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Desalination by pulsed electrodialysis reversal: Approaching fully closed-loop water systems in wood pulp mills

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ABSTRACT

A pulsed electrodialysis reversal (pEDR) process is proposed to desalinate spent water after particle removal, biological and chemical coagulation, which are commonly used as a sequence in Kraft pulp mills. pEDR affords closed-loop processing, reducing the need for freshwater intake while maintaining the quality of recirculating process streams. Compared with conventional electrodialysis, pEDR minimizes production losses (from 5 % to 0.6 %), extending the time for hydraulic reversal (from 15 min to at least 2 h). Simultaneously, the conductivity of the effluent is significantly reduced, from 2100 to 200 μS/cm, reaching a quality similar to the feed water. The operation cost (0.38 US$/$m^3$) is factored in the techno-economic viability of the process water recirculation, which is also demonstrated for its scalability. Additionally, WinGEMS simulation highlights the benefits of installing a pEDR unit, positively impacting mill water under different recirculation rates. Overall, we show remarkable gains in water economy, operation (maintenance and fouling), and quality, which are critical factors in achieving resource sufficiency.

1. Introduction

Water is a key resource for life and human activities, including those associated to processing and manufacturing. Concerns about pollution and scarcity are continuously increasing, especially considering the added effects of climate change. As most industries, those in the forest products sector require large volumes of water; therefore, ensuring the viability of such natural resource and limiting any environmental impact is a mandate. Such factors highlight the important consideration of closed-loop systems for industrial operations (Gavrilescu and Puitel, 2007).

The recovery of wastewater from the pulp and paper industry is a costly and, technically, challenging task. Recirculation is restricted by the accumulation of organics and non-process elements (NPEs) such as K, Si, Ca, Ba, Fe, Cu, Mn, Al, Cl, among others (de Almeida Batista et al., 2020). Water recirculation and related increase in the concentration of organics promote microorganism growth, increase the consumption of bleaching chemicals, and deteriorate the quality of the final product. On the other hand, non-process elements promote corrosion and scaling of processing units, including boilers and piping systems (de Almeida Batista et al., 2020; Gavrilescu and Puitel, 2007). The Kraft process is most widely utilized to produce cellulosic pulp from wood, representing about 90 % of the chemical pulp produced. Some initiatives for closing water circuits are found in literature (Chen and Horan, 1998), although no viable commercial end-of-pipe solutions are available for water recovery, especially relevant in the bleached Kraft pulping process (Bajpai, 2018). Thus, the pulp and paper industries operating worldwide face different challenges, depending on their technologies. The quality and quantity of feed or freshwater and effluent treatment need to be factored in efforts to comply with regulations associated to the quality of discharged water, sustainability, and economic metrics.

Several approaches to reduce water intake are found in literature, including those relevant to sectorial streams, before reaching the effluent treatment plant (de Almeida Batista et al., 2020; Gonzalez-Vogel et al., 2021; Pfromm, 1997). A thorough comprehension of the distribution and reutilization of the water resource inside the process and respective strategic treatments should be cost-effective, for example, compared with end-of-pipe solutions (Gavrilescu and Puitel, 2007). Using this philosophy, pulp mills have reduced their water consumption by at least by 90 % since the eighties (Gavrilescu and Puitel, 2007).

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Table 1
Properties of utilized RALEX membranes.

	Type	Electrical resistance (Ω/cm^2)	Membrane thickness (mm)	Transport number	Ion exchange capacity (IEX, meq/g)	Thermal stability (°C)
RALEX AMH	Anion exchange	7.5 ± 0.5	0.75 ± 0.5	>0.97	1.8	50
RALEX CMH	Cation exchange	9.0 ± 0.5	0.65 ± 0.5	>0.98	2.2	50

Modern mills water consumption is in the range of 10–30 m^3/ADt (air-dried ton of produced cellulose pulp) (Bajpai, 2018). However, decreasing further this consumption is a great challenge and implies added costs, e.g., in efforts to close further water circuits. At some point, an end-of-pipe solution is needed for Kraft mills to comply with more restrictive environmental regulations and to achieve water sufficiency.

Physical and biological treatments are used before returning the treated Kraft effluents to water bodies. In primary (physical) treatment, fibers or particles are separated and the pH of the wastewater is neutralized. The secondary (biological) treatment reduces the digestible organic content (and reduces chlorate species if chlorine dioxide bleaching is part of the process) (Bajpai, 2018; Oliveira-Esquerre et al., 2002). If the effluent is disposed in rivers, a third treatment is applied to remove recalcitrant organics and color. Chemical coagulation and flocculation are used in such tertiary treatment, although advanced oxidation or filtration can be considered as well (Bajpai, 2018). After the above treatments, the quality of the wastewater is suitable for desalination, for example, by using electrodialysis, which is an effective alternative to reclaim water and for its recirculation.

Among the different desalination techniques used to treat industrial effluents, evaporation, reverse osmosis and electrodialysis are commercially available at big scales. In general terms, evaporation is suitable for wastewater treatment when the salinity is very high and thermal energy is available and inexpensive. Membrane technologies, such as electrodialysis (ED) and reverse osmosis (RO), are suitable for desalinization of brackish and brine waters, respectively. RO is the gold standard for sea water desalination; however, if the salinity is below 5000 ppm (Wright and Winter 2014), and silica and microorganism removal are not a concern, ED is a better choice. Compared with RO, ED offers lower maintenance costs, it is less prone to foul (less demanding for pre-treatments) and enables higher recovery ratios (Wright and Winter 2014).

