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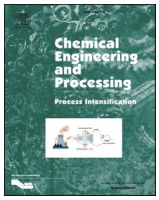

Investigation of ion-exchange membranes and erythritol concentration for the desalination of erythritol culture broth by electrodialysis

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ABSTRACT

Erythritol is a zero-calorie sugar substitute, safe for people with diabetes, that occurs naturally but is also commercially produced. Erythritol produced by fermentation must be separated from the rest of the cultivation broth. Electrodialysis (ED) may be used to separate and purify extracellular fermentation products, allowing simultaneous salt removal from the cultivation broth and generation of saline concentrate solution for reuse in a subsequent fermentation process. In the first stage, this study tested the performance of three membrane stacks and compared them to a reference membrane for erythritol purification. The diffusion of products and by-products was analyzed for the synthetic broth containing 5–25 g/L of erythritol. Product and by-product losses, current efficiency and energy consumption were compared among the tested membranes for the same salt removal rate. Step-wise voltage approach was demonstrated to have fewer product losses than the ED controlled by the constant current approach. Finally, erythritol culture broth after cultivation was treated with selected membranes and ED control based on the findings from the first part of the study. The erythritol losses were only 2% for the 94.8% desalination rate.

1. Introduction

Erythritol is a polyol naturally occurring in small amounts in some fermented food and fruits [29]. At industrial scale it is produced through biotechnological processes, likewise other polyols among which sorbitol, mannitol, xylitol, and maltitol [18]. Erythritol is a zero-calorie sweetener with a small molecular size. Erythritol cannot be broken by enzymatic batteries of the human body, because of that it is absorbed and excreted in the urine without changes [19]. Because it does not affect glucose and insulin levels, erythritol has been declared as a safe sugar substitute for people with diabetes [12,30].

Erythritol is produced at industrial scale by several microorganisms including osmophilic yeasts as *Yarrowia lipolyitica, Moniliella pollinis, Zygosaccharomyces* or *Hansenula*. Glucose is commonly used as a primary carbon source in the culture medium. Besides the carbon source, a mixture of macro- and micronutrients is required to allow yeasts' growth and efflux of osmolyte compounds. The production of osmolytes such as glycerol (considered the main by-product) and sugar alcohols (i.e. erythritol or mannitol), is induced when the osmophilic yeasts are exposed to high sugar or salt concentrations [18].

After the cultivation stage, erythritol needs to be purified. Firstly, the cultivation broth is membrane-filtered to remove microorganisms, followed by the treatments with ion-exchange resins (IER) to remove charged impurities. In the final step, the solution is discoloured on activated carbon, then the erythritol fraction is separated by preparative chromatography and concentrated by rotary evaporation to allow the crystallization of pure polyol [8,18,21]. Although IER achieve almost complete ion removal from the culture liquid, they eventually get saturated and require a regeneration step with acids and bases [8,9,21]. The intensive requirements of chemicals for the regeneration of IER lead to the generation of large amounts of waste, having a negative environmental impact. Further disadvantages of IER application are the high cumulative energy demand consisting in the energy required for pumping, regenerants production and wastewater treatment [10].

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Along with circular and green economy goals rises the demand for improvements in downstream technologies of bioprocesses. For the biotechnological production of erythritol, the focus shall be put on reducing the waste and recovering the salts from culture broth for their reuse in subsequent culture stages. Thus, erythritol culture broth can be treated by electrodialysis (ED) for its desalination and product purification. ED is an electro-membrane process that contains a membrane stack composed of pairs of anion- and cation-exchange membranes. Ion-exchange membranes (IEMs) can selectively remove cations and anions while uncharged components remain in the feed on the diluate side of the ED system.

The advantage of ED used for the downstream of the erythritol broth is threefold. Firstly, the broth can be desalted, enhancing the erythritol isolation in subsequent steps. Secondly, the salts removed from the feed can be concentrated in the concentrate chamber and reused in the following culture batch. Thirdly, ED has almost zero discharge and less need for maintenance chemicals compared to the commonly used IER in the purification of culture broths [32]. Additionally, ED can be driven by green energy, lowering the carbon footprint [2,4].

IEMs are polymeric membranes with embedded charged groups that allow the passage of counter-ions while rejecting co-ions [22]. The transport of counter-ions is well described by the extended Nernst-Planck equation comprehending electromigration, convection and diffusion of ions through the membrane phase [15]. Although electromigration is the main constituent of ion transport, IEMs have an interstitial phase between the fixed charged groups within which co-ion transport is possible [15]. These voids in the membrane structure are electro-neutral. Thus, when the membranes get in contact with a feed solution, some of the non-ionic compounds can diffuse from the feed towards the concentrate chamber. The diffusional phenomenon leads to product losses in the separation process. Erythritol's diffusional potential is increased due to its concentration in solution and its molecular size, which may be especially concerning in the ED treatment.

Erythritol diffusion is also influenced by other operational and setup parameters such as current/voltage application mode and IEM characteristics. The regulation of the applied current/voltage may have a direct effect in the control of the diffusional effects. In this regard, a step-wise current/voltage control may reduce diffusional effects compared to the common constant current/voltage approach [3,11].

Properties of ion-exchange membranes in ED strongly differ depending on fabrication method, membrane material and its homogeneity, ion-exchange group and capacity, membrane thickness and swelling [22,31]. Various manufacturers, such as Fumatech GmbH (Germany), SUEZ (United States), PCCell (Germany), offer commercial IEMs for broad applications, always striving to develop products with high ion selectivity, low resistance, and low swelling.

Our previous research assessed ED as an alternative process for removing ions from a synthetic erythritol culture broth containing 5 g/L erythritol, 5 g/L glycerol and 2 g/L glucose. The outcome of this previous study reported low levels of losses in products and by-products ($\leq$ 2%), and 53% current efficiency for obtaining a desalination level of 96% [7]. The conclusions of our previous work led to new questions about the separation performance at different concentration of products, and the current efficiency that we could reach using different membrane stacks. In this work, we aimed to get a better understanding of the product losses and the ED current efficiency. For this, three new membrane stacks were assembled and their performance and response to different erythritol concentrations were evaluated. The results of newly purchased membranes were compared to the reference membrane stack used in the previous study [7]. The limiting current density and the membrane resistance were determined in the first stage of experiments for the investigated membranes. Diffusional phenomena, product losses, current efficiency and energy consumption were compared among four membrane stacks in the second experimental stage to select an optimal membrane for the third stage of the experiments. In the third stage, the focus was put more on the behavior of the chosen membrane stack with increments of product concentration. Further on, fourth stage included step-wise voltage and constant current ED control were compared. Finally, in the fifth experimental stage, erythritol culture broth after cultivation was treated by ED based on the previously obtained parameters.

