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Recovering bioethanol from olive bagasse fermentation by nanofiltration

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ABSTRACT

The aim of this manuscript was the study of the recovery of bioethanol produced by the fermentation of the lignocellulosic biomass (olive bagasse) by nanofiltration. In terms of downstream processing, the nanofiltration permeate stream was expected to be comprised mostly of water and ethanol, and as such, ethanol may be further recovered by conventional distillation. Different nanofiltration membranes (NF90 and NF270) were tested for their efficiency in the separation of bioethanol. Model aqueous solutions of ethanol and sugars, and real liquors were processed by nanofiltration focusing on flux and rejection performance. The results shown that the more complex medium of a real liquor interacts with the membrane and lower the rejection to target solutes. Generally, both membranes tested were suitable for separating and recovering ethanol from a fermentation medium. The diafiltration mathematical model developed in this work shown to be capable of describing experimental results, which may be considered extremely important for process design and scaling up purposes.

Keywords: Bioethanol recovery; Nanofiltration; Diafiltration; Olive bagasse; Sustainable membrane processing

1. Introduction

Last decades world's economy dependency on fossil fuels, such as oil, coal and natural gas and their excessive consumption, led to an excessive pollution and consequently to an increase in greenhouse gases (GHG) emissions [1,2]. The increase in GHG and a dramatic increase in the petroleum price are the main concerns in the search for new renewable alternative energy sources [2–4]. Due to a good adaptation of motor vehicles to the use of biofuels instead of fossil fuels, a possible alternative may be the use of this renewable energy source [5].

First-generation bioethanol is produced using biomass provided by agricultural resources, such as sugar cane, wheat, and rice. However, this is currently being severely criticized due to the extreme competition between food and fuel, and an intensification of agriculture to biofuel ends, causing local environmental damage [6]. The competition between human and animal food, and the environmental production risks open the possibility for the appearance of

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second-generation bioethanol that, comparatively to the first generation, allows to use lignocellulosic materials which represent a decrease on feedstock for biofuels production, allowing a higher saving on production cost and a lower environmental impact [5].

Lignocellulosic materials can be classified in four groups based on the type of resource: forest residues, municipal solid waste, waste paper and crop residue. Different studies are available in the literature to better understand the process of producing bioethanol from lignocellulosic-based material, such as sugarcane bagasse [7], wheat straw [8], rice straw [9] and crop residues [10].

Olives are one of the most important agriculture products in the Mediterranean area [11,12] but the literature refers mostly to olive residues to be used as a raw material for activated carbon production, as a heat source on biogas production or as material for composting processes [13,14]. Olive bagasse, an olive oil production residue, as lignocellulosic material, contain as main components, hemicelluloses, cellulose and lignin. The main challenge described when using lignocellulosic biomass for the production of ethanol is the breaking down of the cellulosic matrix and subsequent release of sugars so that they can be fermented to produce ethanol. The biochemical production of bioethanol from lignocellulosic biomass may include several steps, namely: (1) pretreatment of biomass in order to turn it to be more accessible to chemical or biological treatment which includes physical treatments (mechanical size reduction [15], pyrolysis [16], microwave oven and electron beam irradiation [17,18]), physicochemical treatments (autohydrolysis [19], ammonia fibre explosion [20]), chemical treatments (acid hydrolysis [21], alkali [22], wet oxidation [23]) and biological pretreatment [24], being used in general a combination of these processes in the pretreatment step; (2) enzymatic hydrolysis, where complex carbohydrates are converted to monomers, such as glucose [25]; and (3) fermentation of enzymatic hydrolysate to produce bioethanol [26]. The fermented liquor containing about 5% (v/v) ethanol is distillated where it is concentrated for commercial application to a concentration below the azeotrope [27].

The recovery of the ethanol produced may also be carried out using membrane technology, such as nanofiltration [28–30]. Previous studies showed that it is possible to use membrane processes for the removal of ethanol from alcohol beverages [31].

Nanofiltration is typically used to remove small molecular weight dissolved solutes from a liquid feed stream. For a membrane process to be efficient and economically feasible, it is required that both the flux and the membrane selectivity for the target compounds are as high as possible [32].