Despite the diversity of pulp and paper processes and the wide variety of available technologies for water treatment, feasible solutions are still lacking. Electrodialysis Reversal (EDR), a variant of ED, has been proposed as a suitable technology for desalination of wastewater (Akhter et al., 2018). Compared with conventional electrodialysis, it requires less pretreatment stages and “Cleaning in Place” (CIP) procedures. However, this is at the expense of lower production rates. As an alternative, pulsed electrodialysis has been shown for its promise in reaching higher limits in these systems (Gonzalez-Vogel and Rojas, 2020). Unfortunately, membrane fouling is prevalent in the latter method, which limits its viability, e.g., increases energy consumption and reduces membrane efficiency and operational life (Akhter et al., 2018). Thus, mitigation of fouling is critical when treating Kraft pulping effluents, the latter of which are associated with highly recalcitrant organics. Therefore, pulsed operations in combination with EDR could address these issues in industrial conditions. Hence, here we propose Pulsed Electrodialysis Reversal (pEDR) as a core technology for fully closing the water circuit of a bleached Kraft pulp mill. To our knowledge, this is the first attempt in effluent desalinization *via* pEDR, which we demonstrate to overcome the challenges associated with water management in those related units.

2. Materials and methods

2.1. Electrodialysis pilot plant

An EDR pilot unit (EDR-Y/50-0.8) including a power supply (75VDC/10A), centrifugal pumps, safety cartridge filters (10 μm for each compartment), manual three-way valves and an electrodialysis module EDR-Y were procured from MEGA a.s (Straz pod Ralskem, Czech Republic). The pilot plant included a data acquisition unit and instrumentation to measure pH, conductivity, flow rate, voltage, and current. Fifty pairs of heterogeneous ion exchange membranes RALEX® (Table 1) provided a total surface area of 4.04 m^2 with an individual

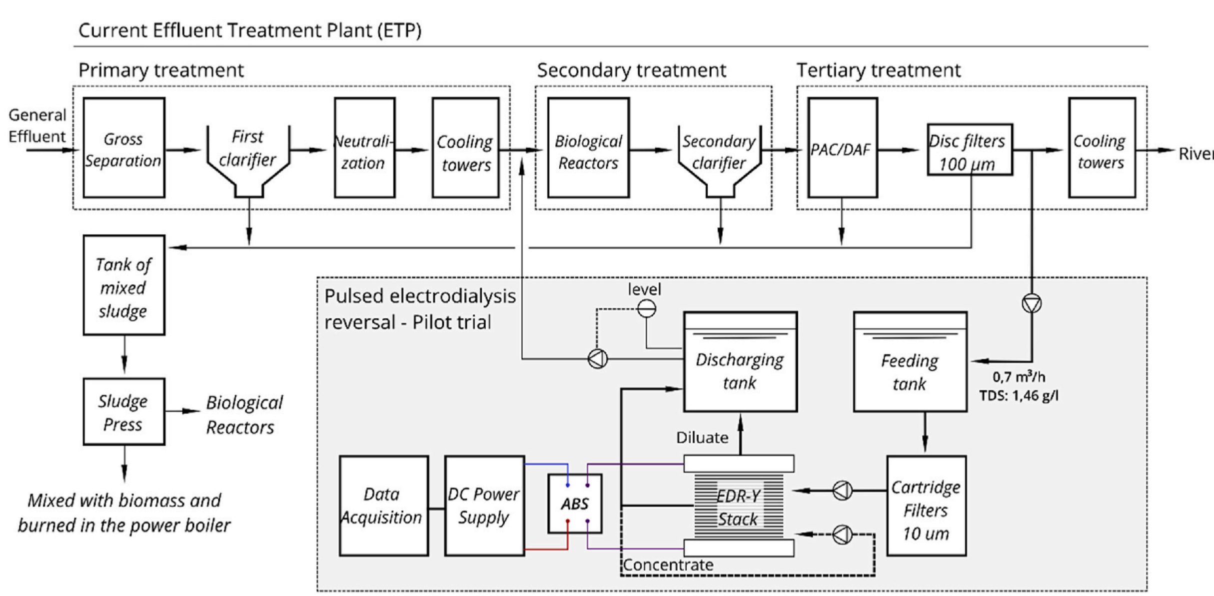

Fig. 1. Effluent treatment process and integration of the electrodialysis pilot plant.

Table 2
Characteristics of water streams.

Parameters	Units	Tertiary effluent	EDR Limits (MEGA)	EDR product	River water
pH		7.60 ± 0.06	>10.0	6.8–7.8	7.2 ± 0.27
Conductivity at 25 °C	μS/cm	1815 ± 81	–	140	36.4 ± 11
Temperature	°C	27.9 ± 1.2	35	–	14.2 ± 4.1
Flowrate	L/s	697.2 ± 25	–	–	–
Total Dissolved Solids (TDS)	ppm	1.278 ± 51	–	<102	48.6 ± 7.2
Chemical Oxygen Demand (COD)	ppm	66 ± 6	100	30	6.9 ± 0.9
Turbidity	NTU	1.31 ± 0.11	5	1	6.08 ± 1.3
Total suspended solids, TSS	ppm	3.2 ± 0.4	10	3.2	7.5 ± 0.7
Total sulfur, as SO_4	ppm	218 ± 18	–	17.4	3.4 ± 1.2
Free chlorine	ppm	<0.03	1	–	0.02
Chloride	ppm	261 ± 23	–	20.1	7.5 ± 3.83
Aluminum	ppm	0.41 ± 0.12	1	0.05	0.09 ± 0.024
Calcium	ppm	11.98	–	1.3	5.4
Magnesium	ppm	2.64	–	0.4	1.8
Barium	ppm	0.057	–	0.01	0.02
Iron	ppm	0.03	3	0.03	0.73
Sodium	ppm	365.9 ± 29.7	–	29.3	4.5 ± 1.4
Manganese	ppm	0.21 ± 0.044	1	0.02	0.02 ± 0.01
Silica, as SiO_2	ppm	13.2	–	13.2	14
Fluoride	ppm	0.04	1	0.02	0.14