2. Materials and methods

2.1. Solutions (synthetic and culture broth)

A synthetic solution containing only salt fractions from the erythritol culture broth was used as an initial solution in all the experiments with the synthetic broth. The composition of initial solution (S4) is presented in Table 1. In all experiments S4 solution was placed in the concentrate chamber as the receiving medium for recovered salts. On the other hand, for those experiments involving non-ionic components, the solution of the diluate compartment was prepared by adding erythritol in different concentrations, glycerol and glucose to the S4 initial solution. The solution S4 with addition of products and by-products represented a synthetic erythritol broth (SEB). Glycerol by-product was selected as the most prominent and likely to be present in the real culture broth, whereas glucose is a reference residual carbon source [8]. Further on, S4 solution was diluted to S1-S3 solutions for the purposes of LCD tests.

All the reagents used in this study were purchased from Merk KGaA (Darmstadt, Germany). The salts $(NH_4)_2\ SO_4$, $MgSO_4\ 7H_2O$, KH_2PO_4, $FeSO_4\ 7H_2O$, $MnSO_4\ H_2O$, $ZnSO_4\ 7H_2O$, $CaCl_2\ 2H_2O$, and NaCl were analytical grade. Erythritol, glycerol and glucose used were HPLC grade.

2.1.1. S1, S2, S3 and S4 solutions for the LCD determination

S1, S2, S3 solutions were prepared diluting the initial S4 solution by dilution factors of 18, 3.9 and 1.7. S1–S4 were used for limiting current density tests and for setting the step-wise ED operating mode.

2.1.2. Solutions for the first experimental stage

S4 solution in the diluate compartment was prepared by adding 5 g/L erythritol ($C_4H_{10}O_4$), 5 g/L glycerol ($C_3H_8O_3$) and 2 g/L glucose ($C_6H_{12}O_6$) (SEB_5 in Fig. 1).

2.1.3. Solutions for the second experimental stage

S4 solution in the diluate compartment was prepared adding 15 g/L erythritol (SEB_{15} in Fig. 1), and in the following experiments the erythritol concentration was increased to 25 g/L (SEB_{25} in Fig. 1). Glycerol and glucose concentrations remained unchanged, 5 g/L and 2 g/L, respectively.

2.1.4. Erythritol culture broth

Final experiments were done with a real erythritol culture broth (ECB) that was prefiltered (microfiltration with 0.3 μm pore size) and placed in the diluate side, whereas S4 solution was in the concentrate chamber for receiving the salts from the culture broth.

2.2. Technical equipment

Laboratory scale electrodialysis ED 64004 (PCCell GmbH,

Table 1
Characterization of initial solution S4.

Compounds in S4	Molecular formula	[g/L]
Ammonium sulfate	$(NH_4)_2\ SO_4$	1.4
Magnesium sulfate heptahydrate	$MgSO_4\ 7H_2O$	0.5
Potassium dihydrogen phosphate	KH_2PO_4	4.2
Ferrous sulfate heptahydrate	$FeSO_4\ 7H_2O$	0.0025
Manganese sulfate monohydrate	$MnSO_4\ H_2O$	0.00085
Zinc sulfate heptahydrate	$ZnSO_4\ 7H_2O$	0.0007
Calcium chloride dihydrate	$CaCl_2\ 2H_2O$	0.001
Sodium chloride	NaCl	0.8

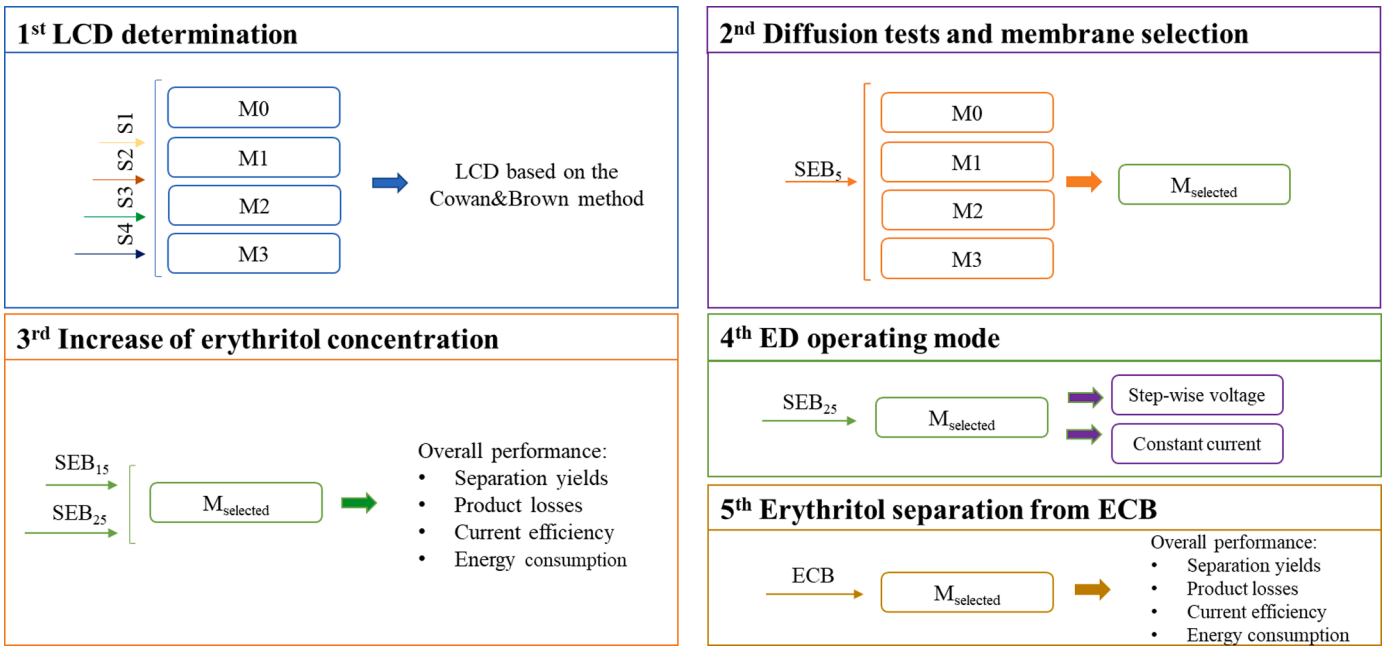

Fig. 1. Scheme of five experimental stages for the membrane selection and overall performance of erythritol separation by electrodialysis under various erythritol concentrations and operating conditions. SEB – synthetic erythritol broth containing 5 g/L (SEB_5), 15 g/L (SEB_{15}) or 25 g/L (SEB_{25}) erythritol; ECB -erythritol culture broth.

