pulping mills, instead of treating the general effluent at the end of the pipe, mainly because of the significantly lower flowrates. In this way, it is also possible to improve the quality of the final (mixed) wastewater. Thus, improvements in effluent quality by desalination of sectorial streams make agricultural irrigation possible with the final, treated effluent, an option that is otherwise prohibited at high salinities (Grattan, 2002; Nackley et al., 2015; Sharma et al., 2014).

One way to treat a given stream in the Kraft pulping process is through the utilization of electrodialysis (ED), a desalination technique that tolerates fouling under certain conditions (Pfromm et al., 1999). This last feature is compulsory, due to the high concentration of organic compounds present in wastewater streams of pulping processes. In ED desalination, the electrolytes in solution are transported through multiple ion exchange membranes, allowing ion concentration and demineralization in separated compartments (Klein et al., 1987). The ion removal efficiency of an ED plant could be theoretically estimated, although it is more effectively studied at laboratory and pilot scales, which also allows to determine the limits of the process and the real ion-removal capacity (Strathmann, 2010). Compared with laboratory experiments, pilot trials are indicated to better understand the technology compatibility and long-term behavior, especially when considering fouling and scaling of the ion exchange membranes. Moreover, based on operational data, it is possible to calculate more precisely the capital and operational expenditures of a full-scale desalination plant.

Conventional ED is usually not compatible with water streams carrying a high content of organic matter; hence, pretreatments are necessary to decrease fouling and to increase membranes lifetime. Thus, the Electrodialysis Reversal (EDR) was introduced five decades ago (Murray et al., 1995). EDR periodically changes the polarity of the system for membrane self-cleaning, decreasing the utilization of chemicals and pre-treatment. However, the reverse in hydraulic polarity inevitably decreases the production rate due to mixing of the demineralized product with the concentrate reject in the pipelines (Tanaka, 2015). Recently, asymmetric pulses of reverse polarity at high-frequency (in the order of kilohertz) (Gonzalez-Vogel & Rojas, 2019), known as high frequency pulsed ED (*hf*-pED), was applied and demonstrated for intensification of ED through the generation of electro-convective vortices (Gonzalez-Vogel & Rojas, 2020). The application of pulses of reverse polarity also mitigates fouling (Merkel & Ashrafi, 2019; Suwal et al., 2016), facilitating its industrial utilization.

In order to study the feasibility of *hf*-pED for treating an internal wastewater stream in a Kraft pulp mill, a pilot plant was designed, constructed, installed and operated in an industrial plant. A pulsed electrodialysis unit operated at high frequency, studied first at laboratory scale to determine the optimal operation, was coupled to the treatment of acidic filtrate, a stream derived from the bleaching of cellulosic pulp, which goes to the effluent treatment plant. Based on the obtained results, the best operation conditions were defined, and scale-up engineering was considered, along with techno-economic evaluation of the dialysis plant. Finally, the quality of the acidic filtrate was studied and its impact on the final effluent calculated and compared with other options. Overall, we propose a viable strategy that reaches a water quality that is more suitable for irrigation.

2. Materials and Methods

2.1. Design of the Electrodialysis Pilot Plant

The ED pilot plant shown in **Error! Reference source not found.** included heat exchangers for cooling down the effluent from 79°C to 35°C to reach the operational range of the ED unit, which had an operation limit of 40°C, and self-cleaning filtration (50 µm discs, Changzhou Duoling Water Treatment Factory, model 3’’ Compact) to remove residual fibers contained in the acidic bleaching filtrate stream (Table 1). The pretreated wastewater was stored in a 1 m^3 tank. Besides, cartridge filters of 5 µm (Vigahome, 10x2.75 inches) were included before entering each compartment of the electrodialysis stack (UAB Membraninės Technologijos LT, model EMA-30). For cleaning of the platinized titanium electrodes (for both cathode and anode, suitable for EDR), a solution of 0.25M Na_2SO_4 (analytical grade, obtained from Merck Chemicals) was pumped with a flowrate of 400 L/h. Both compartments of the ED stack (concentrate and diluate) had their own tanks before discharging, for accumulation of samples and subsequent analysis. The flowrate was varied in the experiments. Mill water was used to dilute the concentrate compartment, according to a pre-defined conductivity threshold, based on the saturation limits of the ionic species in solution. A PLC SIMATIC S7-1200 was the brain of the system, where a control philosophy was adopted for automating the process and data acquisition. Additionally, a GPRS module STM32F1 was used to send information via 4G for remote control and data processing. A 3,000W DC power supply (Powernet model ADC7480/110) operated up to 50V to feed the electrodialysis stack, based on the number of membranes used. The power supply was connected to an Asymmetric Bipolar Switch (ABS) to finely modulate the delivered power (Gonzalez-Vogel & Rojas, 2019).