membrane area of 400 cm^2. The working flow rate was fixed at 700 L/h (linear speed of 4.86 cm/s). The electrode rinsing solution consisted of 0.25 M Na_2SO_4 using a flow of 900 L/h. The temperature was varied between 15 and 30 °C, depending on the effluent and environmental conditions. Every 7 days, the electrodialysis stack was washed with 2 % NaOH and 5M NaCl for 30 min and cleaned with fresh mill water.

2.2. Process integration

The current industrial plant processes hardwood as raw material for production of bleached cellulose pulp. The delignification and bleaching process includes oxygen and chlorine dioxide delignification, caustic extractions, chlorine dioxide and peroxide bleaching stages. The Effluent Treatment Plant (ETP) installed in this mill clarifies, neutralizes the pH, and decreases total organic carbon, AOX, color, and temperature of the effluent before discharging it. On the other hand, the sludge produced from the clarifiers is treated, dried, and burnt together with dried biomass in a power boiler. The effluent treatment plant is composed of three treatments stages. First, a coarse separation removes sand, fibers, and other particles. The effluent is then neutralized to pH 7.0 and cooled down to 35 °C. Secondly, microorganisms remove around 98 % of the organics as Biological Oxygen Demand (BOD) and 99 % of residual chlorate. Lastly, the tertiary treatment separates around 40 % of the remaining organic matter as Chemical Oxygen Demand (COD) and 60 % of color, using a chemical coagulation and flocculation process, followed by dissolved air flotation (DAF), self-cleaning disc filters (100 μm), and cooling towers, before discharging. The tertiary effluent before cooling was used to feed the EDR pilot plant (Fig. 1).

2.3. Operation of pulsed EDR

Coupling of an Asymmetric Bipolar Switch (ABS in Fig. 1) was considered to allow the application of reverse polarity pulses at different frequencies, pulse widths and intensities (Gonzalez-Vogel and Rojas, 2019). These extra degrees of freedom permit a further optimization of the process. Different operation modes were tested. In the ABS system, the pulse width was varied from 10 to 50 ms, the frequency between 1 and 25 Hz and the intensity from 0 (PEF-ED) to 1.5 times the working voltage.

Differences concerning fouling and performance were expected for the conventional and pulsed operations in EDR. These differences can be quantified by operational means such as desalinization efficiency and energy consumption, while fouling can be evaluated *via* the electrical resistance of the stack over time, and the presence of deposits on the surface of the membranes using Scanning Electron Microscopy (SEM). For SEM procedure, membrane samples were dehydrated and coated with carbon (4 nm) before inserting them into a vacuum chamber. The prepared samples were examined with the field emission microscope (FE-SEM, Zeiss SigmaVP, Germany), operated at 3.0 kV, with a working distance of 7 mm. Thus, the surface morphology of the membranes used under different desalination conditions were analyzed.

3. Results and discussion

3.1. Quality requirements and technology selection

Given that Kraft pulping effluents are rich in organic matter and recalcitrant material, we considered ED as a more suitable alternative to RO for desalination. Moreover, the salinity of Kraft effluent after tertiary treatment is in the range of 1400–1600 ppm, making it suitable for ED treatment based on this and other parameters listed in Table 2.

Electrodialysis reversal, reverses every 15–30 min the electrical and hydraulic polarity of electrodialysis, promoting membrane self-cleaning (Pilat, 2003). It is technically possible to go even further with cycle reversal, increasing the reversal frequency. Nevertheless, this strategy is not economically feasible, given that a given time (40 s, for example) are necessary to clean the pipes while inverting hydraulic circuits, representing 5 % of a 15 minutes cycle, losing production time. Modern power electronics could assist in this case, reversing only the electrical polarity for very short times, in a controlled manner, in the order of millisecond to microseconds (Gonzalez-Vogel and Rojas, 2019). Thus, the benefits of EDR are still conserved when reversing hydraulic polarity after longer periods, without compromising production rate. The upgrade from EDR to pEDR only requires the coupling the ABS as a simple device between the power supply and the EDR stack. Considering its robustness and scalability, pEDR is consider further in this discussion, e.g., for desalination of Kraft pulping effluent, as end-of-pipe solution.

