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Selection of membranes for purification of fructooligosaccharides

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ABSTRACT

The aim of this study was to purify fructooligosaccharides (FOS) present in a mixture of sugars, containing also glucose, fructose and sucrose through, nanofiltration membranes. Four membranes were used: NP010 and NP030 (Microdyn Nadir, Germany), Desal–5 DL and Desal–5 HL (GE Water & Process Technologies). Experimental assays were performed in a dead-end cell and tangential cell filtration to select the most appropriate membrane. Then, with the membrane selected performed diafiltration in tangential cell filtration up to a concentration about 80% FOS. In the dead-end filtration cell experiments the NP010, NP030, HL and DL membranes were selected, since they performed the highest retentions of FOS, and lowest retention of glucose. The results showed that NP030 membrane performed the highest differences between the retention of FOS and sucrose, where the retentions of the different saccharides were: fructooligosaccharides (R_{obs} = 0.66), glucose (R_{obs} = 0.18), fructose (R_{obs} = 0.15) and sucrose (R_{obs} = 0.24). The results clearly demonstrate the potential of diafiltration using the NP030 membrane in the purification of FOS from mixtures containing mono and disaccharides.

Keywords: Nanofiltration; Fructooligosaccharides; Separation; Selection of membranes

1. Introduction

Oligosaccharides are functional food ingredients, which have great potential to improve the quality of many foods [1]. Certain oligosaccharides are not digested or absorbed in the small intestine but are metabolized by desirable species of bacteria, mainly bifido and lactobacilli, resident in the colon. These oligosaccharides are classified as prebiotics [2,3]. Fructooligosaccharides (FOS) are oligosaccharides composed by fructose oligomers consisting mainly of kestose, nystose and 1-β-fructofuranosyl nystose, with one to three fructosyl units linked to sucrose in the β–2, 1 position [4]. The FOS are present in the form of mixtures containing mono and disaccharides, so that the purification of FOS from this mixture becomes suitable, by removing the low molecular weight sugars that do not contribute to the beneficial properties of the higher molecular weight oligosaccharides. Nanofiltration (NF) appears to be a potential industrial scale method for purification and concentration of oligosaccharide mixtures because recovering low molecular weight species [5].

Several researchers have been evaluated the potential of nanofiltration to fractionated and concentration the oligosaccharides. According to López Leiva and Guzman [6], the concentration and some purification of oligosaccharides mixtures are possible using NF membranes

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as an alternative to more expensive chromatographic techniques. In addition, Matsubara et al. [7] reported partial concentration of oligosaccharides from steamed soybean wastewater using NF membranes. Sarney et al. [8] used NF for the fractionation of human milk oligosaccharides and produced biologically active oligosaccharide mixtures with very little contaminating lactose. Kamada et al. [9] studied the effectiveness of combined membrane processing with ultrafiltration (UF) and nanofiltration (NF) for purifying and concentrating oligosaccharides from chicory rootstock. Goulas et al. [10] also studied the fractionated commercial oligosaccharides mixtures by applying diafiltration using two nanofiltration and one ultrafiltration membranes. Olano-Martin et al. [11] using the ultrafiltration dead-end membrane reactor to investigate the production of pectin–oligosaccharides.

The aim of this work was the selection of a NF membrane able to purify fructooligosaccharides from a mixture of sugars, which contains glucose, fructose, sucrose and fructooligosaccharides.

2. Material and methods

2.1. Chemicals

Analytical grade purity glucose, fructose and sucrose were purchased from Panreac Quimica S.A (Spain). The commercial oligosaccharide mixture was fructooligosaccharides syrup from BENEO-Orafti (Belgium). The syrup consists of 51–53% of fructooligosaccharides, 25–28% of glucose, 10–13% of sucrose and 8–10% of fructose.

2.2. Membranes

Four membranes were used (Table 1), NP010 and NP030 (Microdyn Nadir, Germany), these membranes were made of polyethersulfone, Desal–5 DL and Desal–5 HL (GE Water & Process Technologies, USA), these membranes were made of aromatic polyamide.

Table 1
Permeabilities at 25 bar pressure in dead-end cell filtration

Membranes	Permeability (m/Pa s)	Retention (%)	MWCO (Da)[c]
NP010	1.01×10^{-12}	25–55[a]	1000
NP030	6.89×10^{-15}	80–95[a]	400
HL	6.84×10^{-14}	98[b]	150–300
DL	2.86×10^{-13}	96[b]	150–300

[a]Na_2SO_4 500 mg/l at 40 bar.
[b]$MgSO_4$ 2000 mg/l at 6.9 bar.
[c]MWCO of the membranes as given by the manufacturer.