The aim of this work is the study of the recovery of bioethanol produced by the fermentation of the lignocellulosic biomass (olive bagasse) by nanofiltration. Two different nanofiltration membranes (NF90, NF270) were tested for their efficiency in the separation of bioethanol. A reverse osmosis membrane (SW30) was also included in this study to clarify the suitability of nanofiltration for the objectives of this work. Model aqueous solutions of ethanol, and aqueous solutions of ethanol and a set of different sugars were prepared. The composition of ethanol and sugar model solution was based on prior data on the hydrolysis and fermentation of the olive bagasse. In terms of downstream processing, the nanofiltration permeate stream is expected to be comprised mostly of water and ethanol, and as such, ethanol may be further recovered by conventional distillation.

2. Materials and methods

2.1. Materials

In this study, two commercial nanofiltration membranes, NF90 and NF270, and one reverse osmosis membrane, SW30, provided by Dow [33] were selected. The molecular weight cut-off (MWCO) of these membranes is shown in Table 1.

Ethanol (p.a.) was obtained from Merck (Germany), cellobiose (⩾98%), glucose (⩾99,5%) and xylose (⩾99%) were obtained from SIGMA (France), and furfural (⩾99%) was obtained from FLUKA (Switzerland).

2.2. Nanofiltration set-up

The nanofiltration experimental set-up used in this work is shown in Fig. 1. It is comprised by a GE-Sepa CF cross-flow module (GE Osmonics, USA) and a high-pressure feed pump (Hydra-cell model G13, Wanner Engineering Inc., USA). The effective membrane area used was of 140 cm^2.

Table 1
MWCO for NF270, NF90 and SW30 membranes

MWCO (Da)		
NF270	NF90	SW30
400 [34]	150 [34]	Salt rejection: 99.80% [34]

Molecular weight cut-off for SW30 membrane is not defined. Membrane properties are defined in terms of salt rejection, specified by manufacturer, Dow.

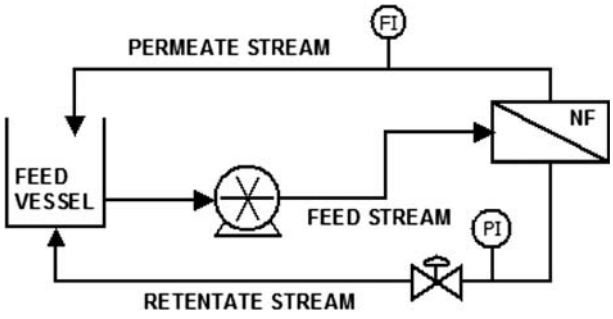

Fig. 1. Experimental nanofiltration set-up (NF). PI and FI are pressure and flow-rate indicators, respectively.

Before starting the experiments, each membrane was compacted at 20 bar until a constant value of flux was obtained. The flux was measured by weighing the volume of water collected in the permeate for a certain period of time. The system was operated under a total recycle mode of operation, in which both the retentate and the permeate streams were recirculated to the feed recipient. In each experiment, the hydraulic permeability value for all the membranes tested was measured after compaction, for a pressure range between 4 and 20 bar, using deionized water. Before a new solution was used, the hydraulic permeability was determined again, in order to evaluate if cleaning of the membrane was necessary. Alkaline cleaning with a 0.1% NaOH solution at 40˚C and low pressure (<2 bar) was carried out when necessary to restore the membrane hydraulic permeability to its initial value.

2.3. Ethanol rejection study for aqueous solutions

Ethanol aqueous solutions of 2L having ethanol percentages in the range between 0 and 25% (v/v) were processed using the previously mentioned membranes (Table 1) for a pressure range between 4 and 20 bar. Feed, retentate and permeate samples for each pressure and concentration were collected and analysed by refractometry (RFM 300 Series module, Bellingham & Stanley Limited).

2.4. Ethanol rejection study for fermentation model solutions

Two fermentation model solutions were prepared using cellobiose, glucose, xylose and furfural at 1 g/L, and with a content of ethanol of 5 or 15% (v/v). The composition of these solutions is aligned with values obtained from hydrolysis and fermentation of olive bagasse. The solutions were processed in the nanofiltration set-up and permeability and rejection were determined for each membrane and for a pressure range between 4 and 20 bar. Permeate, retentate and feed samples were collected for each concentration and pressure tested and were analysed by HPLC (Merck Hitachi LaChrome, Japan).