3.2. Pulsed electrodialysis reversal modes

The application of reverse polarity pulses has been used in electrodialysis, but our initial purpose in including the pulsed operation in EDR was to obtain an extra benefit. For instance, in the robustness that could be gained by decreasing the occurrence of fouling. However, usually pulsed operation requires a more complex electronic system and slightly increases energy consumption, due to back migration of ions (Gonzalez-Vogel and Rojas, 2020; Merkel and Ashrafi, 2019). Moreover, desalination time can be lost when reversing the electrical polarity. To overcome this, different operational modes where chosen with a high effective duty cycle (Eq. (1)) (Gonzalez-Vogel and Rojas, 2020). As comparison, PEF-ED was evaluated as well (Cifuentes-Araya et al., 2011; Ruiz et al., 2007) which by default has a low duty cycle, due to the fact that half of the time the system is paused or not working/desalting.

$$eDC\ (\%) = \frac{T_{ON} - T_{REV}x\left(\frac{A'}{A}\right)}{T_{ON} + T_{REV}} x\ 100 \qquad (1)$$

Effective duty cycle includes pulse width (T_{REV}), intensity (A'/A) and frequency. Thus, different operational modes were tested and firstly

Table 3
Tested operational modes of pulsed EDR. One of the best operational conditions is highlighted in bold.

Operational mode	Pulse width (ms)	Frequency (Hz)	Intensity (x LCD)	Effective duty cycle (%)	LCD (mA/cm^2)
ED	0	0	0	100.0	9.4
PEF ED	10000	NA	0	50.0	9.8
pEDR$_1$	10	5	1	98.3	11.0
pEDR$_2$	30	5	1	94.8	11.6
pEDR$_3$	50	5	1	91.3	12.6
pEDR$_4$	80	5	1	86.1	12.1
pEDR$_5$	50	1	1	98.3	11.1
pEDR$_6$	50	10	1	82.6	13.2
pEDR$_7$	50	15	1	74.0	13.5
pEDR$_8$	**10**	**20**	**1**	**93.1**	**13.9**
pEDR$_9$	50	5	0	95.7	11.1
pEDR$_{10}$	50	5	0.5	93.5	12.0
pEDR$_{11}$	10	10	1	96.5	11.8
pEDR$_{12}$	20	10	1	93.1	11.9
pEDR$_{13}$	20	10	0	96.5	11.2
pEDR$_{14}$	20	10	0.5	94.8	11.5
pEDR$_{15}$	20	10	1.5	91.3	12.8
pEDR$_{16}$	10	25	1	91.3	12.8

Table 4
Desalination performance at different current conditions.

Operational Mode	Current density (mA/cm^2)					
	7.52 (80 % LCD of ED)			11.12 (80 % LCD of pEDR$_8$)		
	ED	pEDR$_8$	pEDR$_{11}$	ED	pEDR$_8$	pEDR$_{11}$
Energy Consumption (kWh/m^3)	0.42	0.47	0.46	0.58	0.68	0.62
Final pH	5.79	5.77	5.77	6.21	5.76	6.12
Residence time (min)	14.3	15.0	15.0	9.23	10.3	9.89

selected based on the calculated Limiting Current Density (LCD) empirically obtained (Cowan and Brown, 1959) (see Table 3).

Among different experimental settings, the "operational mode 8" was selected (pEDR$_8$, Table 3). Compared with conventional ED, higher LCDs were obtained at higher frequencies, although the effective duty cycle rapidly decreased, due to the relatively long times of reverse polarity, in the order of milliseconds. Desalination performance of pEDR$_8$ was also compared with pEDR$_{11}$ (working at lower frequency, and same pulse width and intensity than mode 8) and conventional ED (Table 4). The initial conductivity and pH of the effluent used in all the tests were 2.25 and 5.77 mS/cm, respectively. Changes in pH, energy consumption and residence time were studied after decreasing the conductivity by 60 % (desalination target of 1 ED stage). The shift in pH signals water splitting, which could trigger scaling problems due to changes in solubility, mainly at high pH (Merkel and Ashrafi, 2019). On the other hand, energy consumption and residence time impact the OPEX and CAPEX of the desalination plant.

We observed that pEDR$_8$ operational mode had a slightly higher energy consumption and residence time than conventional ED. Nonetheless, above limiting current density conditions, pEDR was superior when considering pH stability and residence time (10.3 vs 14.3 min), consistent with results from other reports (Gonzalez-Vogel and Rojas, 2020). That means pEDR could boost the desalination process, when working in over-limiting conditions, without compromising the stability of EDR.

Fouling occurrence in cation (CEM) and anion (AEM) exchange membranes was analyzed using SEM, which indicated the deposition of particles after pEDR and conventional ED desalination treatments (Fig. 2). Compared to CEM, anion exchange membranes are prone to foul (Akhter et al., 2018), and some particle deposition might occur in both conventional ED and pEDR, although a clear difference is observed between the two operations. Fouling of cation exchange membrane was not expected, only observed in conventional ED.

Complementary, the occurrence of fouling was evaluated by analyzing the electrical resistance of the electrodialysis stack while performing the desalination. For long term evaluations, we monitored the electrical resistance, given that it increases with time due to the contribution of a gel layer that acts as an insulation material (Akhter et al., 2018), as studied in the following section.

3.3. Tertiary effluent desalination

Pulsed electrodialysis reversal and EDR were tested in the pilot trial to evaluate fouling over time. When desalting, membranes were continuously fouled as expected in any operation. Reversal mode promoted the releasing of accumulated material present on the surface of the membranes, restoring their original function. This effect was observed in every cycle as a decrease in the electrical resistance of the ED stack (see Fig. 3). At some point, the reversal of polarity was not enough for restoring the functionality. Thus, CIP procedures were needed. Chemicals were applied to redissolve, break-down and release