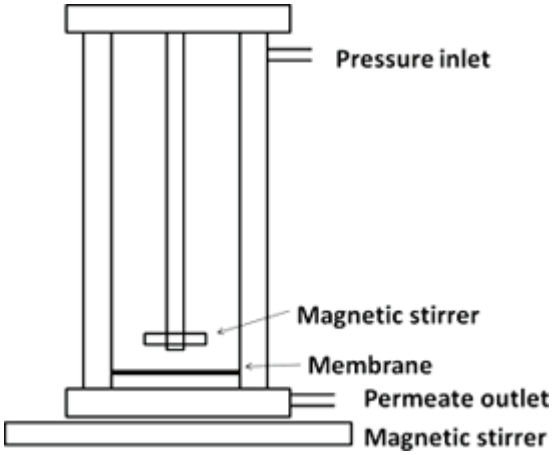

Fig. 1. Dead-end filtration cell.

2.3. Membrane filtration equipment

2.3.1. Dead-end stirred cell

The selection of membranes was performed in a dead-end stirred cell (Model Sterlitech) (Fig. 1). The volume of the stirred cell is 200 ml while the effective membrane surface area is 14.6 cm^2. A magnetic stirrer was used to homogenize the feed solution and to reduce the concentration polarization. The feed of the stirred cell was pressurized using nitrogen gas from a gas cylinder.

At the beginning of each nanofiltration experiment, distilled water was circulated and the pure water permeate flux of the membrane was measured. Pure water fluxes (J_w) were measured as a function of pressure (Δp) using ultra-pure water to determine the permeability of membranes. The permeability of membranes (L_p) were calculated using Eq. (1):

$$L_p = \frac{J_w}{\Delta p} \quad (1)$$

The observed retentions for a given saccharide, based on the concentration determined from the sample analysis, were calculated from Eq. (2):

$$R_{obs} = 1 - \frac{C_p}{C} \quad (2)$$

where C_p is the permeate concentration while C is the feed concentration.

2.3.2. Tangential membrane cell

In order to perform the experiments in a tangential cell a system consisting of a tank for feeding the solution with temperature control (24–28°C), a pump (Tuthill TXS2), two pressure gauges at the membrane inlet and outlet to measure the transmembrane pressure, a needle

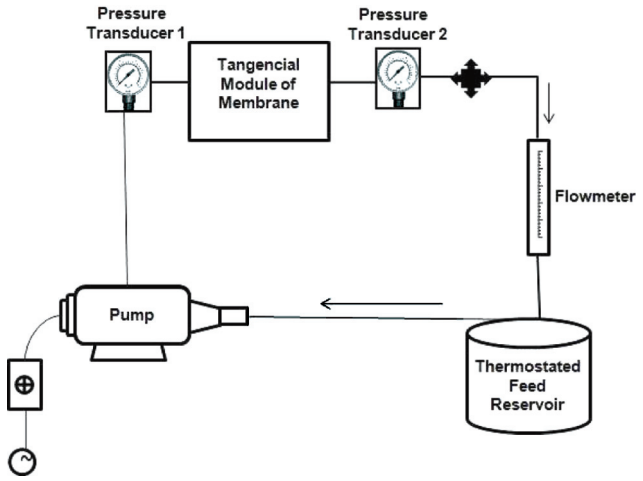

Fig. 2. Experimental set-up of tangential cell filtration.

valve located after the membrane and one flowmeter to measure the retentate flow, was used (Fig. 2) [12]. The effective membrane surface area was 66 cm^2. Samples of permeates and retentates were withdrawn at different times and analyzed by chromatography.

2.3.3. Diafiltration experiments

The diafiltration experiments were performed in tangential cell filtration consisted of a 2.3 l feed tank. The membranes were conditioned by compressing them to steady state with demineralized water as feed, at an intermediate pressure according to their pressure operation limits (40 bar). The feed concentration was about 250 g/l, and operation pressure was 3.5 MPa. The feed volume (2.3 l) was kept constant along the experiment by adding distilled water.

