



Evaluation of fouling phenomena and cation-exchange membrane cleaning in Donnan dialysis for separation of ammonium from fermented solutions rich in volatile fatty acids

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ABSTRACT

Polyhydroxyalkanoates (PHA) are promising biobased and biodegradable alternatives to the petroleum-based plastics. For their production, controlling cell growth is crucial and can be achieved by limiting nutrients, such as ammonium. The use of Donnan dialysis (DD) has been considered for this purpose. However, the effects of long-term DD fermentative operations need to be evaluated since fouling and sorption phenomena can affect the process performance. In this study, DD operations were performed over 10 consecutive batches to separate ammonium from a real fermented stream derived from an acidogenic fermentation process using cation-exchange membranes with distinct properties (a homogenous Fumasep FKS-PET-130 and a heterogenous Ralex CMH-PES) and NaCl or HCl aqueous receiver solutions. A cleaning procedure with acidic and alkaline solutions was proposed for the Ralex. It was verified that sorption and fouling phenomena occurred on/inside both membranes using a NaCl solution as receiver. This occurred more intensely with the Ralex, thus reducing the ammonium percent extraction from 55% (first batch) to approximately 40% in the subsequent batches. On the other hand, Fumasep exhibited higher percent extractions, and its values remained constant at around 65% along the batches when only rinsed with distilled water. The proposed cleaning procedure for Ralex effectively regenerated this membrane and increased the subsequent ammonium percent extractions. However, the acidic and/or alkaline solutions formed cavities on/in the membrane. The use of a HCl solution as receiver led to a lower reduction in the percent extraction throughout the batches when compared to NaCl, but the acidic receiver solution also damaged the membrane. It is suggested the use of the Fumasep membrane for the application evaluated herein or that a milder cleaning procedure is developed and applied for the Ralex membrane.

1. Introduction

Polyhydroxyalkanoates (PHAs) are biodegradable and biocompatible polymers considered as a promising sustainable alternative to traditional petroleum-based plastics due to their unique properties and versatility, enabling their use in numerous applications across various sectors [1,2]. PHA can be produced by mixed microbial cultures (MMCs), whose process typically comprises three distinct stages [1,2]:

(1) Acidogenic fermentation: in this stage, a volatile fatty acids (VFAs)-rich stream is produced. These VFAs serve as precursors for the subsequent PHA biosynthesis; (2) Culture selection: a mixed microbial culture is enriched in PHA-accumulating organisms by applying selective pressures, such as of Feast and famine (F/f) regime; (3) PHA production: the culture selected in stage 2 is fed with the fermented stream produced in stage 1, enabling the production of PHA.

PHA are synthesized by microorganisms when cell growth rate is

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constrained, which can be achieved through nutrient limitation during specific periods of MMC-based PHA production process. Controlling the periods of microorganisms' growth can enhance the efficiency of culture enrichment selection [3,4]. To achieve this, strategies such as uncoupling carbon from nitrogen have been established, where the nutrient, such as nitrogen, is fed solely during the famine phase when all exogenous carbon (VFAs) have been depleted. This approach provides an advantage to PHA-accumulating organisms, as these organisms can utilize stored PHA as carbon and energy sources for growth during the famine phase when nutrients are available. Regarding the PHA production stage, the absence of nutrients maximizes PHA storage yield, as their presence might divert a fraction of available carbon (VFAs) towards cell growth instead of PHA synthesis. When nutrient-poor feedstocks, such as fruit waste [5], are valorized through PHA production, controlling nitrogen availability throughout the production process is straightforward. Conversely, when utilizing nutrient-rich feedstocks, such as protein-rich feedstocks [6], the aforementioned strategy of uncoupling C/N feeding is not viable. Thus, reducing the nitrogen availability by removing it from these nutrient-rich feedstocks will allow to apply the uncoupling C/N strategy during the selection stage and enable PHA production under nutrient limitation, which is essential for achieving higher PHA productivities.

To address this limitation, alternative membrane-based methods have been assessed to remove or decrease the nitrogen content in the fermented stream, such forward osmosis [7], membrane extraction [8], and electrodialysis with monopolar [9] and bipolar membranes [10,11]. Although these techniques have shown to be promising, some limitations have been observed, such as severe membrane fouling, high energy consumption, and low separation rates. Recently, the application of Donnan dialysis (DD) using three different cation-exchange membranes (CEMs) to recover ammonium (NH_4^+) from a feed solution initially rich in VFAs derived from the acidogenic fermentation of cheese whey was evaluated [12]. The study demonstrated that DD can be successfully applied for this purpose, achieving NH_4^+ percent extraction values of up to 96 %. The main advantages of using DD in this application are its low cost and the simplicity of its layout, operation, and maintenance. Since it does not operate under the application of pressure or electric current, it is much less subjected to limitations associated with concentration polarization effects [13]. However, the effects of fouling occurrence at long-term DD operations were not assessed. Besides, the mass balances of NH_4^+ ions for the solutions did not reach 100 % under most conditions tested, indicating the occurrence of NH_4^+ sorption phenomena at/in the membranes. It is well known that fouling is one of the major limitations in membrane separation processes, especially in the case of using complex solutions such as fermentation media. The fouled compounds/particles may significantly reduce the ion separation efficiency due to the reduction in the ion flux through the membrane, deterioration of the separation selectivity, shortening of membrane lifespan, and increase of the energy consumption [14,15]. To overcome these limitations, researchers often evaluate distinct fouling mitigation methods and cleaning procedures of ion-exchange membranes. These studies are generally focused on membranes used in electrodialysis due to the occurrence of water dissociation at the membranes, which intensifies fouling occurrence [16–20]. However, as suggested by Chen et al. [21] and Wang et al. [22] in their recent works on the separation of NH_4^+ ions by DD, although concentration gradient driven processes are less susceptible to membrane fouling, it still may occur at long-term operations and limit the NH_4^+ transfer. Furthermore, sorption of ions at/in the membranes may also affect the DD performance [23–25]. Thus, it is crucial to mitigate sorption and fouling phenomena and/or develop cleaning strategies to make the DD process feasible.

In the present work, the effects of long-term DD operations were evaluated over 10 batches to recover NH_4^+ from a real solution derived from the acidogenic fermentation of cheese whey to be used in the PHA production. Initially, the DD tests were conducted using a NaCl receiver solution and a cation-exchange membrane that was only rinsed with

distilled water after each batch. In this stage, two cation-exchange membranes were tested: Ralex CMH-PES and Fumasep FKS-PET-130. Subsequently, the DD tests were performed using a NaCl solution as receiver and the Ralex membrane, which was subjected to a chemical cleaning procedure in acidic and alkaline medium after each batch. Lastly, the DD tests were conducted with a HCl receiver solution and the Ralex membrane, which was rinsed only with distilled water after each batch. The DD operations performances were evaluated in function of the percent extraction of NH_4^+ from the feed solution, the flux of NH_4^+ reaching the receiver solution, and the NH_4^+ mass balance. After the tests, the structural condition of the membranes was evaluated by means of Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR), Scanning Electron Microscope with Energy Dispersive Spectrometry (SEM-EDS) and ion-exchange capacity measurements.

