Nanofiltration and reverse osmosis membranes for purification and concentration of a 2,3-butanediol producing gas fermentation broth

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Abstract

For sustainably produced fuels and chemicals to become viable resources they need to be cost comparable with crude oil based products. 2,3-Butanediol is an important commodity chemical that can be produced *via* gas fermentation alongside acetate and ethanol. The current recovery of 2,3-butanediol is an energy intensive process, to which membranes could be incorporated, to achieve energy and monetary savings through partial purification and / or concentration of the desired products. This paper investigates for the first time a number of nanofiltration and reverse osmosis membranes for this purpose. Three membranes (NF270, NF90 and BW30) were investigated for their applicability to concentrate 2,3-butanediol, acetate and ethanol within a gas fermentation broth. BW30 was identified as a suitable membrane for the concentration of 2,3-butanediol and acetate within the gas fermentation broth with rejections of 96.1 and 94.6 % respectively at pH 6.5. Rejection of other possible alcoholic fermentation products was also screened with BW30 for the concentration of these products.

Overall, this work demonstrates how NF and RO membranes could be implemented within a membrane series to potentially replace part of the distillative separation of low volatility organics from fermentations.

Keywords:

Nanofiltration, Reverse Osmosis, Separations, 2,3-Butanediol, Acetate, Biofuel, Biochemical, Fermentation, Concentration, downstream processing

1. Introduction

There is a growing need to reduce dependency on crude oil based products due to both the negative environmental impacts these produce [1] and the finite nature of this feedstock.[2] Microbial fermentation can be used as an alternative for the production of fuels and chemicals from a variety of substrates. Gas fermentation uses gases rich in carbon monoxide, with varying levels of hydrogen and carbon dioxide, as a source of carbon and energy. As these gases can be sourced from either steel mill flue gas or the gasification of biomass / municipal waste, gas fermentation provides a sustainable route to a variety of commodity chemicals.[3]

2,3-Butanediol is an important commodity chemical with downstream products having an estimated market of 32 million tons a year, valued at around $43 billion in sales.[4] Gas fermentation can be used to produce 2,3-butanediol alongside acetate and ethanol which are also important commodity chemicals with markets of 9 and 60 million tons per year respectively.[5] The recovery of these desired organics from the fermentation broth however is an energy intensive process limiting its cost effectiveness. This is due to these fermentation products being produced at low concentration and having to be separated from a complex broth mixture of metabolites, proteins, salts, sugars and other nutrients used as growth media. Distillation is still the dominant separation technology, but for the purification of high-boiling organics such as 2,3-butanediol (b.p. = 183 ^{o}C) it is not desirable since it contributes to over half the cost of its microbial production.[6]

A variety of low energy recovery techniques have been investigated for the fermentative production of 2,3-butanediol, [6-9] acetate and ethanol.[10, 11] For 2,3-butanediol, specific examples include demonstration of liquid-liquid extraction,[12, 13] reactive extraction,[14, 15] salting out,[16] aqueous two phase extraction [17-19] and gas stripping.[7] Membrane technologies however present an attractive low energy alternative to these methods.[20, 21]

Nanofiltration (NF) and reverse osmosis (RO) are pressure driven membrane processes that are suitable for the downstream purification and concentration of fermentation products. Examples exist for the purification / concentration of various acidic products from fermentations such as lactate,[22, 23] acetate[24, 25] and succinate.[26] Other examples include the removal of sugars from an ethanol fermentation [27] and purification and concentration of glycerol [28]. Although NF and RO have been studied for the removal of 2,3-butanediol and other fermentation by-products from distillery condensates,[29, 30] to our knowledge no comparison of the purification and concentration of these alcohols as the main target for separation as fermentation products has been undertaken. Consequently, this paper aims to provide insight into the use of NF and RO into the membrane fractionation (Figure 1) of 2,3-butanediol and its co-fermentation products, acetate and ethanol, in the context of gas fermentation. The identified membranes could be implemented for purification and concentration of the broth to enable energy savings in further downstream separation processes (such as distillation). The membrane BW30 has also been compared for its potential suitability in the concentration of other alcoholic metabolites.

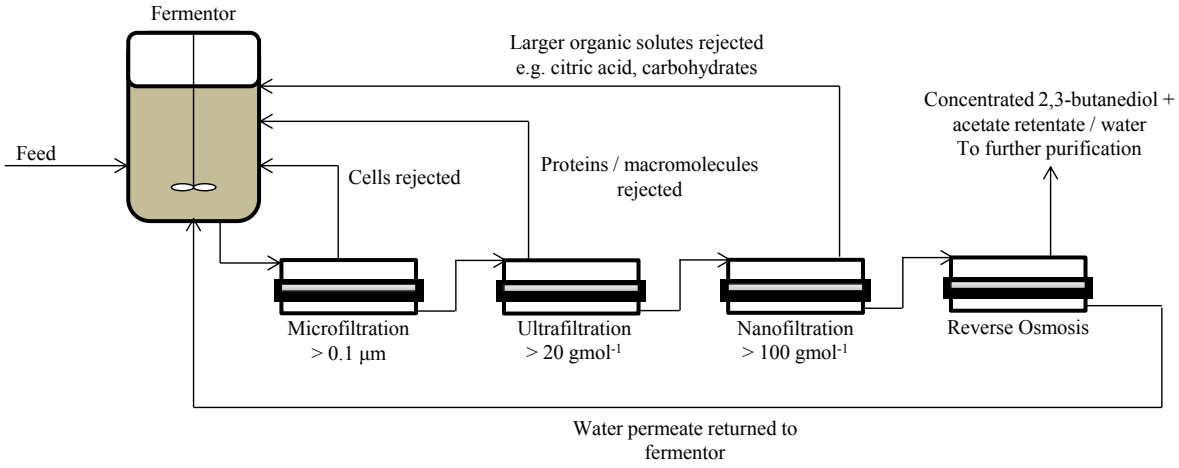

Figure 1. Schematic of membrane series for broth purification and concentration using 2,3-butanediol as an example of a dilute organic target product.

