



# Comparison of ion removal from waste fermentation effluent by nanofiltration, electro dialysis and ion exchange for a subsequent sulfuric acid recovery

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## ARTICLE INFO

Editor: G. Palmisano

### Keywords:

Pretreatment  
Nanofiltration  
Electrodialysis  
Ion-exchange resins  
Nutrient recycling  
Fermentation wastewater  
Downstream process

## ABSTRACT

Nutrient recovery from wastewater in the form of acids/bases by electro dialysis with bipolar membranes or diffusion dialysis facilitates the current demand for a green economy and circular production. However, bipolar membranes are sensitive to scaling, mainly by calcium and magnesium salts, as well as to biofouling caused by microbial growth and linked aspects. This work aimed to reduce divalent cations to a value below 10 ppm and DOC content of a residual liquid waste stream after microbial fermentation and before a bipolar electro dialysis/diffusion dialysis step for nutrient and acid/base recovery. In this context, three pretreatment technologies were analyzed: nanofiltration, electro dialysis with monovalent cation-exchange membranes, and ion-exchange resins. Nanofiltration and electro dialysis with monovalent cation-exchange membrane were demonstrated to be suitable pretreatments with 92–96 %  $Mg^{2+}$  and  $Ca^{2+}$  removal and 86–94 % DOC removal. Ion-exchange resins had excellent divalent cation removal but no DOC removal, therefore requiring additional treatment to remove organic substances and prevent membranes' biofouling. Electro dialysis with monovalent cation-exchange membranes was preferable over nanofiltration due to the 1.6-fold concentration factor for sulfate ions. In contrast, nanofiltration had lower energy consumption and higher stability in divalent cation rejection. Results obtained in this study are valuable for selecting an appropriate treatment for resource recovery and water reclamation from industrial wastewater and for biotechnological downstream processes.

## 1. Introduction

Liquid wastes of different industrial production processes often contain high concentrations of nutrients and ions which need to be removed in conventional wastewater treatment plants before the discharge to the environment. Otherwise, nutrient loading into water bodies can cause eutrophication, toxic effect and other health issues [1], [2]. Alternatively, nutrients could be recovered for reuse, following the European Green Deal for a zero-pollution ambition [3].

Several membrane processes, such as electro dialysis (ED), bipolar electro dialysis (EDBM) and diffusion dialysis (DD), have been recognized as feasible technologies for resource recovery at source from diverse wastewaters [4–9]. Moreover, these technologies comprise numerous cation- and anion-exchange membranes for selective ionic transport. ED and EDBM are electro-membrane processes that require an electrical field as a driving force for ionic removal. On the contrary, the driving force in the DD process is a concentration gradient. Furthermore,

ions from industrial waste streams can be recovered as acids/bases by EDBM and DD [10–14].

Besides cation- and anion-exchange membranes commonly applied in conventional ED and DD, EDBM contains bipolar membranes where an external electrical field initializes water splitting. Evolved protons and hydroxyl ions combined with their counter-ions occurring in the feed result in a corresponding acidic or caustic stream. In DD, the ions transfer through the membrane by dissolution and then diffusion down a concentration gradient, while the ion exchange membranes (IEM) reject the larger co-ions [15], [16]. However, small size co-ions with low valence ( $H^+$  and  $OH^-$ ) can migrate through the IEM [14]. Both EDBM and DD offer resource recovery and reuse even in the same processes e.g. for pH control, ion-exchange resin regeneration, etc. [17–19].

The competitiveness between ED and DD was lately researched regarding the acid recovery rate, metal rejection rate, energy consumption and the process economy [20]. EDBM can achieve much larger acid/base concentrations and recovery ratios in a short time, allowing a

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higher treatment capacity than DD. On the other hand, the advantages of DD are lower energy consumption, lower membrane fouling and higher environmental friendliness [16], [20]. Although DD membranes are less prone to fouling, both EDBM and DD require pretreatment to protect IEMs when applied in wastewater treatment. Additionally, adequate pretreatment can increase acid/base concentrations and recovery ratio in both technologies.

Industrial liquid waste streams often contain significant amounts of additional organic and inorganic substances that cause fouling as a general term on IEMs. In fact, IEM fouling can be classified into four groups – colloidal fouling, organic fouling, inorganic scaling, and biofouling [21]. The formation of deposits on and in the IEMs has adverse effects on the process performance – especially on membrane characteristics, increasing electrical resistance, decreasing membrane permeability and selectivity, and altering its physical properties [22]. Colloids in wastewater are non-dissolved suspended solids ranging in particle size from 1  $\mu\text{m}$  to 1 nm. Organic fouling is caused by the dissolved organic matter of a treated solution, such as carbohydrates, proteins, and humic acids [21], [23], [24].  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are the major scaling ions that tend to precipitate on the membrane surface mainly as carbonates, especially in the EDBM system, due to the strong pH changes of the produced streams [25–27]. Precipitation of  $\text{Al}(\text{OH})_3$  on the membrane can occur in NaOH extraction by DD [28]. Finally, biofouling is particularly disturbing as bacteria form biofilms on IEMs, increasing the membrane thickness and reducing the available area for ion exchange.

Fouling is not only a problem in IEMs but also in pressure-driven membrane processes for drinking water production and wastewater treatment [29–32]. Latter has been more researched considering the broad and long applications of pressure-driven membranes in diverse applications. In contrast, IEM fouling mechanisms and cleaning procedures gained more attention only in recent years [21], [33]. Ion exchange resin is not excluded from the issues mentioned above. Namely, their capacity decreases over time due to fouling phenomena, particularly by organic foulants in the water purification assembly [34].

Different strategies for preventing or reducing IEM fouling have already been studied [21]. There are approaches in IEM modifications [35–37], implementation of advanced membrane spacers [38], changes in ED/EDBM operating conditions [26], mechanical and chemical cleaning methods [33], [39], as well as the pretreatment of feed solutions [40], [41].

Frequently, pressure-driven membrane processes are used for ED/EDBM/DD pretreatment, including micro-, ultra-, and nanofiltration [28], [42]. Micro- and ultrafiltration can remove colloids from wastewater and reduce organic matter, providing sufficient pretreatment for the ED feed. In the study of Wang et al. [10], ultrafiltration was applied for removing proteins, mycelium, and carbohydrates from a microbial fermentation broth, followed by activated carbon for discoloration before further treatment via EDBM. However, feeds containing scaling ions demand more sophisticated pretreatment because IEMs of EDBM/DD systems are more prone to scaling. In some studies, ion-exchange resins have also been coupled with EDBM, e.g., to remove hydroxycarboxylic acids and thiosulfates from spent pulping liquors [18] and to remove nickel ions [43]. Developed strategies for antifouling of IEMs, including e.g., synthesis of nanocomposite materials [44] and periodic air sparging [45], indicate even the feasibility of a direct ED application before EDBM/DD in the treatment of some industrial wastewater.

In general, ED is an emerging membrane separation technology beneficial for its selective ion separation from various feeds and near-to-zero liquid discharges [46]. IEMs are ongoingly investigated, modified, and optimized for specific usages, such as separating monovalent and multivalent ions [35] or enhancing ionic flux and ion perm-selectivity [47]. The fabrication of the monovalent-selective membranes offers a multitude of innovative ED applications in seawater desalination, acid recovery in hydrometallurgy, and removal of specific ions from liquid

**Table 1**  
Physicochemical analysis of the fermentation effluent.

Parameter	Fermentation effluent
pH	2.83
Conductivity (mS/cm)	19.2 $\pm$ 1.4
DOC (mg/L)	1058.7 $\pm$ 68.9
Na <sup>+</sup> (mg/L)	1195.5 $\pm$ 164.5
K <sup>+</sup> (mg/L)	319.3 $\pm$ 122.2
NH <sub>4</sub> -N (mg/L)	1709.6 $\pm$ 113.1
Ca <sup>2+</sup> (mg/L)	36.8 $\pm$ 2.8
Mg <sup>2+</sup> (mg/L)	44.5 $\pm$ 0.9
Cl <sup>-</sup> (mg/L)	122.5 $\pm$ 51.2
SO <sub>4</sub> <sup>2-</sup> (mg/L)	9541.8 $\pm$ 663.9
PO <sub>4</sub> -P (mg/L)	146.8 $\pm$ 5.7

waste [35].