2. Materials and methods

2.1. Donnan dialysis cell

The DD experiments were conducted in a two-compartment plexiglass cell with a cation-exchange membrane separating the compartments, as represented in Figure S1 (see Supplementary Material). Two membranes were tested: Ralex CMH-PES (MemBrain s.r.o, Stráž pod Ralskem, Czech Republic) and Fumasep FKS-PET-130 (Fumatech BWT GmbH, Bietigheim-Bissinge, Germany). The main properties of the membranes are shown in Table 1. Each compartment had a volume of 150 mL, and the effective area of the membranes was 11.2 cm², which were positioned vertically. Two mechanical stirrers were placed in the center of each compartment, respectively, for mixing the solutions under a rotation speed of 100 rpm. The DD tests were performed for 17 h at room-controlled temperature (~25 °C).

2.2. Working solutions

The feed solution initially rich in NH_4^+ and VFAs was a real solution derived from the acidogenic fermentation of cheese whey obtained as described in [12]. The fermented solution was clarified using a hollow fiber ultra-filtration module (5 × 105 MW cut-off, UFP-500-E-4 × 2MA, GE Healthcare). The chemical composition of the feed solution is shown in Table 2.

The receiver solution was composed of NaCl or HCl at a concentration of 0.35 mol/L, which is approximately ten times greater than the initial concentration of NH_4^+ in the feed solution. The receiver solution was freshly prepared with NaCl (Panreac, Barcelona, Spain) or HCl (Fisher Scientific, Loughborough, UK), and distilled water.

Table 1

Main characteristics of the Ralex CMHPES and Fumasep FKS-PET-130 membranes.

	Ralex CMHPES [26,27]	Fumasep FKS-PET-130 [28–30]
Type	Heterogeneous	Homogeneous
Ion-exchange group	R – SO ₃	Not specified
Thickness of dry membrane [μm]	450	90 – 100
Thickness of swelled membrane [μm]	700	127
pH stability	0 – 10	0 – 8
Ion-exchange capacity [meq/ g]	2.2	0.74
Water content [%]	55	19
Specific resistance (0.5 M NaCl) [Ω.cm ²]	<120	2.6 – 4.6
Transport number (0.5/0.1 M KCl)	>0.95	99
Permselectivity (0.5/0.1 M KCl)	>90	>96

Table 2
Chemical composition of the feed solution.

	Component	Concentration
Solids (g/L)	TSS*	0.38 ± 0.12
	VSS**	0.23 ± 0.01
Nutrients (mmol/L)	N-NH ₄	35.9
	P-PO ₄	0.6
VFAs (Cmmol/L)	Acetic acid	172.5
	Propionic acid	7.6
	Isobutyric acid	30.2
	Butyric acid	250.2
	Valeric acid	2.1
	Caproic acid	25.6
Other species (mmol/L)	Aluminium	0.00593
	Boron	0.01235
	Calcium	3.31146
	Copper	0.00248
	Iron	0.01336
	Magnesium	1.16394
	Potassium	15.4332
	Silicon	0.10071
	Sodium	39.2258
	Strontium	0.00364
	Zinc	0.01829
	Chloride	36.5823
	Nitrite	0.56448
	Sulfate	0.33916

* Total suspended solids.

** Volatile suspended solids.

2.3. Donnan dialysis experiments and chemical cleaning procedure

A flowchart showing the DD experiments and chemical cleaning procedure is shown in Figure S2 (see Supplementary Material). First, two DD tests were carried out with the Ralex and Fumasep membranes, respectively, using a NaCl solution as receiver in 10 batches without subjecting the membranes to the chemical cleaning step. In this case, the membranes were only rinsed with abundant distilled water for 7 h after each batch.

Then, a DD test was performed using the Ralex membrane and a NaCl solution as receiver in 10 batches, subjecting the membrane to the chemical cleaning procedure after each batch. The chemical cleaning procedure was carried out in both acidic and alkaline medium. In this case, after each DD batch, the membrane was rinsed with distilled water for 1.5 h (the solution was changed twice). Then, the membrane was immersed in a 1 % v/v NaOH solution for 2 h, rinsed with abundant distilled water, and then immersed in a 1 % v/v H₂SO₄ solution for 2 h. Lastly, the membrane was again rinsed with abundant distilled water for 1.5 h, before being used in the next DD batch. This cleaning procedure was based on the protocols generally used for cleaning cation-exchange membranes from fermentative processes [31,32].

Lastly, a DD test was performed with the Ralex membrane and HCl solution as the receiver solution in 10 batches. The membrane was not subjected to the chemical cleaning procedure, being only rinsed with abundant distilled water for 7 h after each batch.

Each experiment was conducted with a new sample of membrane. Before the experiments, the new membranes were equilibrated in a 0.5 mol/L NaCl solution for 72 h and rinsed with distilled water.

2.4. Analytical methods

2.4.1. Evaluation of the solutions

The analytical methods used for quantifying the total suspended solids (TSS) and volatile suspended solids (VSS) of the feed solution, the initial and final concentration of NH₄⁺, phosphate, organic acids, and

other cationic and anionic species in the solutions, besides the determination of their pH values, are described in detail in [12].

2.4.2. Evaluation of the membranes

The chemical structure, morphology and ion-exchange capacity of the new and used membranes were evaluated. The new membranes were already present in their dry form, whereas samples of the used membranes were soaked in distilled water and dried at 40 °C for 15 h before being analyzed.

The chemical structure of the membranes was evaluated by Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (Spectrum Two FT-IR Spectrometer, PerkinElmer, Waltham, USA). Their morphology and chemical composition were evaluated by means of Scanning Electron Microscope (Hitachi S2400, Tokyo, Japan) with Bruker (Billerica, Massachusetts) light elements EDS detector using different magnifications.

The ion-exchange capacity (IEC) of the new and used membranes was calculated by acid-base titration using Equation (1) [33]. In the equation, C_{NaOH} and V_{NaOH} are the molar concentration and volume of the NaOH solution consumed in the titration, respectively, and m_{dry} is the mass of dry membrane sample. Firstly, the dry membrane samples were weighted for determining the m_{dry} term of Equation (1). Then, the membrane samples were soaked in 100 mL of 1 mol/L H₂SO₄ for 24 h to be converted into their H⁺ form. Then, the membranes were soaked in abundant distilled water to remove any trace of the acid solution from their surface (the solution was changed several times). Then, the membrane samples were equilibrated in 100 mL of 1 mol/L NaCl solution for 24 h to allow for the exchange of H⁺ ions present in the membrane and Na⁺ from the solution. Lastly, the NaCl solution containing the released H⁺ ions was titrated with 0.01 mol/L NaOH solution (C_{NaOH} of Equation (1) using phenolphthalein as pH indicator, and the V_{NaOH} term of Equation (1) was then determined.

$$IEC = \frac{V_{NaOH} \cdot C_{NaOH}}{m_{dry}} \quad (1)$$

2.5. Calculations of percent extractions, molar fluxes, and mass balances

The NH₄⁺ extraction from the feed solution after each batch was evaluated by calculating the percent extraction (PE%) using Equation (2). In the equation, C_{F_0} and C_{F_f} are the concentration of NH₄⁺ in the feed solution (F) at the beginning and the end (after 17 h), respectively, of the experiments.

$$PE(\%) = \left(1 - \frac{C_{F_f}}{C_{F_0}}\right) \cdot 100 \quad (2)$$

The flux (J) of NH₄⁺ that reached the receiver solution was calculated using Equation (3), where C_{R_0} and C_{R_f} are the concentration of NH₄⁺ in the receiver solution (R) at the beginning and the end (after 17 h), respectively, of the experiments, V is the volume of the receiver solution, A_m is the membrane area, and t is time.

