

Investigation of nanofiltration as a purification step for lactic acid production processes based on conventional and bipolar electro dialysis operations

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Abstract

Nanofiltration was investigated for usability in a specific lactic acid production process based on conventional and bipolar electro dialysis operations. Industrial fluids, corresponding to two potential integration levels and coming from an existing installation, were investigated. The commercially available DK nanofiltration membrane was used and performances in terms of lactate/lactic acid recovery rate and purification efficiency are reported. Nanofiltration was able to efficiently remove magnesium and calcium ions from a sodium lactate fermentation broth before its concentration and conversion by electro dialysis (first potential integration level). Maximum impurities rejections and lactate recovery were obtained at maximum transmembrane pressures. Mg^{2+} and Ca^{2+} rejections were 64 ± 7 and $72 \pm 7\%$, respectively and lactate recovery rate reached $25 \pm 2 \text{ mol m}^{-2} \text{ h}^{-1}$ for $\Delta P = 20 \text{ bar}$. Sulfate and phosphate ions were also partially removed from the broth (40% rejection). At the invert, chloride ions were negatively retained by the membrane and were consequently more concentrated in the permeate. Nanofiltration also led to a nearly total decolouration of the fermentation broth. On the other hand, sulfate and phosphate rejections obtained from the filtration of a converted broth containing the lactic acid under its neutral form (second potential integration level) were also satisfactory, i.e. 47 ± 5 and $51 \pm 5\%$, respectively. High recovery rates were observed in that case, i.e. $48 \pm 2 \text{ mol m}^{-2} \text{ h}^{-1}$ at 20 bar. It indicated that NF could also be used as final purification step in the process.

Keywords: Downstream processing; Lactic acid; Nanofiltration; Fermentation broth; Electro dialysis

1. Introduction

Lactic acid has become an essential additive for flavor and preservation in a large number of industries including food manufacturing and pharmaceuticals. Additionally, its derivatives and polymers start to be used in various applications ranging from drug delivery [1] to the production of biodegradable plastics on an industrial scale [2]. As a result, lactic acid is generating more and more interest and the market, which represented 86,000 tonnes in 2001, is now expected to reach more than 500,000 tonnes in 2010 [3]. Because of this increasing demand, and also because of the more and more drastic environmental constraints in our societies, more efficient lactic acid production processes that lead to less by-products are needed. Almost

all the processes now adopted are based on an initial biological fermentation step followed by several downstream operations. Thus, part of the work consists of optimizing the fermentation conditions [4–7]. But improving the downstream processing efficiency is also of great interest. To that respect, a large number of recent studies proposed new combinations of traditional and/or innovative operations to be used after fermentation (liquid–liquid extraction [8,9], ion-exchange [10], adsorption [11], electro dialysis [12–14] and other membrane separation operations [15–17]).

This work focuses on a widely adopted process, called two-stage electro dialysis recovery process, and described by Lee et al. [18] and Bailly [19] (Fig. 1). In order to increase the fermentation yield, the pH is adjusted by addition of a base. The resulting fermentation broth contains the lactic acid as a calcium, ammonium or sodium salt and several organic and inorganic fermentation residues. The largest impurities (i.e., bacterial cells, high molecular weight residues) are first of all eliminated in a first step of clarification that can be done by microfiltration (MF) for instance [20]. The fluid is then concentrated by

conventional electro dialysis (CED), a technology based on the electromigration of ions through a stack of cation- and anion-exchange membranes. The concentration's goal is to improve the global yield of the process (a partial purification in terms of non-migrating species – remaining sugars for instance [12] – also occurs during this operation). After CED, the acid salt is then converted into its free acid form by bipolar electro dialysis (BED). BED uses a stack of cation-exchange and bipolar membranes and allows to efficiently convert the acid salt without addition or production of any by-product. It is now commonly used for the conversion of organic acids [21–23].