The main drawbacks of electro-membrane compared to pressure-driven processes are still the increased specific energy consumption costs, especially for feeds with TDS  $\geq$  5000 ppm, and higher membrane and maintenance costs [48], [49]. The greater capital and operating costs of ED/EDBM/DD can be, however, outweighed by their advantages when applied for nutrient recycling after conventional wastewater treatment, selective ion separation, water-saving, and quantitative reduction of waste streams.

This research analyzed the performance of three pretreatment technologies applied to a bio-fermentation effluent from the archaea *Sulfolobus acidocaldarius* before an EDBM or DD treatment. As described above, an adequate EDBM/DD pretreatment may decrease the IEM fouling and increase the concentration and recovery ratio of the sulfuric acid retrieved from the fermentation broth. Emphasis was put on the ED pretreatment technology for the selective ionic separation and concentrating ions from the treated waste stream. A particular ED stack was assembled for this study, containing standard anion-exchange membranes (AEM) and monovalent cation-exchange membranes (mCEM), that provide an optimized feed for EDBM/DD by resulting in enrichment with specific ions and reduction of organic molecules. The removal of the divalent cations to a value below 10 ppm and a DOC reduction from the fermentation effluent is necessary due to the afore-mentioned IEMs fouling issues occurring in EDBM systems. The first technology applied was nanofiltration, assessing membranes from two manufacturers. The second technology investigated was ED stacked with AEM and mCEM configuration, which enables to pre-concentrate sulfates for a more efficient subsequent sulfuric acid production by EDBM/DD. Thirdly, three types of chelating ion-exchange resins were applied to remove divalent cations. Results obtained from the three technologies were studied in terms of their removal efficiency for DOC,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , selectivity between mono- and divalent ions, ionic fluxes and energy consumption.

## 2. Materials and methods

### 2.1. Wastewater – fermentation effluent used in the study

Wastewater samples were collected from the residual fermentation broth after a bio-fermentation with the archaea *S. acidocaldarius* in a lab-scale [50]. After fermentation, the residual broth was microfiltered via  $\text{Al}_2\text{O}_3$ -coated ceramic filter (0.2  $\mu\text{m}$  pore size, Deltapore, Netherlands) to separate the biomass containing the desired fermentation products from the surrounding medium. The waste permeates from several fermentation replicates were collected and mixed to obtain sufficient material with uniform conditions for the EDBM experiments. The high-volume sample was then split into 5 L subsamples and stored at  $-20^\circ\text{C}$ . Samples were thawed at room temperature separately before applying various subsequent pretreatment technologies. Additional ionic analyses were done for each thawed subsample to ensure that the ionic composition did not change e.g., by precipitation during freezing. These

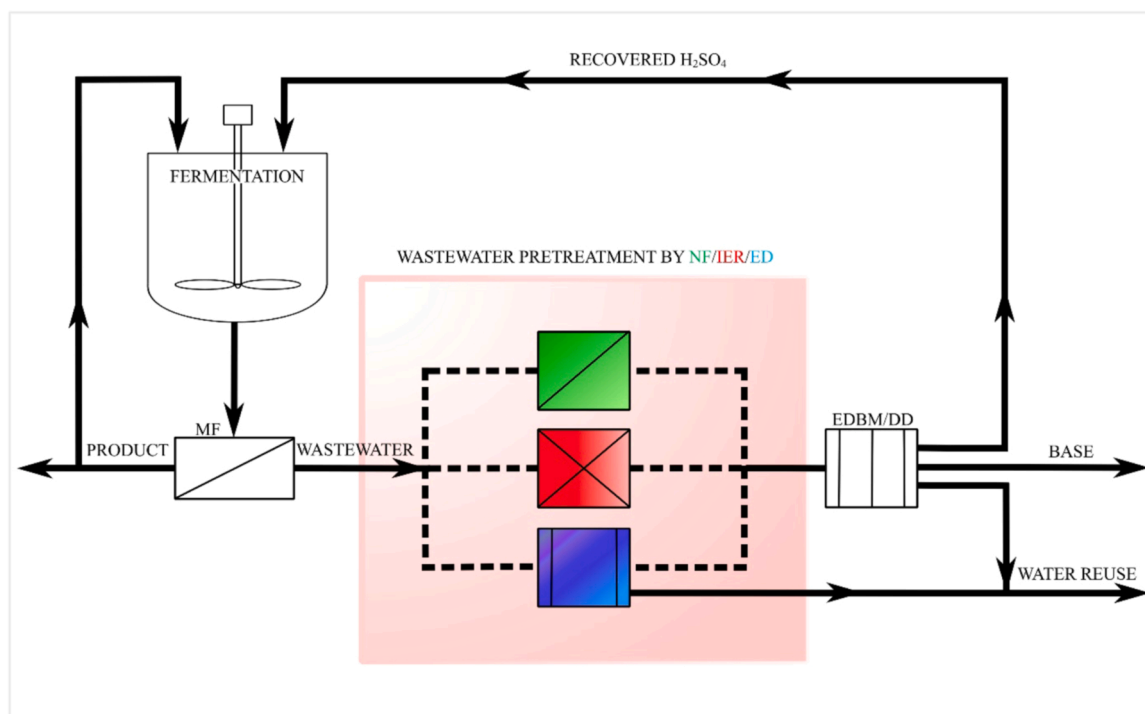


Fig. 1. Process design and the experimental set-up for three technologies tested in this research (in the pink box). MF-microfiltration, NF-nanofiltration, IER-ion exchange resin, ED- electro dialysis with standard AEM and mCEM.

**Table 2**  
NF membrane characteristics as specified by the producer.

Membrane class	Manufacturer	Model	Material	Stabilized salt rejection (%)	pH 25°C	MWCO (Da)	Max P (bar)	Max. Temp. °C
NF	SUEZ	DK	PA-TFC	98 % MgSO <sub>4</sub>	2–10	200	40	80
NF	DUPONT	NF270	PA-TFC	> 97 % MgSO <sub>4</sub>	2–11	200–400	41	45

re-measurements are the base for characterizing the chemical composition of the fermentation effluent provided in Table 1.

## 2.2. Experimental set-up

The whole process scheme depicting the fermentation, product separation by microfiltration, wastewater source (fermentation effluent), three tested pretreatment technologies, and intended final treatment by either EDBM or DD (out of the research scope) is shown in Fig. 1. A sufficient amount of the fermentation effluent stored in the freezer was thawed at room temperature before applying the pretreatment technology to be tested. Experiments were performed individually for NF (DK) and NF270 filtration, ED, and three types of IER (C100E, MTS9300, and CR11). The aim was to obtain a treated solution with less than 10 ppm of divalent cations and reduced DOC values for further recovery of sulfuric acid by EDBM/DD. Experimental conditions are described in the following sections of the study, and samples were taken accordingly. Chemical analysis of collected samples and data analysis of all obtained results were done as described in the following section.

**Table 3**  
Characteristics of ion-exchange membrane used in the ED experiments, specified by PCCell producer.

Membrane	Type	Thickness, μm	Transference number	Resistance, Ohm cm <sup>2</sup>	Water content (wt %)	pH stability
PC SA	Anion exchange	100–110	> 0.95	1.8	14	0–9
PC MVK*	Cation exchange	100–120	–	–6	–	0–11
PC MTE	Cation exchange	220	> 0.94	4.5	–	1–13

\* monovalent cation-selective membrane

## 2.3. Equipment and membranes for pretreatment experiments

**Nanofiltration (NF).** A cross-flow test cell (OSMO Membrane Systems GmbH, Korntal-Münchingen, Germany) with a membrane active area of 80 cm<sup>2</sup> was used for the batch NF experiments. The experimental conditions were: 1.7 L of treated feed, a pressure of 23 bars, 20 °C and a circulation flow of 2.2 L/min. Two membranes were tested for the retention of divalent cations and DOC removal from the fermentation effluent until 1.5 L of permeate was gained. The NF membrane characteristics are summarized in Table 2. Both membranes were kindly provided by the manufacturers, the NF(DK) by SUEZ Group (Paris, France), and NF270 DuPont (Wilmington, Delaware, US).