$$J = \frac{(C_{R_f} - C_{R_0}) \cdot V}{A_m \cdot t} \quad (3)$$

The mass balances (MB) of NH₄⁺ were calculated after each DD batch using the final NH₄⁺ mass in the feed and receiver solutions and the initial NH₄⁺ mass in the feed solution (Equation (4)). For the NH₄⁺ flux and mass balance calculations, a possible variation in the volume of the solutions due to the transport of water through the membranes via osmosis was neglected since no noticeable change in the volumes was verified.

$$Mass\ balance = 100 \cdot \left(\frac{finalNH_4^+ mass_{(F+R)}}{initialNH_4^+ mass_{(F)}} \right) \quad (4)$$

3. Results and discussion

The results are presented in three different sections. In the first section (Section 3.1), the influence of the membrane type on the occurrence of fouling and sorption was evaluated. In this case, the DD experiments were conducted using a NaCl solution as receiver and the Fumasep and Ralex membranes without being subjected to a chemical cleaning procedure after each batch. In Section 3.2, the results of the evaluation of the effect of chemical cleaning on the performance of DD conducted with the Ralex membrane and a NaCl solution as receiver are presented. Lastly, Section 3.3 presents the results of DD experiments carried out using the Ralex membrane and a HCl solution as receiver. In this case, the membrane was not subjected to a chemical cleaning procedure. Each of these sections presents the results of DD performance (PE%, flux and mass balance of NH_4^+ , and pH of the solutions) followed by the structural characterization of the membranes (SEM-EDS, FT-IR, and IEC).

3.1. Donnan dialysis with the Ralex and Fumasep membranes, a NaCl solution as receiver, and no chemical cleaning procedure

Firstly, two distinct DD experiments were conducted with the Fumasep and Ralex membranes, respectively, which were only rinsed with distilled water after each batch.

3.1.1. Donnan dialysis performance

The results of percent extraction and flux of NH_4^+ obtained with each membrane are shown in Fig. 1, while the results of mass balance of NH_4^+ are presented in Table S1 of the Supplementary Material. The initial and final pH values of the feed and receiver solutions are shown in Table 3. The pH values for the final solutions shown in Table 3 correspond to the mean of all batches because they were similar.

The percent extraction values were significantly higher with the Fumasep than with the Ralex in all batches, which occurred due to the homogeneity and considerably lower thickness of the former (Table 1). Recently, a similar result was obtained in the extraction of NH_4^+ by DD using both membranes evaluated here [12]. In the previous work, the DD process was evaluated over time in a single batch, and it was found that, up to a certain time, the performance of Fumasep was better than that of Ralex for extracting NH_4^+ . However, the influence of DD operation in multiple batches was not evaluated in the previous work.

As shown in Fig. 1, the membranes showed different behaviors regarding NH_4^+ transfer throughout the batches runs performed. For Fumasep, the percent extraction remained virtually constant at around 65% along the 10 batches, while for Ralex the percent extraction for the first batch was 55%, but reduced to approximately 40% in the subsequent batches. This indicates that the performance of NH_4^+ extraction from the feed solution remains constant throughout the batches with Fumasep when it is rinsed with water, while the NH_4^+ extraction performance of Ralex membrane is hindered along the batches. On the

Table 3

pH values of the initial and final solutions from the DD experiments conducted using the Fumasep and Ralex, a NaCl solution as receiver, and without the membranes being subjected to a chemical cleaning procedure.

Membrane	Initial feed	Final feed (Mean of batches 1 – 10)	Initial receiver	Final receiver (Mean of batches 1 – 10)
Fumasep	4.48	4.53	6.02	3.98
Ralex	4.41	4.48	5.93	4.21

other hand, the NH_4^+ molar flux that reached the receiver solution did not show considerable variations along the batches with both membranes, especially with the Fumasep membrane. These results indicate that, for Fumasep, the NH_4^+ ions that left the feed solution reached the receiver solution in the same proportion in all batches, whereas for Ralex a fraction of NH_4^+ that was extracted in the first batch did not reach the receiver solution. This occurred due to a NH_4^+ ions sorption phenomenon, as confirmed by the mass balance values shown in Table S1 (92% and 84% in the first batch with the Fumasep and Ralex, respectively). According to Fig. 1, this effect was significant only in the first batch, which can be explained by the presence of NH_4^+ sorbed to the functional groups from the second batch onwards. In this sense, the NH_4^+ ions sorbed onto the functional groups in the first batch prevent the NH_4^+ ions from subsequent batches from being sorbed, as shown by the increasing mass balance values throughout the batches. No significant differences in the concentration of VFAs and phosphate ions in the feed solution were verified in all experiments carried out in this work, which means that they were not transferred to the receiver solution, as expected due to their negative charges.

According to Table 3, the pH of the feed solution increased slightly after the batches, while for the receiver solution it decreased with greater intensity. This occurred mainly due to the absence and presence, respectively, of NH_4^+ in the solutions. The pH variation is more noticeable for the receiver solution as it is composed of NaCl, while the complex feed solution presents buffer properties (Table 2). When comparing the membranes, the pH variations were more intense with Fumasep than with Ralex due to the higher intensity of NH_4^+ transport through the former, as shown in Fig. 1.

3.1.2. Structural characterization

3.1.2.1. SEM. Fig. 2 shows SEM images (1000 × magnification) of the new Ralex and Fumasep membranes, while the SEM images obtained using a 500 × magnification are shown in the Supplementary Material (Figure S3). The arrows present in the SEM images indicate the regions analyzed by EDS. The EDS results for the new Ralex and Fumasep membranes are shown in Table S2 of the Supplementary Material. As expected, Fumasep exhibits a homogeneous surface while Ralex presents a heterogeneous structure with dispersed clusters of ion exchange particles. According to the EDS results shown in Table S2, the chemical

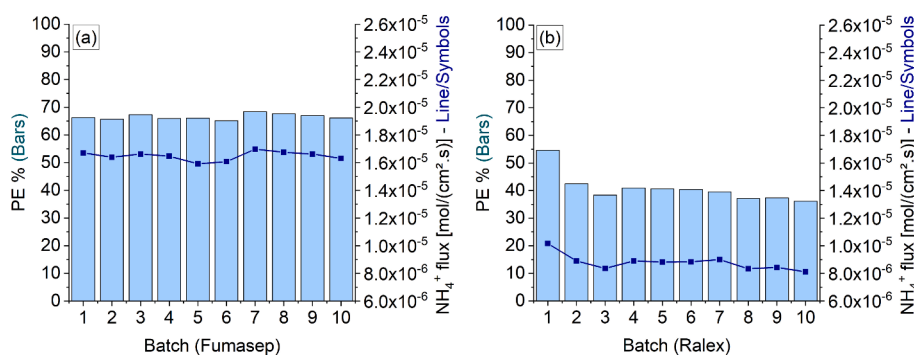


Fig. 1. PE% (bars) and flux (symbols with connecting line) of NH_4^+ obtained with the (a) Fumasep and (b) Ralex using a NaCl solution as receiver and without conducting a chemical cleaning procedure.