Improving the overall efficiency of a two-stage electro dialysis recovery process generally involves adding extra purification operations before and/or after BED. Hardness (calcium and magnesium cations) indeed affects the life time of cation-exchange membranes in the BED stack [24]. A number of patents [13,14,24] propose to use ion-exchange columns and/or nanofiltration to remove these ions before conversion. Purification problems associated with other species than calcium and magnesium can also be encountered. Indeed, depending on the final product specifications, the partial or total elimination of other residual ions (sulfate, phosphate) and remaining sugars (lactose, glucose) is often needed. Nanofiltration, activated carbon and ion-exchange columns are the solutions mentioned in patents [13,14,24,25]. Nanofiltration (NF) as a purification step before and/or after BED is proposed because: (1) typical NF membranes show low rejections of lactic acid (and high rejections of mono- and disaccharides) and (2) the NF rejection mechanisms are traditionally recognized as partly governed by electrostatic interactions leading to high rejections of divalent ions (Donnan effect). However, very few studies clearly quantified the efficiency of the separation applied during the nanofiltration of a real industrial fluid. To our knowledge, only Kang et al. [26] and Jeantet et al. [27] showed in recent publications that NF can efficiently remove magnesium ions (together with glucose or lactose) from a raw lactate fermentation broth. We present here a more systematic study on the possibility of using NF on a clarified fermentation broth but also as a final purification step after lactate conversion. Experiments were done with real industrial fluids corresponding to these two possibilities (Fig. 1):

- Fluid 1: Clarified fermentation broth (MF).
- Fluid 2: Clarified, concentrated and converted fermentation broth (MF–CED–BED).

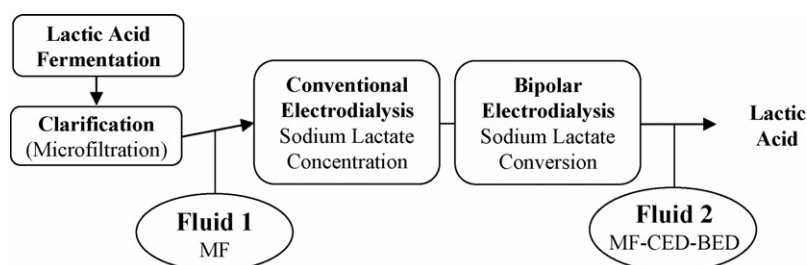


Fig. 1. Schematic diagram of a classical two-stage electro dialysis recovery process for lactic acid production.

For each run, the filtration performances are given in terms of flux, lactic acid/lactate recovery rate, impurities rejection (magnesium, calcium, phosphate and sulfate ions) and separation efficiency. Conclusions about the potential use of NF before and after conversion by BED are drawn from these results.

2. Experimental

2.1. Materials

2.1.1. Membrane

The nanofiltration DK membrane was supplied by GE Osmonics (Le Mée Sur Seine, France) as flat sheets. It is made of polyamide (active layer) and polysulfone and is negatively charged at pH greater than 4 (=isoelectric point) [28]. Other important characteristics, as provided by the supplier, are an average molecular weight cut-off (MWCO) of 150–300 g mol⁻¹, a 98% rejection of Mg₂SO₄ (for [Mg₂SO₄] = 2 g L⁻¹ and ΔP = 6.9 bar), and a hydraulic permeability of approximately 5.5 L h⁻¹ m⁻² bar⁻¹ (hydraulic resistance $R_m = 7.4 \times 10^{13}$ m⁻¹ at 25 °C). The same piece of membrane was used throughout the experiments.

2.1.2. Solutions

All industrial fluids were supplied by Eurodia Industrie (Wis-sous, France). They corresponded to two different levels of a classical two-stage electro dialysis recovery process of lactic acid (Fig. 1). The biological fermentation was conducted from starch residues and NaOH was used for pH adjustment (production of a sodium lactate fermentation broth). The composition and pH of the solutions are given in Table 1 together with the size properties of the solutes present in terms of molecular weight and Stokes radius r_s . This list is non-exhaustive and shows the major compounds found by the analytical methods presented in the next section. No mono- or polysaccharides were identified in the supplied fluids. Model solutions used to characterize the membrane before each run (Section 2.2.3) were made of ultra-pure water, sodium lactate (Prolabo-Merck Eurolab, Fontenay sous Bois, France) and glucose (Acros Organics, Noisy le Grand, France).