2.4. Analytical methods: analysis of sugar

Identification and quantification of saccharides (sucrose, glucose, fructose, and FOS) was achieved by HPLC Shimadzu LC-9A. Shodex KS 801 guard column and column at 22–24°C were used, using software Class-VP. The sugars were eluted in distilled water at a flow rate of 0.8 ml/min and injected volume at 20 µl. The methodology is a standard, defined by the manufacturer and clearly separated the sugars in question.

3. Results and discussion

3.1. Dead-end stirred cell filtration

The stirring velocity used in the dead-end filtration cell experiments was 1110 rpm, was chosen the maximum stirring velocity which reduces the effects of concentration polarization [13], at 25 bar pressure, usual pressure in nanofiltration processes, room temperature and 250 g/l. At low pressures, the relationship between permeate flux and rejection increases in a linear way but as soon as the pressure attains a certain level, the concentration polarization increases and the retention remains constant or decreases. It is not possible to provide a reference value for the optimal flow rate or pressure required using dead-end and membrane separation for saccharide separation, as the optimal value may vary considerably depending on the particular feedstock, i.e., solute properties (as treated above), the volume of the solution, etc. [13].

Table 1 shows the experimental values of permeabilities for the four membranes studied and it can be observed that the NP010 and DL membranes showed the highest permeabilities. Also the characteristics of the nanofiltration membranes provided by the manufacturer are presented in this table.

The selection of membranes was carried out based on the highest observed retentions of FOS and lower observed retention for glucose because the glucose concentration is the highest in the mixture, after the FOS. The observed retentions depending of concentration polarization, depended largely on working conditions, how feed concentration, pressure, and stirring velocity, to decrease the effects of concentration polarization working with high stirring velocities. For the same membrane, with the same working conditions, the concentration polarization should be similar for all sugars and therefore the relative differences between the observed retentions can be considered constant. In these conditions it is possible to compare results of retentions from different membranes through observed retentions, defining the most appropriate for a particular process.

Therefore, the membrane that performed the highest retention of FOS was the DL (R_{obs} = 0.99) (Fig. 3) and presenting an observed retention for glucose of R_{obs} = 0.92,

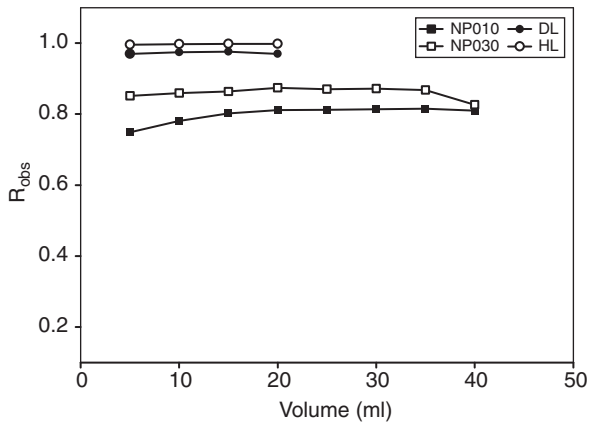

Fig. 3. Observed retentions of FOS versus permeate volume using dead-end stirred cell.

the HL membrane presented the observed retention for FOS (R_{obs} = 0.97) and sucrose (R_{obs} = 0.89). The NP010 and NP030 membranes presented observed retentions of FOS (R_{obs} = 0.81) and (R_{obs} = 0.82) and observed retentions of glucose (R_{obs} = 0.12) and (R_{obs} = 0.10), respectively. These membranes give lower observed retentions of FOS, but the observed retention of sucrose in both membranes (NP010 and NP030) is lower than for the others. In the case of DL and HL membranes, the retention of sucrose is about 90% and it would be very difficult to be separated from FOS with these membranes.

3.2. Tangential membrane cell filtration

For a system of purification of FOS on a large scale were performed the same tests on a tangential membrane cell filtration. Fig. 4(a–d), showed the observed retentions of the saccharides in the NP010, NP030, HL and DL membranes, respectively, using tangential membrane cell filtration at 18 bar pressure, room temperature and 0.55 m/s tangential velocity and feed volume of 1 l at 250 g/l. It can be seen that the membranes NP010 and NP030 showed the lowest retention of glucose, fructose and sucrose, with values for the observed retentions at the end of the experiments of:

– glucose (R_{obs} = 0.26), fructose (R_{obs} = 0.22) and sucrose (R_{obs} = 0.47) for the NP010 membrane and
– glucose (R_{obs} = 0.18), fructose (R_{obs} = 0.15) and sucrose (R_{obs} = 0.24) for the NP030 membrane.