**Electrodialysis (ED).** ED experiments were done in a batch laboratory-scale ED system PCCell ED 64–004 (PCCell GmbH, Germany) with ten cell pairs. Applied membranes were standard anion-exchange membranes (AEM) and monovalent selective cation-exchange membranes (mCEM), with specifications shown in Table 3. One cell pair was comprised of one AEM, spacer, mCEM and again a spacer. Spacers defined repeating diluate and concentrate compartments and allowed better mixing of treated streams. PC MTE cation exchange membrane

**Table 4**

Physical and chemical characteristics of Purolite C100E, Purolite MTS9300 and Diaion CR11, as specified by the producer.

Parameter	Purolite C100E	Purolite MTS9300	Diaion CR11
Polymer structure	Gel polystyrene crosslinked with divinylbenzene	Macroporous polystyrene crosslinked with divinylbenzene	Highly porous styrene-divinylbenzene
Optical appearance	Spherical beads	Spherical beads	Spherical beads
Functional group	Sulfonic acid	Iminodiacetic	Iminodiacetate
Ionic form, as shipped	Na <sup>+</sup> form	Na <sup>+</sup> form	Na <sup>+</sup> form
Total capacity (eq/L)	1.9 (Na <sup>+</sup> form)	nd	nd
Moisture retention	46–50 % (Na <sup>+</sup> form)	52–60 % (Na <sup>+</sup> form)	55–60
Particle size range (µm)	300–1200	425–1000	355–1180
Reversible swelling	10 % (Na <sup>+</sup> to H <sup>+</sup> )	35 % (H <sup>+</sup> to Na <sup>+</sup> )	28 % (H <sup>+</sup> to Na <sup>+</sup> )
Specific gravity	1.27	1.18	nd
Shipping density (g/L)	800–840	750–800	730
Effective pH range	6–10	nd	2–6
Temperature limit	120 C	80	120

was used as an end-membrane in the ED stack (Table 3). The effective membrane area was 64 cm<sup>2</sup>. Spacer thickness was 0.45 mm. Electrodes were Pt/Ir-coated titanium anode and V4A steel cathode, placed in the polypropylene electrode housing material. The process was controlled by a step-wise application of current density based on the limiting current densities estimated via Cowan and Brown curves [51] (Appendix A). Electrode-rinse solution (0.25 M Na<sub>2</sub>SO<sub>4</sub>) was circulated at 120 L/h flowrate. 1.53 L of the fermentation effluent and 0.81 L of the synthetic solution with 250 mg/L Na<sub>2</sub>SO<sub>4</sub> dissolved in deionized water were circulated at a 15 L/h flowrate (linear velocity of 0.012 m/s) in the diluate and concentrate chamber, respectively. The synthetic solution in the concentrate was used to retain the organic substances from the feed solution and attain the ionic species containing macronutrients such as P, N and S. The 1.9 vol ratio between the diluate and the concentrate was selected to concentrate ions from the fermentation effluent. ED experiments were done as duplicates to obtain in total ~1.6 L of concentrate solution. Conductivity and temperature were continuously monitored and recorded at the ED stack outlet for both streams. Additionally, the pH of the diluate was also continuously measured.

**Ion exchange resins (IER).** Three types of IER were used in the experiments, kindly provided by Mitsubishi Chemical (Tokyo, Japan) and by Purolite Corporation (Pennsylvania, USA). The physicochemical properties of the chelating resins are given in Table 4. For each experiment, 50 mL of resins were put in glass columns with an internal diameter of 1.5 cm. The total bed volume (BV) height was 16 cm, including 1 cm glass wool to avoid loss of resins, 0.5 cm glass pearls (diameter 1 mm) for even distribution of the feed and 14.5 cm resin material. The fermentation effluent was manually fed on the top of the column, having gravitational down-flow through the filter bed. The flow was regulated by a bottom valve and maintained at 8.4 BV/h (7 mL/min). The resins were rinsed with 20 BV deionized water before the start of the experiments. Samples of the column effluent for cation analysis were taken every 20 min. The conductivity, pH, and temperature of the column effluent were continuously measured. The endpoint of experiments was achieved when a volume of 1.7 L of treated fermentation effluent was gained.

nd - not defined.

## 2.4. Chemical analysis

Water samples were analyzed for PO<sub>4</sub>-P and NH<sub>4</sub>-N with continuous flow analysis and photometrical detection (Skalar, Netherlands) according to DIN EN ISO 6878 and DIN EN ISO 11732 standards, respectively. Anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) were analyzed according to DIN EN ISO 10304-1 and cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) according to DIN EN ISO 14911 standard, using high performance ion chromatography (Metrohm AG, Switzerland). Dissolved organic carbon (DOC) was analyzed using the combustion method according to DIN EN 1484 standard.

## 2.5. Data analysis

The following equations were used to compare process efficiencies and characteristics among the investigated three different pretreatment technologies.

The rejection rate of a specific ion in the NF ( $R^{NF}$ ) and ED ( $R^{ED}$ ) system was calculated from:

$$R^{NF} = \left(1 - \frac{c_p}{c_f}\right) \times 100\% R^{ED} = \left(1 - \frac{(c_c^t - c_c^0)V_c}{c_d^0 V_d}\right) \times 100\% \quad (1)$$

where  $c_f$  and  $c_p$  (mol/L) are the concentrations of ion  $i$  in the feed and in the permeate, respectively, in the NF system. In the ED system, removal of ion  $i$  was calculated based on the ion concentration  $c$  (mol/L) and volume  $V$  (L) in the diluate  $d$  and concentrate  $c$ , denoted in subscript, at the time 0 and  $t$ , denoted in superscript.

The ion permeation in NF ( $\%p^{NF}$ ) and ED ( $\%p^{ED}$ ) was obtained according to:

$$\%p^{NF} = \frac{c_p}{c_f} \times 100\% \%p^{ED} = \frac{(c_c^t - c_c^0)V_c}{c_d^0 V_d} \times 100\% \quad (2)$$

where the permeation of ions in ED refers to ion migration from the diluate to the concentrate chamber.

The ionic flux in NF ( $J^{NF}$ ) and ED ( $J^{ED}$ ) was calculated using:

$$J^{NF} = \frac{c_p V_p}{A t} J^{ED} = \frac{(c_c^t - c_c^0)V_c}{A t} \quad (3)$$

where  $V_p$  (L) is the permeate volume.  $V_c$  (L) in ED is the concentrate volume.  $A$  (m<sup>2</sup>) is the effective membrane area and  $t$  (h) the process duration time.

The membrane perm-selectivity between monovalent cation  $i$  and divalent cations  $n^{2+}$  (Mg<sup>2+</sup> and Ca<sup>2+</sup>) in NF was obtained according to:

$$S_{n^{2+}}^i = \left(\frac{c_f^{n^{2+}}}{c_p^{n^{2+}}}\right) \left(\frac{c_f^i}{c_p^i}\right) \quad (4)$$

where  $c$  (mol/L) is the ion concentration, for monovalent ion  $i$  and divalent ions  $n^{2+}$ , denoted in superscript, and in feed  $f$  and permeate  $p$ , denoted in subscript. As  $S_{n^{2+}}^i$  increases, the monovalent selectivity of the membrane increases.

The membrane perm-selectivity between monovalent ion species  $i$  and divalent cations  $n^{2+}$  (Mg<sup>2+</sup> or Ca<sup>2+</sup>) in ED was obtained according to:

$$S_{n^{2+}}^i = \frac{J_i c_{n^{2+}}}{J_{n^{2+}} c_i} \quad (5)$$

Where  $J$  (mol/(cm<sup>2</sup> s)) is the ionic flux and  $c$  (mol/L) is the average ion concentration in the diluate chamber during experiment, for monovalent ion  $i$  and divalent ions  $n^{2+}$ , denoted in the subscripts. As  $S_{n^{2+}}^i$  increases, the monovalent selectivity of the membrane increases.