2.2. Methods

2.2.1. Analytical methods

Total lactic acid (lactic acid + lactate) concentrations in fluids 1 and 2 were determined by HPLC using a Shodex

Table 1
Composition of the industrial fluids and size properties of the solutes

	Concentrations		Solute properties	
	Fluid 1, MF	Fluid 2, MF-CED-BED	MW (g mol ⁻¹)	Stokes radius r_s (nm)
Lactic Acid	4 mM	1.57 M	90.1	0.22 ^a
Lactate	0.86 M	40 mM	89.1	0.23 ^a
Cl ⁻	6 mM	11 mM	35.5	0.12 ^b
H ₂ PO ₄ ⁻	12 mM	19 mM	97.0	0.28 ^a
SO ₄ ²⁻	6 mM	11 mM	96.1	0.23 ^b
Na ⁺	1 M	97 mM	23.0	0.18 ^b
K ⁺	41 mM	–	39.1	0.13 ^b
Ca ²⁺	6 mM	–	40.1	0.31 ^b
Mg ²⁺	12 mM	–	24.3	0.35 ^b
pH	6.2	2.3		

Bold values are those corresponding to lactic acid and sodium lactate.

^a Calculated from the Stokes–Einstein relation $r_s = k_B T / 6\pi\mu_0 D_{\infty}$, with $k_B = 1.3807 \times 10^{-23} \text{ J K}^{-1}$, $\mu_0 = 8.9 \times 10^{-4} \text{ Pa s}$, $T = 298.15 \text{ K}$, $D_{\infty, \text{Lactic Acid}} = 1.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [44], $D_{\infty, \text{Lactate}} = 1.06 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [45], $D_{\infty, \text{H}_2\text{PO}_4^-} = 0.88 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [45].

^b See [46].

SUGAR SH1011 column (Showa Denko, Kawasaki, Japan) and a refractive index detector. The column temperature was set to 50 °C and the mobile phase was 0.01N sulfuric acid at a flow rate of 1 mL min⁻¹. Respective quantities of lactate and lactic acid were then determined using the measured value, the solution pH, and the specific lactic acid acid–base dissociation constant ($\text{p}K_a = 3.86$ at $T = 25 \text{ }^\circ\text{C}$ [29]). Mineral ions were analyzed on a Dionex IC system (Sunnyvale, CA, USA) using a CD20 conductivity detector. Chemical separations were achieved using an Ionpac AS11 column (mobile phase = NaOH 14.5 mM at 1 mL min⁻¹) and an Ionpac CS12A column (mobile phase = CH₄O₃S 20 mM at 1 mL min⁻¹) for anions and cations, respectively. Concentrations of sodium lactate and glucose in the model solutions used for membrane integrity check (Section 2.2.3) were determined by refractometry (Atago RX-5000 refractometer, Tokyo, Japan).

2.2.2. Filtration unit and experimental procedure

All experiments were done using a membrane system already described in a previous paper [30]. Briefly, the cross-flow filtration unit uses a Sepa CF II cell (GE Osmonics, Le Mée Sur Seine, France) that allows running filtrations on relatively small flat-sheet membranes (140 cm²) at hydrodynamic conditions close to those encountered in a spiral-wound module (i.e., cross-flow velocity, spacer geometry). All the filtrations were performed at constant cross-flow velocity (1.3 m s⁻¹, i.e. $\text{Re} \approx 1400$ for this cell geometry) and constant feed concentration (permeate and retentate recycling). All feed solutions were kept at $25.0 \pm 0.5 \text{ }^\circ\text{C}$ during the experiments. Transmembrane pressures ranging from 2 to 20 bar were used to get the variations of flux and rejection with ΔP . For each component, rejection R (%) was defined as:

$$R = 100 \times \left(1 - \frac{C_p}{C_f} \right) \quad (1)$$

where C_p is the solute concentration in the permeate and C_f is the solute concentration in the feed.

For all impurities, the separation efficiency was described by a separation factor S defined as:

$$S_{\text{Imp}} = \frac{1 - R_{\text{Lac}}}{1 - R_{\text{Imp}}} \quad (2)$$

with R_{Lac} the lactic acid or lactate rejection and R_{Imp} the rejection of the specific impurity. S represents the increase in the ratio $[\text{Lac}]/[\text{Imp}]$ in the permeate. As an example, $S = 2$ indicates that $[\text{Lac}]/[\text{Imp}]$ doubles in the permeate compared to the feed solution.