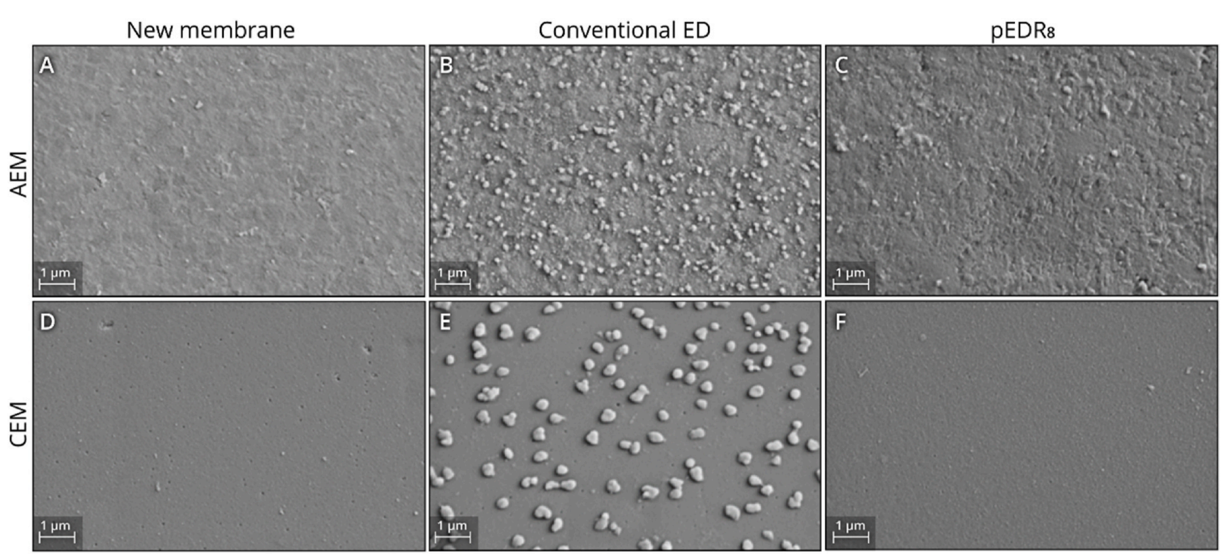

Fig. 2. Fouling occurrence on membranes after desalination of tertiary effluent.

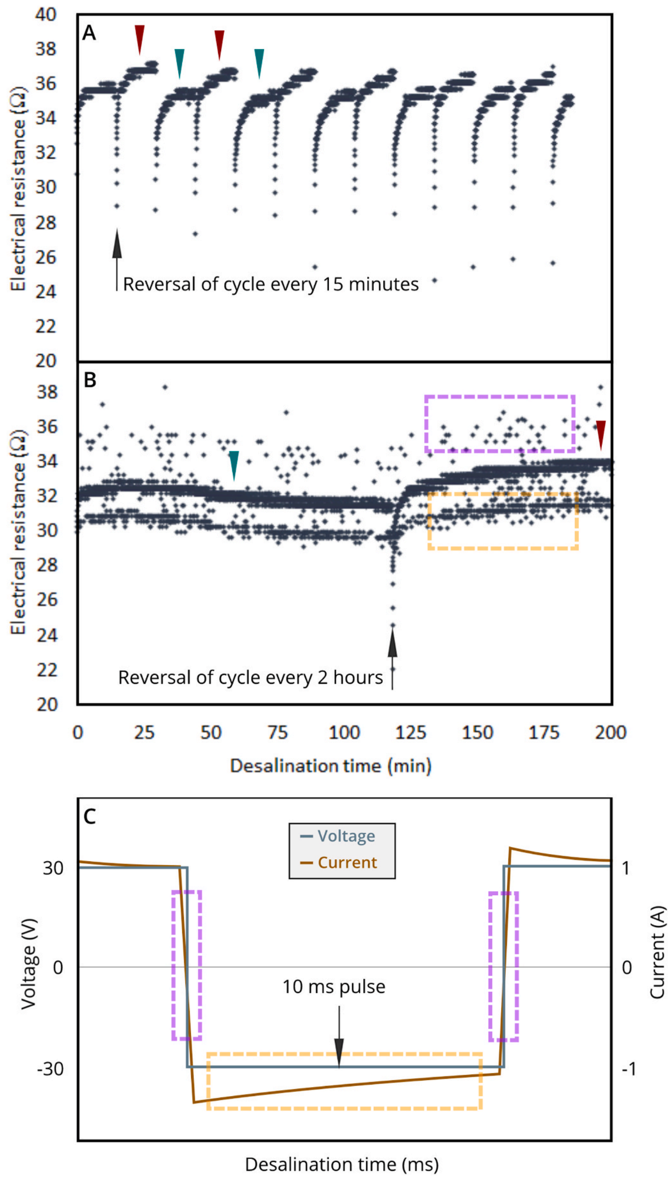

Fig. 3. Electrical resistance over time during the pilot trial A) Electrodialysis Reversal mode where resistance was restored every 15 min, according to the reverse of polarity. B) Pulsed EDR mode, where the whole polarity was reversed every 2 h, and C) Electrical response in a short period of time when reversing polarity in Pulsed EDR mode, the current output explains the uneven measurements obtained in B.

the precipitated fouling or inorganic scaling, reestablishing their function (Bazinet and Araya-Farias, 2005). Fouling might be irreversible and eventually (in a matter of years) those membranes must be replaced.