2. Experimental

2.1 Materials

The membranes used in all dead-end filtration experiments were purchased from Sterlitech (USA). 2,3-butanediol (98 %), ethanol (≥ 99 %), acetic acid (≥ 99 %), 1,3-propanediol (98 %), 2-propanol (≥ 99.8 %), ethylene glycol (≥ 99.5 %) and methanol (≥ 99.9 %) were purchased from Sigma Aldrich (UK). Ammonium Acetate (97 %), 1-propanol (> 99.5 %), 1,2-propanediol (99.5 %), 1-butanol (99 %), 2-butanol (99 %), Isobutanol (99 %), tert-butanol (99 %), 1,4-butanediol (99 %) and 1,3-butanediol (99 %) were purchased from Alfa Aesar (UK). A series of commercial NF and RO membranes were selected with molecular weight cut-offs (MWCOs) lower than ~ 400 $gmol^{-1}$ as defined by the manufacturer. This is larger than the MW of 2,3-butanediol (90.1 $gmol^{-1}$), acetic acid (60.1 $gmol^{-1}$) or ethanol (46.1 $gmol^{-1}$), however a range of membranes with varying MWCOs were investigated due to MW not being the only determining factor to effect rejection of organic solutes by NF and RO membranes.[31] Deionised water was taken from a Purelab Option unit (15 MΩ·cm at 25 °C).

Table 1. Commercial membranes for screening with model solutions

Manufacturer	Membrane	Membrane type	Active Layer Material	Manufacturers stated MWCO range ($gmol^{-1}$)	Supplier or citation stated Salt Rejection (%)
Dow	NF	NF	Polyamide	200 - 400	99 ($MgSO_4$)
	NF245	NF	Polyamide	200 - 400	99 ($MgSO_4$)
	NF270	NF	Polyamide	200 - 400	80 (NaCl), 50 ($CaCl_2$), 99.3 ($MgSO_4$)[32]
	NF90	NF	Polyamide	200 - 400	90 – 96 (NaCl)[32]
	BW30	RO	Polyamide	100	99.4 (NaCl), 99.4 ($CaCl_2$), 99.7 ($MgSO_4$)[32]
	BW30LE	RO	Polyamide	100	99.0 (NaCl)[29]
	BW30FR	RO	Polyamide	100	
TriSep	TS80	NF	Polyamide	150	99 ($MgSO_4$)[33]
	SB90	NF	Cellulose acetate blend	150	97.0 ($MgSO_4$)
GE Osmonics	SG	RO	Thin film	0	98.2 (NaCl)[29]
	SE	RO	Thin film	0	98.9 (NaCl)[29]

	CE	RO	Cellulose acetate	0	97.0 (NaCl)[29]

Gas fermentation broth was provided by LanzaTech (USA) and kept frozen until use. The broth was centrifuged at 5000 rpm for 30 minutes to remove any non-dissolved solids before use. To increase the pH of the gas fermentation broth NaOH was added. The composition of the gas fermentation broth is presented in Table 2 and Table 3.

Table 2. Composition of Organics in LanzaTech gas fermentation broth

Component	**Concentration in Broth (gL^{-1})**	**MW ($gmol^{-1}$)**
Ethanol	8 - 10	46.1
2,3-Butanediol	3 - 8	90.1
Acetic Acid	3 - 8	60.1
Suspended Biomass	2 - 8	-

Table 3. Maximum Inorganic Content of LanzaTech gas fermentation broth

Characteristic	**Fermentation Broth**
COD (mgL^{-1})	80000 - 100000
BOD (mgL^{-1})	75000 - 90000
TSS (mgL^{-1})	2500 - 5000
TDS (mgL^{-1})	3000 - 4000
TN (mgL^{-1})	1500 - 2500
TP (mgL^{-1})	250 - 400
Chloride (mgL^{-1})	250 - 500
Potassium (mgL^{-1})	150 - 400
pH	5.1 - 5.3

Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Total Nitrogen (TN), Total Phosphorous (TP).

2.2 Filtrations

Aqueous solutions of 2,3-butanediol, acetic acid, and ammonium acetate at concentrations similar to those observed in a gas fermentation broth bleed stream were used to determine and compare flux and rejection characteristics of the commercial membranes. Then dead end-filtrations were conducted using the gas fermentation broth outlined above with NF270, NF90 and BW30.

Dead end filtrations were carried out in a Sterlitech HP4750 stirred cell made of stainless steel with an active membrane area of 14.6 cm^2 using the standard methodology that has been applied in numerous other studies[34, 35]A magnetic stirrer just above the membrane surface was used for mixing of the feed and minimizing concentration polarization. The dead end cell was placed in a water bath on a heater-stirrer for stirring speed and temperature control (150 – 300 rpm and 30 ^oC). Pressure was applied using compressed nitrogen (BOC, 99.998 %) and measured with a pressure gauge. Weight of permeate was recorded using a Sartorius LC3201D-00MS balance with a data logging program developed in LabVIEW. Flat sheet membrane discs of 47 mm diameter were either cut out from larger flat sheets with a scalpel using a membrane size template (to prevent scratching of the surface) or used as received as pre-cut discs. NF and RO membranes were conditioned by permeating reverse osmosis water (15 MΩ.cm at 25 ^oC) under pressure before use for ~ 2 hrs, until constant flux was achieved.