2.2.3. Membrane pre-treatment and integrity check

The membrane was compacted before each run by filtering high-purity water at 20 bar until a constant permeation flux was reached. The average hydraulic resistance R_m was then calculated. A constant value of $5.4 \pm 0.2 \times 10^{13} \text{ m}^{-1}$ was obtained throughout all experiments. Prior to the filtration of the industrial fluids 1 and 2, the characteristics of the membrane in terms of glucose (0.1 M) and sodium lactate (0.5 M) rejections were determined from the filtrations of model single-solute solutions. These rejections are linked to the average pore radius (glucose and sodium lactate cases) and the charge density (for sodium lactate case only) of the membrane [31]. Relatively constant rejections were obtained (60 ± 5 and $30 \pm 5\%$ for glucose and sodium lactate, respectively, at $\Delta P = 20$ bar, results not shown), indicating that the membrane characteristics were identical before each experiment.

3. Results and discussion

In the next section, the filtration performances are given in terms of permeation flux, lactic acid/lactate recovery rate, impurities rejection (phosphate, sulfate, chloride, calcium and magnesium ions) and separation efficiency. Conclusions about the potential use of NF before and after conversion by BED are drawn from these results in Section 4.

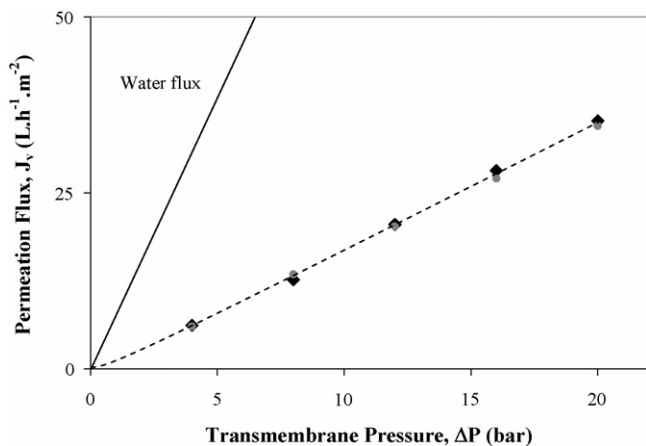


Fig. 2. Permeation flux J_v as a function of transmembrane pressure ΔP after membrane compaction (water flux) and for the two sets of experiments: (●) fluid 1 (MF) and (◆) fluid 2 (MF-CED-BED).

3.1. Permeation fluxes

The volumetric permeation fluxes J_v for the experiments with industrial fluids 1 and 2 showed comparable values and a linear increase of J_v with ΔP ranging from 4 to 20 bar (Fig. 2). The measured fluxes are lower than the water fluxes obtained after membrane compaction. This is typically due to the osmotic pressure difference induced by the separation but also to the higher viscosities of the permeating solutions compared to water. On this last point, viscosities around 1.4–1.7 times the viscosity of water can indeed be estimated for the permeates of runs 1 and 2, respectively (calculation based on the work of Lo Presti et al. [32] and making the assumption that sodium lactate/lactic acid are the major contributors to viscosity).

The permeation fluxes reported are suitable for an industrial application with values close to $35 \text{ L h}^{-1} \text{ m}^{-2}$ at $\Delta P = 20$ bar. These fluxes are comparable to, and even higher than, those obtained by Kang et al. ($20 \text{ L h}^{-1} \text{ m}^{-2}$ at 27 bar, [26]) with a sodium lactate fermentation broth and a membrane showing comparable characteristics with the DK membrane (NF45 membrane [33]).