2.5. Ethanol rejection study for bioethanol produced by fermentation of olive bagace

Olive bagasse fermentation liquor was used to study the suitability of nanofiltration to process real solutions. The solutions were processed using the same nanofiltration set-up as with model solutions, and permeability and rejection values were determined for NF270 membrane and for a pressure range between 4 and 20 bar. For the diafiltration experiments, the permeate was continuously removed and feed volume was kept constant by continuously feeding deionized water to the feed vessel at the same mass flow rate as the permeate. Samples of feed and permeate were collected periodically during the experiment. Diafiltration was conducted for 6 h according to previous modelling results. Permeate, retentate and feed samples were collected for each concentration and pressure tested and were analysed by HPLC (Merck Hitachi LaChrome, Japan).

2.6. Analytical methods

As previously mentioned in Section 2.3, aqueous ethanol solutions obtained in the permeate, retentate and feed were analysed by refractometry. The refractometry system was comprised by a RFM 300 Series module (Bellingham & Stanley Limited) with a temperature control bath regulated to 20˚C.

Fermentation model media samples obtained as described in Sections 2.4 and 2.5 were analysed by HPLC (High-performance liquid chromatography). A Merck Hitachi LaChrome equipment with a L7000 interface module, a L7200 autosampler, a L7490 RI detector, a UV detector, a L7350 column oven and a L7100 pump, was used associated with the D-7000 HSM software. An Aminex HPX-87H (7.8×300 mm) cation exchange column, from Bio-Rad [33] was used at 50˚C, with a flow rate of 0.6 mL/min of 5 mM H_2SO_4 solution used as the mobile phase. H_2SO_4 used was from analytical grade (from Normapur). All the samples were pre-filtered with 0.45 μm pore size filters from Pall, USA.

2.7. Calculation methods

Permeability and rejection were calculated, respectively, using the following equations:

$$J_v = L_p(\Delta P - \Delta\pi) \quad (1)$$

$$R_i = 1 - \frac{C_{i,p}}{C_{i,f}} \quad (2)$$

Where J_v is the solvent volumetric flux ($L\,m^{-2}\,h^{-1}$), L_p, is the membrane permeability ($L\,m^{-2}\,h^{-1}\,bar^{-1}$), ΔP is the transmembrane pressure (bar), and $\Delta\pi$ is the osmotic pressure difference (bar), which is determined by the Van't Hoff equation. R_i is the apparent rejection of solute i (%), and $c_{i,f}$ (g/L) and $c_{i,f}$ (g/L), are the concentration in the permeate and feed of solute i, respectively.

3. Results and discussion

3.1. Hydraulic permeability

The volumetric fluxes for water, obtained for each membrane in the pressure range between 4 and 20 bar, are represented in Fig. 2.

As shown in Fig. 2, there was a linear relationship between the flux and the driving force. According to Eq. (1), the slope of the representation of the flux as a function of driving force corresponds to the hydraulic permeability of each membrane. The values obtained are represented in Table 2. It was observed that the NF270 membrane has the highest hydraulic permeability value when compared with the other membranes. This was an expected result given the distinct MWCO of each membrane. The NF270 membrane, in the group of the three membranes studied, is the one with the highest MWCO (see Table 1).

Table 2
Hydraulic permeability for the NF270, NF90 and SW30 membranes

Lp ($L/m^2\,h\,bar$)		
NF270	NF90	SW30
20.18	8.23	1.1

The permeability values were obtained in this work at 35°C, whereas most data available in the literature were obtained at room temperature. For example, Teixeira et al. [35] obtained hydraulic permeabilities of 13.6 and 7.0 $L/m^2\,h\,bar$ at room temperature for NF270 and NF90, respectively. The manufacturer provides values of 11.09 and 6.6 $L/m^2\,h\,bar$ for these membranes also at room temperature. It can be anticipated that with increasing temperature the membrane polymeric matrix becomes looser while water viscosity decreases—both effects contribute to an increase in permeability, as shown by Sharma et al. [36].

3.2. Ethanol rejection study

The ethanol rejection study was performed for solutions with different ethanol concentrations (between 5 and 25% (v/v) and for a working pressure range mentioned previously (between 4 and 20 bar). Fig. 3 presents the permeability obtained for each membrane as a function of ethanol concentration of the aqueous solution. The hydraulic permeability is also represented, which corresponds to 0% ethanol concentration.