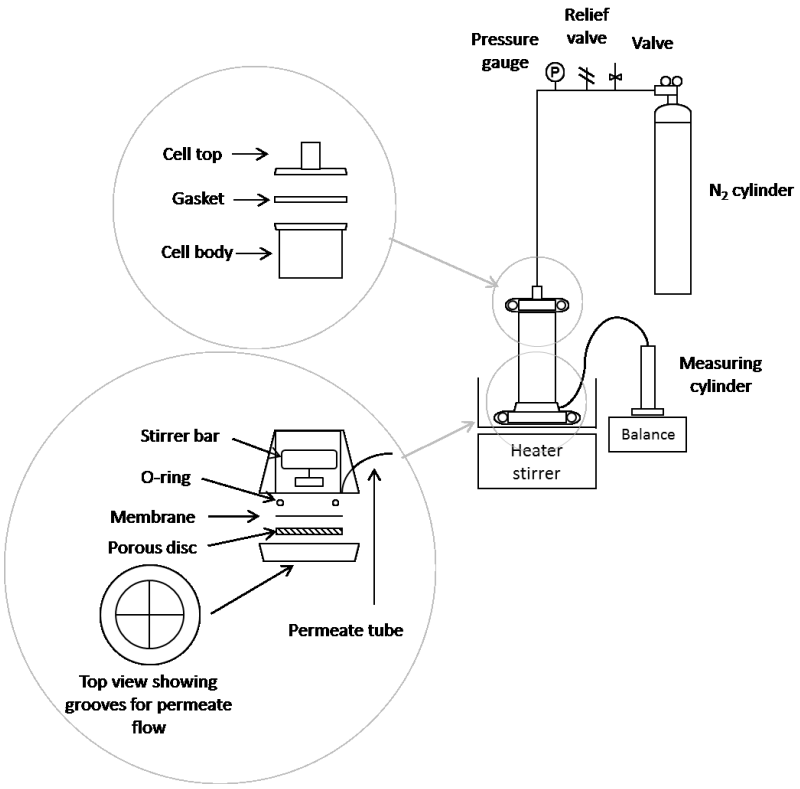

Figure 2. Schematic of Sterlitech HP4750 Dead-end cell used for filtrations.

Observed rejections were characterised by permeating half of a 50 mL feed solution (to account for changing concentration) and calculated using equation 1 after measuring the concentration in feed and permeate.

$$R_{j,i} = \left(1 - \frac{C_{i,p}}{C_{i,f}}\right) \times 100\ \% \qquad (1)$$

Where: $C_{i,p}$ = Concentration of species i in permeate

$C_{i,f}$ = Concentration of species i in feed

So when $R_{j,i}$ = 100 % a complete rejection is observed and when $R_{j,i}$ = 0 % no separation has been achieved.

2.3 High-Performance Liquid Chromatography (HPLC)

The concentration of organic solutes in feeds, permeates and retentates were analysed by HPLC using an Agilent Technologies 1200 series instrument. A Phenomenex organic acids column (7.8 x 300 mm) was used at 60 °C with 5 mM H_2SO_4 as mobile phase and a flow rate of 0.7 mL min^{-1}. Solutes were detected with an RI detector and concentrations interpreted through the peak area using external calibration. Fermentation samples were prefiltered with a 0.22 µm syringe filter (Millipore, UK) before analysis to remove any suspended particles.

2.4 pH Measurements

pH measurements of solutions were conducted on a Denver Instruments 250 pH meter. The pH meter was calibrated to solutions of pH 4, 7 and 10 (Fisher Scientific, UK) before use.

2.5 Conductivity measurements and Apparent Salt Rejection (ASR)

Conductivity measurements were carried out on a Thermo Scientific Orion Versa Star conductivity meter. ASRs were calculated as:

$$ASR\ (\%) = \left(1 - \frac{\mathrm{C_p}}{\mathrm{C_f}}\right) \times 100$$

where $\mathrm{C_f}$ is the conductivity of the feed and $\mathrm{C_p}$ is the conductivity of the permeate.

2.6 Effective Contact Angle Measurements

Static effective water contact angles were measured on air dried membranes using the sessile drop method with a Dataphysics contact angle system OCA goniometer (Dataphysics, Germany). Measurements were taken 1 s after a 20 µL drop of ultrapure water (18.2 MΩ·cm at 25 °C) was placed on the surface of the membrane at room temperature. Effective contact angles represent the average of a minimum of 10 runs.

2.7 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded over the range 4000 – 600 cm^{-1} using a Perkin Elmer Spectrum 100 FTIR spectrometer fitted with an attenuated total reflectance (ATR) detector. Three ATR-FTIR spectra were recorded in different positions on the membrane sample and the spectrum was averaged over 10 scans with a resolution of 1 cm^{-1}.

2.8 Irreversible Fouling Determination

Irreversible fouling was determined by taking the fouled membrane and washing with deionised (DI) water for 5 minutes. Samples of 25 mL of DI water were then permeated through the membrane until the flux stabilised. Then 3 x 25 mL of DI water were permeated through the membrane and an average of the runs was taken.

3. Results and Discussion

3.1 Observed Rejection of 2,3-Butanediol, Acetate and Ethanol

As the gas fermentation studied produces 2,3-butanediol, acetate and ethanol as fermentation products, the individual rejection of these compounds by the selected commercial membranes was investigated at concentrations similar to those found in the broth. Rejection generally correlated well with manufacturers defined MWCOs – however this is not always the case.[35] Initial studies looked at the rejection of aqueous solutions of 2,3-butanediol (Figure 3). High rejections were observed for the denser RO/NF membranes and much lower rejections were observed for the looser NF membranes as expected. One limit to our approach would be the maximum concentration of the fermentation products achievable before permeability declines beyond a useful level. Experiments conducted at concentrations of 20 gL^{-1} 2,3-butanediol were attempted however the extremely low

permeabilities observed indicate that this would be close to the upper limit of concentration with this method.