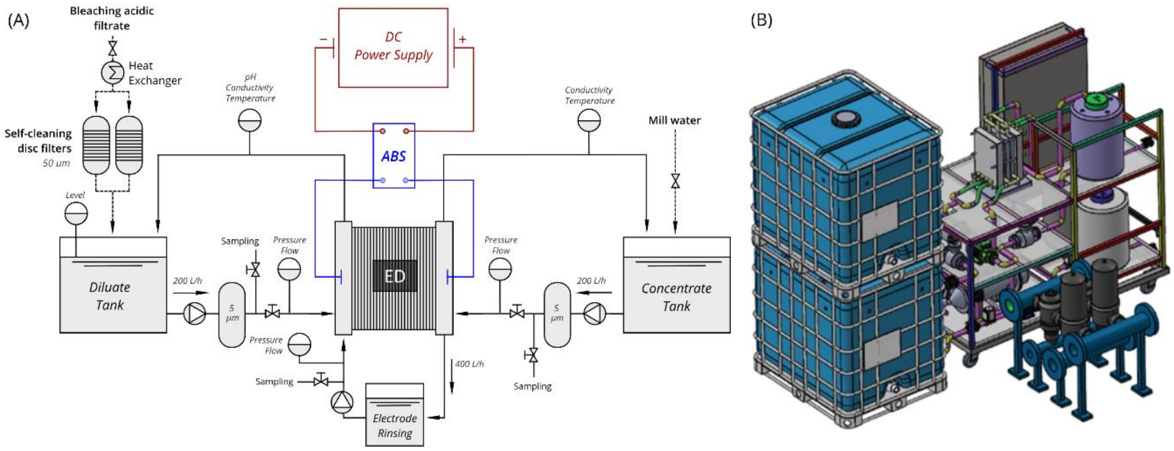

Fig. 1. Electrodialysis pilot plant. (A) Simplified diagram in batch configuration. (B) Design of the pilot plant.

Table 1. Main characteristics of the acidic bleaching filtrate of a Kraft pulping plant.

Flowrate	162	± 17.6	L/s
Conductivity	6,580	± 633	µS/cm
Color	754	± 158	pt-Co
Total Suspended Solids	229	± 73	ppm
COD	3,142	± 3	ppm
pH	2.8	± 0.2	
Temperature	79.4	± 1.5	°C

The ED stack consists of 10 pairs of heterogeneous membranes, namely, 11 cation exchange membranes (CEM), 10 anion exchange membranes (AEM), and 20 spacers with a thickness of 1 mm. UAB Membraninės Technologijos LT provided the cation and anion exchange membranes (Table 2), using an effective dimension of 356 x 226 mm. Platinized titanium electrodes plates are used, to allow reversal of polarity.

Table 2. Characteristics of the commercial ion exchange membranes used in the pilot trial

Membrane	Ion-exchange group	Thickness (mm)	Exchange capacity (mol/kg)	Burst strength (MPa)	Permselectivity (%)	Electrical resistance (Ω/cm^2)	pH range
AEM	$R\text{-}(CH_3)_3N^+$	0.4 ± 0.02	>2	>0.6	>95.0	5-8	1-14
CEM	$R\text{-}SO_3^-$	0.35 ± 0.02	>2.2	>0.6	>95.0	4-7	1-14

2.2. Asymmetric Bipolar Switch (ABS)

A custom-made electronic device was installed in between the DC power supply and the electrodialysis stack , allowing the application of high-frequency pulses of reverse polarity (Gonzalez-Vogel & Rojas, 2019). This device is a H-bridge that has a couple of characteristics that differs from conventional H-Bridges. It can be connected to one or two power supplies to modulate pulse amplitude, and it also includes a charge-pump that feed bootstrap capacitors, to work for longer periods in a defined polarity. By including those features, and by controlling the different switch gates with a microcontroller, it is possible to modulate frequency, amplitude, and duration of the reverse polarity pulses according with the process requirement. By contrast, a conventional H-bridge it is not able to use such asymmetric operation because the power output is adjust with pulse width modulation (PWM), which function is focused in energy saving and control of velocity in motors (Gonzalez-Vogel et al., 2017; Gonzalez-vogel & Rojas, 2019).

2.3. ED operation with pulses at high frequency

The ABS device was coupled to the pilot plant, keeping the same membranes for comparison with conventional ED. The influence of reversing the polarity at a high frequency was studied first at a laboratory scale. Conventional ED was compared with *hf*-pED and pulsed electrodialysis reversal (pEDR) at 2,000 Hz, meaning 490 µS of working (desalination) time and 10 µs of pauses using *hf*-pED, or electrical polarity reversal using pEDR, with a duty cycle of 98%. The limit current density (LCD) for each operational mode was first determined. Then, using 80% of this LCD, the energy consumption for 90% chloride removal was determined in desalination experiments. These experiments were repeated three times for each condition. The temperature was kept at 35°C in all the laboratory tests.