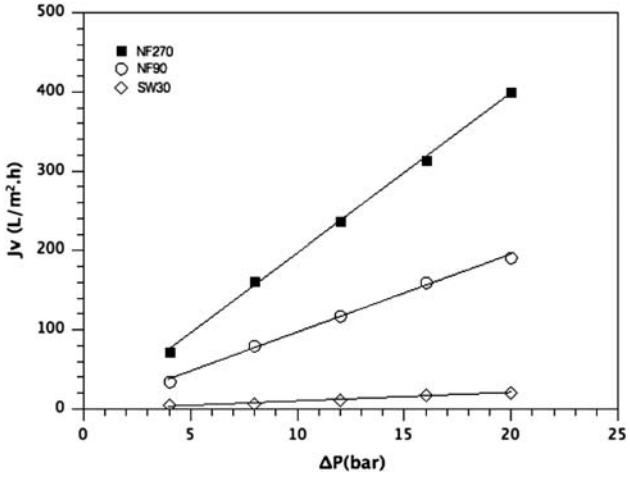

Fig. 2. Volumetric fluxes for water at different transmembrane pressures for the NF270 (square), NF90 (circle) and SW30 (diamond) membranes.

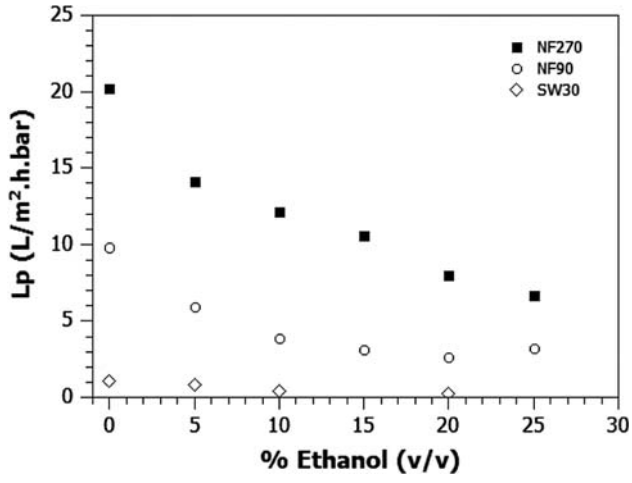

Fig. 3. Permeability of the NF90, NF270 and SW30 membranes, as a function of ethanol concentration (v/v).

By the analysis of Fig. 3, it can be verified that in general membrane permeability decreases in a logarithmic fashion with an increase in ethanol concentration. For the SW30 membrane, it was not possible to obtain the permeability values for 15 and 25% (v/v) ethanol concentration, because the permeate flux was rather erratic.

Comparing the results obtained for the hydraulic permeability for all the membranes tested (0% ethanol concentration) with those obtained for ethanol solutions (Fig. 3), it is observed that the permeability is lower when ethanol is present. Geens et al. [32] studied the influence on flux and rejection for nanofiltration membranes of binary mixtures of water and organic solvents. It was concluded that the addition of a low content of alcohol (less than 20% (v/v)) to pure water strongly influences the polarity of the solution, which leads to a decrease in permeability for hydrophilic membranes. The membranes tested in this work (NF270, NF90 and SW30) are reported to have a hydrophilic character, given their low contact angle with water [37–39]. Hence, the results obtained in this work were aligned with the results obtained by Geens et al. [32].

One of the most critical aspects of this process is to guarantee a low ethanol rejection. Table 3 compiles maximum rejection values obtained for each membrane and for each ethanol concentration. The rejection was calculated according to Eq. (2). It is clear that there is as decrease in rejection with an increase in the MWCO of the membrane. For lower pressures, the SW30 membrane presents a very low flux, and the values obtained are within the experimental error.

It was interesting to note that ethanol rejection decreases with an increase in ethanol concentration, indicating that size exclusion was not the main separation mechanism. This suggest that a higher ethanol concentration improves the selectivity of the membranes for the purposes of this work, enabling the production of a permeate stream with a similar ethanol composition as that of the feed stream.