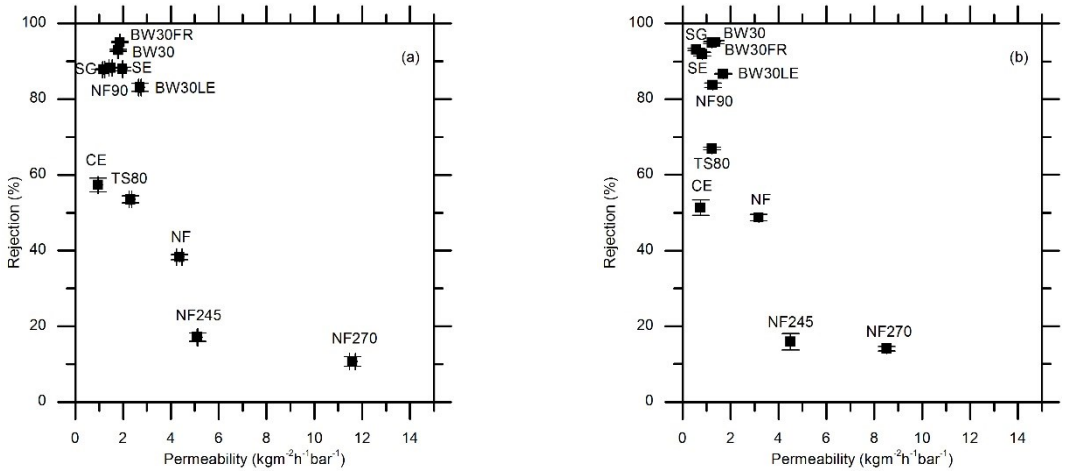

Figure 3. Observed Rejection of (a) 4 gL^{-1} and (b) 10 gL^{-1} 2,3-butanediol by various membranes; 15 bar, 30 °C, 150 rpm

Acetate rejection was also characterised for each membrane. Every membrane studied exhibited poor rejection (< 40 %) of acetic acid (Figure 4. a), whereas for ammonium acetate rejection for some membranes was high (> 90 %) (Figure 4. b). The difference in the rejection is due to Donnan Exclusion, based on the charge of the acetate ion and membrane surface.[24] As the pH of the solution is lower than the pK_a of acetic acid (pH = 3.39 vs. AcOH pK_a = 4.75), it will exist mainly as AcOH in solution. When ammonia is present, the pH of the solution increases (pH = 6.81) and therefore acetic acid exists mainly as its conjugate base AcO^-. As the majority of membranes studied exhibit negatively charged surfaces (e.g. BW30, NF90 and NF270)[36], the increase in rejection is thought to be mainly due to an increase in electrostatic repulsion between the membrane surface and the acetate anion. However MWCO is still an important factor in the rejection of acetate, as the membranes with a smaller MWCO still exhibit a higher rejection than those with a greater MWCO. Therefore for this particular separation, the membrane selection has been based in the main on both charge and MWCO / pore size – the authors however acknowledge that the other criteria are also important for membrane selection (long term robustness and performance, cost, availability, fouling, ease and robustness to cleaning etc) many of which are beyond the scope of this work. During the filtration of the fermentation broth, however, it is possible that further interaction effects and membrane fouling may alter the rejection and has been investigated in more detail in Sections 3.2 and 3.3.

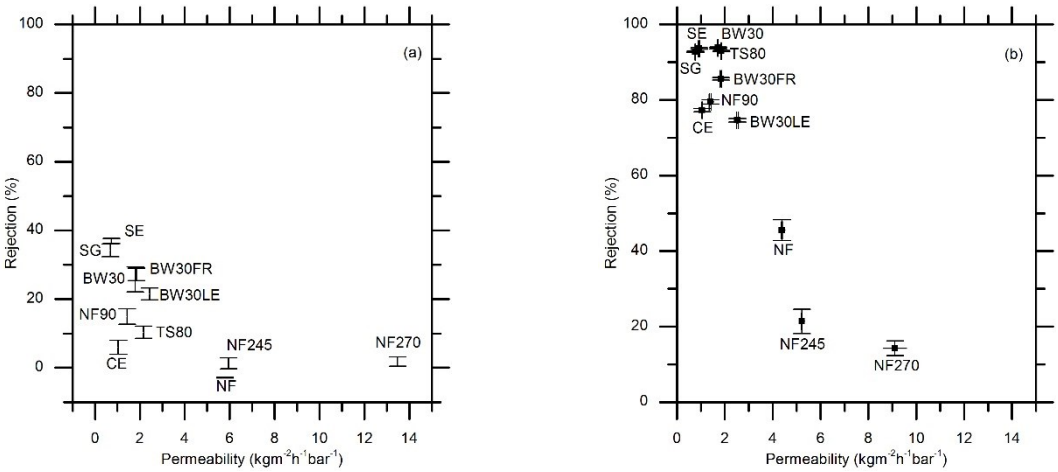

Figure 4. Observed rejection of (a) 5 gL^{-1}acetic acid and (b) 2.5 gL^{-1} ammonium acetate by various membranes; 15 bar, 30 ^{o}C, 150 rpm

Three membranes were chosen for further investigation NF270, a poorly rejecting membrane, NF90, a high flux medium rejection membrane, and BW30, a high rejection low flux membrane. The performance of NF270, NF90, and BW30 were investigated at different pressures to investigate the variance in rejection performance with flux (Figure 5). BW30 exhibited a general increase in rejection of 2,3-butanediol with flux whereas NF270 exhibited the opposite behaviour with a decrease in rejection with an increase in flux. NF90 exhibited a relatively stable rejection with increasing flux. Each membrane exhibited a linear relationship between flux and pressure.