Heusweiler, Germany) with built-in pH, temperature and electrical conductivity probes was used for this study. 1.5 L of diluate and 1.5 L of concentrate were circulated with a flow rate of 15 L/h (linear velocity of 0.012 m/s), and the electrode-rinse solution (0.25 M Na_2SO_4) with a flow rate of 150 L/h, in all ED experiments. ED outlet pipes were adjoined for the limiting current density tests in order to achieve stationary conditions. On the contrary, the concentrate and diluate streams were completely separated in the erythritol purification experiments and diffusion analysis. The temperature was controlled with cooling water to maintain 22.5 ± 1 ºC throughout all experiments.

2.3. Membranes

A 10-cell pair ED stack was assembled from different cation- (9xCEM) and anion-exchange membranes (10xAEM) to test them for erythritol purification. Membranes were cut to the active membrane area of 64 cm^2. The reference membrane pair (M0, PCCell GmbH, Heusweiler, Germany) was from the previous research on the erythritol broth treatment by electrodialysis [7]. Membrane stacks M1 (SUEZ Water Technologies & Solutions, Pennsylvania, United States), M2 and M3 (Fumatech GmbH, Bietigheim-Bissingen, Germany) were tested in this study. All tested membrane stacks had the same end-membranes (End-M in Table 2) and polypropylene spacers (0.45 mm). Membrane specifications are presented in Table 2.

2.4. Experimental approach

Fig. 1 depicts five experimental stages performed within this study. The first stage obtained LCD tests for S1-S4 solutions in M0-M3 ED membrane stacks (LCD determination). The criteria for selecting an ion-exchange membrane embraced results from LCD tests and second experimental stage (2nd). 2nd stage included diffusion tests and erythritol separation of 5 g/L erythritol from a synthetic erythritol broth (SEB_5). Erythritol concentrations were increased to 15 g/L (SEB_{15}) and to 25 g/L (SEB_{25}) in the third experimental stage (3rd), that included diffusion tests and erythritol separation. Step-wise voltage and constant current ED operating mode were compared in the fourth experimental stage (4th) and finally erythritol was separated from a real erythritol culture broth in the fifth experimental stage (5th).

2.5. First stage - Limiting current density (LCD) determination

Synthetic solutions S1–S4 without products and by-products were put in both diluate and concentrate chambers to define LCDs of each

Table 2
Membrane characteristics of the reference membrane stack (M0) and tested membrane stacks (M1-M3).

Membrane stack	Membrane	Type	Thickness [μm]	Resistance [Ω cm^2]	Selectivity[a] [%]	Ion-exchange capacity[b] [meq/g]
M0	PC-SA	AEM	100–110	~ 1.8	>95	0.1/1.2[c]
	PC-SK	CEM	100–120	~ 2.5	>96	3
M1	AER103P	AEM	570	9.4	92	2.4
	CR61P	CEM	580	10	94	2.2
M2	FAS-PET-130	AEM	120–140	1.7–3.0	93–97	1.0–1.3
	FKS-PET-130	CEM	120–140	2.4–4.0	96–99	0.8–1.0
M3	FAB-PK-130	AEM	115–138	<4	95	0.8
	FKL-PK-130	CEM	120–140	3–10	96–99	0.6–0.8
End-M	PC-MTE	CEM	220	~ 4.5	>94	1.8

[a] selectivity 0.1 / 0.5 mol/kg KCl at $T = 25$ °C, determined from membrane potential measurement in a concentration cell.
[b] AEM: ion exchange capacity (in Cl^- form), CEM: ion exchange capacity (Na^+ form).
[c] strong basic (meq·g^{-1})/weak basic (meq·g^{-1}).

tested membrane stack. LCD is mainly governed by the salt content, while uncharged molecules have a minor impact on LCD when other parameters (i.e., temperature, flow) are maintained constant. The steady-state condition was achieved by mixing the membrane outlets and evenly distributing the mixed solution in the diluate and concentrate inlet. The voltage was increased step-wise from 3 – 29 V in 0.5 V increments. LCD was determined based on the Cowan and Brown method [6].

The same LCD experiments were done for the reference membrane stack M0. The ED operation mode was determined based on the M0 results for the second stage of experiments – testing M1–M3 performances in erythritol purification.

2.6. Second stage - Diffusion experiments and membrane selection

Three membranes M1-M3 were tested for diffusional behavior of erythritol, glycerol and glucose from the diluate towards concentrate. The solution containing salts, products and by-products (SEB) was placed on the diluate side, whereas salt solution (S4) was placed in the concentrate chamber. Both feeds were circulated (15 L/h) for 80 min without applying an external electrical field. Samples were taken from the diluate and concentrate every 20 min for product/by-product analysis.

Three ED membrane stacks M1–M3 were tested for the erythritol separation from the salt content in the culture broth (Table 1) by ED with external electrical field and compared to the reference membrane M0 (Table 2). Step-wise voltage was applied for the ED control, as explained in the previous research, where four different voltages were applied accordingly with the reduction of conductivity [7], until the 94% desalination was reached. Samples were taken from the diluate and concentrate at the beginning and end of the ED desalination for ion analysis, and every 20 min for product/by-product analysis. The assessed ED operation parameters were: salt removal efficiency, current efficiency, product and by-product leakage from the diluate to the concentrate, and energy consumption.

2.7. Third stage – effects of increase in erythritol concentration

The ED stack with the lowest product losses, highest current efficiency and lowest energy consumption was applied for further experiments in the second stage. Ideally, the erythritol concentrations are high, whereas the by-product and remaining glucose concentrations are low in an optimized cultivation for erythritol production. The membranes need to retain the products and by-products, inhibiting their diffusion and passage towards the concentrate.