At the pilot scale, two operational modes were compared, conventional and pulsed ED at high frequency. For each mode, LCD was determined under three different flow rates (150, 200 and 300 L/h i.e. 2.19, 2.92 and 4.39 cm/s, respectively) using the minimum value of the 4th order polynomial regression curve, obtained by plotting the electrical resistance of the stack *vs* the reciprocal current (Rapp & Pfromm, 1998). Then, to evaluate fouling over time, five batch tests using fresh acidic filtrate in the diluate compartment tank (21.5 L of feed volume at a flow rate of 200 L/h) were conducted for each operational mode. The same current density was used in all the experiments, which was defined as 80% of the LCD obtained in conventional ED. Galvanostatic mode (constant current) was employed in all the experiments until reach 50V, and then the trial was finished when reaching 60% of the initial diluate conductivity. Membranes were not cleaned between tests to evaluate fouling, except when changing from normal ED to pulsed ED, in order to restore the ion-exchange capacity. The concentrate tank was also replenished with fresh acidic filtrate after changing the operational mode.

Fouling was assessed based on the electrical resistance of the stack, which increases as the membranes accumulate deposits (organic particles or mineral scales). Around 100 mL of samples of the dialyzed acidic bleach filtrate, obtained at the beginning and at the end of the desalination tests, were collected to perform elemental analysis.

2.4. Analytical methods

Cation elemental analysis was performed using an Atomic Absorption Spectrometer (PerkinElmer PinAAcle 500) and Inductively Coupled Plasma (Agilent 5110 ICP-OES). Anions were measured with Ionic Chromatography (Metrohm AG 930 Compact IC Flex). Treatment of the sample and measurements are based on Standard Methods for the examination of wastewater Ed.23, using 3030E and 3120B for sample treatment.

For in-line measurements of conductivity, flow and pH in the pilot plant the following probes and sensors were installed: HI1001, Hanna Instruments pH electrode; K1 and K2 type conductivity sensor, EZO model, Atlas Scientific; RS PRO Radial flow turbine flow meter, RS Model 257-133.

2.5. Energy consumption

Energy consumption was calculated for the laboratory and pilot trials using Equation 1 [17], and normalized by volumetric unit of treated water (kWh/m^3):

$$E = \int \frac{UIdt}{V} \tag{1}$$

where U is the voltage across the electrodialysis stack; I is the current measured while running the process (initially fixed in galvanostatic mode), and V is the volume of treated acidic filtrate, in m^3. The time was defined when a 90% reduction of Cl^- was achieved.

2.6. Design of the industrial electrodialysis plant

The main goal of this investigation was to study the feasibility of treating acidic bleach filtrate with ED and *hf*-pED. Therefore, the design of an industrial plant must consider the required membrane area to reach the desired levels of ion removal and all the complimentary systems to properly operate the ED stacks, such as filters, piping, pumps, and tanks.

The design was based on a 90% removal of the salts contained in the bleaching filtrate. The flow rate employed for the calculations was taken as the mean, plus one standard deviation of the measured flows in the Kraft mill during a certain period (around five months). The membrane area required was computed using Equation 2 (Strathmann, 2010):

$$A_{m\_req} = \frac{Q\ F\ (C_{in} - C_{out})}{i\ \xi} \quad (2)$$

where Q is the feed flow rate, F the Faraday constant, i the current density, ξ the current utilization efficiency and C_{in} and C_{out} the normality of the feed solution at the inlet and outlet of the process, respectively. Equation 2 assumes constant current density throughout the whole process. However, as desalination takes place, the feed solution becomes more diluted and its conductivity diminishes, raising the electric resistance of the stack and lowering the electric current, considering that the voltage is at its highest admitted value. A lower current density means a lower desalination rate. Thus, if Equation 2 is applied with the initial value of i, the required membrane area will be underestimated. To overcome this problem, we divided the process into sections in which the conductivity decreased linearly, which we relate it to pseudo-constant desalination rates. For each section, i was defined as the average between the initial and final current density. Finally, the total required membrane area was the sum of all A_{m_req} computed in each section.

2.7. Cost estimation

When studying feasibility of a treatment, economical aspects are of major importance. Thus, operational (Opex) and capital expenditures (Capex) were estimated for the designed plant. Opex were estimated based on a published method (Sajtar & Bagley, 2009), where costs included those of electricity, labor, chemicals, membrane replacement and required miscellaneous parts. On the other hand, Capex were estimated based on mandatory main equipment (ED units, pumps, filters) and complimentary works, considering costs of materials, labor and installation.