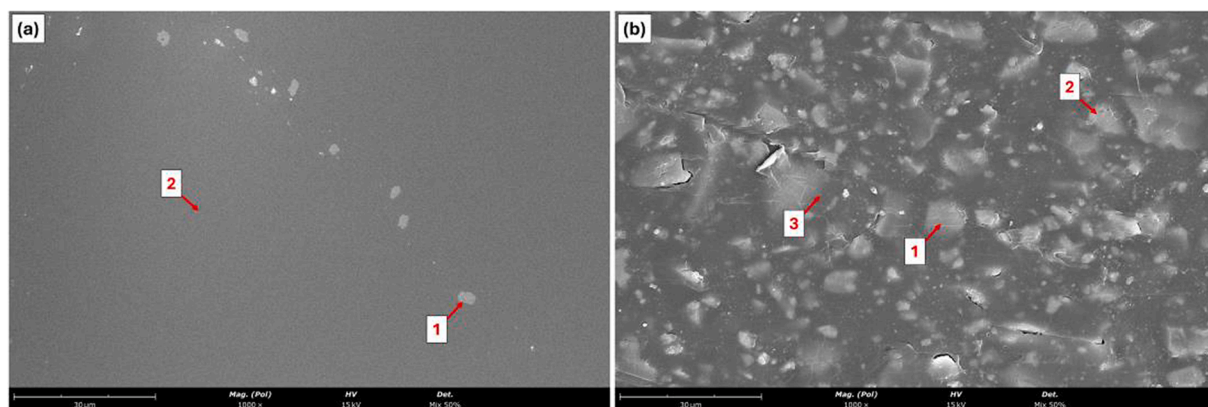


Fig. 2. SEM images (1000 × magnification) of the new (a) Fumasep and (b) Ralex membranes, respectively.

composition of the membranes is similar, so that the C and O in both membranes are from the polymer, while the S in Ralex is due to the sulfonic acid functional group. To the best of our knowledge, there is no information about the functional group of the Fumasep membrane published in the open literature, but the presence of S in this membrane at high concentrations (~12 %) indicates that their functional groups are also SO_3^- .

Fig. 3 presents SEM images (1000 ×) of the surfaces of the used Fumasep that were in contact with the feed and receiver solutions, respectively, Table S3 of the Supplementary Material presents the EDS results, and Figure S4 of the Supplementary Material shows the SEM images obtained using a 500 × magnification. A difference between the two surfaces of Fumasep was verified, as nitrogen was present only on the feed side despite their concentration being higher in the receiver solution after the 10 DD batches. The presence of Ca was observed at both membrane surfaces, which were counter-ions initially present at high concentrations in the feed solution (Table 2). These results indicate that the mass balance value of approximately 90 % shown in Table S1 is due to the retention of part of the NH_4^+ ions on the feed surface of the Fumasep, which did not impair the process since the percent extraction remained virtually unchanged at all batches. The absence of NH_4^+ at the receiver surface of the membrane may indicate that the NaCl solution is able to desorb it from the Fumasep.

Fig. 4 shows SEM images (1000 × magnification) of both surfaces of the used Ralex membrane after 10 batches of DD, the EDS results are shown in Table S4 of the Supplementary Material, and the SEM images obtained using a 500 × magnification are shown in Figure S5 of the Supplementary Material. Fouling occurrence and NH_4^+ sorption was much more intense at the receiver surface of the Ralex than at the feed surface, despite the SEM image of the receiver side resembling the new

membrane more closely. Nitrogen was present on both surfaces of the Ralex, mainly on the receiver side, indicating that it may have become adsorbed within its interior. Thus, the NaCl receiver solution was not able to desorb the NH_4^+ ions from the Ralex. The filaments shown on the feed surface consist of carbon and oxygen, which can be explained by the presence of a small fraction of VFAs adhered to the membrane. Lastly, species of Ca were present at the receiver membrane surface since they were counter-ions transferred from the feed solution.

3.1.2.2. FTIR. The Fumasep and Ralex membranes used in 10 batches of DD without being subjected to the chemical cleaning procedure were characterized by FTIR, and the spectra are shown in Fig. 5. For each membrane, three spectra are presented in the figures, referring to the membrane surface that was in contact with the feed and receiver solutions, respectively, in addition to the spectra of a new membrane. The assignments of the peaks shown in Fig. 5 are presented in Table S5 (Fumasep) and Table S6 (Ralex) of the Supplementary Material.

For the Fumasep membrane, the vertical shift of the receiver surface spectrum is greater than that of the feed surface. This can be explained by the higher dispersion of the fouled species on the receiver surface as shown in the SEM images of Fumasep (Fig. 3). Most peaks did not show differences in their wavelength numbers (Table S5), except for the peak at 2804 cm^{-1} (C-H) of the new membrane, which disappeared in the used membrane. Peaks between 2902 cm^{-1} and 2989 cm^{-1} were verified only at the used membrane, which may be associated with the interaction between the Fumasep- NH_4^+ from the NH_4^+ sorbed, as verified by Karelin et al. [34] for Nafion- NH_4^+ between $2870 \pm 10 \text{ cm}^{-1}$ and $3212 \pm 4 \text{ cm}^{-1}$, or due to the presence of Ca at both surfaces, as shown in Table S3. The unchanged values of most peaks of the Fumasep despite the presence of NH_4^+ and other species at its surfaces agree with the

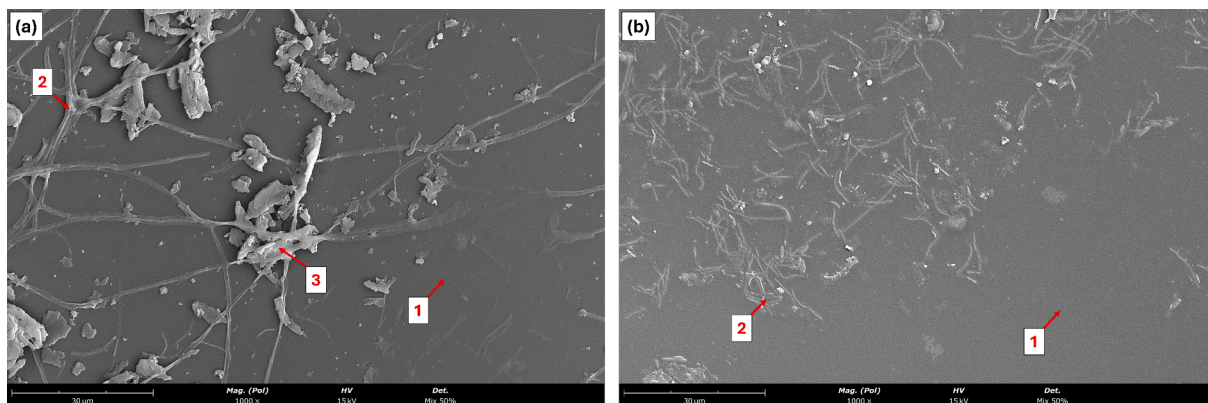


Fig. 3. SEM images (1000 × magnification) of the (a) feed and (b) receiver surfaces of the Fumasep after 10 batches of DD using a NaCl solution as receiver and without conducting a chemical cleaning procedure.

