INTRODUCTION OF NANOFILTRATION IN A PRODUCTION PROCESS OF FERMENTED ORGANIC ACIDS

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1. Introduction

Nanofiltration (NF) is known to be a separation technique lying between ultrafiltration (UF) and reverse osmosis (RO) which presents a selectivity governed both by steric hindrance effects and electrostatic repulsions. Most NF membranes have therefore the particularity to strongly retain compounds of molecular weight up to 150-250 $g.mol^{-1}$ and charged molecules, especially multivalent ions. Due to these interesting separation properties, NF begins to be used in a wide range of applications in the food industry. More particularly, and according to the numerous works published in the last years, the use of NF as a downstream operation in organic acids production processes is going to be a large and new application field of this technology [1, 2].

Organic acids (acetic, lactic, gluconic acids), which are increasingly used in food industries, are mainly produced starting from a fermentation. This fermentation generates an acid salt solution (sodium, ammonium or calcium salt) containing different impurities like residual sugars and mineral salts. Further operations are needed afterwards to get the acid in a suitable form. As it is presented in a previous work, bipolar electrodialysis (EDBM) can for instance be used in order to convert the organic salt in its "neutral" form, the organic acid [3]. According to its separation properties, NF can theoretically be considered as an appropriate operation of purification before this conversion. In the case of acetic acid production, Han and Cheryan explained for instance that NF has the ability to let permeate the acetate while other fermentation broth components are retained and recycled to the fermentation tank [4].

In this work, this possibility is investigated in the case of a sodium lactate fermentation broth containing glucose as residual sugar. Indeed, a high retention of glucose could be achieved together with a lower retention of sodium lactate, that has a low molecular weight (two times lower than glucose) and is present at concentration for which electrostatic repulsions are expected to be very weak.

An experimental investigation was carried out. . We present here the principal results obtained with solutions of glucose and sodium lactate at average concentrations that can be found in a fermentation broth. Since retentions obtained in a mixture can slightly differ from those found as solutes are considered separately [5-7], experiments were performed with solutions of different compositions, i.e. single-solute solutions (containing either glucose or sodium lactate) and mixed-solute solutions (containing both solutes).

2. Material and methods

Desal 5 DK membranes, supplied by Osmonics as flat sheets, were used for this study. These are negatively-charged membranes made of polyamide (active layer) and polysulfone. Average characteristics are a molecular weight cut-off of 150-300 g.mol^{-1} and a hydraulic permeability about 7 to 9 l.h^{-1}.m^{-2}.bar^{-1}.

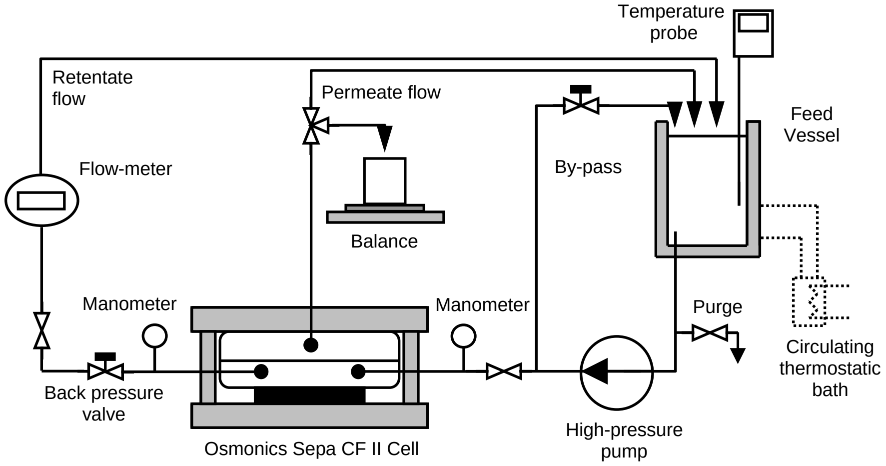
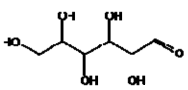
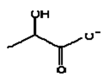


Figure 1. Schematic diagram of the NF pilot plant

Fig. 1 is a schematic diagram of the cross-flow filtration unit used in this work. Experiments were performed with the Sepa CF II cell (Osmonics) providing a membrane area of 137 cm^2. The solution was pumped into the cell from a five liters feed vessel kept at 25 ± 0.5 °C. The retentate and the permeate were recycled into the feed vessel in order to work at constant feed concentration.