In the case of EDR, the cycle was reset every 15 minutes and the variation of the electrical resistance was monitored between cycles (red and cyan arrows in Fig. 3a). The observed difference is explained considering that one side of the membranes in the ED stack was more fouled than the opposite one, and it was more difficult to restore its function (red arrow). The same behavior was found with pEDR, where the first cycle (0–120 min) had less overall electrical resistance than the following cycle. Additionally, more noise was observed in pEDR, presenting lower and higher resistance values than expected (orange and purple dashed rectangles in Fig. 3b). These uneven values are explained by the fact that the current changes with the time of measurement. Considering a 10 ms pulse width, with a frequency of 20 Hz, at some point the current is measured while the system is being pulsed, generating irregular values. This contrasts with the results that are typical in EDR, which show smooth signals (Fig. 3c).

EDR by itself is a robust technique compared with conventional ED, although 5 % of the product is lost due to hydraulic reversal. To overcome this problem and to preserve the benefits of self-cleaning, we applied pulsed operation with increased periods between reversal cycles. By using pEDR, it was possible to work for 2 h before reversing the whole cycle. Thus, the production loss was reduced to 0.6 % of the feeding water, considering the same 40 s of hydraulic reversal.

$pEDR_8$ was tested for longer operation times. However, the optimal operation could vary according to the characteristics of the feeding water (pH, temperature, conductivity, organics, etc.) and electrodialysis stack performance, including fouling or deterioration state. For instance, recent studies have shown that by working at high frequencies, in the order of kHz, it was possible to exploit electroconvective vortices to improve the performance of desalination (Gonzalez-Vogel et al., 2021; Gonzalez-Vogel and Rojas, 2020). In practice, it is not possible to manually try different modes. Future work will be focused on including learning sequences and automatic optimization embedded in the ABS unit.

3.4. pEDR scaling up

For scaling up the application, a flowrate of ~65000 m^3/d must be considered, with a Total Dissolved Solids (TDS) of 1278 ppm (Table 1). Based on the characteristics of the fresh or inlet water to the mill, we set a target desalination level (cut-off) of 92 % to avoid accumulation of NPE's. Taking into consideration the solubility limits of the removed salts, it was possible to calculate a maximum recovery of 95 % using pEDR, in a feed and bleed operation and 92 % cut-off (Fig. 4). Thus, four EDR stages were required to reach this desalination level, considering about 60 % desalination per stage.

pEDR showed a high effluent recovery (95 %) relative to the feed water, avoiding accumulation of salts and associated risks, e.g., by removal of 92 % of the salts. pEDR can reach up to 90–95 % recovery,

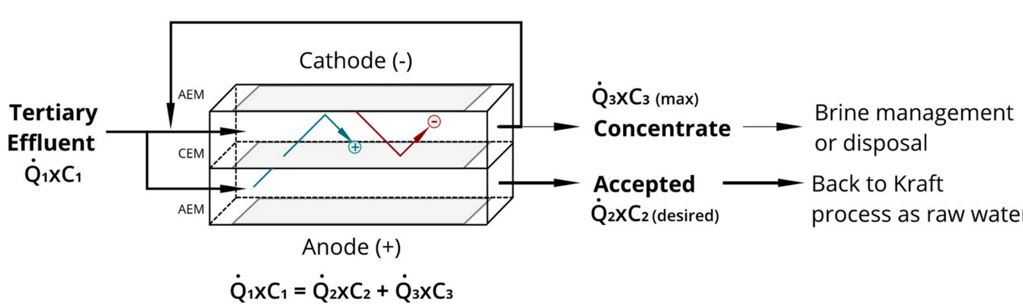

Fig. 4. Diagram showing the mass balances for determining the maximum recovery rate in a feed and bleed mode. C_3 and $\dot{Q}_3$ are determined based on the saturation index of the removed salts, while C_2 depends on the desired level of remotion. $\dot{Q}_2$ is calculated from the mass balance.