Current efficiency in the ED process was calculated from the following equation:

$$CE = \frac{F \times \sum_i z_i (c_i - c_0) \times V}{N \times I \times t} \quad (6)$$

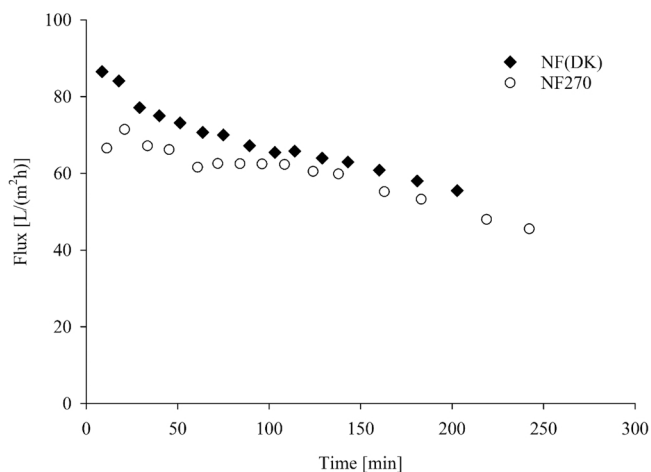


Fig. 2. Decline of permeate flux over time for two tested membranes: NF(DK) and NF270. Pressure: 23 bar; temperature: 20 °C; circulation flow: 2.2 L/min.

where  $F$  is the Faraday constant (96,485 sA/mol),  $z_i$  the valance of ion  $i$ ,  $N$  the number of ED cell pairs (10 in this study),  $I$  (A) applied current.

In the ED the energy is consumed for the feed desalination ( $E_d$ ) and for the pumps of the diluate, concentrate and electrode-rinsing solutions

( $E_p$ ). Therefore, the total energy consumption for the experimental conditions of the batch ED mode were calculated as follows:

$$E = E_d + E_p = \frac{U \times I \times t}{V} + \frac{Q \times \Delta p}{\eta \times V} \quad (7)$$

where  $U$  (V) is the applied voltage,  $I$  (A) is the applied current,  $t$  (h) is the desalination duration, and  $V$  ( $m^3$ ) is the treated volume of the feed solution. Energy consumed by the pumps ( $E_p$ ) in the diluted, concentrated, and electrode-rinsing solutions was calculated accordingly, where  $Q$  ( $m^3/s$ ) is the flow of the diluted, concentrated, or electrode-rinsing solution,  $\Delta p$  (Pa) is the differential pressure between the inlet and outlet of the ED stack,  $\eta$  is the pump efficiency (assumed as 75 % for all three pumps), and  $V$  ( $m^3$ ) is the treated volume of the diluted solution. The same  $E_p$  equation was used for calculating energy consumption in nanofiltration.

### 3. Results and discussion

The following section presents the results obtained from the treatment of the fermentation effluent by nanofiltration, electrodialysis and ion-exchange resins. The investigated parameters were subsequently compared to define the quality of the streams obtained by three different technologies.

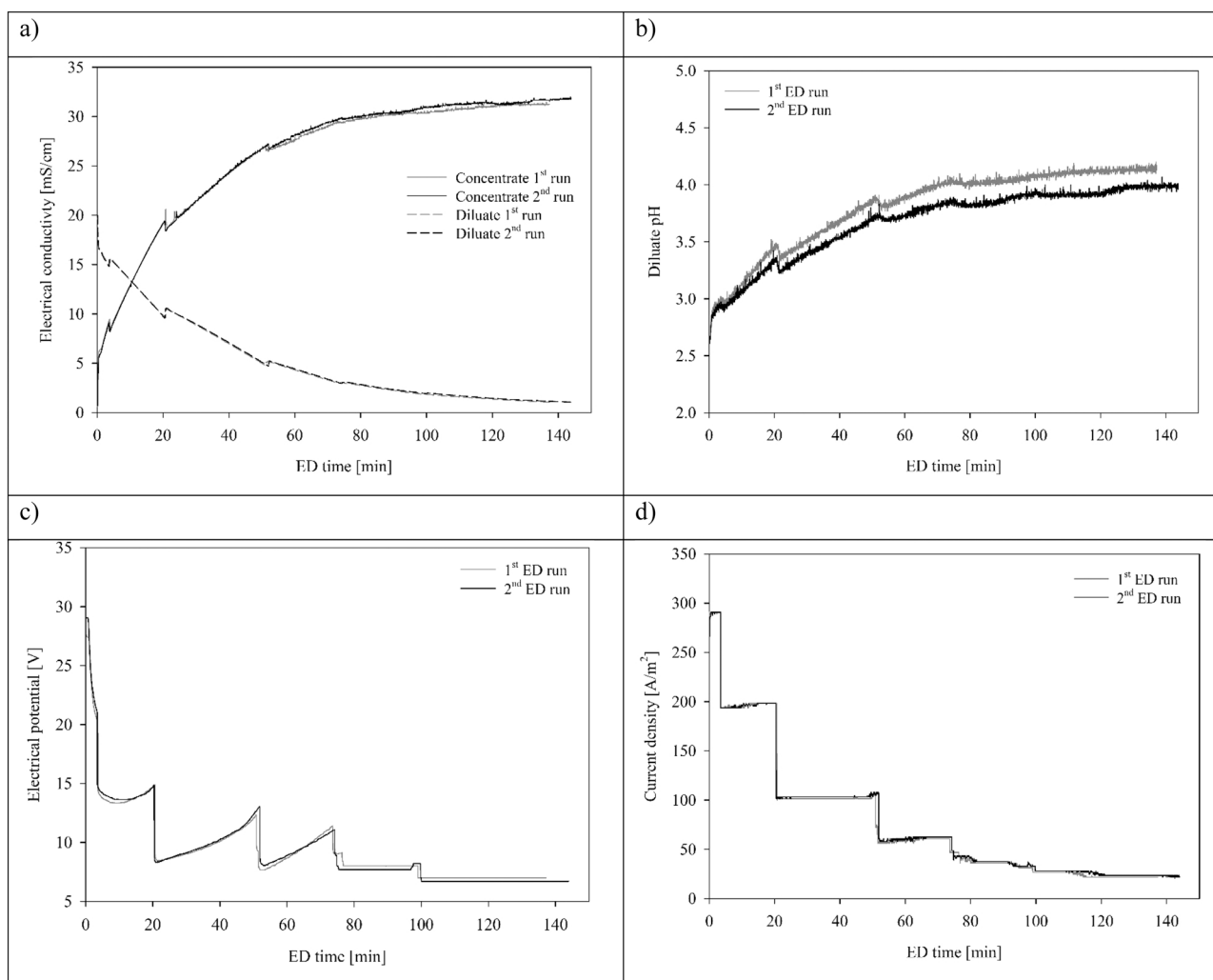


Fig. 3. a) Evolution of the diluate and concentrate conductivities in the first and second ED run; b) Diluate pH during the demineralization; c) Voltage applied to the ED stack; d) The step-wise current density trend for wastewater demineralization.