3. Results and Discussion

3.1. Process integration and treatment strategy

The acidic filtrate stream, coming from the bleaching of fiber, is compatible with electrodialysis, showing a low potential of fouling based on previous studies (Tsai et al., 1997). The acidic pH of the stream (~3) hinders the occurrence of colloids, and consequently the fouling of membranes in ED. In previous applications, the treated water was recovered as process water, decreasing the water consumption of the mill. However, a small amount of chloride is not separated from this stream often producing a large chloride load in the treated water. For instance, with a typical concentration of 100 ppm of chloride in the treated bleaching filtrate (after 90% of chloride removal) at an average flowrate of 130 L/s, 1.12 t/d of chloride would end in the recovery circuit of liquors (Fig. 2). Moreover, aluminum is not well separated by ED membranes (Rapp & Pfromm, 1998), therefore, some elements could cause scaling in the causticizing area if recirculated and enriched in the recovery cycle and causticizing.

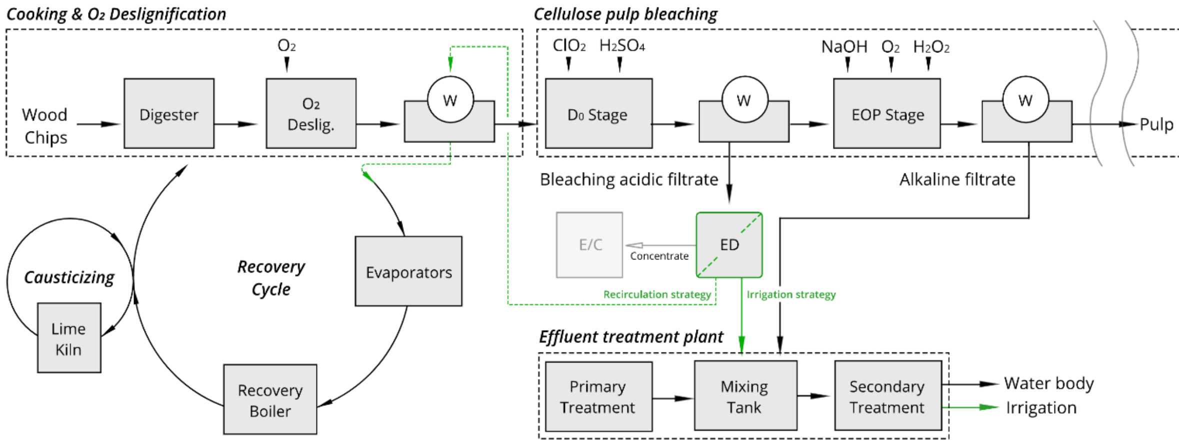

Fig. 2. Integration of ED for desalination of the internal stream "acidic filtrate", and application strategies

In order to avoid corrosion and scaling problems, we decided to use another strategy: desalinate the sectorial stream for quality improvement of the general effluent. In this way, we can evaluate the cost of desalinating an internal stream to comply with irrigation standards, instead of applying an end-of-pipe solution. With this strategy it is possible to potentially reduce up to 23% of sodium, 64% of chloride and 22% of sulfate of the final effluent, based on mass balances of a conventional Kraft pulping mill (Figure 3).

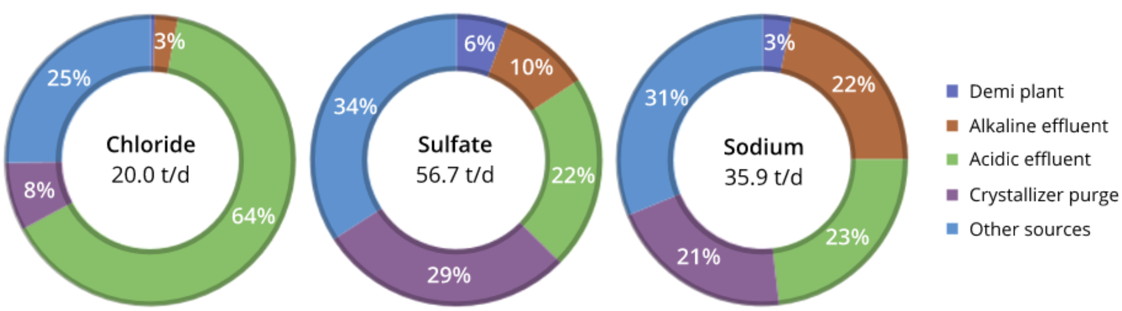

Fig. 3. Percentage contribution of different sectorial streams in the final effluent of a Kraft pulping mill.