Table 3
Maximum value obtained for ethanol rejection for the NF270, NF90 and SW30 membranes

Ethanol concentration (% (v/v))	NF270	NF90	SW30
	Rejection (%)		
5	15.8	25.0	47.7
10	12.5	22.7	30.9
15	9.86	21.3	37.5
20	7.07	12.37	12.0
25	7.20	9.60	11.1

3.3. Sugar rejection study using fermentation model solutions

As result of the fermentation of the olive bagasse hydrolysates, residual sugars and ethanol are obtained as main products. In order to use ethanol as fuel, it is necessary to recover it from the liquor resultant from the fermentation step. For evaluating if nanofiltration is efficient for this separation, two fermentation model solutions were prepared. The rejection of sugars for each membrane and the recovery of ethanol in the permeate stream was determined. The rejection study for the solutions containing sugars (cellobiose, xylose, glucose and furfural at a concentration of 1 g/L) was only performed for the NF270 and NF90 membranes. The reason for this was that the permeability for SW30 membrane was very low, and more importantly, ethanol rejection was relatively high for the objectives of this work (please see Section 3.2).

Table 4 shows the permeability of the NF270 and NF90 membrane for the solutions studied. As before, a higher permeability value was obtained for the NF270 membrane.

The rejection values obtained for the solutions containing 1 g/L of sugars and between 5 and 15% (v/v) of ethanol for the NF270 and NF90 membranes are represented in Figs. 4 and 5, respectively. Generally, both NF270 and NF90 presented rejections between 80 and 100% for cellobiose, xylose and glucose, and lower rejections for furfural and ethanol. The compounds studied have the following molecular weights: Cellobiose—343 g/mol; Xylose—150.13 g/mol; Glucose—180.16 g/mol; Furfural—96.09 g/mol; Ethanol—46.02 g/mol. Therefore, as expected, the membrane rejection for sugars follows the trend of the solutes molecular weight. In the case of furfural and ethanol, molecular weight may not be the most adequate parameter to describe rejection as these molecules are less spherical than sugars. Although furfural presents a higher molecular weight comparatively to ethanol, it presents a lower rejection (please see Figs. 4 and 5). Bellona et al. [40] and Van der Bruggen et al. [41] studied the influence of molecular

Table 4
Permeability of NF270 and NF90 membrane for the solution containing sugars (1 g/l) and ethanol with different concentrations

Ethanol concentration (% (v/v))	Lp ($L/m^2 h bar$)	
	NF90	NF270
5	6.31	12.46
15	4.95	10.96

size on retention for molecules having a molecular weight below the MWCO. They showed that Stokes diameter may be a more adequate parameter for characterization of solute rejection. Stokes diameter for furfural and ethanol is 0.44 [42] and 0.62 [41], respectively. NF270 membrane pore size is 0.84 [43], while NF90 membrane pore size is 0.68 [43]. Therefore, according to Stokes diameter, it should be expected that furfural presents a lower rejection in comparison with ethanol, which is consistent with the results obtained.

The results presented in Figs. 4 and 5 indicate that both NF270 and NF90 fit the objectives of this work by presenting a relatively low rejection to ethanol, and a high rejection to the sugars. A benefit of NF270 is a higher permeability, whereas NF90 shows comparatively higher sugar rejection, which is important in a diafiltration operation.

In order to evaluate the recovery of ethanol from a fermentation medium by nanofiltration, a diafiltration process was simulated to study the time needed to recover most of the ethanol from a feed solution. It has been shown in the literature that diafiltration with nanofiltration membranes is an efficient process to recover/remove micro solutes from feed solutions [34,44,45]. The diafiltration model implemented in this work assumes operational constant applied pressure and constant volume of feed solution. A mass balance to the system gives:

$$\frac{d(V_f C_{s_i f})}{dt} = -J_v A C_{s_i p} \quad (3)$$

Where V_f is the feed volume (m^3), C_{sf} is the concentration in feed of solute i (mol/m^3), C_{sp} is the concentration in the feed of solute I (mol/m^3), J_v is the permeate volumetric flux (m^3/m^2 h), A is the membrane area (m^2) and $t(h)$ is the diafiltration time.

The rejection (R) may be considered to be constant during the course of the experiment. Therefore Eq. (3), can be solved as,

$$C_{sf} = C_{sf_o} \exp\left(-\frac{J_v A(1-R)}{V_f} t\right) \quad (4)$$

The diafiltration model was simulated for NF270 and NF90 membranes in order to understand the behaviour of both membranes on a diafiltration mode and compare them in terms of diafiltration time and purity of permeate stream. The feed volume tank was assumed to be 10 L, the membrane area was assumed as 140 cm^2, the rejection values of cellobiose, xylose, glucose, furfural and ethanol were fixed at the values obtained in the previous experiments at 20 bar (please see Figs. 4 and 5) and J_v was assumed to be constant and equal to 0.219 m^3/m^2 h for NF270 and 0.099 m^3/m^2 h for NF90, for a transmembrane pressure of 20 bar. The ethanol concentration in the feed solution considered was 15% (v/v). The results for the diafiltration simulation are represented in Fig. 6.