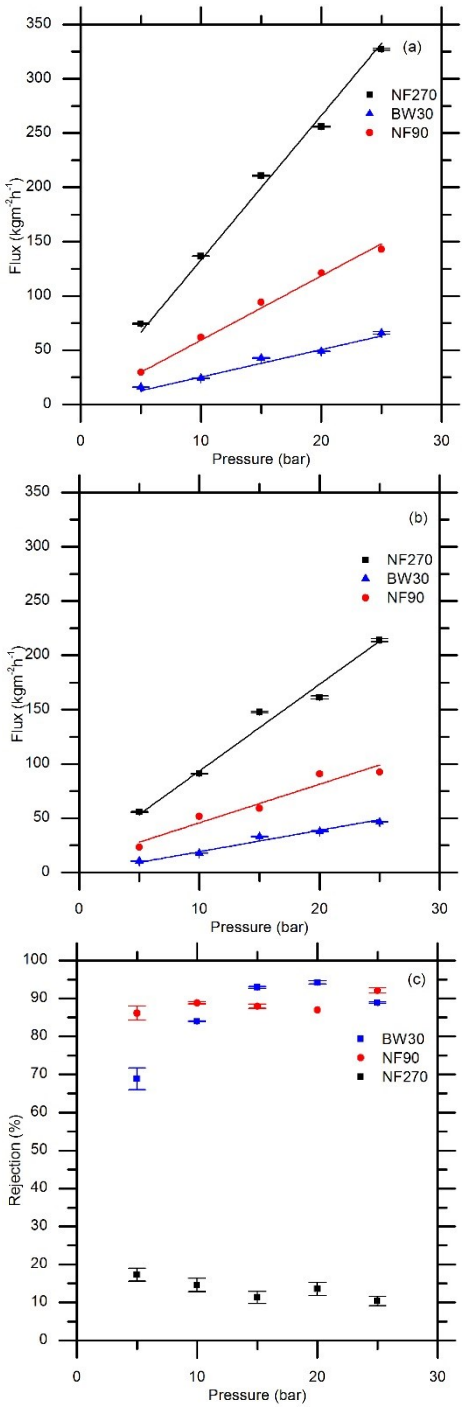

Figure 5. (a) Pure water flux and (b) flux and (c) rejection of 4 gL^{-1} 2,3-butanediol with different applied pressures; 30 °C, 150 rpm

The rejection of ethanol was investigated for these membranes (Table 4) that had different performances in the rejection of 2,3-butanediol and acetate. Each membrane tested showed very low rejection (< 15 %) of ethanol, this is in accordance with previous literature.[37] It is envisaged that ethanol could not be concentrated within the gas fermentation broth, as for 2,3-butanediol and acetate, and therefore would need to be recovered from the purified permeate stream from one of these membranes.

Table 4. Ethanol Rejection and Permeability data, 10 gL^{-1} Ethanol, 30 °C, 150 rpm, 15 bar

Membrane	Permeability ($kgm^{-2}h^{-1}bar^{-1}$)	Ethanol Rejection (%)
NF270	11.0 (± 0.0814)	2.50 (± 1.69)
NF90	4.29 (± 0.690)	14.8 (± 0.382)
BW30	1.56 (± 0.382)	14.5 (± 1.07)

3.2 Rejection of mixtures of 2,3-Butanediol and Acetate

The rejection of mixed component solutions by NF270, NF90 and BW30 was investigated to ascertain any effect the combination of solutes may have on the rejection of the organic species. The rejection of 2,3-butanediol by BW30, NF90 or NF270 (Table 5) was unaffected by the addition of either acetic acid or ammonium acetate. Likewise the rejections of acetic acid or ammonium acetate were unaffected by the presence of 2,3-butanediol (Table 5). As the pK_a of 2,3-butanediol (pK_a = 14.9) is much higher than the pH of either the acidic or neutral solution (pH 3.40 and 6.95 respectively), 2,3-butanediol does not form its conjugate base in either solution, so rejection is still mainly based on molecular size / MW. On the other hand, the addition of 2,3-butanediol has negligible effect on the pH of the solution, so the rejection of acetate is unaffected for its respective solutions. This indicates that the membranes and selectivity's obtained in the single component runs are applicable still in the mixtures and further justifies the selection of these membranes. Figure 6 shows the reduction in flux for each membrane over the concentration of a mixed solution of 2,3-butanediol and ammonium acetate demonstrating only a small reduction in flux over the course of the experiment.

Table 5. Permeability and rejection of a mixed solution of 2,3-butanediol and ammonium acetate

Membrane	Permeability ($kgm^{-2}h^{-1}bar^{-1}$)	2,3-Butanediol Rejection (%)	Acetate Rejection (%)
NF270	7.92	14.3	37.8
NF90	2.53	80.8	76.1
BW30	1.27	96.0	94.2

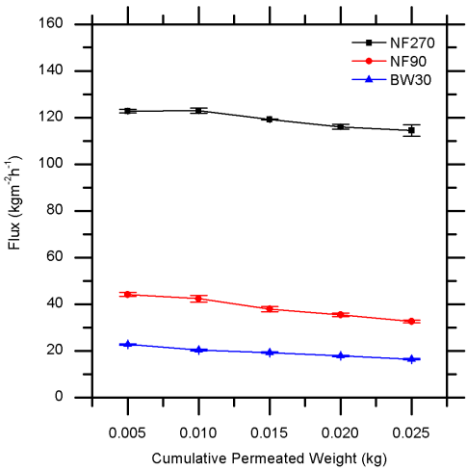

Figure 6. Reduction in flux by a mixed solution of 2,3-butanediol (4gL^{-1}) and ammonium acetate (2.5 gL^{-1}), 30 °C, 15 bar, 300 rpm (±SD)