Fig. 3 shows the contribution of chloride, sulfate, and sodium in the given streams, including acidic filtrate. The demineralization plant uses ion exchange resins, whose regeneration with sulfuric acid and caustic contributes with sodium and sulfate to the final effluent. On the other hand, crystallization is a commonly used technique to recover sodium sulfate from ashes, which produces a purge discharged into the general effluent. This purge has a very low flowrate (around 0.7 L/s) and contains many inorganics, including sodium, sulfate, and chloride. Finally, alkaline filtrate, rich in sodium, is hard to treat with electrodialysis, due to the colloids present in this stream at high pH (~12). Other effluent sources such as condensates, backwashes from the raw water treatment plant, sealing water, etc. are not identified as having an important individual contribution of ions to the final effluent.

3.2. Pulsed electrodialysis operation

Acidic filtrate was treated at laboratory scale using *hf*-pED and pEDR for determining the optimal operation parameters. As expected, LCD increased under a pulsed regime, especially when using pulsed electrodialysis reversal (Table 3). However, energy consumption increases by 10% or 35% when comparing *hf*-pED or pEDR with conventional ED, respectively, using 80% of the original LCD (12.3 mA/cm^2). The initial pH of the acidic bleaching filtrate remained constant at pH 3.2 throughout the whole desalination experiments, for all the tested conditions. In previews reports it was shown that the utilization of pEDR could prevent pH swings in the ED stack, improving its performance and robustness (Gonzalez-Vogel & Rojas, 2020). However, in this case, the filtrate acts as a buffer and the beneficial effect of pEDR is not fully exploited.

Table 3. Electrodialysis conditions and main results obtained at laboratory scale

	Adjusted parameters in ABS			Experimental results	
Experiment	Pause/Reverse Pulse (µs)	Frequency (Hz)	Intensity (A')	LCD (mA/cm^2)	E. consumption (kWh/m^3)
Conventional ED	0	0	0	12.3 ± 0.9	2.0 ± 0.2
Pulsed ED	10	2,000	0	13.0 ± 0.8	2.2 ± 0.1
Pulsed ED Reversal	10	2,000	1	14.5 ± 0.1	2.7 ± 0.1

Therefore, *hf*-pED and pEDR did not significantly improve the electrodialysis process as expected, especially pEDR due to the high-energy consumption compared to conventional ED. Consequently, only pulsed electrodialysis was considered in the pilot trial for further research, looking for fouling mitigation in the long term (compared with laboratory trials) rather than process intensification.

3.3. Limiting current density at pilot scale

Limiting current density (LCD) is a parameter that must be determined for each condition because it depends on the water characteristics, spacer geometry, membrane chemistry, temperature, etc. Two of the most important parameters that influence LCD are the fluid velocity and concentration of the feed solution in the diluate compartment. At high velocities, the thickness of the boundary layer in the diluate compartment is reduced by hydraulic turbulence, decreasing the occurrence of a phenomenon called concentration polarization and consequently increasing the LCD. Furthermore, a high ion content decreases the occurrence of a depleted layer, reaching high current intensities (Lee et al., 2006). This is expressed in the following Equation 3:

$$\mathrm{LCD} = \mathrm{a}\ \mathrm{C}_{\mathrm{dial}}\ \mathrm{u}_{\mathrm{dial}}{}^{\mathrm{b}}, \quad (3)$$

Where C_{dial} is the normality of the diluate compartment (meq/L), u_{dial} is the linear velocity (cm/s) in the same compartment, and a and b are empiric coefficients that are adjusted by estimating LCD at different velocities.

To analyze the effect of flowrate in the LCD under *hf*-pED vs conventional ED, experiments were performed with bleaching acidic filtrate at 35°C, having an initial conductivity of 6,000 µS/cm. From Table 4, it is possible to observe that the LCD using *hf*-pED is higher than the LCD determined with conventional ED in pilot trial conditions. This is consistent with the laboratory experiments and previously reported results (Gonzalez-Vogel & Rojas, 2020).

Table 4. LCDs at different flowrates measured in pilot trials:

Flowrate (L/h)	Velocity (cm/s)	LCD ED (A/m^2)	LCD *hf*-pED (A/m^2)	Times LCD increased
150	2.19	41.9	70.1	1.67
200	2.92	51.5	73.9	1.43
300	4.39	64.2	78.2	1.22

The impact of *hf*-pED depends on the velocity of the fluid. That can be explained because under low flowrates, the depletion of ions on the surface of the membranes is more prominent. Thus, the turbulence caused by a pulsed electrical field becomes more significant. Even though higher linear velocities promote turbulence, the residence time of the wastewater would decrease inside the stack (decreasing the time for desalination in a continuous process). Therefore, an optimal value exists for balancing flowrate and LCD which was not the focus of the current study. For subsequent desalination experiments, 2.92 cm/s and an 80% of the LCD of 51.5 A/m^2 were chosen to compare the different operational modes.