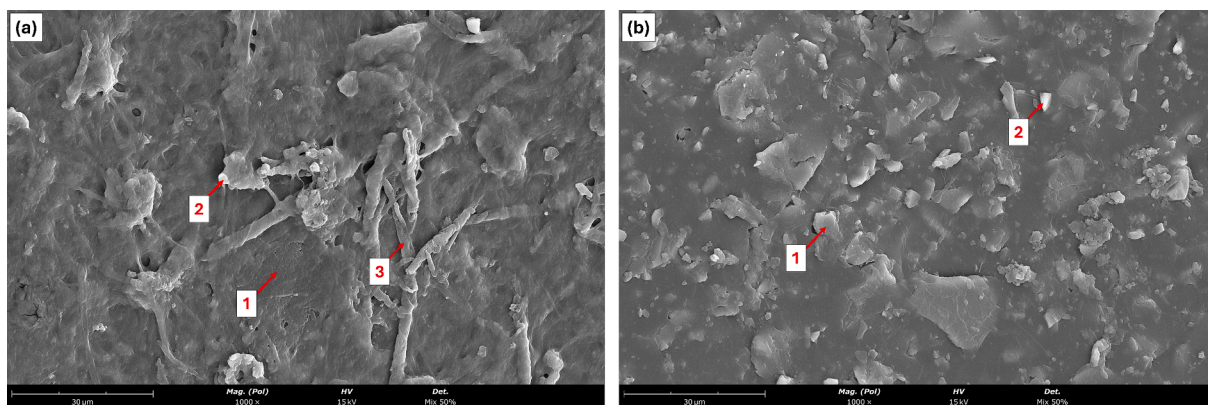


Fig. 4. SEM images (1000 × magnification) of the (a) feed and (b) receiver surfaces of the Ralex after 10 batches of DD using a NaCl solution as receiver and without conducting a chemical cleaning procedure.

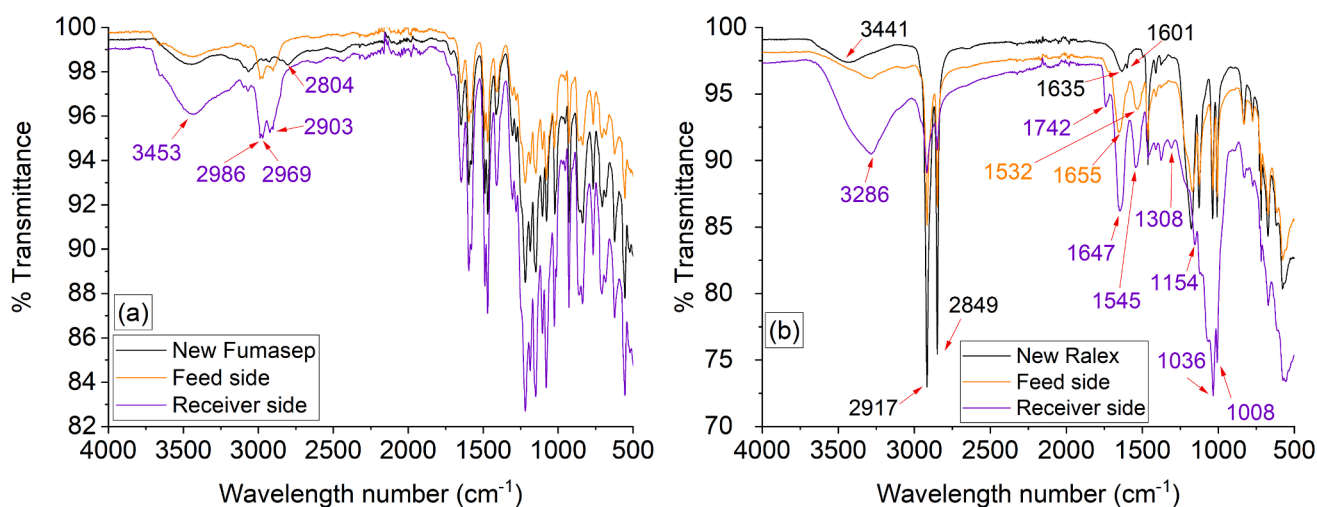


Fig. 5. FTIR spectra of the new and used (a) Fumasep and (b) Ralex after 10 batches of DD using a NaCl solution as receiver and without conducting a chemical cleaning procedure.

maintenance of the constant percent extraction after 10 DD batches.

For the Ralex, the spectra of both surfaces of the used membrane also shifted vertically in relation to the new membrane. Unlike Fumasep, the used Ralex exhibited significantly different behaviors from the new membrane. As shown in Fig. 5 and Table S6, some peaks initially present at the new membrane, such as at 3441 cm^{-1} ($\nu(\text{O-H})$ of the bounded water), 1635 cm^{-1} (C-H stretching), and 1601 cm^{-1} (C-H stretching vibration), disappeared or were shifted after DD, which may have occurred due to the NH_4^+ sorption or fouling, while some peaks appeared after the process. The peak at 3286 cm^{-1} appeared on both surfaces due to the N-H stretching from the NH_4^+ sorbed [35]. The peaks at 1655 and 1532 cm^{-1} appeared at the feed surface, while the peaks at 1742 , 1647 , 1545 , 1308 and 1154 cm^{-1} appeared at the receiver surface. It is suggested that the peaks at 1532 and 1545 cm^{-1} are related to the N-H stretching from the sorbed NH_4^+ [35], but dedicated studies must be conducted to confirm it. The peaks at 1655 cm^{-1} (feed) and 1647 cm^{-1} (receiver) (related to C-H stretching vibration) may have been shifted from 1635 cm^{-1} as a consequence of sorption/fouling. No information was found in the literature regarding the other peaks detected at the used membrane, which may have appeared due to the interaction of NH_4^+ ions with the membrane or the presence of the species verified in Table S4. Lastly, the spectrum of the receiver surface of Ralex shows that the peaks related to the SO_3^- functional groups of the membrane, between $1178 - 1008\text{ cm}^{-1}$, emerged and shifted considerably when compared to the new membrane. This most probably occurred because

of the intense sorption and fouling occurrence at/in the Ralex, which was more noticeable at the fixed groups due to the higher attraction between the fixed groups and counter-ions. The greater intensity of NH_4^+ sorption and fouling occurrence at the Ralex when compared to the Fumasep explains the reduction in the Ralex percent extraction after the first batch. The SEM-EDS and FTIR results indicate the need for chemical cleaning of the Ralex membrane.

3.1.2.3. Ion-exchange capacity. The IEC obtained for the new Fumasep and Ralex membranes were 1.45 meq/g and 2.22 meq/g , respectively, which are in accordance with the literature [27,28]. The final IEC values were 1.41 meq/g for the Fumasep and 2.15 meq/g for the Ralex, indicating a reduction of approximately 3 % for both membranes after 10 batches of DD. The similar IEC trend verified for the membranes, despite the more intense occurrence of sorption and fouling at/in the Ralex, can be explained by the desorption of species by the H_2SO_4 solution used for the IEC calculation.

3.2. Donnan dialysis with the Ralex membrane, a NaCl solution as receiver, and a chemical cleaning procedure

Considering the reduction in the NH_4^+ percent extraction because of the NH_4^+ sorption and intense fouling occurrence at/in the Ralex, the DD performance was evaluated subjecting the membrane to the chemical cleaning procedure after each batch.

3.2.1. Donnan dialysis performance

Fig. 6 shows the values of percent extraction and flux of NH_4^+ obtained with the Ralex membrane, which was chemically cleaned after each batch, while the results of mass balance of NH_4^+ are presented in Table S7 of the Supplementary Material. The initial and final pH values of the feed and receiver solutions are shown in Table 4. For the final solutions, the pH values shown in Table 4 correspond to the mean of batches 2–10.