Analysis of the diafiltration simulation results in Fig. 6(a) shows that for NF270 about 10 h of operation are sufficient to remove most of the ethanol from the fermentation solution (99%). In the first two diafiltration hours, there is a decrease in about 40% of initial ethanol in the feed tank. On the other hand, NF90 appears to be more efficient on what concerns the retention of sugars, due to their high rejection. Diafiltration is expected to take about 25 h to achieve the

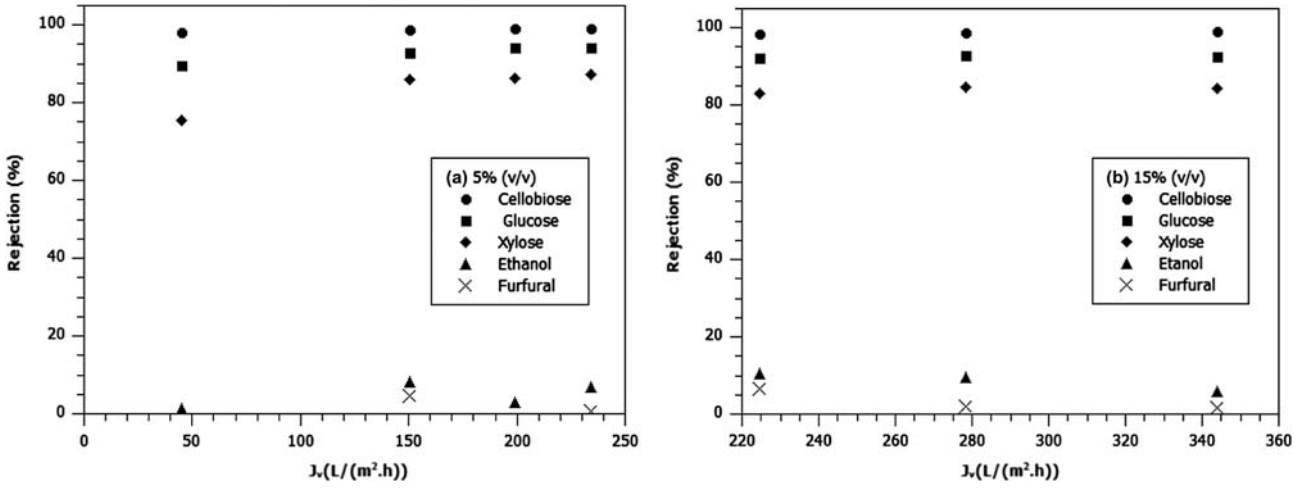

Fig. 4. Rejection profile for cellobiose (circle), glucose (square), xylose (diamond), ethanol (triangle) and furfural (cross) of the NF270 membrane, (a) for the 5% (v/v), and (b) and 15% (v/v)) ethanol's concentration.