3.4. Ion removal profiles under selected regimes

Desalination was performed until reaching 90% of chloride removal. Chloride was selected as the quality criteria due to its detrimental effects when looking for recirculation or irrigation purposes. Thus, real-time measurements of chloride were necessary to detect the removal target concentration. Nevertheless, no ion selective electrode (ISE), in-line continuous measurement device nor techniques were available. Therefore, a relationship between chloride concentration and conductivity was established using data from five measurements of the bleaching effluent treated with ED in the pilot plant (**Error! Reference source not found.**).

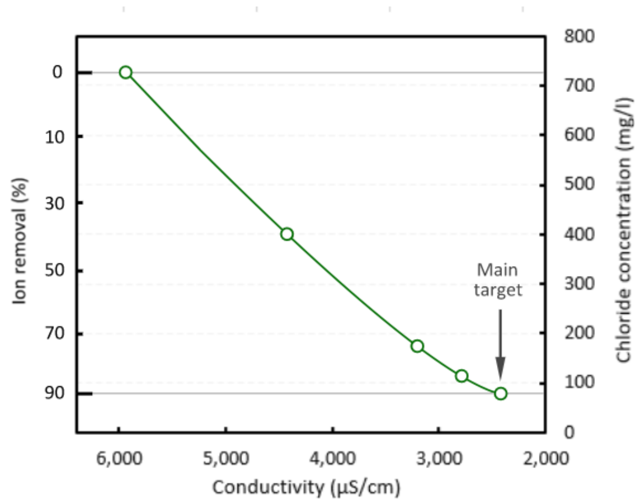

Fig. 4. Chloride removal as criteria for finishing the desalination process

From Fig. 4 it is possible to observe that 90% of chloride removal is not equivalent to 90% of conductivity reduction, down to ~2,300 µS/cm. The pH of the acidic filtrate stayed at 3.2, and organics were not removed in the process. Therefore, remaining charged species were still contained in the diluate compartment which was reflected in its conductivity. Thus, it was determined that a reduction of 60% of the initial conductivity represents 90% chloride removal.

When desalting with *hf*-pED and conventional ED, clear differences are appreciated on the ion removal profiles. For some ions, especially sodium, the profiles differ with the different operational modes (**Error! Reference source not found.**). In this particular case, the higher removal of sodium was not expected, although it has some benefits for the final effluent quality, because sodium is one of the biggest concerns in irrigation (Grattan, 2002; Nackley et al., 2015; Sharma et al., 2014). On the other hand, calcium, magnesium, zinc, and other minerals are removed from the acidic filtrate as well. These ions are useful minerals for plants and would be ideal to conserve them in the treated effluent instead of the concentrate. Perhaps the utilization of monovalent cation exchange membranes could help in retaining those multivalent ions, while removing sodium from the diluate stream.

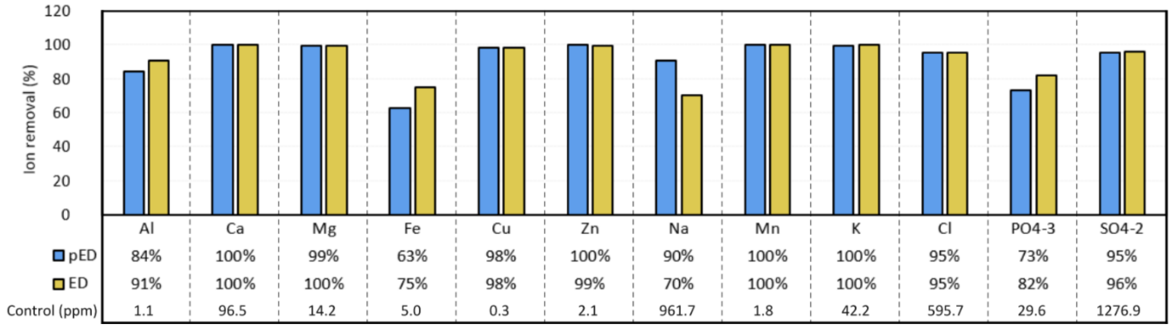

Fig. 5. Comparison of different ions removal levels between *hf*-pED and conventional ED

3.5. Fouling mitigation and energy consumption with hf-pED

The occurrence of fouling in both, conventional ED and pulsed ED at high frequency (2,000Hz), was determined based on the electrical resistance of the whole electrodialysis stack using Ohm´s Law. To be certain that the differences in electrical resistance of the stack are produced by changes in the resistance of the membranes, all other factors must be held as constant as possible. Assuming that ohmic losses in the electrodes, spacers and other components of the stack remain the same throughout the experiments, the only additional factor is the resistance of the solution, which is defined by its conductivity. Since the initial conditions were not the same due to variability in the acidic filtrate composition, a fixed conductivity value was used to properly compare the batch tests. Therefore, an arbitrary value of 4 mS/cm (close to a 40% conductivity decrease for all the experiments) was defined as the comparison point for all the tests. Thus, the experiments were performed for consecutive days to observe the effect in the fouling of the membranes (Fig. 6).