3.3 Performance of Membranes for Concentration of a Gas Fermentation Broth

The rejection and flux characteristics of each organic component by the membranes NF270, NF90 and BW30 within a gas fermentation broth was determined. Figure 7 shows the flux profiles for BW30, NF90 and NF270 for the concentration of the gas fermentation broth at natural pH (pH = 5.1). It can be seen that the concentration of the fermentation broth greatly reduces the flux of the membranes compared to that of the model solutions of 2,3-butanediol and acetate (Figure 6, Table 5). Rejections of each component reflected those of the model solutions (Table 6) with BW30 and NF90 exhibiting high rejections (94.6 and 92.6 % respectively). The rejection of acetate by BW30 and NF90 is between that of the model solutions with values of 74.4 and 70.5 % respectively.

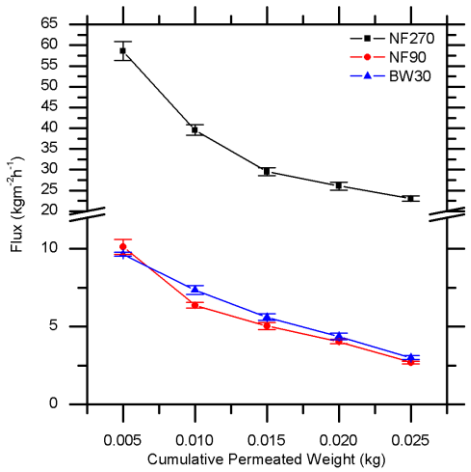

Figure 7. Reduction in flux by gas fermentation broth, 30 °C, 15 bar, 300 rpm (±SD)

Table 6. Rejection data for filtration of the gas fermentation broth

Concentration	Feed	NF270		NF90		BW30	
		Permeate	Retentate	Permeate	Retentate	Permeate	Retentate
2,3-butanediol (gL^{-1})	3.34	2.31	3.67	0.25	5.62	0.18	5.58
Rejection (%)		**30.9**		**92.6**		**94.6**	
Acetate (gL^{-1})	6.51	4.72	7.01	1.92	10.3	1.67	9.93
Rejection (%)		**27.5**		**70.5**		**74.4**	
Ethanol (gL^{-1})	9.2	8.0	8.74	7.11	9.29	7.51	9.47
Rejection (%)		**13.2**		**22.7**		**18.4**	
ASR (%)		**25**		**82**		**88**	
pH	5.1	5.0	5.2	4.3	5.3	4.1	5.2

The reduction in flux from irreversible fouling can be seen in Figure 8. After the rejection experiments, membranes were washed with deionised water and the pure water flux measured. NF90 experienced the greatest amount of irreversible fouling with a decline of pure water flux by 55 %, followed by BW30 exhibiting a decline of 43 %. NF270 experienced the least amount of fouling with a decrease in pure water flux of 9.0 %. The greater decline in flux exhibited by NF90 compared to BW30 may be attributed to an increase in fouling from the rougher surface of NF90[36] creating more grooves to trap potential foulants from the fermentation broth. The FTIR of NF90 also indicates irreversible fouling due to a general increase in absorbance of the cleaned membrane due to foulants on the membrane surface (Figure S1; Supplementary material). The contact angles for BW30 and NF90 also indicate at some fouling due to an increased hydrophilicity of the fouled and cleaned membranes compared to the virgin membrane (Figure S2; Supplementary Material). An increase in contact angle was observed for NF270 from conditioned to fouled to cleaned (Figure S2). As can be seen from the ATR-FTIR of the used NF270 membranes (Figure S1) there is an increase in the peaks at 1640 cm^{-1} and 1533 cm^{-1}. This has been attributed to the partial breaking down of the polyamide barrier layer (Figure S3; Supplementary Material). The shoulder at 1635 cm^{-1} in the conditioned NF270 FTIR is due to polyamide C=O stretching,[38] the increase in the absorbance and shift to 1640 cm^{-1} has been attributed to an increase in carboxylic acid C=O stretching shifting, increasing and pronouncing the absorbance. The increase in amide II N-H stretching, not present in the tertiary amide structure, has been attributed to the increase in absorbance at 1533 cm^{-1}.

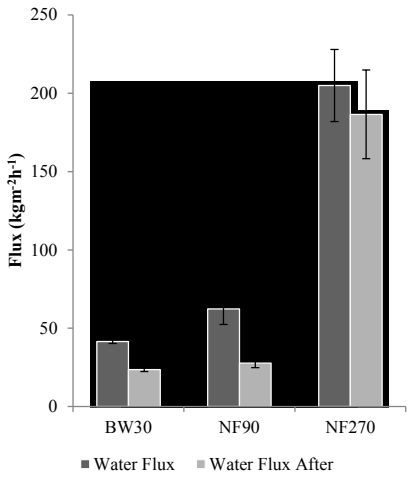

Figure 8. Pre-use and post-cleaning water fluxes for membranes after concentration of broth dead-end filtration, 30 °C, 15 bar, 300 rpm (±SD)

Avoiding irreversible fouling is important for a robust membrane separation. Changing solution pH will also change the zeta potential of the membrane surface, altering the interaction of foulants with the membrane. Moreover, changing pH can also affect acid-base species equilibrium, altering rejection of these species in solution. For acetate as discussed earlier increasing the pH of the solution will also increase the rejection. Consequently, the pH of the broth was increased to 6.5 to increase acetate rejection and an increase to 94.6 % by BW30 was observed (Figure 9a). An increase in transmembrane pressure was also utilised to increase membrane flux. The filtration observed a lower reduction in flux during the experiment (81 % reduction compared to pure water flux; Figure 9b). The amount of irreversible fouling measured by the post-cleaning pure water flux was also found to be less: a 36 % reduction as opposed to the natural pH broth experiment. The reduction in irreversible fouling of the membrane is thought to be due to the higher pH of the broth creating an increased number of deprotonated foulants, therefore increasing the number of foulants repulsed by the negatively charged membrane surface. This increased repulsion could create less membrane surface fouling and pore blocking.

