EVALUATION OF NANOFILTRATION FOR THE PURIFICATION OF AN ORGANIC ACID FERMENTATION BROTH

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Abstract: This study focuses on a possible elimination of glucose from a sodium lactate fermentation broth by nanofiltration (NF). The results obtained with single-solute solutions indicate that glucose is clearly more retained that sodium lactate. Nevertheless, glucose retention strongly decreases when the two solutes are present in the same solution and the separation becomes unachievable. Such a incidence of a solute on another in NF has rarely been reported before.

Keywords: membrane processes, nanofiltration, organic acids, selectivity, mass transfer mechanisms

A. 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 of purification, concentration, and conversion are needed afterwards to get the acid in a suitable form.
According to its separation properties, NF can theoretically be considered as an appropriate operation of purification before the conversion of the organic salt. 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 [3]. The purpose of this study is to evaluate this possibility in the

case of a sodium lactate fermentation broth containing glucose as residual sugar. Glucose is indeed classically highly retained by NF while sodium lactate is a low molecular weight solute (two times lower than glucose) and is present at such a concentration in a fermentation broth that electrostatic repulsions due to the membrane charges can be considered as weak.
However, several authors noticed that the solute retentions obtained in a mixture of two compounds can slightly differ from those found for each solute taken separately [4-6]. Experiments reported in this work were consequently carried out with solutions of increasing complexity, i.e. single-solute solutions (containing either glucose or sodium lactate) and mixed-solute solutions (containing both solutes). In this manner, the separation efficiency was investigated as well as any solute interaction.

B. Materials and methods

A Desal 5 DK membrane, supplied by Osmonics as a flat sheet, was used for this study. It is a negatively-charged membrane made of polyamide (active layer) and polysulfone. Its average characteristics are a molecular weight cut-off of 150-300 $g.mol^{-1}$, 98% retention of Mg_2SO_4 (with $[Mg_2SO_4] = 2\ g.l^{-1}$ and $\Delta p = 6.9$ bar), and a hydraulic permeability lying between 7 and 9 $l.h^{-1}.m^{-2}.bar^{-1}$.

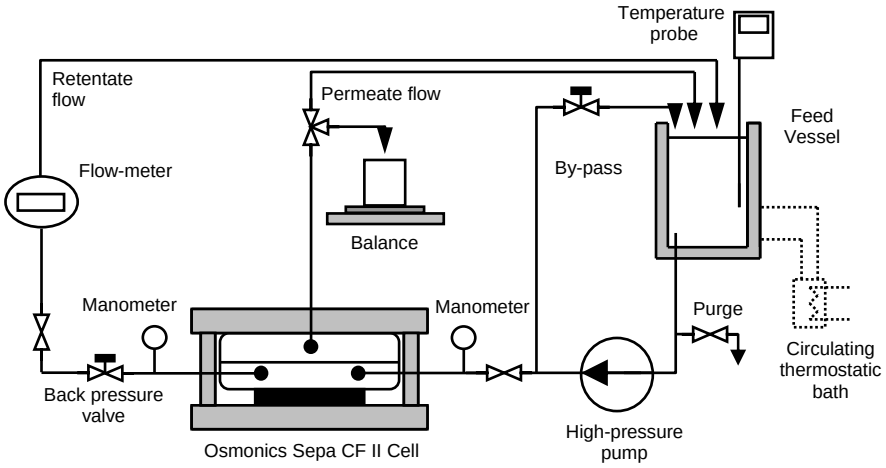
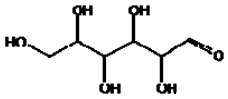
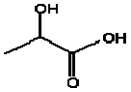


Figure 1. Schematic diagram of the membrane system.

Fig. 1 is a schematic diagram of the cross-flow filtration unit used in this work. Experiments were performed with the Osmonics Sepa CF II membrane cell providing a membrane area of 137 cm^2. The solution was pumped from a five liters feed vessel kept at 25 ± 0.5 °C into the cell. The transmembrane pressure was controlled by the mean of a stainless steel control mounted on the retentate outlet. 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 - (Prolabo - Merck eurolab), glucose - Glu - (Acros Organics) and water. The characteristics of these compounds in term of size (molecular

weight and Stokes radius) are reported in Table 1. (As sodium lactate is used under its dissociated form, the ions lactate and sodium are listed).
Concentrations close to those found in a real fermentation broth were used [7], i.e. from 0.025 M to 0.1 M for glucose and from 0.1 M to 1 M for sodium lactate. The pH of single-solute solutions of glucose fluctuated between 4 and 5 (pH of the de-ionized water used). The presence of dissociated sodium lactate in the other solutions fixed a pH lying between 6.5 and 7.