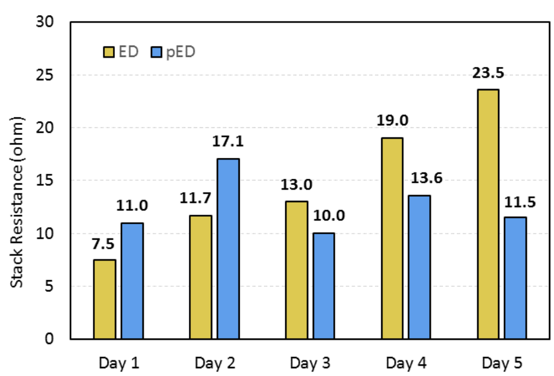

Fig. 6. Stack electrical resistance (ohm) at a standard diluate conductivity of 4 mS/cm

Accordingly, electrical resistance continuously increased after each test during normal ED operation. On the other hand, resistance remained low throughout the tests with pED, although an isolated major increase occurred in Test 2. This shows the potential of this pulsed operational mode to minimize membrane fouling.

Energy consumption of *hf*-pED was lower than conventional ED at pilot scale, giving a consumption of about 8.3 kWh/m^3 of treated acidic filtrate for ED, whereas *hf*-pED required 6.1 kWh/m^3. This differs with laboratory results, where the energy consumption was slightly higher for *hf*-pED. In the laboratory trials, the energy consumption represents the behavior at initial conditions of desalination, while a continuous increase of electrical resistance in conventional ED points to the continuous fouling at the pilot scale (Fig. 7). The pulsed operational mode at high frequency aids in keeping the electrical resistance low, which results in reduced energy consumption. Note that in **Fig.** B the current begins to decrease once the voltage reaches 50 V in conventional ED (the maximum level to safely operate this membrane stack), due to the continuous increase of electrical resistance. In the case of *hf*-pED, the voltage did not reach the 50V, in any of the tests. No significant differences were observed in the desalination time of five consecutive batch experiments. While conventional ED reached a reduction of 40% in conductivity (equivalent to 1 stage of electrodialysis) in 65.7 minutes on average, it was possible in 64.2 minutes with *hf*-pED.

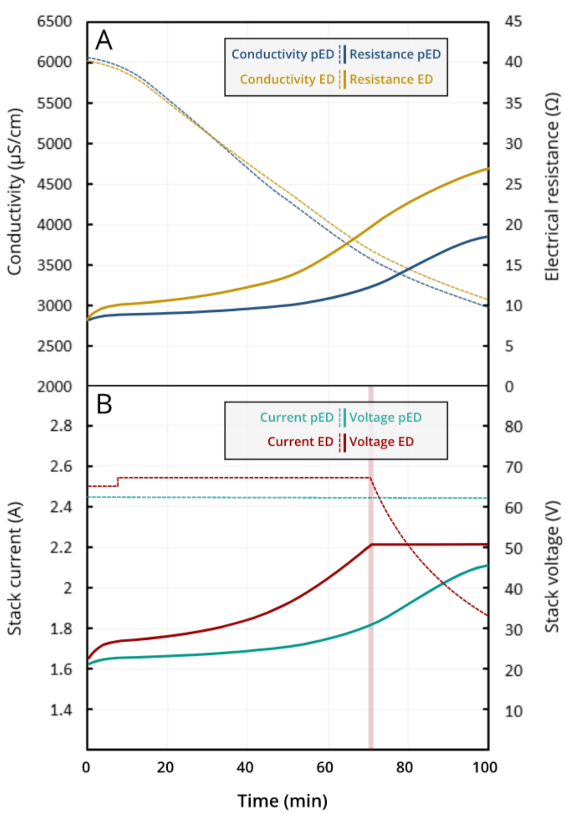

Fig. 7. Desalination performance of pilot trials of conventional and pulsed ED. A) Conductivity reduction and energy consumption. B) Voltage and current behavior.