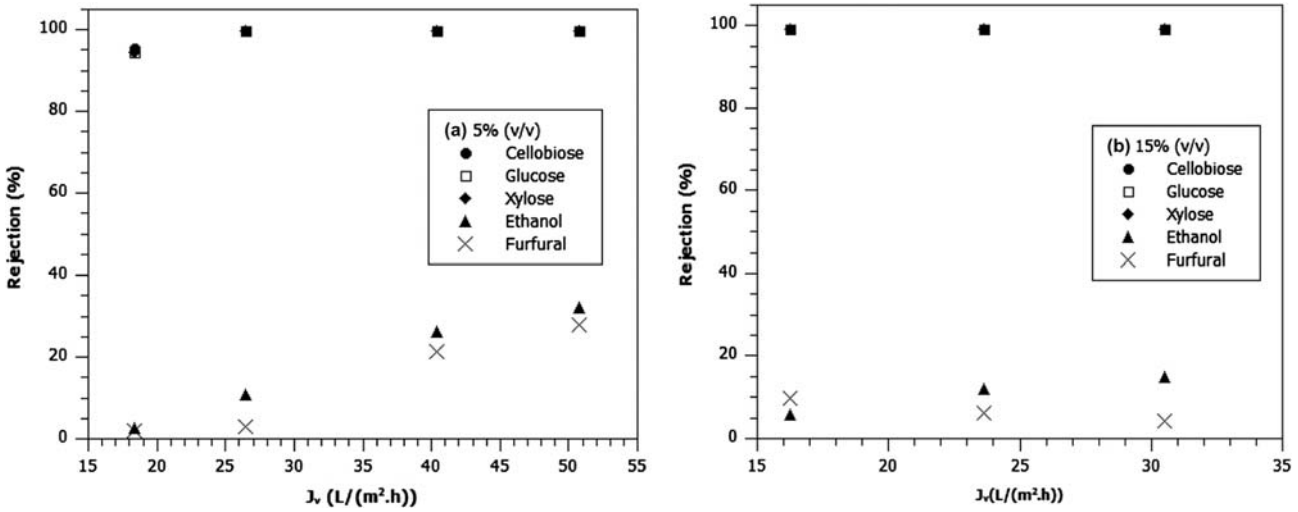

Fig. 5. Rejection profile for cellobiose (circle), glucose (square), xylose (diamond), ethanol (triangle) and furfural (cross) of the NF90 membrane, (a) for the 5% (v/v), and (b) and 15% (v/v)) ethanol's concentration.

ethanol concentration obtained by NF270 after 10 h, given the different permeability values for both membranes. In what concerns the selectivity of the diafiltration process, the use of the NF90 membrane allows for a better separation of ethanol from the sugars (rejection values shown in Figs. 4 and 5 further detail this point).

Table 5
Composition of olive bagasse fermentation liquor

Compound	Concentration
Glucose	0.2 g/L
Xylose	0.7 g/L
Ethanol	3.1% (v/v)

3.4. Sugar rejection study using fermentation model solutions

In order to understand the suitability of nanofiltration for processing a real liquor resultant from olive bagasse fermentation, rejection studies were carried out. This study was performed using the NF270 membrane, since it enables a more significant variation of solute's concentration (namely sugars) during a diafiltration operation.

The composition of olive bagasse fermentation liquor, in terms of the main compounds, is described in Table 5.

Fig. 7 presents the rejection profile for glucose, xylose and ethanol present in fermentation liquor.

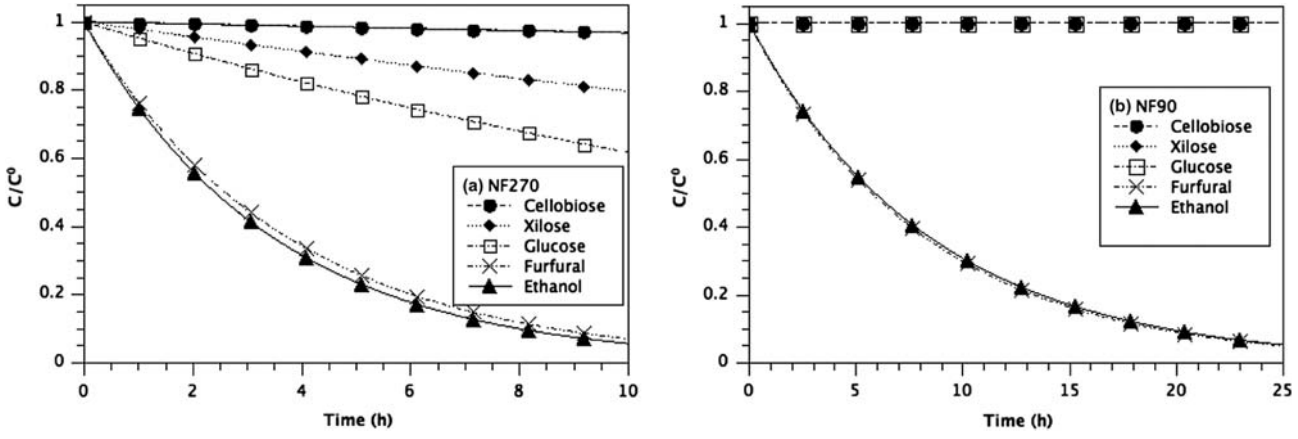

Fig. 6. Diafiltration simulation for: (a) NF270 and (b) NF90 membranes.