Each experiment was performed at constant cross-flow velocity for six transmembrane pressures from 2 to 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 using the following definition :

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

C. Results and discussion

Results obtained with single-solute and mixed-solute solutions are successively presented and compared in this section. As it is commonly done in membrane filtration, experimental results are presented as variations of the retention versus the permeation flux J_v.

- Effect of hydrodynamic conditions :

Fig. 2 shows the observed retentions of sodium lactate as a function of the permeation flux for different cross-flow velocities. The retention decreases as cross-flow velocity decreases. This observation, common to all experiments, is characteristic of the concentration polarization effect. Indeed, a cross-flow velocity decrease leads to an increase of the concentration at the membrane surface. A higher solute transfer consequently occurs so that retention decreases.

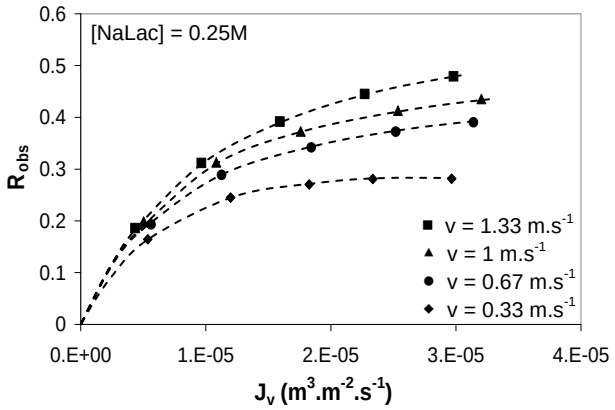


Figure 2. Variations of R_{obs} versus J_v
Influence of the cross-flow velocity

The following results are those obtained at a constant cross-flow velocity, i.e. at a constant level of concentration polarization.

- 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. On the one hand, no significant dependence of the retention with respect to the concentration is observed for glucose solutions. The retention of a neutral solute is indeed only due to steric hindrance effects which do not depend on the concentration of the solute but only on the solute and membrane pores radii. On the contrary, the observed retention of sodium lactate clearly depends on its concentration. The retention decreases as sodium lactate concentration increases from 0.1 M to 0.5 M. For concentrations beyond this value, the retention seems to reach a plateau value. Such a decrease of retention with concentration for a charged solute is a well-known effect in NF. Indeed, the retention of such solutes comes from a combination of both steric and

electrostatic effects, this last depending on the ionic strength, and so on the solute concentration. Then, as the concentration increases, electrostatic interactions become weaker and the solute retention decreases. The lower limit of the retention is thus fixed by steric-hindrance effect.