Diffusion tests were also done in the second stage of testing the M2 membrane. The erythritol concentration was increased to 15 g/L and 25 g/L, while glycerol and glucose concentrations remained the same as in the second experimental stage. Samples were taken from the diluate and concentrate every 20 min for product/by-product analysis.

Erythritol from SEB containing 15 g/L and 25 g/L of erythritol were separated with M2 membrane stack and the same stepwise voltage control as in the second stage. Samples were taken from the diluate and concentrate at the beginning and end of the ED desalination for ion analysis, and every 20 min for product/by-product analysis.

2.8. Fourth stage - ED operating mode

Besides choosing an optimal ion-exchange membrane, the ED operating conditions may impact the transport mechanisms of charged and uncharged particles from the diluate towards the concentrate. Thus, the variations in current density, constant current (21.9 A/m^2) and step-wise voltage (10 V, 9 V, 7 V, 6 V) were compared in the scope of this study. Step-wise voltage was regulated based on the online measurements of the diluate conductivity to prevent exceeding current densities, and according to the LCDs values (see Supplement). Samples were taken from the diluate and concentrate at the beginning and end of the ED desalination for ion analysis, and every 20 min for product/by-product analysis.

2.9. Fifth stage - Treatment of the erythritol culture broth

A real erythritol culture broth (ECB) was treated by ED with M2 membrane stack and step-wise voltage control (10 V, 9 V, 7 V, 6 V). Samples were taken from the diluate and concentrate at the beginning and end of the ED desalination for ion analysis, and every 20 min for product/by-product analysis.

2.10. Analytics

PO_4-P and NH_4–N were determined with continuous flow analysis and photometrical detection (Skalar, Netherlands) according to DIN EN ISO 6878 and DIN EN ISO 11,732 standards, respectively. Anions (Cl-, SO_4^{2-}) were analyzed according to DIN EN ISO 10,304–1 and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) according to DIN EN ISO 14,911 standard, using high performance ion chromatography (Metrohm AG, Switzerland). Erythritol, glycerol, and glucose were determined using High-Performance Liquid Chromatography (HPLC) (Shimadzu, Kyoto, Japan), equipped with a refractive index detector RID-20A (Shimadzu, Kyoto, Japan). The mentioned compounds were separated on a Aminex HPX-87H column (78 × 300 mm) with a guard column Shodex Sugar SH-G (6.0 × 50 mm). The separation was performed at an isocratic flow of 0.6 mL/min. The mobile phase used was 5 mM H_2SO_4. The retention time of glucose, erythritol and glycerol are 9.021 min, 11.696 min and 13.447 min respectively. The oven and RID temperature were 50 °C.

2.11. Data analysis and calculations

The overall diffusion and flux [mmol/(m^{2}s)] of products and by-products through the membrane were calculated by the following equation:

$$J = \frac{V_c c_c^i}{ANt} \tag{1}$$

Where V_c [L] is the concentrate volume; c_c^i [mmol/L] is the concentration of component i that diffused to the concentrate solution; A [m^2] is the effective area of a single membrane; N is the number of membranes ($N = 19$); t [s] is the ED process time.

Energy consumed [kWh/m^3] for the desalination of the erythritol broth was calculated as follows:

$$E = \int_0^t \frac{U_t I}{V_d} d_t \tag{2}$$

Where U_t [V] is the voltage drop at time t [h]; I [A] is the electrical current; V_d [L] is the diluate volume.

Current efficiency [%] was calculated according to the following equation:

$$CE = \frac{(c_t - c_0) z V F}{NIt} * 100 \tag{3}$$

Where c_0 and c_t are the concentration of ionic species at time zero and time t in the diluate; z is the ionic valence; F is the Faraday constant [96,485 C/mol].

3. Results and discussion

3.1. First stage - LCD determination

3.1.1. Membranes' resistance and limiting current density

Fig. 2 demonstrates the resistance of each tested membrane stack

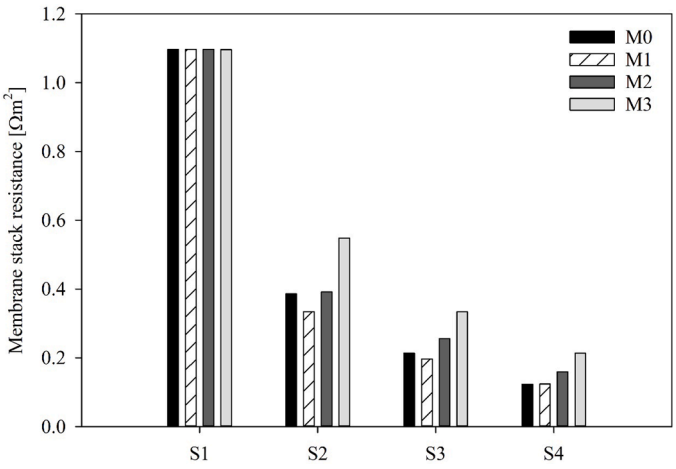

Fig. 2. The resistance of M0–M3 membrane stacks for applied 12 V in LCD test of four salt solutions with increasing salt content. S4 is the initial solution to be treated, whereas S1 represents the desired final solution after the ED treatments.

treating S1-S4 solution for the applied 12 V, which represents a middle value of the applied voltage range (3 – 29 V). The overall resistance was very high (1.1 Ωm^2) and equal in M0–M3 stack for S1 solution, representing the desired final diluate quality, due to its low ionic strength. In general, the resistance decreased and the LCD increased with an increasing salt concentration of the treated feed. At the low salt concentrations (<1 mol/L) the overall resistance is high and the contribution of the concentration boundary layer at the membrane/solution surface should not be neglected [25]. High resistances are reasonable as the S4 solution has the salt concentration of 0.1 mol/L. Additionally, diffusional transport is expected to have a high contribution to the transmembrane ion transport. The membrane stack resistance in LCD experiments had the same trend among the tested membranes for the whole diapason of applied voltages 3 – 29 V. Cowan&Brown plots with indicated membrane resistance are in Supplement.