Table 1: Principal characteristics of investigated compounds

Compounds	Formula	Molecular weight (g.mol^{-1})	Stokes radius r_s (nm)
Glucose		180.16	0.35-0.37
Lactate		89.07	0.23
Na^+	-	22.99	0.16 - 0.19

Solutions were prepared using high purity sodium lactate - NaLac - , glucose - Glu - and water. The relevant characteristics of these compounds are reported in Table 1. Concentrations close to those found in a real fermentation broth were used [8], i.e. from 0.025 M to 0.1 M for glucose and from 0.1 M to 1 M for sodium lactate. Sodium lactate and glucose concentrations were determined by refractometry for single-solute solution and HPLC (Shodex SUGAR SH1011 column + refractive index detector) for mixed-solute solutions.

xperiments were performed at a constant cross-flow velocity of 1.33 $m.s^{-1}$ and at different transmembrane pressures lying between 2 and 20 bar. A volume of 5 ml of permeate was collected for each pressure and timed to estimate the permeation flux. The observed retention R_{obs} was then calculated from the solute concentrations using the following definition :

$$R_{obs} = 1 - \frac{c_p}{c_r} \quad \text{with} \quad \begin{cases} c_p = \text{concentration in the permeate} \\ c_r = \text{concentration in the retentate} \end{cases}$$

3. Principal results

We present here the results obtained with solutions at concentrations close to the average ones in a real fermentation broth, i.e. sodium lactate at 0.5 M and glucose at 0.1 M. Single-solute and mixed-solute solutions experiments are successively presented and compared. As it is commonly done in membrane filtration, experimental results are presented as variations of the observed retention R_{obs} versus the permeation flux J_v.

- *Single-solute solutions:*

The plots of the observed retention versus permeation flux for single-solute solutions of glucose and sodium lactate are presented in Fig. 3 with 3 different pieces of membrane (A, B and C).

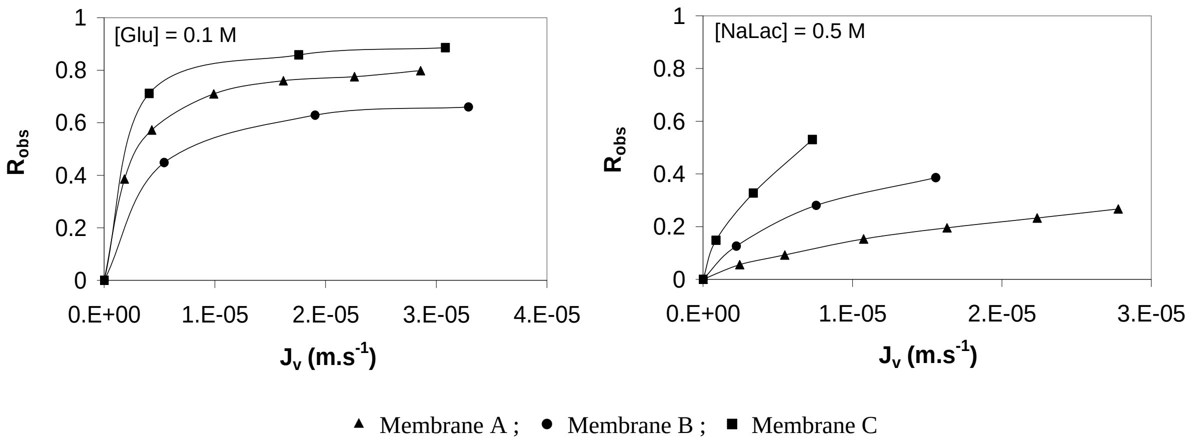


Figure 2. Variations of R_{obs} versus J_v for single-solute solutions
Variability between different membranes

One can observe that quite different curves are obtained for the 3 membranes. Membrane C has the highest retention for both solutes. Membrane B has the lowest glucose retention but an intermediate retention of lactate. Finally, membrane A has the lowest lactate retention but an intermediate retention of glucose. Then, no direct correlation comes out between the retention of the two solutes. Nevertheless, whatever the membrane, Fig.2 shows that the glucose retention is always superior to the sodium lactate one. Consequently, one can expect to achieve in the permeate a higher concentration ratio [NaLac]/[Glu] than that in the feed. In that case, a partial purification could be obtained.