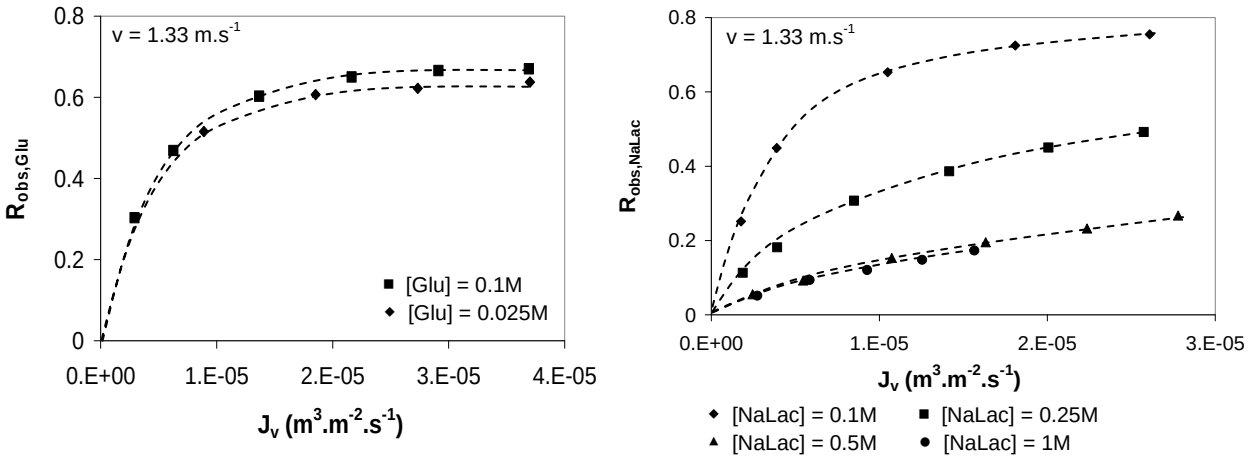


Figure 3. Variations of R_{obs} versus J_v for single-solute solutions
Influence of the solute concentration

From these single-solute results, one can expected a glucose retention greatly exceeding the sodium lactate one in the case of a highly concentrated fermentation broth. A higher ratio [NaLac]/[Glu] could then be achieved in the permeate compared to the feed and a partial purification could therefore be realized. For instance, at a value of $J_v = 3.10^{-5}$ $m^3.m^2.s^{-1}$ ($\Delta P \approx 20$ bar) this ratio could increase from 5 to 15 in the case of a fermentation broth containing 0.1 M of glucose and 0.5 M of sodium lactate.

- Mixed-solute solutions :

The results obtained with the mixed-solute solutions are plotted in Fig. 4. Single-solute solutions results are also reported in comparison (empty symbols). According to the first graph, the retention of sodium lactate is not significantly affected by the presence of glucose. Inversely, the second graph shows that glucose retention is strongly affected by the presence of sodium lactate. As the sodium lactate concentration increases, the glucose retention decreases until values inferior to 0.2.

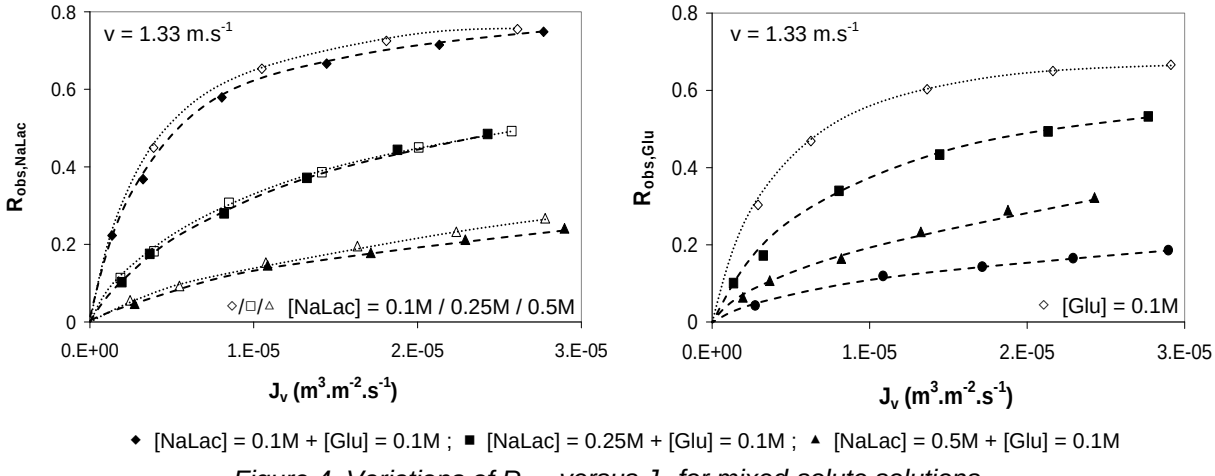


Figure 4. Variations of R_{obs} versus J_v for mixed-solute solutions
Comparison with single-solute results

These observations are in qualitative agreement with those of Wang [5] or Freger [4]. However, the effect is much more pronounced in our case (the decrease of glucose retention does not exceed 15% of the initial value in the work of Wang and al. against 70% here). This difference comes probably from the different type of salt and also from the higher concentrations used in this study. Such a strong

incidence of a solute on another has consequently never been reported in the literature until now. No rigorous explanation is available at that time. Experiments with other salts and neutral solutes have to be done in the future to understand the mechanisms responsible of such an effect.