The DL membrane has a low retention of glucose and fructose (R_{obs} = 0.25) and (R_{obs} = 0.26), respectively, but has a similar retention of FOS (R_{obs} = 0.98) and sucrose (R_{obs} = 0.91). The HL membrane has a similar behavior even with somewhat lower values of retention for all sugars.

The NP010 and NP030 membranes were chosen to perform tangential filtration because these membranes showed greater differences in observed retention of FOS and sucrose, and they can be used to define a

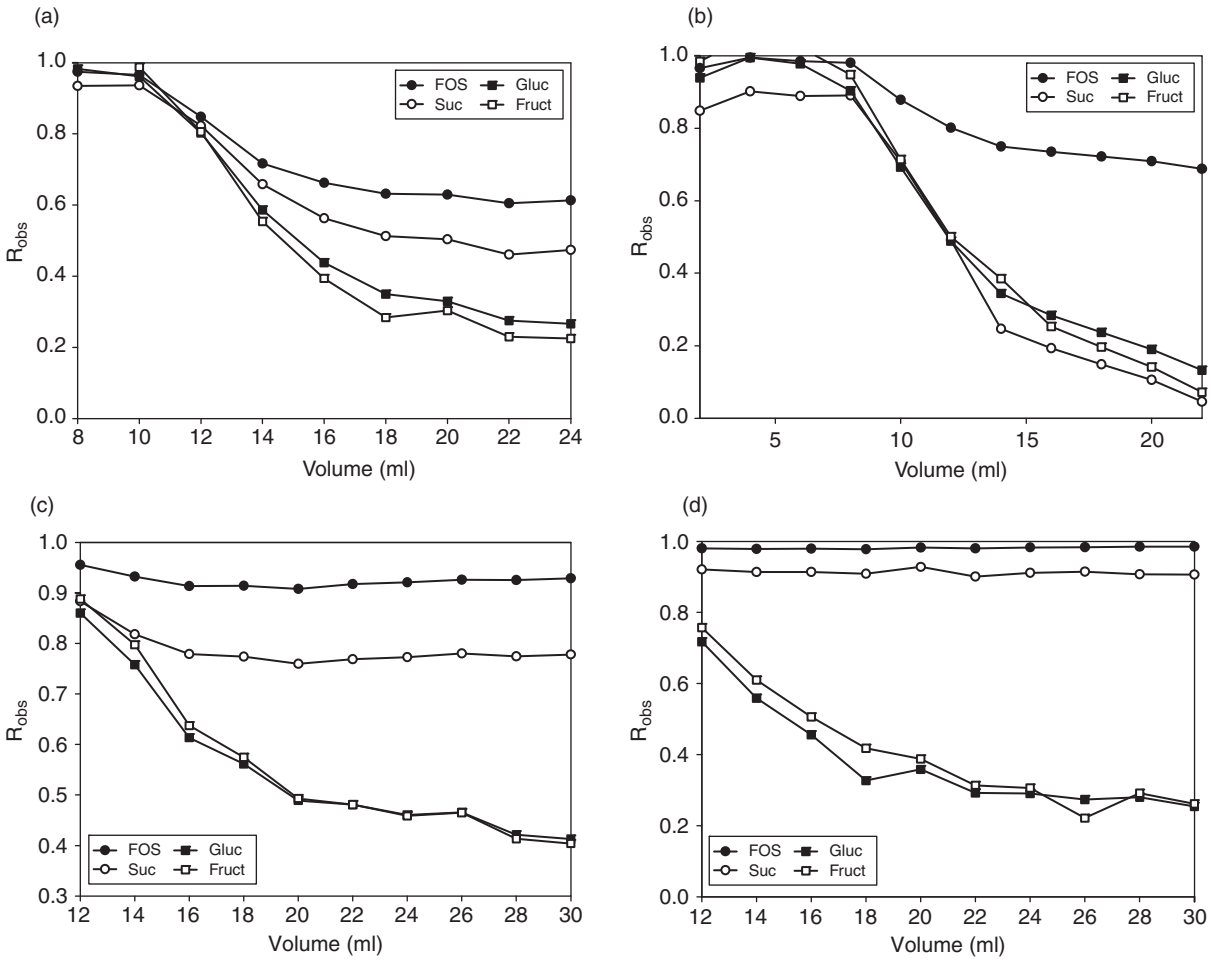

Fig. 4. Observed retentions of saccharides versus permeate volume using tangential membrane cell filtration (a) NP010 (b) NP030 (c) HL and (d) DL membranes.