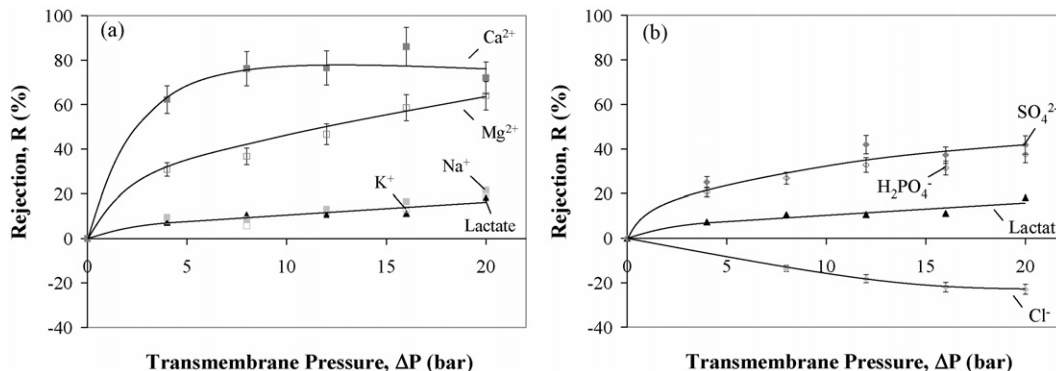


Fig. 3. Solute rejections R as a function of transmembrane pressure ΔP for fluid 1 (MF). (a) Cationic content: (■) Ca^{2+} , (□) Mg^{2+} , (▨) Na^+ , (□) K^+ , (▲) lactate. (b) Anionic content: (◆) SO_4^{2-} , (◇) H_2PO_4^- and (◊) Cl^- .

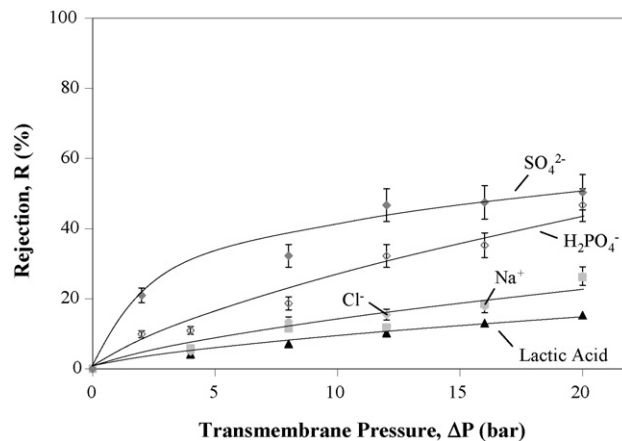


Fig. 4. Solute rejections R as a function of transmembrane pressure ΔP for fluid 2 (MF-CED-BED): (■) Na^+ , (▲) lactic acid, (◆) SO_4^{2-} , (◇) H_2PO_4^- and (◊) Cl^- .

3.2. Lactic acid/lactate recovery

As expected, low rejections of lactate (fluid 1) and lactic acid (fluid 2) were observed in both cases (Figs. 3 and 4). Maximum rejections at $\Delta P = 20$ bar reached 18 ± 2 and $15 \pm 2\%$, respectively (Table 2). In the first run, it has to be noted that lactate permeates through the membrane together with associated sodium ions. Sodium rejection, i.e. $22 \pm 2\%$ at 20 bar, is consequently similar to lactate rejection (Fig. 3). Potassium ions, slightly smaller in size (Table 1) and identical in charge to sodium ions, are nearly equally retained ($18 \pm 2\%$).

Lactic acid is primarily present as a neutral molecule in fluid 2 (1.57 M of lactic acid molecules versus 40 mM of lactate ions, Table 1). It is only retained by size effects and presents a sufficiently small size to permeate through the membrane. Lactic acid molecular weight is indeed 90 g mol^{-1} against a typical MWCO of $150\text{--}300 \text{ mol g}^{-1}$ for the Desal DK membrane. Conversely, lactic acid is almost exclusively present as lactate ion in fluid 1 (Table 1). Rejection of charged molecules in nanofiltration is typically explained by a combination of size effects and electrostatic interactions between the solute and the charged membrane. It is well-known that charge repulsion effects become less important at increasing bulk ionic concentrations and/or decreasing mem-

Table 2

Lactate, lactic acid and ions rejection, recovery rate and separation factor data for the two industrial fluids investigated at $\Delta P = 20$ bar

	Fluid 1, MF			Fluid 2, MF–CED–BED		
	Rejection (%)	Recovery rate ($\text{mol m}^{-2} \text{h}^{-1}$)	Separation factor	Rejection (%)	Recovery rate ($\text{mol m}^{-2} \text{h}^{-1}$)	Separation factor
Lactate	18 ± 2	24.7 ± 2.0	–	–	–	–
Lactic acid	–	–	–	15 ± 2	48.0 ± 2.0	–
Cl^-	-23 ± 2	–	0.7	27 ± 3	–	1.2
H_2PO_4^-	38 ± 4.0	–	1.3	47 ± 5	–	1.6
SO_4^{2-}	42 ± 4	–	1.4	51 ± 5	–	1.7
Na^+	22 ± 2	–	(1.0)	27 ± 3	–	1.2
K^+	18 ± 2	–	(1.0)	–	–	–
Ca^{2+}	72 ± 7	–	2.9	–	–	–
Mg^{2+}	64 ± 7	–	2.3	–	–	–