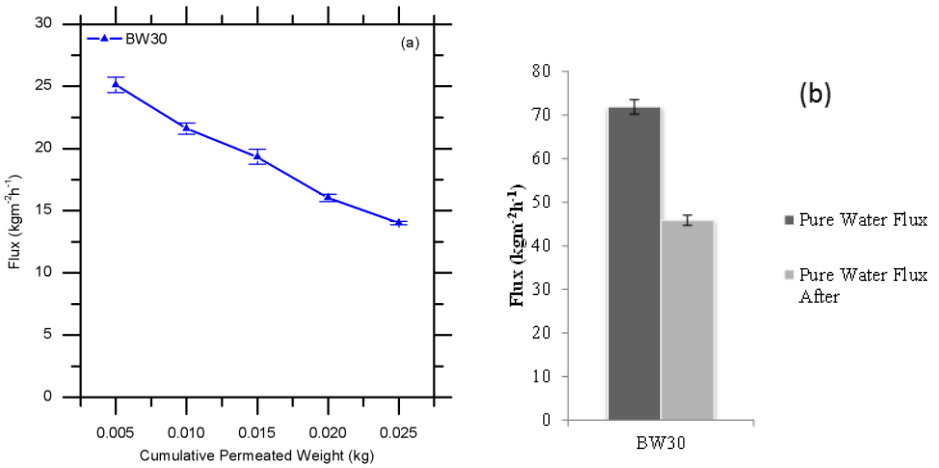

Figure 9. (a) Reduction in flux of a gas fermentation broth at pH 6.5, 30bar (b) Pre-use and post-cleaning water flux for BW30 after concentration of broth.

Table 7. Rejection of fermentation products by BW30 at pH 6.5

	Feed	Permeate	Retentate	Rejection / ASR (%)
2,3-butanediol (gL^{-1})	2.77	0.11	4.85	96.1
Acetate (gL^{-1})	5.38	0.29	9.77	94.6
Ethanol (gL^{-1})	7.64	5.47	8.82	28.3
Conductivity (mS/cm)	12.5	0.934	20.2	92.5
pH	6.5	6.3	6.5	-

Overall these results show that a membrane fractionation purification approach is possible in order to concentrate and purify 2,3-butanediol as per Figure 1. NF270 gives good clarification of the media with relatively low rejections of 2,3-butanediol and acetate so can be used to purify the broth. NF90 and BW30 exhibited high rejection of 2,3-butanediol and good rejection of acetate, however NF90 exhibited slightly higher irreversible fouling compared to BW30. When the pH of the broth was increased to 6.5, the rejection of acetate was increased by BW30. Therefore BW30 is the more suitable membrane for the concentration of 2,3-butanediol and acetate within a gas fermentation broth.

3.4 Separation of Alcohols by BW30

As the library of potential fermentation products from gas fermentation is extensive and BW30 had been identified as a suitable membrane for rejection of 2,3-butanediol, it was hypothesised that this membrane could be used to reject other alcoholic products in a gas fermentation broth. For this, the relationship between rejection, flux and MW for BW30 of a number of different alcohols was determined. The general trend of solutes follows - with increasing MW in general a greater rejection is exhibited by BW30, however flux is compromised by this increase in rejection due to fouling, concentration polarisation and an increase in osmotic pressure, hence it decreases with increasing MW (Figure 10). This would indicate that pore flow is the major rejection mechanism in controlling the selectivity in this separation.

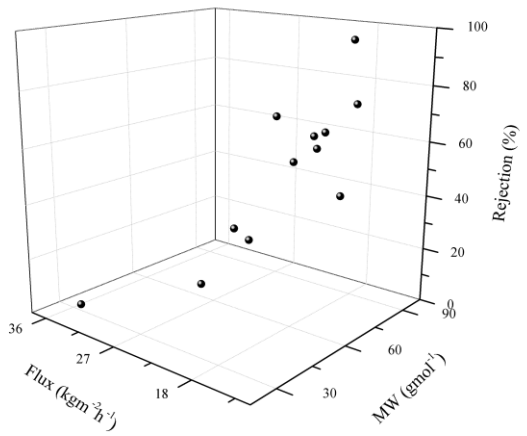

Figure 10. Relationship between flux, molecular weight and rejection for BW30.

Figure 11 further illustrates the obtained relationship between MW and rejection for the alcohols tested. This clearly shows that although rejection increases with increasing MW, the role of sterics of the alcohols also plays a part in their rejection by BW30. Change in pH with rejection was not investigated because of the relatively high pK_a's of alcohol (~16), the pH would have to be increased beyond an acceptable degree for a fermentation media to achieve dissociation of the alcoholic protons.