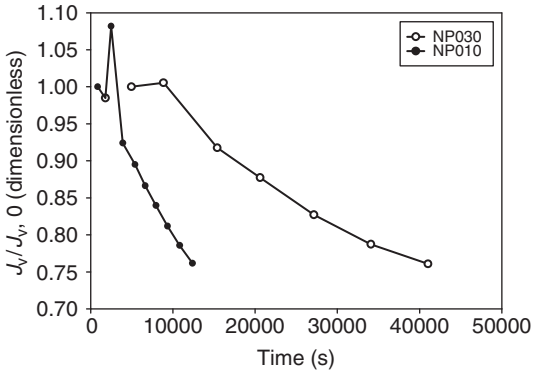

Fig. 5. Relation between permeate flux versus time and the initial flux to the membranes NP010 and NP030 in the process of tangential filtration.

methodology for purification of FOS. Although we are not considering the concentration polarization in these experiments, considering only the observed retentions, we do not believe that have relative differences between the true and observed retentions in this case. Fig. 4 shows the results for the permeate volume, in these cases the permeate volume is very small and not change the feed concentration during the filtration.

The fouling is confirmed by an analysis of the flux versus time, in Fig. 5 shows a decrease of the flux of both membranes. It can observe that the NP010 membrane has a higher initial flux, then the process is faster, but the flux is decreased much faster too.

In the purification experiments the feed concentration can be changed, then others experiments were conducted to NP010 and NP030 membranes, at 18 bar pressure, room temperature and feed volume 2 l at 300 g/l. The first filtration was permeated half the original volume, about 1 l. Fig. 6a shows the observed retentions of FOS (R_{obs} = 0.64), sucrose (R_{obs} = 0.38), glucose (R_{obs} = 0.28) and fructose (R_{obs} = 0.31) in the NP010 membrane and Fig. 6b shows the observed retentions of FOS (R_{obs} = 0.72), sucrose (R_{obs} = 0.40), glucose (R_{obs} = 0.15) and fructose (R_{obs} = 0.27) in the NP030 membrane, it can be concluded that the NP030 membrane has the largest retention of FOS, whereas the observed retentions of sucrose and fructose are the same in both membranes, then this seems to indicate that the NP030 membrane is most suitable for the process of purification.

Fig. 6 shows the observed retentions in the NP010 and NP030 membranes, it can be observed that the membrane NP010 has an increased observed retention during filtration, since the membrane NP030 remains constant, this can be explained by fouling in the NP010 membrane.

Fig. 7 shows the observed retentions for the solution more diluted, this experiment was performed because the filtration has been slow due to high osmotic pressures generated by high concentrations of sugar, and then more dilute solutions were used to demonstrate that the relationship between retentions of sugars is the same. Then the feed volume was 2 l at 200 g/l, the volume permeate was 1 l. The observed retentions for the NP010 membrane were: FOS (R_{obs} = 0.57), sucrose (R_{obs} = 0.31), glucose (R_{obs} = 0.16) and fructose (R_{obs} = 0.31) (Fig. 7a), and for the NP030 membrane the observed retentions were: FOS (R_{obs} = 0.71), sucrose (R_{obs} = 0.31), glucose (R_{obs} = 0.02) and fructose (R_{obs} = 0.001) (Fig. 7b). The standard deviation between different experiments is less than 10%.

With these results we can define a methodology for the purification of FOS through diafiltration using the NP30 membrane. The diafiltration process seems more appropriate because for low concentrations, the observed retention is greater and, at the same time, when the filtration is advancing, there is a decrease of the