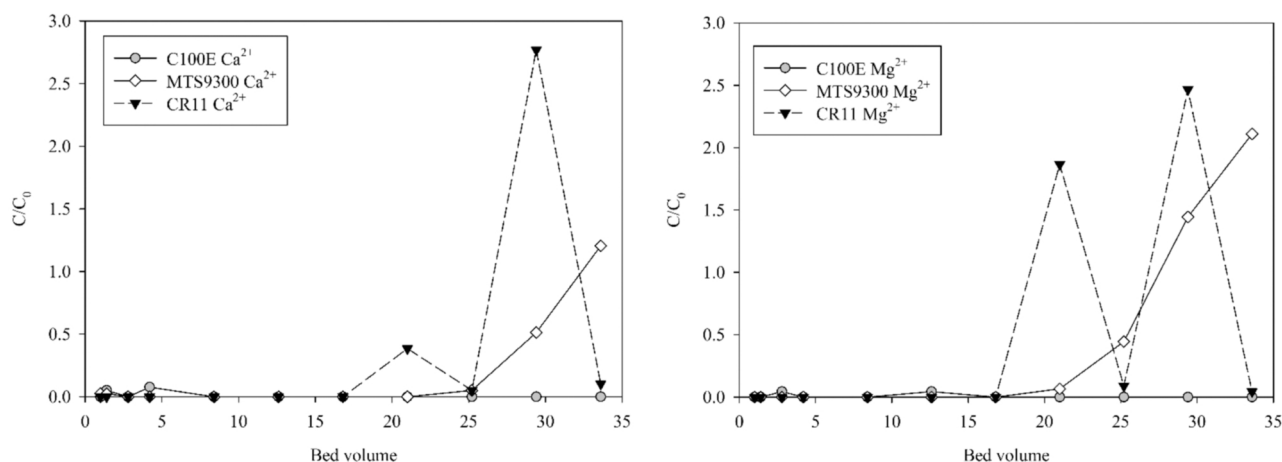


Fig. 4. Breakthrough point for three types of IER applied for: a)  $\text{Ca}^{2+}$  removal and b)  $\text{Mg}^{2+}$  removal from the fermentation effluent. The temperature was kept at 22 °C.

### 3.1. NF - nanofiltration

NF was performed in batch mode, using NF(DK) and NF270 membranes to treat the fermentation effluent. The filtration time for NF(DK) and NF270 was 203 min and 242 min, respectively. Fig. 2 shows the evolution of the permeate flux for two NF membranes tested until 1.5 L of the filtrate was obtained. The measured fluxes are similar to the values obtained from literature [52–55]. The permeate flux continuously declined due to the continually higher concentrations in the feed and organic fouling of the membranes. The more the organic molecules adsorbed on the membrane, the higher the decline in the flux [56]. The mass balance of DOC revealed adsorption of 1.3 g DOC to the NF(DK) surface and 1.1 g DOC to the NF270 surface, from 1.7 L of the treated feed containing  $1 \pm 0.07$  g/L DOC. The molar quantities retained by NF (DK) and NF270 from the feed were 0.20 mol and 0.34 mol, respectively. The volume reduction factor of 8.5 led to retentate densities of 1.07 g/mL for NF(DK) and 1.49 g/mL for NF270, both rich with  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions and organic matter. The water recovery factor was 90 % and 87 % for NF(DK) and NF270, respectively.

### 3.2. ED - electrodialysis

ED experiments were done in batch mode and duplicates. Initial volumes were 1.5 L of the fermentation effluent in the diluate chamber and 0.81 L of 250 mg/L  $\text{Na}_2\text{SO}_4$  model solution in the concentrate chamber. The demineralization rate of the diluates was 94.7 % and ED lasted  $140.6 \pm 3.3$  min. The concentrate/diluate volumes were monitored to restrain volume variations during ED. Thus, ED was aborted when the diluate reached a conductivity of 1.05 mS/cm. This value prevented significant concentrate volume increments but still provided a diluate fulfilling the irrigation water requirements (e.g. diluate conductivity < 3 mS/cm) [57]. Otherwise, the large difference between the diluate and concentrate conductivities initializes osmotic water flux from the diluate towards concentrate [58]. Consequently, the uncharged pollutants from the feed may increasingly diffuse towards the concentrate [59]. The final concentrate conductivity was  $31.5 \pm 0.3$  mS/cm. Conductivity trends, representing the total ionic strength, are shown in Fig. 3a for the diluate and concentrate of both ED runs. In the ED set-up, the mCEM retained divalent cations in the diluate, whereas the standard AEM allowed the transport and concentration of sulfates toward the concentrate solution. The molar quantities of salt removed from the diluate were  $0.44 \pm 0.003$  mol and transferred to the concentrate  $0.41 \pm 0.002$  mol. The remaining difference makes up for the retained divalent cations (0.0039 mol) and ion leakage to the electrode-rinsing solution (explained in 3.5 and 3.7). A total concentration factor of

$1.59 \pm 0.02$  was achieved, comparing the initial diluate and concentrate conductivities. The concentration factor of sulfates was  $1.6 \pm 0.1$ . Diluate pH rose from 2.6 to 4 pH with increased ion removal (Fig. 3b). Step-wise current was applied for the ED control, as described in Appendix A. Trends of electrical potential and current density can be seen in Fig. 3c and Fig. 3d. The current efficiency CE for anion removal from the diluate was  $72.7 \pm 7.1$  %, whereas the cationic removal CE was  $61.3 \pm 3.5$  % due to the retention of divalent cations. CE values are in the range provided in literature [4], [60], [61].

### 3.3. IER - ion exchange resins

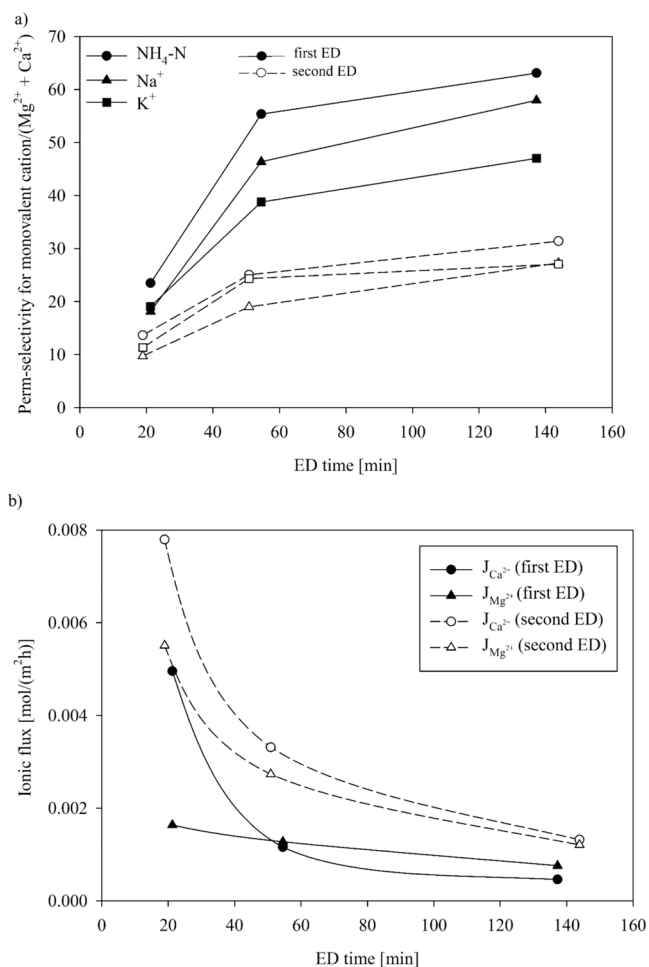
Three types of chelating cation exchange resins were tested for the removal of divalent cations in the scope of this research. In initial experiments, the content of anions in the treated fermentation effluent was proven to remain unchanged as expected. Thus, the IER column outlet samples were analyzed for cations only. A volume of 1.7 L was collected after 240 min (33.6-bed volumes) with the wastewater down-flow rate of 7 mL/min. The measured  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations in the column outlet were divided by their inlet concentration and plotted against the bed volume in Fig. 4. The breakthrough curves for  $\text{Ca}^{2+}$  removal (Fig. 4a) and  $\text{Mg}^{2+}$  removal (Fig. 4b) were observed for MTS9300 and CR11 resins, while the C100E resins remained unsaturated. Thus, the C100E resins had complete removal of divalent cations (0.0046 mol), whereas the molar quantities removed by MTS9300 and CR11 resins before the breakthrough point were 0.0028 mol and 0.0023 mol, respectively.