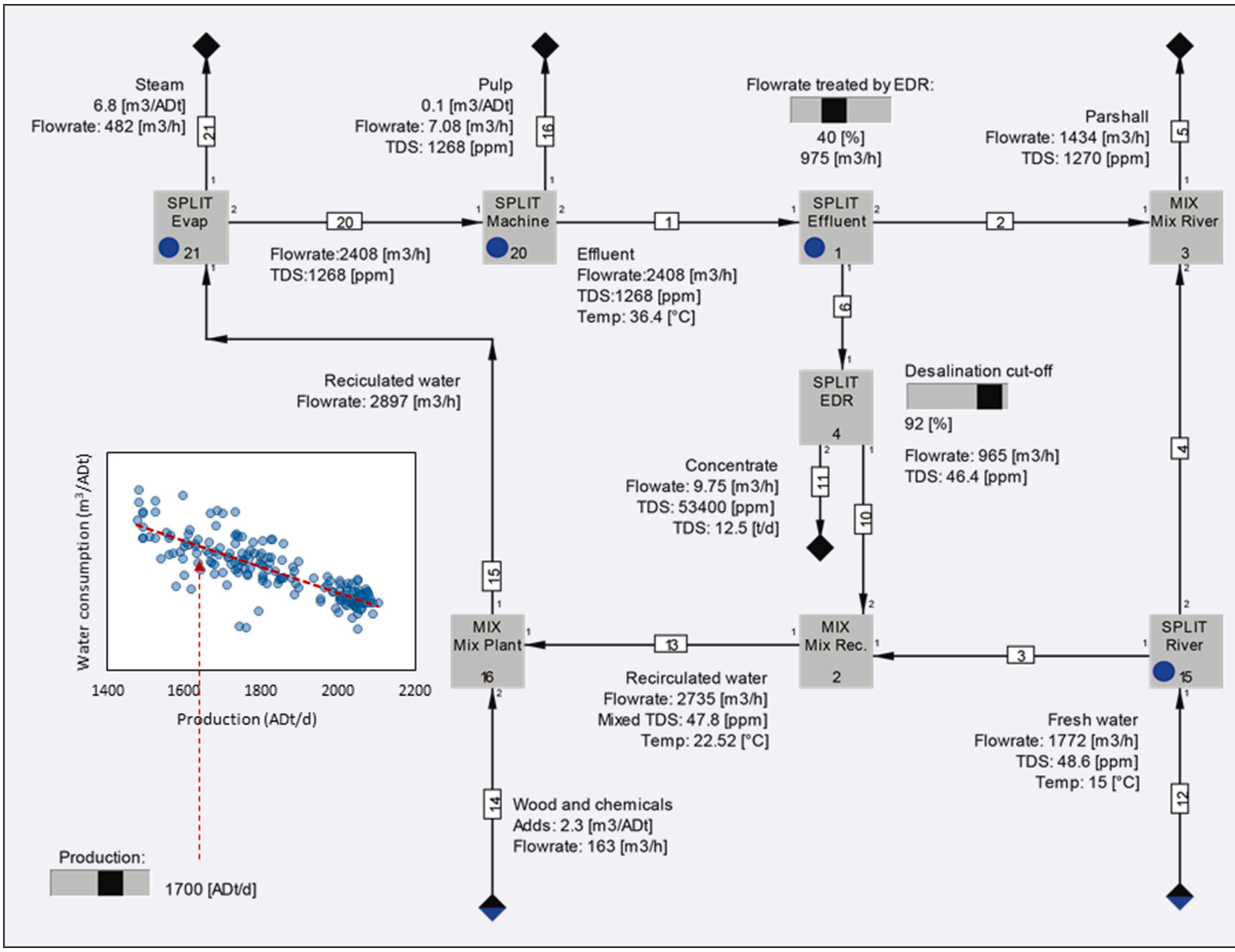

Fig. 5. WinGEMS model employed to simulate the impact of the recirculation of effluent in a conventional Kraft pulp mill. The model was constructed using SPLIT blocks, to simulate removal of water and salts, and MIX blocks, to calculate the different components after mixing defined streams. Linear regression of water consumption vs production and specific consumption per areas of the mill were used to adjust the model.

meaning a concentrate (brine) with a flowrate equivalent to 10-5% of the incoming feed water and 11000–22000 ppm of salt concentration using a desired 92 % desalination cut-off, according to mass balances.

3.5. Recirculation impact

Depending on the selected mill and location, several brine management alternatives can be considered. These options include disposal of the concentrate in water bodies, deep well injection, evaporation/crystallization, mechanical evaporation, and valorization of brines using bipolar membrane or metathesis electrodialysis, among others (Fernandez-Gonzalez et al., 2016; Morillo et al., 2014; Reig et al., 2016). The evaluation of these alternatives is not the focus of this study. Instead, recirculation scenarios were evaluated without considering the treatment and disposal of the generated brine. Thus, to evaluate the impact in the mill process when recirculating the desalinated effluent, a model was built in process simulation of the pulp mill by using WinGEMS, which values were adjusted considering historical data of the mill production rate (Fig. 5).

As expected, with a desalination cut-off of 92 % it is possible to keep the TDS of the original freshwater, even under different recirculation rates (Fig. 6a). If the desalination cut-off is reduced, an accumulation of salts is expected to occur in the mill, mainly from sodium, sulfate, and chloride ions. Nevertheless, silica and other NPE's are always less concentrated than the freshwater, as shown in Table 1. Therefore, the accumulation of detrimental species is not a mayor concern; on the contrary, according to mass balances and compared with original freshwater, problematic species such as Ca, Mg, Fe, were kept low (Fig. 6b). The only problematic NPE with increased concentration is chloride, which can be controlled if chlorine dioxide bleaching is replaced with elemental chlorine-free (ECF) or total chlorine free (TCF) bleaching sequences. On the other hand, the temperature of the mill freshwater is expected to increase after recirculation. This effect is the main issue if the process is scaled up. Therefore, the effluent must pass through the already installed cooling towers (placed at the end of the effluent treatment plant) to reduce the temperature of the recirculated water.

3.6. Economics and scaling up challenges

pEDR capital and operational expenditures to treat 100 % of the effluent were calculated using a previously reported model (Larson and Leitner, 1979), adjusting the prices to the year 2020. For instance, computed equipment cost was 32.5 MUSD for a 90%-recovery pEDR plant (using water type #3 (Larson and Leitner, 1979)). The total CAPEX considering installation cost was calculated as 56.8 MUSD, for 90%-recovery. Total operational cost was estimated as 0.32 USD/m^3 or 12.3 USD/ADt. For the latter, a flow rate of 64800 m^3/d and a production of