A clear inflection point in ED stack resistance with increasing current density was observed for all ran experiments of the LCD assessment. The obtained LCD values of each tested membrane stack depending on the solution's conductivity are presented in Table 3. M1 membrane was expected to have the lowest LCDs due to the largest membrane thickness and the highest specific membrane resistance (Table 2). However, the highest ion exchange capacity of the M1 membrane stack led to the lowest overall resistance. Conversely, the M3 stack had the highest overall resistance for S2–S4 solutions (Fig. 2). M3 are polyketone reinforced membranes with high proton and hydroxyl blocking capability and low ion exchange capacity that resulted in low LCDs (Table 3).

Among the membranes, the LCD progression for a particular salt solution (S1–S4) could not be correlated to the membrane-specific thickness, resistance, or ion exchange capacity. M1 and M2 membrane stacks had the most similarities with the reference membrane M0, whereas M3 had up to 70% lower LCDs.

Table 3
LCDs reached within M0–M3 membrane stacks for salt solutions S1–S4 with their measured electrical conductivities.

Solution	Conductivity [mS/cm]	LCDs [A/m²]			
		M0	M1	M2	M3
S1	0.3	6.2	6.2	6.2	6.2
S2	1.4	35.9	42.2	35.9	10.9
S3	3.0	70.3	56.2	51.6	21.9
S4	5.6	157.8	156.2	157.8	135.9

3.2. Second stage – diffusion tests and membrane selection

3.2.1. Diffusion of products and by-products

Diffusion experiments were done as a single run, without current/voltage application. Diluate, containing salts, products and by-products (SEB), and concentrate, containing salts only (S4), were circulated for 80 min. The overall diffusion of erythritol (5 g/L), glycerol (5 g/L) and glucose (2 g/L) from the diluate to the concentrate solution was not detected in M2 and M3. The presence of products in the first sample of M1 concentrate indicates the insufficient cleaning procedure before the experiments. However, after the mass balance of initial and final samples there was no indication of diffusional phenomena. More thorough cleaning is required for the ED system treating erythritol broth. Cleaning steps depend on the characteristics of the treated feed and some cleaning strategies are suggested in the study of Merino-Garcia et al., [17]. There was no detection of non-ionic compounds in the electrode-rinsing solution of all performed diffusion experiments.

3.2.2. Desalination of synthetic erythritol broth (SEB)

The set endpoint of the ED process was 93.6% feed desalination based on the online conductivity measurements. However, the desalination velocity (% removed salts/min) varied between the membrane stacks. The highest desalination velocity was for the reference membrane M0 (1.1%/min), followed by M1 (1%/min) and M2 (0.97%/min), whereas M3 had a significantly lower salt removal velocity (0.51%/min) for the same applied electrical field. M3 contains CEMs and AEMs with lower ion exchange capacity compared to M0–M2 membranes, which significantly prolonged the desalination time.

The average desalination rate for individual ions had the same trend at the end of ED in all tested membrane stacks (Table 4):

Only phosphates and sodium ions had removal efficiencies below 90% in M1–M3 experiments. PO_4-P was less removed due to the increased presence of H_3PO_4 at the pH < 4 [5,24]. Namely, the diluate pH dropped from ~4.6 to ~3.7 in M1–M3. In the M0 serial, the diluate pH did not drop below 4, having the complete fraction of $H_2PO_4^-$ that led to the higher P removal. K^+ was better removed than Na^+ because of the feed's two times higher potassium molar concentration and its higher electrical mobility [1,23]. The electrostatic attraction between the membrane and ions increased with increased ionic charge. Thus, almost all performed experiments achieved complete removal of divalent cations and above 95.4% of sulfate removal.

3.2.3. Product purification

Product and by-product losses were observed in M1, similar to the reference M0 [7]. Higher concentrated erythritol and glycerol (~5 g/L) started permeating towards concentrate between 60 and 90 min of the processing time. 1.3 ± 0.05% of erythritol and 1.8 ± 0.02% of glycerol losses were recorded in M1 experiments. In the reference membrane, less than 2% of products were found in the concentrate after 40 min of treatment (Daza-Serna et al., [7]). Contrary, glucose (~2 g/L) was not detected in the concentrate of M1–M3 experiments. This behavior can be assigned to the lower initial glucose concentration. Steric exclusion mechanisms [13,14] might also impact the permeation of non-ionic species. For example, glucose is a molecule with six carbon atoms existing mainly as pyranose cyclic form in aqueous solutions (>99%). Thus, the ion exchange membranes may block the passage of bigger glucose molecules better than the four-carbon erythritol and three-carbon glycerol. However, this study could not thoroughly analyze steric effects due to the other governing transport mechanism. The concentrate of M2 and M3 runs remained pure saline until the end of the feed desalination, performing even better than M0–M1 membranes. The advantage of the M2 membrane was a significantly lower resistance (Fig. 2) and a shorter process time (97 min) than ED with the M3 stack (184 min).

A concentration factor of 1.8 was reached for the ions in the concentrate of all (M0–M3) experiments. The maximum recorded

Table 4
Average desalination efficiency of anions and cations using four different membrane stacks (M0-M3).

Membrane stack	PO_4-P %	NH_4–N %	Cl %	SO_4 %	Na %	K %	Ca %	Mg %
M0	91.0	91.8	99.0	95.4	88.4	95.0	n.d.	93.7
M1	86.7	94.9	93.9	98.2	68.1	94.2	100	100
M2	86.3	96.3	92.4	98.2	88.0	93.9	100	97.1
M3	89.8	99.9	94.1	96.5	87.7	97.5	100	100

decrease of diluate volume was 4.7%, caused mainly by sample uptake and partially by the osmotic water transport from the diluate towards the concentrate [26]. The diluate densities dropped by 0.32 ± 0.017% from the average value of 1.005 g/cm^3 due to the salt removal, and the concentrate densities increased for 0.34 ± 0.018% from the average value of 1.002 g/cm^3 with increased salt concentration.

The current efficiency was the lowest for the reference M0 membranes (53%), and the highest for the M2 membrane stack (71.9%), as shown in Fig. 3. The current efficiency trend among M0–M3 membranes could not be correlated to the operational current, charge or membrane resistance. The higher ion-exchange capacity of AEMs of M1 and M2 membrane stacks had a major impact on the higher current efficiency compared to M0 and M3 membranes (Table 2). The M0–M2 had lower resistance than M3 membranes (Fig. 2) and, followingly, the shorter desalination time (81–98 min) and lower energy demand. The energy consumption for desalination of synthetic erythritol broth was the lowest in the ED assembled with M2 membranes (Fig. 3).