The ion breakthrough in the CR11 resins started at around 20 BV for both magnesium and calcium, followed by subsequent adsorption of these ions at 25 BV, another desorption at 30 BV and again adsorption at 33 BV. The desorption of divalent cations is possible due to the 34 times higher monovalent cation equivalents compared to divalent cation equivalents in the fermentation effluent and low adsorption in the resin. The behavior of the resins could also be affected by a possible nonideal fluid mixing and flow through the column geometry. For all resins, the selectivity for cations was:  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+$ . The dynamic ion exchange capacity for divalent cations was  $\text{C100E} > \text{MTS9300} > \text{CR11}$ , with exchange capacities between 0.12 eq/L and above 0.19 eq/L of resins. The sorption of divalent cations depends on the solution pH values and can reach higher or lower values for the pH other than 2.8 [62], [63]. A recent study by Suwannahong et al. [64] indicated a decreased adsorption ability of the iminodiacetic acid functional group in IERs when treating highly acid solutions, similar to the MTS9300 and CR11 chelating resins researched in this paper. In contrast, C100E resins have sulfonic acid as the functional group

**Table 5**

The rejection rate for DOC, Ca<sup>2+</sup>, and Mg<sup>2+</sup> from the fermentation effluent, performed via different technologies.

R (%)	NF (DK)	NF270	ED1&2	IER		
				C100E	MTS9300	CR11
DOC	85.9	85.6	94.1 ± 0.14	~0	~0	~0
Ca	93.9	97.6	89.3 ± 6.0	100	100	100
Mg	93.5	95.3	95.3 ± 2.2	100	100	100



**Fig. 5.** a) Perm-selectivity between individual monovalent cations (Na<sup>+</sup>, NH<sub>4</sub>-N, or K<sup>+</sup>) and sum of divalent cations (Mg<sup>2+</sup> and Ca<sup>2+</sup>) for the mCEM during the ED operation time; b) Fluxes of Mg<sup>2+</sup> and Ca<sup>2+</sup> in the first and the second ED run, depicted over ED operation time.

(Table 4) and exhibited the highest softening capacity for the wastewater treated within this study. The obtained results indicate preferential application of the resins with the sulfonic acid functional group to remove divalent cations from the fermentation effluent with a low pH value.

### 3.4. Removal of divalent cations and organic compounds by the three investigated technologies

This aspect of the research focused on removing divalent cations and DOC from the fermentation effluent via three technologies under investigation. Mg<sup>2+</sup> and Ca<sup>2+</sup> removal was obtained by their rejection rate in NF and mCEM and the exchange rate in IER. The obtained removal efficiencies are summarized in Table 5 and decreased in the following order for DOC: ED>NF(DK)>NF270>IER; for Ca<sup>2+</sup>:

IER>NF270>NF(DK)>ED and for Mg<sup>2+</sup>: IER>ED=NF270>NF(DK). IER had 100 % removal of divalent cations; however, the organic matter remained in the column effluent. Therefore, IERs require additional posttreatment, such as activated carbon, for DOC reduction and discoloration. Both NF membranes and ED had very high DOC and divalent cation removal values.

### 3.5. Perm-selectivity of monovalent cations

The monovalent cations together with hydroxide anions in the EDBM system result in a caustic stream. As the fermentation effluent mainly contains NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup> ions (Table 1), the bases produced via bipolar membranes are predominantly NH<sub>4</sub>OH and NaOH, and at a lower rate KOH. In order to increase the yield for the caustic stream, it is desired to have high concentrations of monovalent cations after the pre-treating step before forwarding it to EDBM.

The mCEM retains divalent cations in the diluate and shifts monovalent cations towards the concentrate. The concentrate is supposed to be fed to the EDBM for the acid/base production. Fig. 5 shows the development of the mCEM perm-selectivity between individual mono- and the sum of divalent cations in ED against the operation time. A detailed picture of perm-selectivities determined individually for Mg<sup>2+</sup> and Ca<sup>2+</sup> ions can be found in Appendix B. Perm-selectivities were determined for three sampling points during the ED process, at average current densities of 209.4 A/m<sup>2</sup>, 143.8 A/m<sup>2</sup> and 78.1 A/m<sup>2</sup>, for both first and the second ED run (Fig. 5a). The perm-selectivity between monovalent (NH<sub>4</sub>-N, Na<sup>+</sup> or K<sup>+</sup>) and divalent cations increased with the ED demineralization time, reaching maximum values of 63.1, 58.0 and 47.0 for NH<sub>4</sub>-N, Na<sup>+</sup>, and K<sup>+</sup>, respectively. With decreasing diluate ion concentration and current density, the perm-selectivities were increasing, indicating a positive effect of these two parameters on the overall membrane selectivity. Further on, prolonged ED operation time led to a progressive diffusion boundary layer formation near mCEM on the diluate side. This layer promoted diffusional transport mechanisms, favoring the transport of monovalent over multivalent counter-ions.

However, the perm-selectivities decreased drastically (~50 %) in the second ED run. Effects of ion concentrations and current densities on the mCEM selectivity can be excluded, as the exact same conditions were applied in the first and the second ED run. The mCEM has a specified 0–11 pH stability (Table 3), therefore excluding the impact of the low feed solution pH (pH 3) on the membrane properties. When the fluxes of divalent cations through the mCEM of the first and the second ED run were compared, a significant increase was observed in the second ED run (Fig. 5b). The increased fluxes of Mg<sup>2+</sup> and Ca<sup>2+</sup> ions indicate the damage of the mCEM surface layer that usually hinders the transport of divalent ions and the absence of its electrostatic repulsion towards multivalent ions. The strong binding of divalent cations to the sulfonic acid group led to the inactivation of mCEM exchange layer [65]. Once the divalent cations enter the membrane matrix, the membrane characteristics alter strongly. Adsorption of organic molecules may have also impacted the mCEM characteristics in the second ED run, as the instability of the IEM charged layer during ED has already been noticed [65–67]. These behaviors need further research. In this study, commercial IEMs were used, but recent studies show the improvements of the modified monoselective IEMs compared to the commercial ones, with promising selectivity, stability and antifouling potential [47], [68], [69].

Nevertheless, the perm-selectivities obtained in the second ED run were in the range of those obtained in NF experiments. Perm-selectivities for NH<sub>4</sub>-N, Na<sup>+</sup>, and K<sup>+</sup> were 12.6, 12.2 and 16.7 in NF (DK) and 7.1, 9.6 and 9.1 for NF270, respectively, and similar to the literature values [25]. NF(DK) membrane had relatively high perm-selectivity for monovalent over divalent cations. The differences in the permeates obtained by NF(DK) and NF270 can be seen in the change of the conductivity (Fig. 6a) and in pH measurement (Fig. 6b). The conductivity of the NF270 permeate is significantly lower compared to

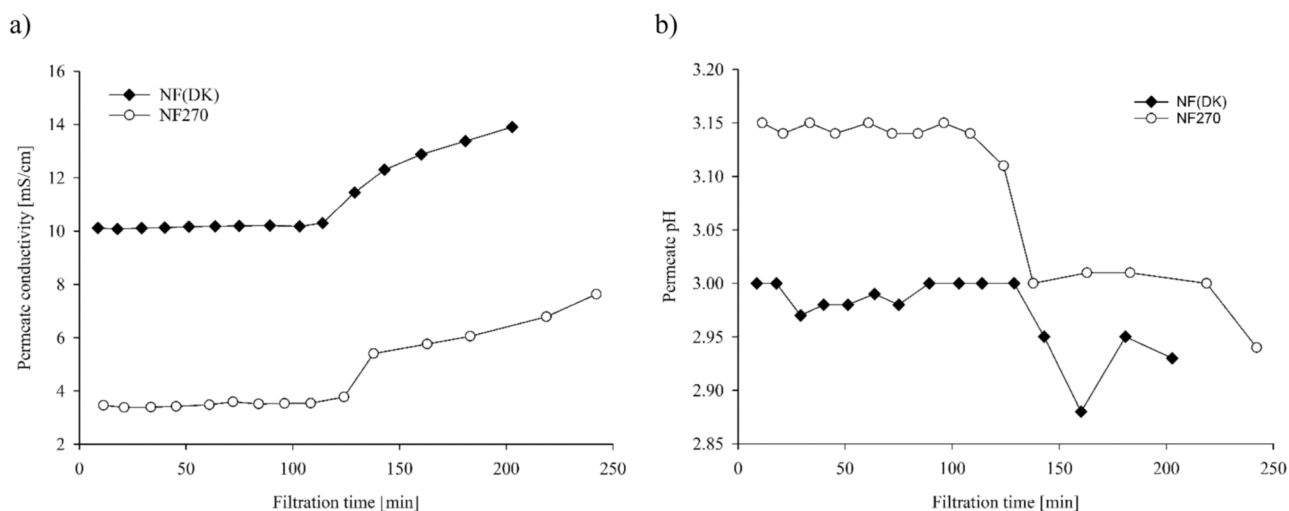


Fig. 6. Characteristics of the NF permeates represented by a) the electrical conductivity and b) the pH measurements.