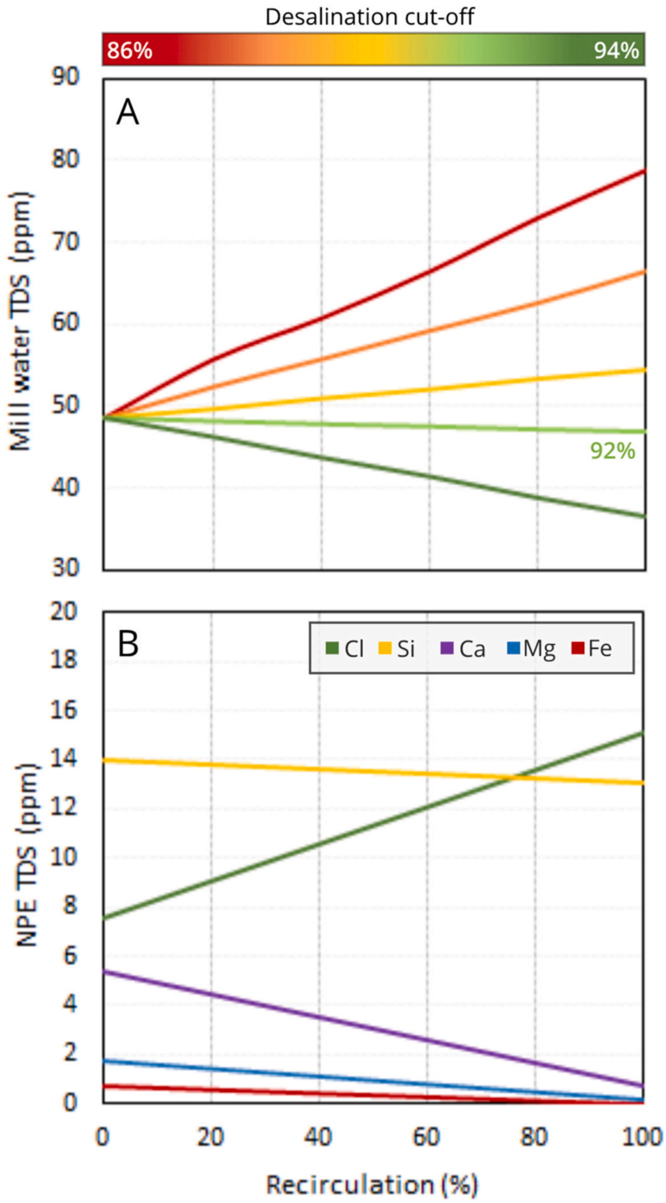

Fig. 6. Results from WinGEMS simulation under different recirculation scenarios. A) Mill water quality, in terms of TDS, for varied recirculation rates and using different desalination cut-off values of pEDR. B) Final concentration of some common NPE's after mixing the treated effluent with freshwater reaching up to 100 % recirculation, using 92% of desalination cut-off.

1700 ADt/d were considered. On the other hand, with a 95 % recovery using pEDR in the first phase, the estimated equipment costs were 37.7 MUSD (using water type #4 to represent higher salinity (Larson and Leitner, 1979)). In this last option, an OPEX of 0.38 USD/m^3 or 14.4 USD/ADt was determined.

During our pilot trial, flocs from PAC treatment were still present after DAF and self-cleaning discs of 100 μm (Fig. 1). Those flocs clogged pumps and safety filters; thus, frequent replacement of the cartridge filters was needed to comply with the quality required by pilot pEDR. Improvements in the DAF process and/or a better filtration system would be required to avoid clogging of the ED spacers. The utilization of advanced oxidation technologies as tertiary treatment is preferred, instead of coagulation, since the use of chemical coagulants increases the amount of inorganic salts in the effluent, and consequently, a larger dialysis plant would be needed to deal with these extra TDS.

From the electrodialysis viewpoint, it is necessary to protect the electrodes from scaling. As pEDR reverses the electrical polarity, both electrodes are prone to scale, because they work as anode and cathode in different cycles and it is well known that hydroxyl ions in the cathode could trigger the formation of insoluble species such as $CaCO_3$, $Ca(OH)_2$ and $Mg(OH)_2$ (Han et al., 2019). Some scaling was observed in the pilot trials, which was easily prevented by using diluted hydrochloric acid. However, in industrial conditions and in the long term, other measures, such as acidification of the electrode rinse solution and blocking the pass with monovalent cation exchange membranes, could protect these electrodes.

Finally, pEDR requires an ABS device to run at industrial scale. Alternatively, this function could be integrated with the power supply. Scaling up efforts are being carried out to address such aspects. The electronics must be adapted to work with high power applications (800VDC/100A), considering power supply protection against harmonics and thermal dissipation, thus complying with industrial safety standards.

4. Conclusions

pEDR is identified as a suitable technology for the desalination of wastewater in a Kraft pulp mill. Particularly, pEDR is as a robust solution to reduce fouling and pH swings at the end of each reversing cycle. Moreover, the utilization of pEDR allowed the extension of complete reversal (hydraulics) cycles, which translates into minimum production losses. For instance, compared to EDR, the production losses were reduced from 5 % to 0.6 %.

WinGEMS simulation indicated the accumulation of TDS, NPE's and heat, which are factors that may affect the mill under increased recirculation rates. The closing of circuits presents given challenges that must be addressed when scaling up, corroborating the models and adjusting the calculated parameters.

Finally, the brine management subprocess remains open. The additional treatment and disposal of this brine represents an extra cost and technical challenge, depending on the mill, a topic that was not considered in this study. Given the added costs of more extensive recovery, future work should be focused in affordable ZLD systems combining available technologies.

Author contributions

A. Gonzalez-Vogel: conceptualization and design of study, acquisition of data, formal analysis and/or interpretation of data, writing of the original draft, review & editing critically for important intellectual content, and approval of the version of the manuscript to be published. **J.J. Moltedo:** acquisition of data, formal analysis and/or interpretation of data, writing of the original draft, and approval of the version of the manuscript to be published. **O. J. Rojas:** conceptualization and design of study, formal analysis and/or interpretation of data, writing of the original draft, and approval of the version of the manuscript to be published.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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