Finally, M2 membranes outperformed reference and other tested membranes (M0, M1 and M3) regarding higher current efficiency and high retention of products and by-products. The membrane resistance and energy consumption were in the range of values obtained in M0 and M1 and lower than in M3. The results from the first stage of experiments indicate a preferable selection of the M2 membrane stack for further ED investigation in erythritol isolation.

3.3. Third stage – effect of increase in erythritol concentration

Based on the results from the previous section, the M2 membranes were applied for further experiments on the optimization of the erythritol purification step. Effects of the increments in the product concentration and the current application were analyzed in the ED desalination with the M2 stack.

3.3.1. Diffusion of products and by-products

Ideally, cultivation processes are optimized to intensify erythritol production and to minimize the evolution of by-product. Thus, diffusion tests were also done in the second stage of testing the M2 membrane, increasing the erythritol concentration from 5 g/L to 15 g/L and 25 g/L in SEB. On the contrary, the by-product concentrations remained the same as in the first stage. As previously reported, with 5 g/L of erythritol in the feed, no detectable amounts were measured in the concentrate fraction. The overall diffusion of the erythritol increased with increased initial erythritol concentration (Fig. 4a) and increased contact time between the feed and the membrane surface (Fig. 4b). The overall erythritol diffusion was 1.2 × 10^{-6} mol/(m^{2}s) and 2.1 × 10^{-6} mol/(m^{2}s) for 0.00045 mol/L (15 g/L) and 0.00079 mol/L (25 g/L), respectively. Interestingly, the overall diffusion of the glycerol (5 g/L) appeared with the increased erythritol concentration, but it remained at the same rate for the feed containing 15 g/L and 25 g/L of erythritol (Fig. 4). Therefore, a co-transport of glycerol with erythritol diffusion was observed, but it reached its limiting diffusional rate of 1.2 × 10^{-6} mol/(m^{2}s). Most probably the membrane swelling was altered with increased erythritol

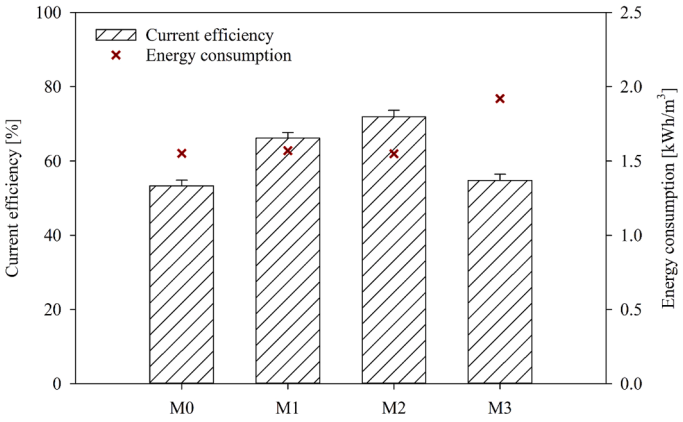

Fig. 3. Comparison of current efficiency and energy consumption for desalination of erythritol broth among four tested membranes (M0–M3).

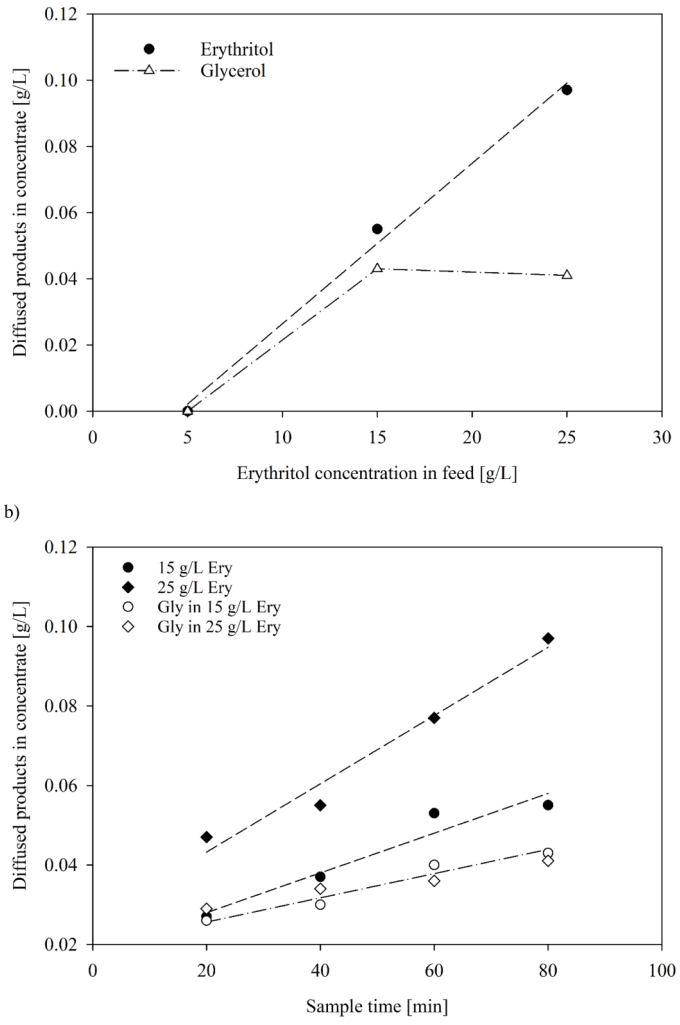

Fig. 4. a) Diffusion of erythritol and glycerol from the feed towards concentrate depending on the erythritol concentration in the feed; b) Evolution of erythritol and glycerol diffusion over circulation time. "Ery" stays for erythritol and "Gly" for glycerol.

concentration, which further caused glycerol diffusion. A decrease in membrane volume with increased salt concentration of feed was already reported in literature [27], but the impact of the uncharged compounds on the membrane swelling needs further research. The results of this research show a clear dependence of diffusional rate on the molar concentration of carbon compounds as dominating transport effect (molar glycerol concentration was 0.00045 mol/L).

Erythritol losses of 0.36% and 0.41% were recorded for the feeds containing initially 15 g/L and 25 g/L of erythritol, respectively. The glycerol losses were 0.84% in both cases. Diffusion is concentration-dependent, thus, glucose (2 g/L) remained in the diluate for all performed experiments.

