Assessing nanofiltration and reverse osmosis for the detoxification of fermentable solutions

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Introduction

Lignocellulosic materials provide abundant and renewable energy sources: cellulose and hemicellulose hydrolysis releases fermentable sugars allowing ethanol production through micro-organisms such as *Saccharomyces cerevisiae.* However, during hydrolysis – generally performed with diluted acid solutions – fermentation inhibiting substances are also produced. The fermentation efficiency of the obtained hydrolysates depends upon their composition and the micro-organism used. The mainly found inhibitors include furan derivatives (furfural and 5-Hydroxy methyl furfural (5-HMF)), phenolic compounds, weak acids (formic, acetic and levulinic acids), raw material extractives (acidic resins, tannic and terpen acids), and heavy metal ions (iron, chromium, nickel and copper).

Many methods have been tested to remove inhibitors from hydrolysates such as membrane extraction, trialkylamine extraction, over liming, ion-exchange resins, active charcoal, enzyme treatment or *in situ* detoxification (1,2,3). None of them proved able to remove simultaneously all types of inhibitors. Moreover, the most efficient present environmental drawbacks (reactant consumption, waste release). Membrane technologies have recently drawn much interest, as most inhibitors have molecular weight lower than monosaccharides (4,5). This study examined the feasibility – using NF and RO membranes – of detoxifying fermentable solutions by combining simultaneously high rejection of sugars and low rejection of inhibitors.

Methods

A model solution (Table 1) was elaborated based on the information found about the composition of lignocellulosic hydrolyzates from different raw material. Solution pH was 3.

Table 1. Composition of model solution

	Xylose	Arabinose	Glucose	Acetic acid	Furfural	HMF	Vanillin
Concentration (g L^{-1})	15	5	10	5	0.5	1	0.05
MW (g mol^{-1})	150	150	180	60	96	126	152

Five reverse osmosis (CPA2, CPA3, ESPA2 (Hydranautics), XLE (Dow Filmtec), and SG (GE Osmonics)) and five nanofiltration (NF90, NF270, NF-, NF245 (Dow Filmtec), DK (GE Osmonics)) membranes were selected from literature and suppliers' data and from our experience on condensates detoxification (6). Filtration experiments were carried out with LabStak M20 pilot scale membrane filtration equipment of Alfa Laval at a flow rate of 400 L h^{-1} and a temperature of 20 ºC. They were performed in a total recycling mode with transmembrane pressures (TMP) increased from 5 to 30 bar by 5 bar step.

Retention Ri was calculated for each solute as Ri=100*(1-Cp,i/Cf,i) with Cp,i and Cf,i concentrations of solute i in the permeate and in the feed, respectively.

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Concentrations were analyzed by HPLC.

Results and discussion

For NF as well as for RO membranes, permeate flux increases linearly with TMP. Table 2 shows values of permeate fluxes for TMP of 5 and 30 bars. For RO, permeability increases as follows: SG < CPA3 < CPA2 < XLE < ESPA2. For NF membranes: NF90 < NF245 < NF ≈ DK < NF270. Regarding permeability, NF 90 presents an atypical behaviour and will be considered as a RO membrane in the discussion.

Table 2. Permeate fluxes (L h^{-1} m^{-2}) for RO and NF membranes at different TMP (bar)

TMP	SG	CPA3	CPA2	XLE	ESPA2	NF90	NF245	NF	DK	NF270
5	0.21	0.38	0.45	0.33	0.2	3.3	7.9	11.0	10.4	22.2
30	20.8	27.2	30.9	34.7	46.3	43.9	83.3	125.1	138.9	192.3

With RO membranes and TMP >10 bar, sugar's retention achieves values higher than 97% whatever the sugar. Regarding inhibitors' retention, CPA3 and CPA2 retain the less, followed by NF 90, ESPA 2, SG and XLE, in this order. However, the retention of inhibitors increases strongly with TMP (except for vanillin almost completely rejected probably due to its large MW). Table 3 compares rejection values for all RO membranes around 18 L h^{-1} m^{-2}: for CPA3, rejection is already 28% for furfural, 40% for acetic acid, 66% for HMF and 87% for vanillin. Inhibitors rejection follows more or less the order of molecular weight. Furfural (MW=96) goes through better than acetic acid (MW=60) because it has a much stronger affinity with the aromatic polyamide active layer of the membrane (7).

For nanofiltration membranes and TMP >10 bar, a high retention (>94%) is observed for glucose whatever the membrane. Considering arabinose and xylose, NF 270 would lead to significant loss of these sugars with retention ranging from 78 to 83% for arabinose and 69 to 83% for xylose. These results are in accordance with data on Stokes diameter of sugars (arabinose: 0.635 nm, xylose: 0.638 nm, glucose: 0.726 nm) and average pore radius of the membranes (NF 270: 0.84 nm). Regarding inhibitors' retention, all nanofiltration membranes show low to very low retention of inhibitors: at a permeate flowrate around 65 L h^{-1} m^{-2}, furfural is the less retained (<3%), followed by acetic acid (<8%), HMF (<13%) and vanillin (<20%) (Table 3). As for RO, rejection follows more or less the order of molecular weight. However, it can be noticed that with similar molecular weight, vanillin (MW=152) and xylose and arabinose (MW=150) are very differently retained, stressing the influence of physico-chemical interactions between solutes and membranes. At 65 L h^{-1} m^{-2}, NF 270 and DK give the lowest retention for all inhibitors. Although DK should be operated at higher pressure (15 bar instead of 10), it should be preferred for its lower loss of sugars.

Table 3. Retention of sugars and inhibitors (obtained for flux permeate around 18 L h^{-1} m^{-2} for reverse osmosis and 65 L h^{-1} m^{-2} for nanofiltration)

	SG	CPA3	CPA2	XLE	ESPA2	NF90	NF245	NF	DK	NF270
Pressure (bar)	30	20	20	20	15	10	20	15	15	10
Xylose	98.4	97.5	97.4	98.5	98.8	100.0	89.8	91.6	90.1	82.9
Arabinose	97.7	96.9	96.7	97.4	98.0	100.0	91.3	93.7	93.3	83.6
Glucose	98.8	97.8	97.3	98.8	98.8	100	95.5	97.3	96.6	94.8
Acetic acid	60.5	40.1	43.5	79.8	54.5	50.0	6.7	7.8	4.9	4.5
Furfural	50.7	28.1	31.4	87.6	47.0	42.1	2.3	0.5	-0.9	0.5
HMF	84.1	66.5	31.4	98.0	85.8	81.6	12.7	12.8	7.1	6.5
Vanillin	92.0	86.7	89.2	94.3	93.9	84.0	19	13.3	9.8	7.8

Conclusion and perspectives

Nanofiltration offers at higher flow rates and lower pressure a better detoxification effect of lignocellulosic hydrolyzate model solution than reverse osmosis. With suitable inhibitor removal and low sugar loss, DK should be preferred to NF 270. The impact of increasing volumetric reduction ratio (VRR) is currently in progress to check the effect of concentration on rejection and on separation between sugars and inhibitors.

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