According to Fig. 6, the percent extraction and flux of NH_4^+ remained constant throughout all batches when chemically cleaning the Ralex membrane after each batch. The mass balance values of NH_4^+ (Table S7) were slightly lower than those obtained without chemically cleaning the membrane, as the cleaning procedure removed the sorbed species from the functional groups, allowing new ions from the feed solution of each batch to be sorbed. The pH of the feed slightly increased while the pH of the receiver significantly decreased after the first batch due to the transfer of NH_4^+ ions. From the second batch onward, the pH of the feed and mainly the receiver solution decreased more intensely due to the H^+ ions from the membrane cleaning process being released into the solutions throughout the DD.

3.2.2. Structural characterization

3.2.2.1. SEM. Fig. 7 shows SEM images of the used Ralex membrane that was subjected to the chemical cleaning step after each batch, while the EDS results are presented in Table S8. The SEM images obtained using a $500\times$ magnification are shown in Figure S6 of the Supplementary Material.

Both surfaces exhibited similar morphologies and compositions, showing small concentrations of Ca, Mg, and Al that were not removed from the membrane by the cleaning solutions. The higher concentration of these metals at the receiver solution when compared to the DD operated without chemical cleaning (compare Table S4 to Table S8) can be explained by the release of H^+ ions from the acid solution throughout the DD after the cleaning procedure and the consequent pH reduction of the receiver solution (Table 4). In this sense, the presence of H^+ in the receiver solution and their consequent transfer to the feed solution may have intensified the transport of the metallic counter-ions in the opposite direction from the feed to the receiver solution. On the other hand, the NH_4^+ ions were desorbed from the membrane since no nitrogen was detected in the EDS analysis, which increased the percent extraction after the 1st batch (compare Fig. 1b with Fig. 6). The constant percent extraction values shown in Fig. 6, the presence of metallic species and

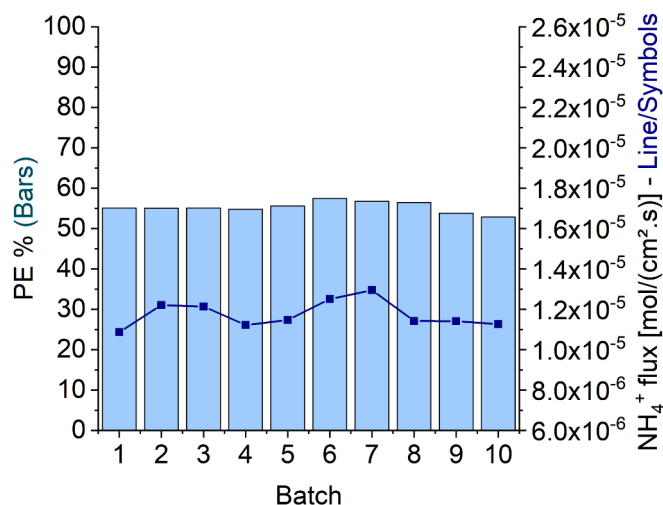


Fig. 6. PE% (bars) and flux (symbols with connecting line) of NH_4^+ obtained with the Ralex using a NaCl solution as receiver and conducting a chemical cleaning procedure.

Table 4

pH values of the initial and final solutions from the DD experiments conducted using a NaCl solution as receiver with the membrane being subjected to a chemical cleaning procedure.

Membrane	Initial Feed	Final feed (batch 1)	Final feed (means of batches 2 – 10)	Initial receiver	Final receiver (Batch 1)	Final receiver (Means of batches 2 – 10)
Ralex	4.51	4.59	4.49	5.87	4.41	2.9

the absence of nitrogen at the membrane suggest that NH_4^+ sorption hinders the DD performance with the Ralex more intensely than fouling of the metallic species. It is worth mentioning that the NH_4^+ ions removed from the membrane were transferred to the cleaning solutions, therefore, they must be recovered from these solutions. The SEM image ($500\times$ magnification) shown in Figure S6 of the Supplementary Material shows the presence of small cavities at the membrane indicating polymer structure degradation, which may have occurred due to the exposure of the membrane to the acidic and/or alkali medium of the cleaning solutions used after each batch [20].

3.2.2.2. FTIR. The FTIR spectra of both surfaces of the Ralex membranes used in 10 batches of DD subjecting the membrane to the chemical cleaning procedure after each batch are shown in Fig. 8. The assignments of the peaks shown in Fig. 8 are presented in Table S9 of the Supplementary Material.

Fig. 8 and Table S9 show that the FTIR spectra of the two membrane surfaces that underwent chemical cleaning after each batch were very similar to the new membrane. All peaks have virtually the same wavelength number and did not show vertical displacements, indicating that there were no significant amounts of fouled or sorbed species. Three peaks were observed at each surface of the used membrane that were not present in the new membrane: 1730 cm^{-1} (feed), 1726 cm^{-1} (receiver), 1646 cm^{-1} (feed), 1653 cm^{-1} (receiver), 1551 cm^{-1} (feed), and 1537 cm^{-1} (receiver). The peaks at 1646 cm^{-1} (feed) and 1653 cm^{-1} (receiver) may have been shifted from 1635 cm^{-1} (new membrane) due to sorption or fouling occurrence, as verified in the previous section, while the peaks at 1551 cm^{-1} and 1537 cm^{-1} may be related to the N–H stretching from the sorbed NH_4^+ [35]. As specific FTIR peak data for interactions of NH_4^+ or metallic species with membranes are scarce in the literature, dedicated studies must be carried out to confirm these suggestions. Unlike the previous results, the intensity of some peaks of the receiver surface are lower than those of the feed, such as at 2916 cm^{-1} ($\nu_{\text{as}}\text{CH}_2$), 2848 cm^{-1} ($\nu_{\text{s}}\text{CH}_2$), 1177 cm^{-1} , 1125 cm^{-1} , 1043 cm^{-1} , 1007 cm^{-1} (SO_3 functional group). This indicates that part of the polymer was degraded by the cleaning solutions, including the functional groups, which was also verified in the SEM images (Figure S6).

3.2.2.3. Ion-exchange capacity. The IEC of the Ralex membrane that was subjected to the chemical cleaning procedure was 2.01 meq/g , which was a lower value than that of the membrane that was only rinsed with distilled water (2.15 meq/g) and the new one (2.22 meq/g). This can be explained by the degradation of part of the fixed functional groups of the membrane by the cleaning solutions, as verified in the SEM images and FTIR spectra.

3.3. Donnan dialysis with the Ralex membrane, HCl solution as receiver, and no chemical cleaning procedure

Lastly, the DD performance was evaluated using a HCl solution as receiver in order to verify whether the receiver's acidic medium was capable of cleaning the Ralex membrane. After each batch, the membrane was rinsed with only distilled water, preventing it from being

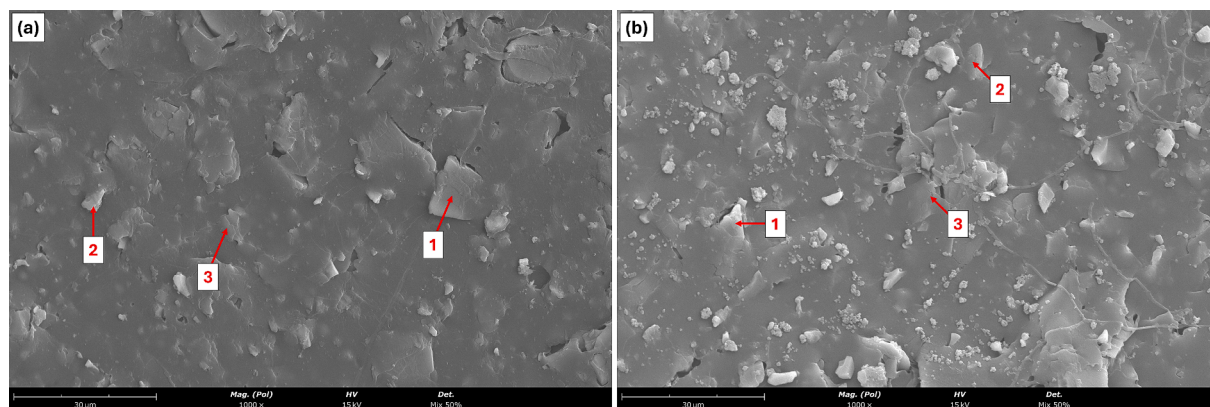


Fig. 7. SEM images (1000 × magnification) of the (a) feed and (b) receiver surfaces of the Ralex after 10 batches of DD using a NaCl solution as receiver and conducting a chemical cleaning procedure.