- *Mixed-solute solutions:*

The results obtained with the mixed-solute solutions with membranes A and B are plotted in Fig. 4. For comparison, the results obtained with single-solute solutions are also reported on the same graph.

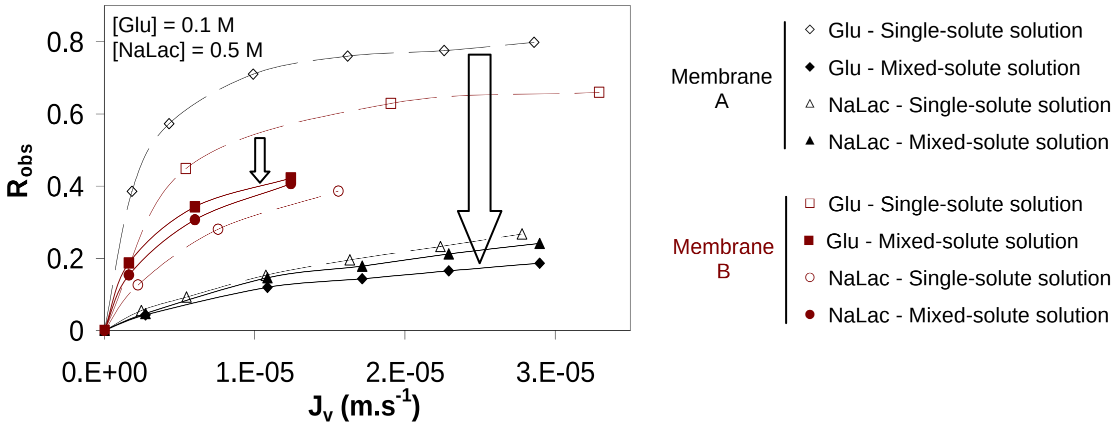


Figure 4. Variations of R_{obs} versus J_v for mixed-solute solutions (full symbols) Comparison with single-solute results(empty symbols)

From the qualitative point of view, identical results are obtained for both membranes.The retention of sodium lactate is found to remain almost the same for single and mixed solute solutions. Then it is not significantly affected by the presence of glucose. On the opposite, the glucose retention is strongly affected by the presence of lactate. Indeed, significantly lower retentions are observed for the sugar in mixed solutions (decrease symbolized by a arrow). These observations are in qualitative agreement with those published by Wang [5] or Freger [4] for the same type of solutions. However, from the quantitative point of view, the comparison is much more difficult. Indeed, in the results reported by Wang et al for instance, the decrease of glucose retention does not exceed 15% of the initial value. A stronger effect is observed here, since the retention of glucose can reach 70%. This could be due to the higher concentrations used in this study. However, Fig. 4 also clearly points out that different values can be obtained for a given membrane and identical operating conditions, depending on the membrane sample. Such a strong incidence of a solute on another as that reported here has never been reported in the literature. Different results show the dependence of the solute retention on the presence of another solute. But no satisfactory explanation is available at that time concerning the mechanisms involved in such solute interactions.

Finally, contrary to the conclusions drawn from experiments with single-solute solutions, the [NaLac/Glu] concentration ratio is not increased in the permeate compared to the feed. Indeed, the glucose retention is very close to and even slightly lower than that of sodium lactate.

4. Conclusion

An experimental study was carried out to investigate the possibility to use NF as a purification step to remove glucose from a sodium lactate solution. Solutions of increasing complexity were used. The retention of a charged and a neutral solute obtained from single-solute experiments showed a typical behavior. Moreover, glucose retention was found to be greater than that of sodium lactate at concentrations close to those in a fermentation broth. Nevertheless, the results obtained with mixed-solute solutions showed that the retention of glucoseis strongly decreased in the presence of sodium lactate. Consequently, the purification, which was expected to be possible according to single-solute results, is finally unachievable.

Such differences between single- and mixed-solute results were already reported. But those obtained in this work are much more significant. Further investigations will aim at understanding the involved mechanisms.

5. References

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