brane charge density. This phenomenon is generally explained by assuming a Donnan equilibrium between the bulk solution and the membrane [31,34,35]. Ideally, at a sufficient ionic concentration, electrostatic interactions become negligible so that charged solutes are only retained via size effects. The lactate rejection obtained for fluid 1 shows that this limit in concentration is almost reached. Indeed, results from a former study conducted with sodium lactate model solutions on the same membrane showed that lactate rejection can reach up to 0.8 at low concentrations (0.1 M, [30]). This clearly indicates that charge effects are strongly affected by lactate concentration in the present case. Moreover, lactate rejection, although still higher by a small extent, is very close to lactic acid rejection (fluid 2). As we can reasonably assume that lactic acid and lactate ion present the same size (Table 1), this result furthermore indicates that electrostatic effects are not of major importance in this case.

Of course, due to the complexity of the solutions investigated, other mechanisms could be, directly or indirectly, involved in the rejection of lactate and lactic acid. We could mention for instance the possible swelling of the membrane pores at low pH [36] and the adsorption of specific ions onto/into the membrane leading to changes in membrane characteristics (charge and/or pore size [37]). However, and even if these effects probably play a role in the cases presented here, it is difficult to assess their relative importance from the results obtained.

In order to look at the overall performances of the two runs, the recovery rates for runs 1 and 2, i.e. quantities of product recovered in the permeate per unit of time and membrane surface, are given in Table 2. They are important values for the filtration evaluation and are typically higher than those reported by Kang et al. with another membrane at transmembrane pressures higher than 20 bar [26].

3.3. Mineral ions rejections

As lactate/lactic acid are the desired products of the filtrations, phosphate, sulfate, chloride, calcium and magnesium ions constitute impurities. Calcium and magnesium are only present in the clarified fermentation broth (fluid 1) as sulfate and phosphate are present in the two processed fluids. Because they follow the lactate ions through the membrane, potassium and sodium ions cannot be considered as impurities in fluid 1 (Sec-

tion 3.2). Nevertheless, sodium is undesirable in the final product and consequently in fluid 2.

All impurities were initially present at low concentrations (less than 50 mM for the great majority). Moreover, all these ions are different in terms of charge and size. Their rejection was consequently the result of numerous and complex mechanisms. These mechanisms are difficult to explain and/or predict and related to charge/size repulsion effects as well as charge equilibriums. The negative chloride rejections observed with fluid 1 (Fig. 3b) are one perfect illustration of such complex mechanisms. At $\Delta P = 20$ bar, chloride rejection was $-23 \pm 2\%$ (Table 2). This effect has been widely encountered during nanofiltration of model mixtures of mono- and divalent ions [28,36,38–41]. However, it has been rarely reported in filtration of more complex fluids (dairy process water [42]). This phenomenon is due to the competition for permeation between co-ions (ions showing the same charge sign as the membrane) with different mobility, i.e. size and number of charge [36]. In the case presented here and knowing that the membrane is negatively charged at this pH ($\text{pH} > 4$), chloride ions permeate through the membrane more freely than lactate and sulfate ions, which are solutes of higher size and/or charge (Table 1). It results in this negative rejection, i.e. a chloride enrichment in the permeate, and consequently in a separation factor S lower than 1 (Table 2). At the opposite, chloride ions become clearly rejected in the second run (fluid 2, Fig. 4 and Table 2). In this case, none of the conditions leading to chloride negative rejection is satisfied. Lactic acid is indeed present in its neutral form and chloride ions are membrane counter-ions (as the membrane is positively charged at $\text{pH} < 4$). The resulting chloride rejection is higher than lactic acid one by a small amount so that a small purification occur (separation factor close to 0.2). It can also be noted here that sodium ions show the same rejection ($27 \pm 3\%$) and consequently the same separation factor.