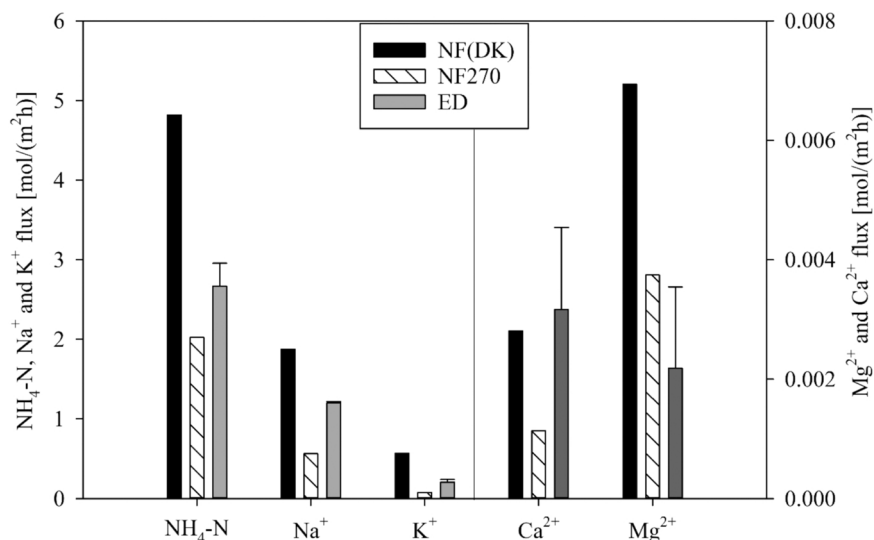


Fig. 7. Average flux of cations through NF(DK), NF270 nanomembranes and mCEM in ED. Flux values for ED are based on two ED runs.

the NF(DK) permeate because more ions were retained. The high retention of monovalent cations (e.g. 63 % for NH<sub>4</sub>-N, 65 % for K<sup>+</sup>) by NF270 membrane is comparable to the literature results [70]. An increase of the conductivity in both permeates occurred after a water recovery ratio of ~50 %, indicating the impact of the ion concentration in the retentate on the permeation of ions. High retention and concentration of Mg<sup>2+</sup>, Ca<sup>2+</sup>, and SO<sub>4</sub><sup>2-</sup> ions in the retentate forced other ions from the fermentation medium to permeate through the NF membranes.

### 3.6. Cationic fluxes

The perm-selectivity of mCEM and NF membranes was demonstrated in the previous section, and the ionic fluxes of mono- and divalent ions strongly influence it. Ionic fluxes through the applied membrane depend on the membrane and feed physicochemical characteristics, ion concentrations, driving force, operating conditions, etc. Thus, cationic fluxes were compared among the tested pretreatment technologies. Fig. 7 reveals higher cationic fluxes for the more concentrated cations in the feed (Table 1) for both pressure-driven and ion-exchange membrane processes.

The fluxes obtained correspond to the molar ratios between NH<sub>4</sub><sup>+</sup> against Na<sup>+</sup> and K<sup>+</sup> ions in the feed, which led to flux reduction factors

of 0.4 and 0.1 for Na<sup>+</sup> and K<sup>+</sup>, respectively, compared to the NH<sub>4</sub><sup>+</sup> flux:

$$M_{(\text{Na})}/M_{(\text{NH}_4)} = 0.4 \rightarrow J_{(\text{Na})} = 0.4 * J_{(\text{NH}_4)}.$$

$$M_{(\text{K})}/M_{(\text{NH}_4)} = 0.1 \rightarrow J_{(\text{K})} = 0.1 * J_{(\text{NH}_4)}.$$

The only exemption was in the case of the NF270 membrane, with 1.2–2.5 lower fluxes than through the NF(DK) membrane, for both mono- and divalent cations. The lowest Ca<sup>2+</sup> and Mg<sup>2+</sup> fluxes during the NF270 filtration step were beneficial for divalent cation removal. However, the NF270 membrane retained a significant amount of monovalent cations, as seen in their low fluxes in Fig. 7. The low mono- and divalent cationic fluxes can be assigned to the positively charged NF270 membrane surface when the solution pH is less than 3.3–4 [71], as is the case for the fermentation effluent treated in this study. The resulting electric charge repulsion increased the retention of the monovalent cations that otherwise pass through the NF membrane at neutral conditions [72].

The average fluxes of the monovalent cation through mCEM were between the ranges of fluxes through NF(DK) and NF270. Ca<sup>2+</sup> flux was higher, whereas Mg<sup>2+</sup> flux was lower in ED compared to NF membranes. According to Fig. 7 selection of NF(DK) membrane is preferential due to the highest monovalent cation flux and higher capacity than the other tested technologies for the same membrane area.



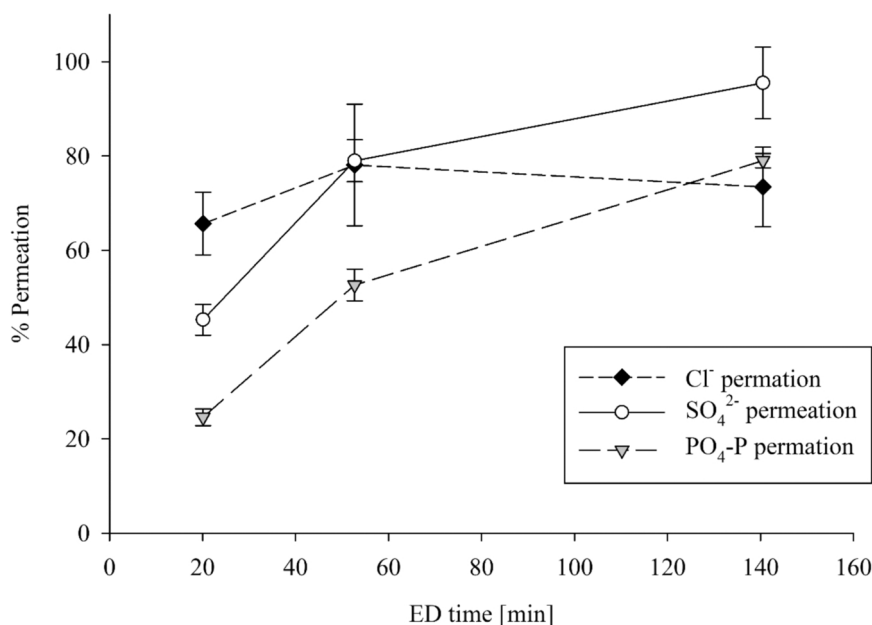


Fig. 8. Permeation (migration) of anionic species from the diluate to the concentrate solution through AEM during ED.

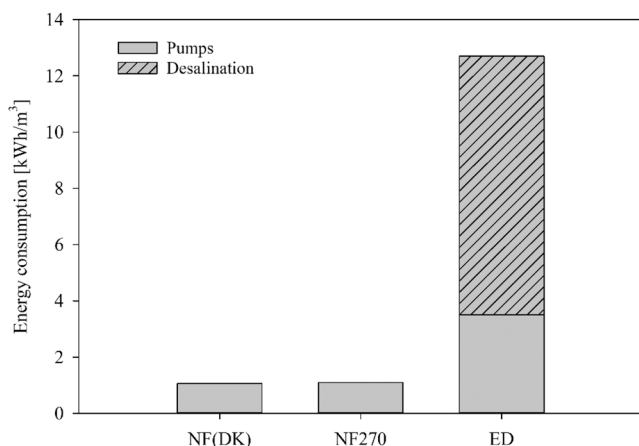


Fig. 9. Energy consumption for pumps in nanofiltration, and for pumps and external electrical field for desalination in ED.