3.3.2. Erythritol purification and conservation

SEB containing 15 g/L and 25 g/L erythritol were desalinated by ED and compared. In Fig. 5, the erythritol flux in ED desalination and its diffusional rate from previous experiments increased with increasing initial concentrations. The transport of erythritol was intensified with the application of the external electrical field, although the desalination time for 15 g/L and 25 g/L was prolonged for only 5–8 min compared to the diffusion experiments (80 min). The product losses increased from ~0.4% (only diffusion) to 0.53% due to the co-transport with ion migration through ion-exchange membranes. Ions are surrounded by water molecules that enable some non-ionic compounds to pass through the membrane matrix beside their diffusion through the interstitial membrane phase. Molar flux of glycerol was slightly higher (1.3×10^{-6} mol/(m^{2}s)) than its diffusional rate of (1.2×10^{-6} mol/(m^{2}s)). Thus, the glycerol losses were 0.98–1.1%.

The current efficiency and the energy consumption remained in the same range, 70% and 1.5 kWh/m^3, respectively, for the desalination of the feed containing 5–25 g/L erythritol. Thus, the membrane characteristics and the salt content were the major factors impacting the current efficiency, desalination duration and energy demand.

3.4. Fourth stage - ED operating mode

The previous experiments showed that the erythritol diffusion from the feed to the concentrate increases with the increasing contact time between the feed and the membranes (Fig. 4a). Thus, the step-wise voltage control was adopted for the erythritol purification in order to intensify the ED process and reduce the product losses. Commonly, a low current density corresponding to 75 – 80% of the limiting current density determined for the final feed quality (S1 in this case) is applied throughout the desalination process [11,16,25]. Therefore, the step-wise voltage approach was compared with the constant current approach within this research. The applied constant current density was 21.9 A/m^2 and the M2 membrane stack was utilized. Normally, 6.2 A/m^2 would be adopted according to

Table 3 for S1 solution. However, the current density between S1 and S2 solutions was chosen due to the very high membrane stack resistance when treating S1 solution.

The 93.6% desalination rate of 25 g/L erythritol broth was prolonged 1.5 times for constant current versus step-wise voltage approach (Fig. 6). Although the diffusional rate was somewhat lower in the ED controlled by the constant current approach (2.4×10^{-6} mol/(m^{2}s)), the product and by-product escape towards concentrate was higher due to the prolonged membrane/feed contact time. The losses of erythritol were 0.78% and of glycerol 1.2%, whereas the glucose was not detected in the concentrated fraction. On the contrary, losses of erythritol were 0.53% and of glycerol 0.98% in the step-wise controlled ED. The current efficiency for ED with constant current dropped to 55%, whereas the energy consumption was slightly reduced to 1.38 kWh/m^3. Current density has insignificant role in salt transport number [25], but the increased current density, as it was in the step-wise approach, increased the current efficiency. The salt removal velocity was 0.72%/min and lower than in the step-wise ED (1%/min).

3.5. Fifth stage - Erythritol culture broth

In the final step, erythritol was separated from the culture broth (ECB) by ED adjusted according to the previously obtained results. M2 membranes and step-wise voltage were used to minimize product losses. The feed contained 23.81 g/L erythritol, 37.92 g/L glucose and 0.99 g/L glycerol. Some other polyols were found in the culture broth, but they remained at the same concentration level in the feed during the entire desalination. The ECB treated in this work did not present a complete glucose consumption. The ionic content of the real broth was: 610 mg (PO_4-P)/L, 729 mg (NH_4—N)/L, 444 mg (Cl^-)/L, 419 mg (SO_4^{2-})/L, 224 mg (Na^+)/L, 996 mg (K^+)/L, 21 mg (Ca^{2+})/L, 4 mg (Mg^{2+})/L. The same S4 solution as used in previous experiments, containing salts solely, was placed on the concentrate side.

The desalination rate was 94.8% and the ED time was 241 min. The removal efficiency for specific ions was: 95.7% PO_4-P, 90.8% NH_4—N, 94.8% Cl^-, 89% SO_4^{2-}, 92% Na^+, 95.7% $K^+$and 100% for $Ca^{2+}$and Mg^{2+}, and similar to the values obtained in Table 4.

The transport of glucose and erythritol from the feed towards the concentrate was recorded already after one minute of the circulation

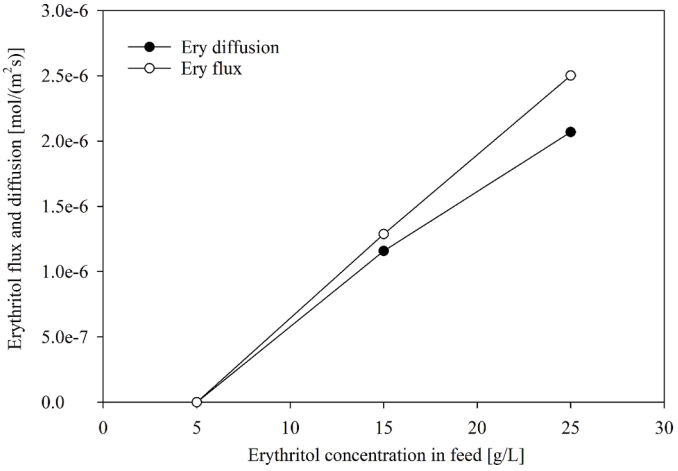

Fig. 5. Diffusion of erythritol from the feed containing 5 g/L, 15 g/L and 25 g/L of erythritol towards the concentrate solution (black circles); Erythritol flux in the ED desalination that includes overall diffusion and co-transport with ionic species driven by the external electrical field (white circles).