The rejections of the ions with higher molecular weights and/or charges, i.e. phosphate, sulfate, magnesium and calcium, are presented in Figs. 3 and 4 and reported in Table 2 for $\Delta P = 20$ bar. All these solutes were highly rejected compared to any other species. Phosphate and sulfate ions were equally retained along the pressure range for the raw and concentrated fermentation broth (fluid 1, Fig. 3b). As already mentioned in Section 3.2, rejection mechanisms in such a concentrated salt solution are mainly due to size effects. Nevertheless, we can

presume that electrostatic effects are still partly responsible for the observed sulfate rejection (Fig. 3b). Charge repulsion effects are indeed more significant with divalent co-ions and high sulfate rejection on negatively charged membrane is a classical result in nanofiltration [34]. Moreover, the rejection obtained cannot be explained through size effects only since sulfate ion shows the same size as lactate ion (Table 1). On the other hand, steric-hindrance effects are clearly visible when looking at the phosphate rejection compared with lactate. These two solutes indeed present the same charge but a clear difference in size (Table 1). For fluid 2, i.e. when lactic acid is present as a neutral molecule, sulfate and phosphate rejections reached about 50% at $\Delta P = 20$ bar with separation factors > 1.5 (Fig. 4). Such values are higher, by a small extent, to those obtained with fluid 1. These results cannot be explained by size exclusion phenomenon only and the mechanisms responsible of these rejections are not clear in that case. The membrane is indeed supposed to be positively charged at this pH and should attract these ions more than repel them (Donnan effect). But, as it was already mentioned, effects of pH and/or specific ion adsorption on membrane structure [36,37], as well as complex ionic equilibriums, could be responsible for the observed results.

Finally, calcium and magnesium ions present in fluid 1 were highly rejected by the membrane (Fig. 3a). Rejections of 72 ± 7 and $64 \pm 7\%$ were observed at 20 bar, respectively. As a result, magnesium and calcium separation factors at $\Delta P = 20$ bar are relatively high in fluid 1 (2.3 and 2.9) and indicate good NF performances. Again, size effects are probably the main contributors to these rejections. These divalent cations indeed show high Stokes radii compared to all the other species in solution (Table 1). However, we can speculate that adsorption phenom-

ena will also contribute to this overall rejection of magnesium and calcium. From streaming potential measurements, Childress et al. indeed showed that divalent cations can form complexes with the surface of negatively charged nanofiltration membrane [43]. It is not possible here to quantify the effect of adsorption on the overall Mg^{2+} and Ca^{2+} rejections. Nevertheless, it could be relatively important since size effects alone cannot explain the relative positions of Ca^{2+} and Mg^{2+} rejections (Fig. 3a). Calcium ions were indeed more retained than magnesium ions (which is in contradiction with their relative size, Table 1) and calcium is known to be more easily adsorbed than magnesium onto polyamide nanofiltration membranes [37]. Nevertheless, it has to be noted that no firm conclusion can be drawn here since previous studies relating to adsorption in nanofiltration were conducted with diluted model solutions of a mineral salt, and not a complex and concentrated solution like in the present work.

4. Nanofiltration potentialities and conclusion

Two main conclusions can be drawn from the former results in terms of potential use of nanofiltration in a two-stage electro-dialysis recovery process of lactic acid (Fig. 1):

- (a) Nanofiltration was able to partially remove magnesium and calcium ions from a raw, clarified fermentation broth with high lactate recovery rates (fluid 1). Results obtained at $\Delta P = 20$ bar showed Mg^{2+} and Ca^{2+} rejections reaching 64 ± 7 and $72 \pm 7\%$, respectively for a lactate recovery rate of $24 \pm 2 \text{ mol m}^{-2} \text{ h}^{-1}$. Moreover, as former studies only focused on magnesium removal until now [26,27], we