### 3.7. Behavior of anions

Retaining a high concentration of anions in the pre-treated fermentation medium is important because it directly affects the concentration of the acid produced by the subsequent EDBM treatment. The fermentation effluent contains a high concentration of sulfates (~9.5 g/L), whereas the molar concentration of chlorides and phosphates is about 40 times lower. Therefore, the acid produced by EDBM is mainly composed of H<sub>2</sub>SO<sub>4</sub> and significantly less of H<sub>3</sub>PO<sub>4</sub> and HCl. The concentration of the anions in the purified fermentation medium varies considering the technology applied for its pretreatment. Therefore, this section compares the performance of NF, ED, and IER regarding anions by calculating the permeation of anionic species.

Fig. 8 shows the anion migration over time through the anion-exchange membranes (AEM) in ED. The permeation of SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub>-P increased during the ED process time and ultimately reached 95.5 ± 5 % and 79.0 ± 1 %, respectively. Cl<sup>-</sup> was less concentrated than the other anions and was already efficiently removed (78.1 ± 9 %) in the first 60 min of the ED process. Afterward, the Cl<sup>-</sup> permeation decreased to 73.4 ± 6 %, most probably due to the co-ion leakage through the end-

membrane towards the electrode-rinsing solution [20], [73], [74]. The electrical conductivity of the electrode-rinsing solution increased by 0.8 mS/cm until the end of the demineralization.

Permeation of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub>-P was 95.8 %, 68.6 % and 89.2 % for NF(DK) and 90.5 %, 28.8 % and 73.3 % for NF270, respectively. The obtained values are comparable to the ones from literature [75]. Anionic content of the feed treated by IER remained unchanged.

SO<sub>4</sub><sup>2-</sup> permeation through the AEM in ED was the highest. Comparing NF membranes, SO<sub>4</sub><sup>2-</sup> permeation was 2.4 times higher in the NF(DK) than in the NF270 membrane. Thus, if applying a pressure-driven membrane process before EDBM, NF(DK) membrane would be preferable.

### 3.8. Energy consumption

A simplified economic evaluation was conducted based only on the energy consumption calculations for NF and ED technologies but not for IER. Results are presented in Fig. 9. The energy consumption for the pumps in the NF(DK) process was 1.06 kWh/m<sup>3</sup> of the treated waste stream and 1.1 kWh/m<sup>3</sup> for the NF270 process, respectively. Energy consumption for demineralization in the ED was 9.2 kWh/m<sup>3</sup>, and 12.7 kWh/m<sup>3</sup> when the diluate, concentrate and electrode-rinse circulation pumps were included.

ED energy consumption values are comparable to literature values falling in the range of 3.7–15 kWh/m<sup>3</sup> [48] and significantly increasing with increasing feed salt concentrations [76]. The energy costs also increase with the increasing current density while the required membrane area accordingly decreases. Reduction in energy requirements can be achieved by optimizing ED operating mode via e.g., application of pulse electric field [77], or segmented electrode system of the ED stack [78]. According to the recent study of Severin et al. [79], optimization of the electrode rinsing solution also increases the overall ED process efficiency.

Greiter et al. [80] did an elaborative study regarding the sustainability and cumulative energy demand for why desalination by ED versus IER. The final conclusion was that the ED was preferred due to significantly lower cumulative energy demand, lower effluent volume, and lower total salt discharge. Finally, the investment, operation and maintenance cost, as well as the waste generation, should be considered when calculating a complete economic evaluation.

**Table 6**

The final composition of the pre-treated fermentation effluent meant to be forwarded to EDBM or DD for acid/base recovery.

EDBM Feed	Volume	DOC	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	NH <sub>4</sub> -N	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> -P
	L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
NF(DK)	1.5	154.0	2	3	764.0	395.0	1,201.0	91.0	5,987.0	123.3
NF270	1.5	136.7	1	2	283.0	67.0	623.0	86.9	2,767.0	106.3
ED1	0.8	124.8	4	2	2,489.0	446.0	2,571.0	330.0	15,777.0	225.0
ED2	0.8	116.3	11	6	2,423.0	672.0	2,718.0	165.0	16,544.0	235.0
IER*	1.6	1058.0	0	0	1,450.3	195.7	2,068.8	95.0	8,732.0	138.3

\* Each effluent from the three tested IER had the final composition in the similar range

#### 4. Summary and conclusion

EDBM/DD is a system sensitive to fouling and scaling when applied in the treatment of wastewater containing various organic and inorganic pollutants. This research experimentally compared three EDBM/DD pretreatment technologies (NF, ED, IER) for divalent cation reduction to values below 10 ppm and a DOC removal from a fermentation effluent. Assessment of investigated technologies was performed in terms of their removal efficiency for DOC, Mg<sup>2+</sup> and Ca<sup>2+</sup>, selectivity between mono- and divalent cations, ionic fluxes and energy consumption. The obtained results are valuable for designing wastewater treatment and downstream processes in biotechnology.

Table 6 comprises the ionic and DOC composition of the fermentation medium after treatment by NF, ED, and IER.

Both NF membranes had a high removal of divalent cations (95.3 ± 1.6 %) and organic compounds (85.8 ± 0.1 %). However, NF(DK) performed better in permeating sulfates and monovalent cations. The sulfate reduction was 31 % for NF(DK) and 71 % for NF270. Results indicate a possibility of coupling NF(DK) with NF270 for filtering the fermentation effluent. In this case, the NF(DK) permeate would be forwarded to NF270 filtration. Based on the experimental results and rough estimations, NF270 would retain ~50 % of the feed's initial SO<sub>4</sub><sup>2-</sup> and monovalent cations content and concentrate it ~3.4 times. Thus, NF270 retentate could be forwarded to the EDBM for acid/base recovery. Still, the feed treated in this manner would result in higher divalent cation concentrations (above 33 ppm) compared to the ED concentrate (6–17 ppm).

ED technology modified with monovalent CEM had the highest DOC removal (94.1 ± 0.14 %). Mg<sup>2+</sup> and Ca<sup>2+</sup> concentrations were sufficiently low after the first ED run, whereas in the second ED run divalent cations concentration exceeded the limiting 10 ppm. Thus, the ED membrane perm-selectivity decreased in the second run and approached the values of NF membranes' perm-selectivity. ED treatment resulted in a concentration factor of up to 1.9 for monovalent cations, beneficial for the succeeding base production. The major advantage of ED compared to NF was the higher permeation of the SO<sub>4</sub><sup>2-</sup> ions and the concentration factor of 1.6 for SO<sub>4</sub><sup>2-</sup>, providing favorable conditions for sulfuric acid production via EDBM/DD. Concentration factors can be further increased by the addition of multi-stage ED treatment.

All three tested IERs had 100 % removal of Mg<sup>2+</sup> and Ca<sup>2+</sup> until the breakthrough point, among which IER C100E with the sulfonic acid functional group had the highest capacity. There was no DOC removal of the IER effluent, thus, it does not prevent EDBM/DD membranes from biofouling.

According to the energy consumption evaluation, NF requires less energy than ED. Therefore, further optimization of the ED process and membrane stability is needed to reduce energy consumption and increase membrane stability, respectively. Even though the IERs had the highest Mg<sup>2+</sup> and Ca<sup>2+</sup> removal, they are not as feasible as ED and NF due to the absence of DOC removal and requirements for an additional posttreatment and resin regeneration that generates waste.

#### CRedit authorship contribution statement

**Katarina Knežević:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Visualization. **Ernis Saracevic:** Methodology, Formal analysis, Data curation, Writing – review & editing. **Jörg Krampe:** Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Norbert Kreuzinger:** Conceptualization, Validation, Resources, Funding acquisition.

#### 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.

#### Data Availability

Data will be made available on request.

#### Acknowledgment

The authors acknowledge TU Wien Bibliothek for financial support through its Open Access Funding Program. The authors acknowledge the “Bioactive” project, TU Wien, under which the study was performed. The special thanks are forwarded to the NovoArc GmbH based at TU Wien, for providing spent culture broth and to Amal Ahmed for the technical support.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2022.108423](https://doi.org/10.1016/j.jece.2022.108423).

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