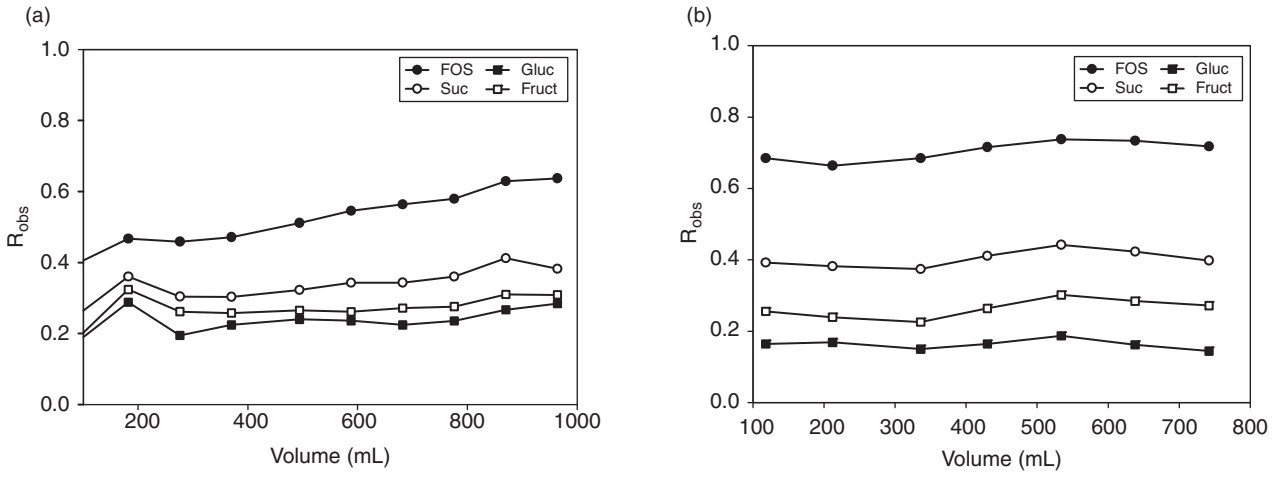

Fig. 6. Observed retentions of the saccharides versus permeate volume using tangential membrane cell filtration (a) NP010 (b) NP030 membranes.

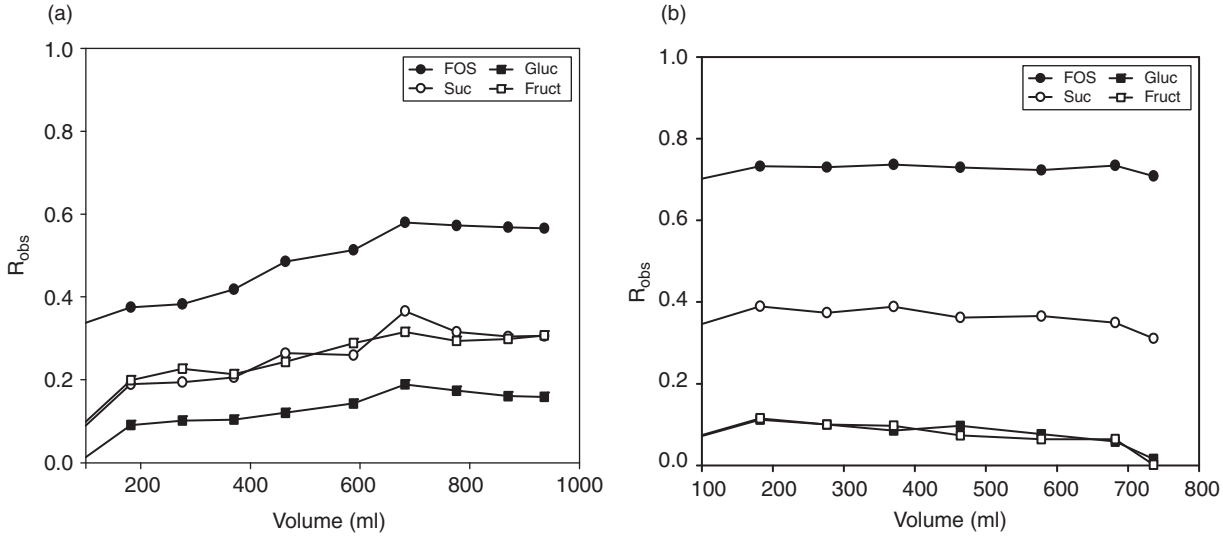

Fig. 7. Observed retentions of the saccharides versus permeate volume using tangential membrane cell filtration with low feed concentration (a) NP010 (b) NP030 membranes.

osmotic pressure. The NP030 membrane is more suitable because this membrane shown that the biggest difference between the retentions of FOS and other sugars.

Goulas et al. [10] observed that membranes composed for polyethersulfone appears to exert better separation characteristics than cellulose membranes, in this work the same was observed then the polyethersulfone membrane was presented the better separation of mixture of sugars. This is because the sugars to be separated have a small molecular size difference that requires a more uniform pore size distribution in order for such separation to be achieved.