The observed retentions of glucose and sodium lactate at respectively 0.1 M and 0.5 M (mean concentrations in a fermentation broth) in both mixed- and single-solute solutions are summarized in the following figure.

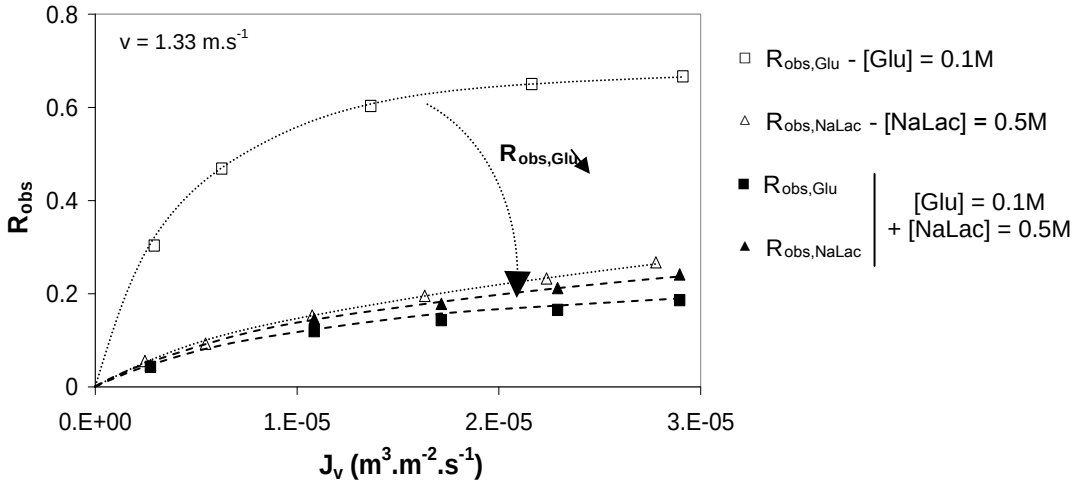


Figure 5. Variations of R_{obs} versus J_v for single- and mixed solute solutions of NaLac - 0.5M and Glu - 0.1M
Evaluation of the separation efficiency

Contrary to the conclusions drawn from the single-solute solutions results, glucose retention is actually close to and even lower than the sodium lactate one. The selectivity towards glucose is consequently totally lost and the separation becomes unachievable.

D. Summary and 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 typical behavior. Moreover, glucose retention was found to be much 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 glucose retention is strongly modified in the presence of sodium lactate. Indeed, glucose is less retained that sodium lactate and 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. Those obtained in this work are however much more significant. Further investigations will aim at understanding the involved mechanisms.

References:

1.Moresi M., Ceccantoni B.,Lo Presti S., Modelling of ammonium fumarate recovery from model solutions by nanofiltration and reverse osmosis, Journal of Membrane Science, 209, 2, 405-420, 2002.

2.Timmer J.M.K., Kromkamp J.,Robbertsen T., Lactic acid separation from fermentation broths by reverse osmosis and nanofiltration, Journal of Membrane Science, 92, 2, 185-197, 1994.

3.Han I.S.,Cheryan M., Nanofiltration of model acetate solutions, Journal of Membrane Science, 107, 1-2, 107-113, 1995.

4.Freger V., Arnot T.C.,Howell J.A., Separation of concentrated organic/inorganic salt mixtures by nanofiltration, Journal of Membrane Science, 178, 1-2, 185-193, 2000.

5.Wang X.-L., Zhang C.,Ouyang P., The possibility of separating saccharides from a NaCl solution by using nanofiltration in diafiltration mode, Journal of Membrane Science, 204, 1-2, 271-281, 2002.

6.Vellenga E.,Tragardh G., Nanofiltration of combined salt and sugar solutions: coupling between retentions, Desalination, 120, 3, 211-220, 1998.

7.Bailly M., Roux-de Balmann H., Aimar P., Lutin F.,Cheryan M., Production processes of fermented organic acids targeted around membrane operations: design of the concentration step by conventional electrodialysis, Journal of Membrane Science, 191, 1-2, 129-142, 2001.