3.6. Economic aspects of irrigation strategy

Required membrane area depends on the current density that can be applied to the ED stacks. To have a safety margin, 80% of the LCD was assumed as working condition. However, according to Equation 3, the LCD depends on flow velocity and concentration of the diluate compartment. Velocity can be estimated from the flow rate passing through each of the stacks. In this case, since the design flow is high compared to the maximum allowed of industrial units stacks, a minimum number of 13 stacks are required in parallel using 3 stages (39 stacks in total), resulting in an effective membrane area of 14,98 m^2. If more parallel stacks are placed, flow speed diminishes, resulting in lower values of LCD and higher requirements of membrane area. Considering the cost of membranes, pumps, electrodialysis frames, tanks, filters and pipes, a capital cost of around 14.7 MUSD was calculated for treating 160 L/s of acidic filtrate. Operational costs of conventional ED and *hf*-pED were estimated as 0.61 and 0.54 USD/m^3, of which 0.35 USD/m^3 corresponds to electricity and 0.14 USD/m^3 to membrane replacement in *hf*-pED. Energy consumption was calculated based on the results of the pilot trial. No treatment of the ED concentrate (with evaporation/crystallization for instance) was included.

The quality of the final effluent could be improved after treating the acidic bleaching effluent with pulsed electrodialysis. A total amount of 11.0, 7.7, 12.0 t/d of sulfate, sodium and chloride can be removed from the final effluent, decreasing the concentration of those components by 20, 21, and 59 % respectively, based on mass balances (Fig. 8). In this way, it is possible to obtain a better water quality for irrigation purposes, based on chloride concentration, which decreases from 290 ppm (base case) to 117 ppm, below the maximum allowed value of 200 ppm defined by Chilean law (NCh 1333). However, sodium levels are still high, and other sectorial streams should be treated to decrease sodium levels down to 270 ppm, at least (second target). Sulfate could be problematic or beneficial (considered as fertilizer), depending on the type of soil and applied normative. The concentration range could vary between 250-1,000 ppm. Other sectorial treatments such as alkaline filtrate, demineralized water (salts from regeneration of ion exchange resins), and crystallizer purge could be also treated with other methods to further improve the effluent quality. This could vary depending on the mill; for instance, if reverse osmosis is used instead of ion exchange resins for production of demineralized water (consumed in power boilers), the amount of salts discharged in the effluent would be negligible.

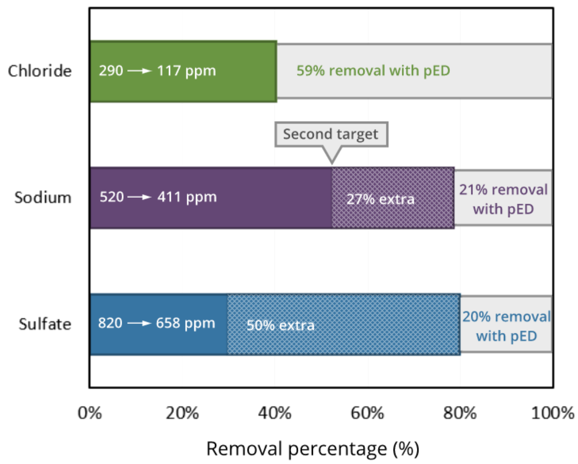

Fig. 8. Final effluent quality estimation after removal of chloride, sodium, and sulfate from the sectorial acidic filtrate stream.

It will be always less expensive to treat streams with low flowrates compared with the final effluent. In the current example, a common Kraft pulping plant, the final flowrate reaches 800 L/s, while the acidic bleaching filtrate has a flowrate of 160 L/s. Electrodialysis allows to treat this stream without extensive pretreatments (except for a filtration stage for removal of fibers), in contrast to desalination plants at the end of the pipe. Thus, the Capex and Opex of *hf*-pED, specifically treating the acidic streams, is far lower (at least 10 times for both costs) than the treatment of the final effluent. Nevertheless, replacement of chlorine dioxide with ozone in bleaching, specific treatment of other streams, and internal recirculation could tremendously help to improve the effluent quality as well. The options must be considered case by case.

4. Conclusions

The treatment of sectorial streams is presented as an effective way to improve the quality of the final effluent in terms of sodium, sulfate, and chloride concentrations. This strategy, in combination with the treatment of other sectorial streams, would allow in the future the reutilization of pulping effluent as irrigation water or for other purposes. Nevertheless, the full-scale integration of the ED process requires the evaluation of the brine management, and subsequent disposal or reutilization of this salt.

Pulsed ED at high frequency reduces fouling and decreases Opex of the desalination process compared with conventional ED. Upgrading of the system requires only one external device per membrane stack. Intensification is also achieved, reflected in the higher limiting current densities. Nevertheless, intensification was not studied in the current pilot trial. Future tests could include the effect of the intensification when using *hf*-pED, to decrease capital costs and footprint of the industrial plant.

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