3.3. Diafiltration

The tests were carried out in the tangential cell filtration with the NP030 membrane because this membrane showed the highest observed retention of FOS and lower retention of others saccharides (glucose, fructose and sucrose). The diafiltration experiments were carried out with 2.3 l feed solution of the syrup, at 35 bar pressure, and feed concentration 350 g/l at room temperature with a recirculation flux of 6 l/min. The feed volume was kept constant along the experiment by adding distilled water up to a maximum concentration of FOS in the retentate. During this process the permeate flux increases significantly. This occurs because the fouling of the membrane is negligible and the difference in osmotic pressure decreases during the process. Table 2 shows the results of two filtrations, where the first was performed as a diafiltration up to a concentration about 80% FOS. In the second filtration, the permeate volume of the first filtration was filtrated and it was obtained a concentration of FOS in the retentate, this retentate volume could be added to a continuous process.

Fig. 8 shows the sugar concentration versus the cumulative volume of the permeate. Results showed that it was possible to obtain a purity greater than 80% in the first retentate and when permeate was filtered again the concentration of FOS obtained in the second retentate is concentrated, which would minimize losses of product, with the adding the retentate in the first tank.

Table 2
Permeate and retentate concentrations using NP030 membrane in the diafiltration process

	First filtration				Second filtration	
	Conc. init. (g/l)	Conc. init. %	Retentate (g/l)	Retentate (%)	Retentate (g/l)	Retentate (%)
FOS	180.3	51.44	250.9	80.11	96.80	51.55
Sucrose	35.32	10.08	27.09	8.65	21.20	11.29
Glucose	98.02	27.96	25.73	8.22	55.80	29.71
Fructose	36.86	10.52	9.48	3.03	13.99	7.45
Total conc	350.5		313.2		187.79	

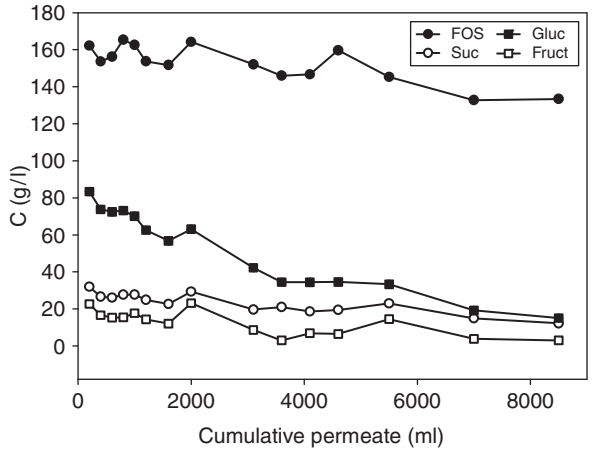

Fig. 8. Retentate concentrations of the saccharides versus cumulative permeate flux in the NP030 membrane using tangential cell filtration.

According to the results of the NP030 membrane, one can conclude that the NP030 membrane is able to produce, by diafiltration, FOS solutions with high purity, thus increasing its applicability in foods.

4. Conclusions

According to the experiments performed in dead-end stirred filtration cell was performed a classification of four membranes for their capacity for the purification of FOS.

The NP010, NP030, DL and HL membranes were used in tangential cell filtration. From these experiments, the NP030 membrane was selected, since it presented the higher differences between the observed retentions for FOS and sucrose. From filtration results it is apparent that the most appropriate membrane for purifying fructooligosaccharides from mono and disaccharides is the NP030 membrane.

Diafiltration experiments with the NP030 membrane led to a concentrate with 80% of fructooligosaccharides. This study clearly demonstrates the potential of diafiltration using the NP030 membrane for the purification of fructooligosaccharides from mixtures containing mono and disaccharides.

The more regular, as far as pore size is concerned, the polyethersulfone membrane appears to exert better separation characteristics than the polyamide membranes. This is because the compounds to be separated have a small (as far as membrane separations are concerned) molecular size difference that requires a more uniform pore size distribution in order for such separation to be achieved.

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Symbols

J_w — Pure water flux (based on the membrane area), m/s
ΔP — Applied pressure drop, kN/m^2
R_{obs} — Observed retentions
C_p — Concentrated of the solute in the permeate, g/l
C — Concentrated of the solute in the feed, g/l

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