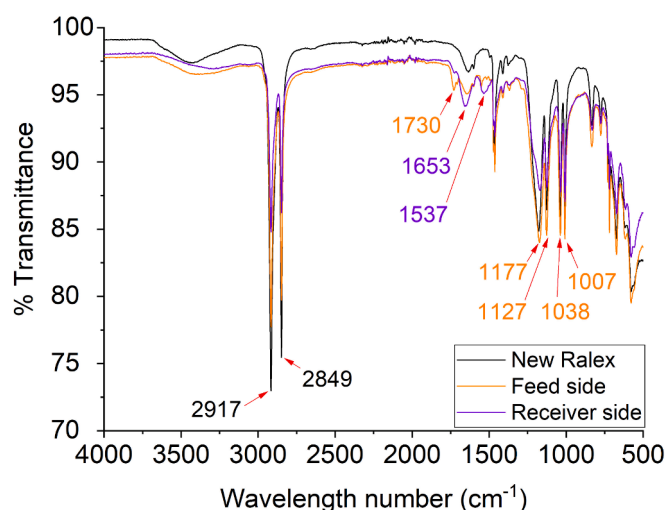


Fig. 8. FTIR spectra of the new and used Ralex after 10 batches of DD using a NaCl solution as receiver and conducting a chemical cleaning procedure.

exposed to the acidic and alkaline solutions of the chemical cleaning procedure.

3.3.1. Donnan dialysis performance

Fig. 9 shows the values of percent extraction and flux of NH_4^+ obtained with the Ralex membrane and a HCl solution as receiver, while the results of mass balance of NH_4^+ are presented in Table S10 of the Supplementary Material. The initial and final pH values of the feed and receiver solutions are shown in Table 5. For the final solutions, the pH values shown in Table 5 correspond to the mean of batches 1–10 because they were similar.

The percent extraction obtained in the first batch was approximately 60 %, which was slightly higher than that obtained with NaCl (Fig. 1b and Fig. 6). The greater transfer of NH_4^+ using HCl when compared to NaCl was also observed by Chen et al. [21] under some concentration conditions, and can be explained by the greater diffusivity of H^+ compared to Na^+ ions [36]. The percent extractions obtained from the second batch onwards decreased slightly reaching 52 % at the 10th batch. This decrease was lower than the decrease verified in the DD operated with NaCl solution without subjecting the membrane to the chemical cleaning, indicating a greater NH_4^+ desorption and/or membrane cleaning by the H^+ than Na^+ ions from the receiver solution. The desorption effect of NH_4^+ by H^+ ions can be verified by the higher mass balance values obtained with HCl when compared to NaCl (compare Table S1 with Table S7).

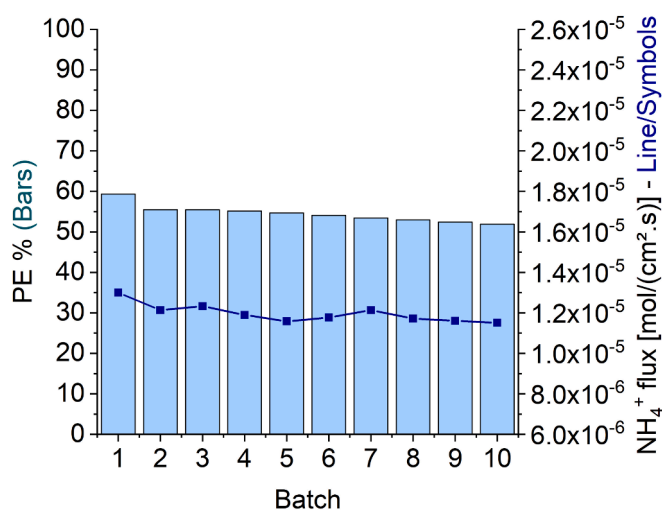


Fig. 9. PE% (bars) and flux (symbols with connecting line) of NH_4^+ obtained with the Ralex using a HCl solution as receiver and without conducting a chemical cleaning procedure.

Table 5

pH values of the initial and final solutions from the DD experiments conducted using a HCl solution as receiver without the membranes being subjected to a chemical cleaning procedure.

Membrane	Initial feed	Final feed (Mean of batches 1 – 10)	Initial receiver	Final receiver (Mean of batches 1 – 10)
Ralex	4.52	1.89	0.99	1.04

According to Table 5, the pH of the feed solution decreased considerably after the DD batches, as expected, due to the migration of H^+ ions from the receiver solution. The receiver solution pH remained practically constant because although the H^+ ions migrated to the feed solution, the acidic NH_4^+ ions from the feed solution migrated in the opposite direction reaching the receiver solution.

3.3.2. Structural characterization

3.3.2.1. SEM. Fig. 10 presents SEM images of the Ralex membrane after 10 batches of DD using a HCl solution as receiver, while Table S11 presents the EDS results. SEM images obtained using a 500 × magnification are shown in Figure S7 of the Supplementary Material.

The SEM image of the feed surface shows the presence of small clusters of particles throughout the membrane surface, which are

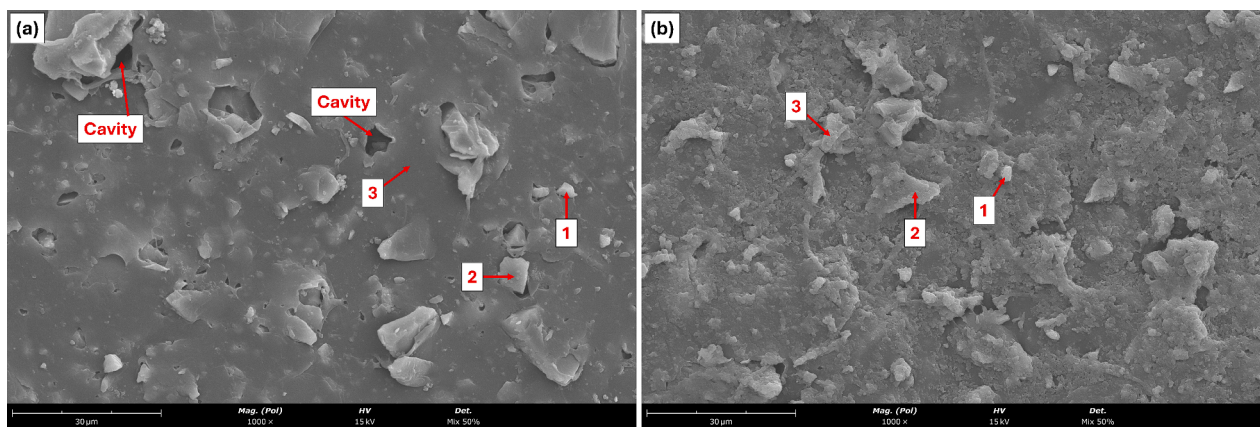


Fig. 10. SEM images (1000 × magnification) of the (a) feed and (b) receiver surfaces of the Ralex after 10 batches of DD using a HCl solution as receiver and without conducting a chemical cleaning procedure.