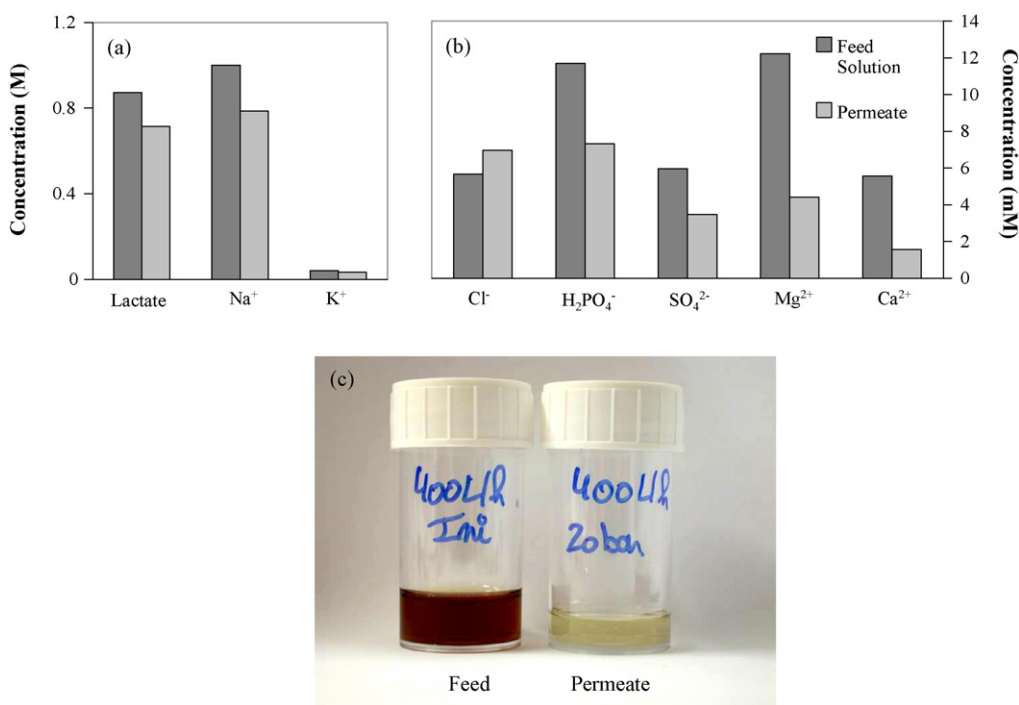


Fig. 5. Histograms showing the fluid 1 initial composition (Feed solution) and the permeate composition. (a) Lactate, Na⁺ and K⁺ content in M. (b) Cl⁻, H₂PO₄⁻, SO₄²⁻, Mg²⁺ and Ca²⁺ content in mM. (c) Evidence of the decoloration induced by the filtration.

showed that sulfate and phosphate ions were also partially removed from the broth (40% rejection). The compositions of the feed solution used in this work and the permeate after filtration at $\Delta P = 20$ bar are presented in Fig. 5a and b. As it was noticed previously, the fluid purification in terms of phosphate, sulfate, magnesium and calcium comes with slight chloride enrichment. As it was already mentioned by Kang et al. [26], Fig. 5c also shows that nanofiltration is able to remove the brown color of the fermentation broth (Fig. 5c). Finally, because the fermentation conducted by our supplier was optimized, the broth we used in this work did not contain any remaining sugars. Consequently, we could not rigorously establish here if NF can also remove mono- and polysaccharides from a fermentation broth that contains some sugar(s). According to the Desal DK specifications, we speculate that this membrane will totally retain di- and polysaccharides of molecular weight higher than 300 g mol^{-1} (e.g. sucrose, maltose). However, it is not unusual to find some glucose, monosaccharide, in fermentation broths [12]. In that case, we believe that NF could not be efficient to retain this sugar. Former results of our group indeed showed that glucose rejection is unexpectedly low in presence of sodium lactate [30].

(b) Nanofiltration could be used as a final purification step after concentration and conversion of the process fluid. We indeed showed that about 50% of the phosphate and sulfate ions were retained by the membrane at an operating pressure of 20 bar (51 ± 5 and $47 \pm 5\%$, respectively). High recovery rates were also observed in that case, i.e. $48 \pm 2 \text{ mol m}^{-2} \text{ h}^{-1}$ at 20 bar. Naturally, the NF integration at this level will depend on the desired properties of the final lactic acid solution. In some particular cases, remaining sugars can still be present in the converted solution [12]. Because glucose rejection is not affected by lactic acid when neutral [30], we speculate that nanofiltration could also efficiently remove any remaining sugars after BED.

In a general manner, and as it was proposed in a certain number of patents but rarely verified, we showed in this study that nanofiltration can play an important role for lactic acid production. Naturally, the final integration of this technology into a specific existing industrial process will depend on many factors. Among them, the fermentation conditions, the available electro-dialysis equipment and inevitable economic considerations will have to be taken into account.

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