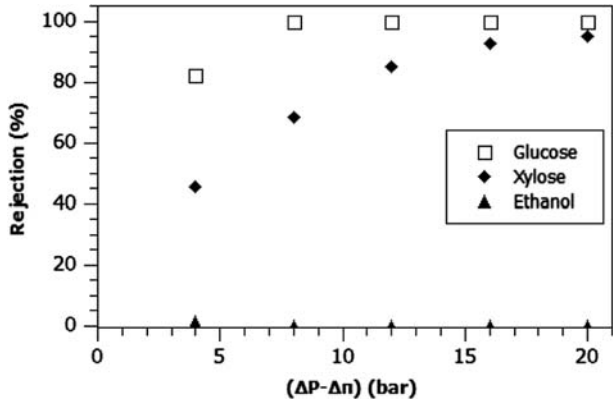

Fig. 7. Rejection profile for glucose (square), xylose (diamond) and ethanol (triangle) of the NF270 membrane.

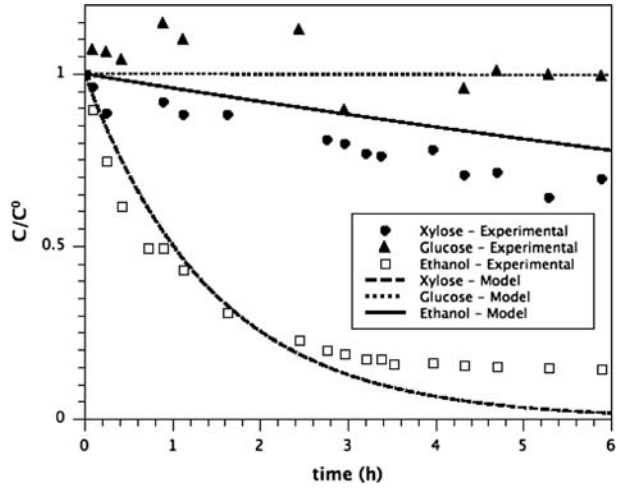

Fig. 8. Diafiltration experiment for fermentation liquor with NF270 membrane.

Results shown in Fig. 7 indicate an increase in glucose and xylose rejection with an increase in transmembrane pressure, as expected. Comparatively with results obtained with model solutions (please see Fig. 4), the rejection obtained for sugars and ethanol in a real liquor follow a different trend than the one obtained with model solutions. This fact may be explained by the more complex nature of the liquor, that is, comprised of a larger number of components, that are expected to interact with the membrane differently that in the case of a model solution. Rejection is generally lower for all components in the case of a real liquor, which may be considered positive from an ethanol recovery stand-point, but being negative for the diafiltration process, since the components that are to be retained are in this way partially lost to the permeate stream.

A diafiltration study for bioethanol produced by olive bagasse fermentation was also conducted. Taking into account, ethanol rejection and permeate flux obtained at 20 bar under total recycle mode of operation, diafiltration time was estimated to be 6 h. The volume in the feed tank was 1.3 L, and the membrane area was assumed as 140 cm^2.

Experimental results obtained in the diafiltration experiment for a real liquor are shown in Fig. 8. Also shown are the numerical predictions obtained through the use of the diafiltration mathematical model previously described.

Results obtained show that after 6 h there was a recovery of about 90% of the bioethanol present in the feed liquor. For the same time period, about 30% of the xylose initially present in the feed was lost to the permeate stream. As expected, glucose concentration was approximately constant throughout the whole operation given the very high rejection values. It is important to note that after about 3 h of operation experimental values start to deviate from the numerical predictions. This could be tentatively related to a change in the permeability and rejection performance of the membrane during operation, which is not captured in the mathematical model applied. These results show that the diafiltration mathematical model developed may be used with confidence for process design and scaling up purposes, provided that permeability and rejection relations are determined beforehand.

4. Conclusions

In this study, nanofiltration showed to be an efficient process to separate ethanol from other compounds present in a typical fermentation medium. The results obtained suggest that ethanol can be recovered from fermentation model solutions, with ethanol rejections in the range between 28 and 5% and an average rejection of 98% for sugars. The final product obtained in the permeate stream may be considered therefore a product with an acceptable level of purification. Taking into account the compromise between membrane permeability and selectivity for the purposes of this work, both membranes tested in this work (NF90 and NF270) present advantages and drawbacks for the recovery of bioethanol from fermentation liquors of olive bagasse. Given that a real liquor interacts with the membrane material and reduces rejection to all solutes, it can be tentatively assumed that NF90 is the most suitable membrane if a total sugar rejection is envisaged, while NF270 is the most efficient membrane if higher ethanol permeation rates are looked for.

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