composed of Ca, Cr and Fe (Table S11). The SEM image of the receiver side shows a rough surface considerably different from the new membrane. According to Table S11, this occurred due to the intense presence of NH_4^+ ions sorbed at the receiver surface of the Ralex. Unlike the results for the NaCl receiver solution, the NH_4^+ sorption occurrence using HCl did not hinder the DD performance throughout the batches, which can be explained by the continuous desorption of NH_4^+ by the H^+ ions during the DD. No filaments related to the presence of VFAs were observed on the membrane, unlike the DD conducted with NaCl without the cleaning procedure. This can be explained by the pKa value of the VFAs (~4.8) and lower pH of the solutions from the DD conducted with HCl (compare Table 3 with Table 5). In this sense, at pH values lower than approximately 4.8, the VFAs are predominantly negatively charged, being repelled by the membrane, whereas at pH values close to 4.8, they are neutral and can adhere more easily to the membrane. Fig. 10(a) and Fig. S7(a) show the presence of cavities at the feed surface indicating polymer degradation, which occurred due to the acidic pH of the receiver solution (Table 5). It is worth mentioning that the cavities may not have been seen at the SEM image of the receiver surface due to its intense coverage by NH_4^+ ions.

3.3.2.2. FTIR. The FTIR spectra of the Ralex membranes used in 10 batches of DD with a HCl solution as receiver without being subjected to the chemical cleaning procedure after each batch are shown in Fig. 11. The assignments of the peaks shown in Fig. 11 are presented in

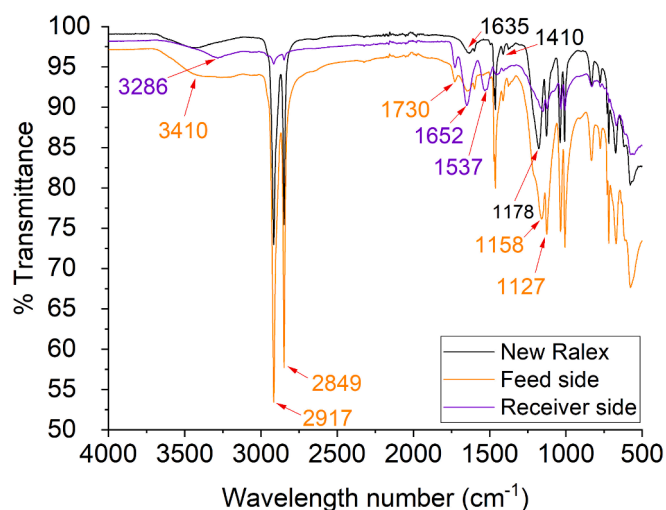


Fig. 11. FTIR spectra of the new and used Ralex after 10 batches of DD using a HCl solution as receiver without conducting a chemical cleaning procedure.

Table S12 of the Supplementary Material.

The spectrum for the feed surface of the Ralex shown in Fig. 11 indicates a strong vertical shift, which is associated with the intense fouling observed at the SEM image in Fig. 10 and Table S11. The region of the spectrum relative to the SO_3^- functional groups exhibited a behavior similar to the Ralex membrane that was not subjected to chemical cleaning (Fig. 5b), as the peaks at 1158 and 1127 cm^{-1} were displaced and became less defined. This could be attributed to the fouling of the metallic counter-ions such as Ca, Cr, and Fe at the feed surface of the membrane (Table S11). The overall spectrum of the receiver surface showed, except for the peaks at 1652 and 1535 cm^{-1} , peaks with considerably lower intensities when compared to the new membrane, especially the peaks at 2917 and 2849 cm^{-1} , related to $\nu_{\text{as}}\text{CH}_2$ and $\nu_{\text{s}}\text{CH}_2$, respectively. The peaks at 1410, 1376, and 1178 cm^{-1} were present at the new membrane and disappeared at some of the surfaces after DD. These disappearances or reductions in the intensity of the peaks may be associated with polymer degradation due to exposure of the membrane to the acidic solution, as verified in the SEM images. Several additional peaks were verified at both surfaces. The peak at 3410 cm^{-1} present at the feed surface may have been shifted from the new membrane (3441 cm^{-1}) being related to the $\nu(\text{O-H})$ of the bounded water. The peak at 3286 cm^{-1} appeared at the receiver surface due to the N-H stretching [35] from NH_4^+ ions sorbed at/in it, as occurred for the Ralex used from the DD using NaCl solution without subjecting the membrane to the chemical cleaning. The peaks at 1647 cm^{-1} and 1652 cm^{-1} may have been shifted from 1635 cm^{-1} (C-H stretching vibration at the new membrane) due to the sorption or fouling occurrence, as also verified in the previous section. The peaks at 1554 cm^{-1} and 1537 cm^{-1} may be related to the N-H stretching from the sorbed NH_4^+ [35]. No information was found in the literature on the peaks at 1158 cm^{-1} (feed) and 1150 cm^{-1} (receiver), which may be related to sorption/fouling occurrence.

3.3.2.3. Ion-exchange capacity. The final IEC of the Ralex after 10 batches of DD using a HCl solution as receiver was 2.03 meq/g, which was similar to the value obtained for the Ralex that was subjected to the cleaning procedure after each DD batch using a NaCl solution as receiver (2.01 meq/g) and lower than for the new membrane (2.22 meq/g). The lower IEC when compared to the new membrane may be related to the membrane degradation due to the contact with the acidic receiver solution throughout the 10 DD batches.

4. Conclusions

The effects of long-term DD operations to recover NH_4^+ from a real fermented solution derived from an acidogenic fermentation process for producing PHAs were evaluated using the Fumasep FKS-PET-130 and

Ralex CMH-PES membranes with NaCl or HCl solution as receiver. A chemical cleaning procedure in acidic and alkaline media was proposed for the Ralex membrane. The obtained results showed that NH_4^+ sorption and fouling occurred on/inside both membranes using a NaCl solution as receiver, which limited the DD operation. This was more intense with the Ralex, particularly at its functional groups, thus impairing the NH_4^+ extraction since its percent extraction decreased from 55 % (first batch) to approximately 40 % in the subsequent batches. The percent extraction values obtained with the Fumasep were considerably greater than with Ralex and remained constant at around 65 % throughout the consecutive batches being only rinsed with distilled water. The chemical cleaning of Ralex after each batch overcame the reduction in the percent extractions caused by the sorption/fouling occurrence, maintaining a nearly constant NH_4^+ percent extraction in all batches. However, the cleaning solutions degraded the Ralex, creating cavities at its surface. The use of a HCl solution as receiver with the Ralex reduced the negative effects of fouling, increasing slightly the NH_4^+ percent extractions (between 60 % and 52 % from the first to the 10th batch, respectively) when compared to NaCl. Nonetheless, the HCl solution also degraded the Ralex membrane. It is therefore suggested that the Fumasep is more appropriate for the application evaluated in this study. On the other hand, a new cleaning procedure should be developed for the more cost-affordable Ralex membrane using less concentrated acidic and/or alkaline solutions.

Declaration of competing interest

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

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2024.129834>.

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