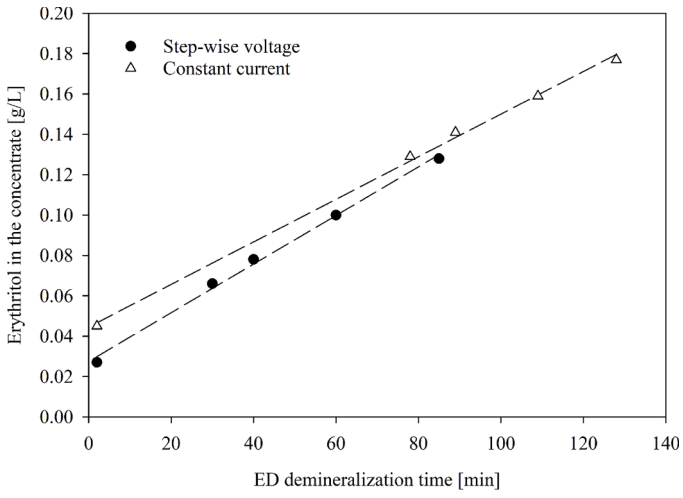

Fig. 6. Evolution of erythritol in the concentrate during the desalination of 25 g/L erythritol broth by ED with applied step-wise voltage vs. constant current.

step, and it gradually increased over the ED process time (Fig. 7). Both glucose and erythritol molar fluxes decreased over ED time as their concentration in the feed decreased and as the ionic transport decreased. The erythritol and glucose molar fluxes significantly differed with the desalination time. Glucose molar flux was lower, although the initial molar concentration of glucose in the feed was higher (0.21 mol/L) than erythritol (0.19 mol/L). Differences in molecular structure and properties led to divergences in molar fluxes [33]. Erythritol is a smaller (~0.4 nm) and open-chain molecule compared to glucose (~1 nm) that appears in cyclic form in solutions. These chemical properties allow higher erythritol transmembrane migration. Erythritol flux was eventually the same as in the experiments performed with the synthetic solution (Fig. 5 and Fig. 7). The glucose and erythritol losses from the real culture broth were 4.7% and 5.6%, respectively. However, only 1.2% glucose and 2% erythritol from the feed were detected in the concentrate compartment. Therefore, it should be concluded that the remained polyol losses adsorbed in the IEMs, blocking the membrane-free volume [24,28]. IEM fouling leads to poorer desalination performance, lower current efficiency, and higher energy consumption [17,20,33]. The effects of membrane fouling by erythritol and glucose require further research. Glycerol was not detected in the concentrate fraction.

The salt concentration factor in the concentrate was 2.6 due to the higher ionic content of the real culture broth (7.9 mS/cm) compared to the synthetic one (5.6 mS/cm). The 1.3 times increased salt content of the real broth led to 82% higher energy consumption than the M2 trials with the synthetic culture broth. The presence of polyols and other organic compounds originating from microbial cells may have also prolonged the desalination process. The lower current efficiency (51%) may be assigned to the higher concentration of by-products and to the possible remains of microbial cells.

4. Conclusion

This research investigated membrane performance for erythritol broth desalination by electrodialysis to reduce erythritol losses and increase current efficiency. Afterward, the best-performing membrane pair was further investigated for the treatment of feeds with higher erythritol concentrations.

Limiting current density was in a similar range for M0–M2 membrane stack, whereas the M3 had up to 70% lower values due to the higher stack resistance. M2 membrane pair, composed of FAS-PET-130 (AEM) and FKS-PET-130 (CEM) (Fumatech GmbH, Germany), had higher current efficiency (79.1%) and high retention of products and by-products (100% for the feed containing 5 g/L erythritol), while the membrane resistance and energy consumption (1.5 kWh/m^3) were in the range of values obtained in M0 and M1 and lower than in M3. Thus, M2 was applied in the second experimental stage for the purification of higher concentrated synthetic erythritol broth. Erythritol losses increased from 0% to 0.36% and 0.41% for the feeds containing initially 5 g/L, 15 g/L and 25 g/L of erythritol, respectively. Additionally, erythritol losses increased by ~0.1% under the electrical field compared to solely diffusion.

Step-wise voltage control of the ED process showed better results than constant current control because of the reduced product losses, mainly governed by the reduced contact time between the feed and the ion-exchange membranes. The energy consumption was similar for the same desalination rate performed with lower constant current and step-wise voltage (1.4 – 1.5 kWh/m^3). In contrast, the current efficiency was higher for the step-wise approach (70%) compared to the constant current (55%).

Finally, optimized ED operation was applied for the desalination of the erythritol culture broth after cultivation, containing almost the same erythritol and glucose molar concentrations (~0.2 mol/L). Erythritol molar flux was higher than glucose due to the smaller molecular size. 1.2% glucose and 2% erythritol from the feed were detected in the concentrate compartment. The higher salt content in the culture broth led to higher product and by-product losses because of the prolonged desalination time.

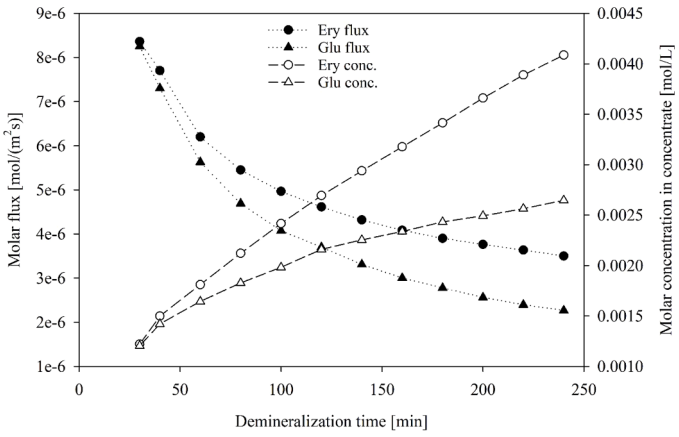

Fig. 7. Evolution of the erythritol (Ery) and glucose (Glu) molar fluxes from the feed to the concentrate in the ED desalination of the real erythritol culture broth. The evolution of Ery and Glu-concentrations in the concentrate is on the right y-axis.

Author contributions

Conceptualization: K.K. and L.D.; methodology: K.K. and L.D.; validation: K.K., L.D., N.K., J.K., A.F., A.M., and R.M.; formal analysis: K.K.; investigation: K.K and L.D.; resources: A.F., A.M., R.M., J.K., and N.K.; data curation: K.K. and L.D.; writing-original draft preparation: K.K.; writing-review and editing, L.D., A.M., A.F., R.M., J.K., and N.K.; visualization, K.K.; supervision: A.F., A.M., R.M., and J.K.; project administration: A.F., A.M., R.M., J.K.; funding acquisition: A.F., A.M., R.M., J. K., and N.K. All authors have read and agreed to the published version of the manuscript."

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Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Laura Daza-Serna reports financial support was provided by Conzil Estate GmbH. Conzil Estate GmbH filed a patent (EPO application no. 21 216 448.7) related to the content of this study. has patent #EPO application no. 21 216 448.7 issued to Conzil Estate GmbH.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cep.2023.109494.

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