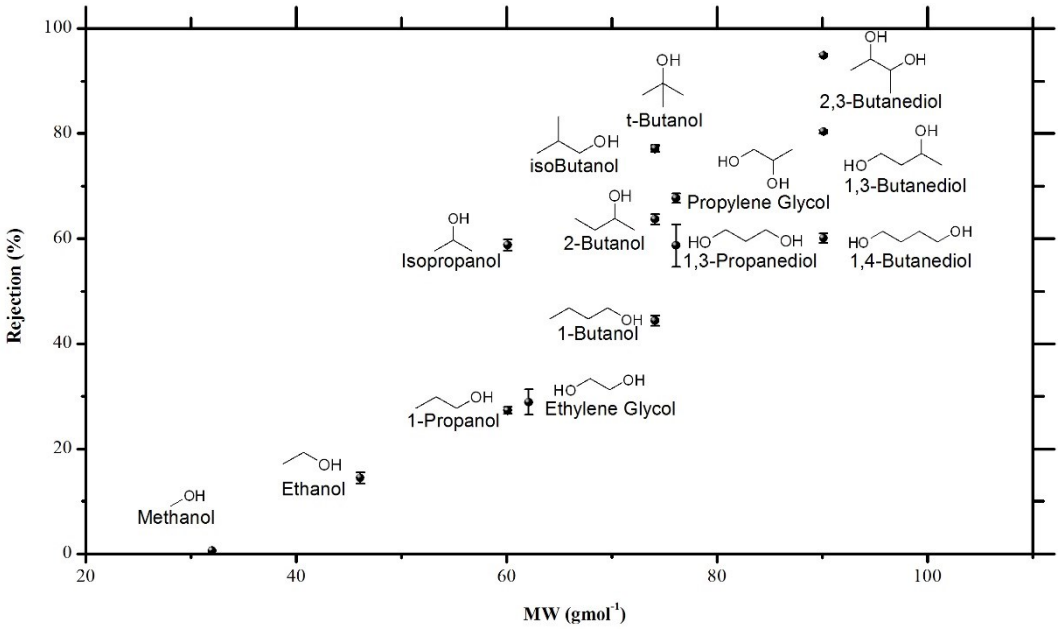

Figure 11. Rejection of Different Solutes by BW30.

The relatively high rejection of isobutanol ~ 77 % would be sufficient for concentration using BW30 as membrane modules could be numbered up to increase the efficiency of rejection. In addition to this, the property of isobutanol to be only partially soluble in water (8.7 mL / 100 mL) requires the concentration of the solution to < 10 wt% before it will partition out of the aqueous solution. It should be noted however, that data on the chemical stability of these membranes towards various alcohols is limited and the long term performance will need to be characterised before implementation. It has previously been shown that solutions of high concentration of alcohols can have a detrimental effect on the flux and rejection properties of RO and NF membranes.[39, 40]

These results indicate that the membrane fractionation strategy purification approach investigated in detail for 2,3-butanediol in this work could be applied more widely to the range of alcohol molecules being produced from renewable feedstocks and across Industrial Biotechnology, hopefully enabling lower energy, more sustainable separations. Future work will require investigating the long term stability of the membranes within these applications. As well as this the effect of concentration of different components of the fermentation broth (e.g. citric acid) on the productivity of the continuous fermentation will need to be studied.

4. Conclusions

A number of commercially available membranes have been investigated for the first time for the concentration of a gas fermentation broth producing 2,3-butanediol, acetate and ethanol as fermentative products. The rejection and flux characteristics of each membrane were determined

for aqueous solutions of 2,3-butanediol, acetic acid and ammonium acetate at 15 bar and 30 °C. A number of membranes were identified to exhibit high rejection of 2,3-butanediol (BW30FR, BW30, SE, SG) as well as a number with very poor rejection (NF270, NF245, NF). Acetate rejection varied with pH for each membrane with a number exhibiting high rejection of ammonium acetate (BW30, SE, BW30FR, SG), but all membranes exhibited a relatively poor rejection of acetic acid.

NF270, NF90 and BW30 were investigated for the purification / concentration of a gas fermentation bleed stream. Results indicate NF270 can purify the broth due to relatively low rejections of 2,3-butanediol and acetate but good clarification of the media. NF90 and BW30 exhibited high rejection of 2,3-butanediol and good rejection of acetate, however NF90 exhibited slightly higher irreversible fouling compared to BW30. When the pH of the broth was increased to 6.5, the rejection of acetate was increased by BW30. BW30 has been identified as a suitable membrane for the concentration of 2,3-butanediol and acetate within a gas fermentation broth.

By investigating the rejection of other alcohols by BW30 it was identified that its exceptional rejection of 2,3-butanediol can be attributed to the steric properties of the molecule and not solely upon its MW. Isobutanol was also identified as a possible fermentation product that could be concentrated within a fermentation bleed stream by BW30 due to its relatively high rejection (77 %).

Overall this work has shown that NF and RO membranes could potentially be used to replace part of the distillation separation of low volatility alcohols from fermentations. This membrane fractionation purification approach to fermentations can be more widely applied across Industrial Biotechnology, hopefully enabling lower energy, more sustainable separations.

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5. References

[1] L.R. Radovic, Energy and Fuels in Society: Analysis of Bills and Media Reports, 1997

[2] P. Vasudevan, M. Gagnon, M. Briggs, Environmentally Sustainable Biofuels – The Case for Biodiesel, Biobutanol and Cellulosic Ethanol, in: O.V. Singh, S.P. Harvey (Eds.) Sustainable Biotechnology, Springer Netherlands, 2010, pp. 43-62.

[3] F.M. Liew, M. Köpke, S.D. Simpson, Gas Fermentation for Commercial Biofuels Production, in: Z. Fang (Ed.) Liquid, Gaseous and Solid Biofuels - Conversion Techniques, InTech, 2013, pp. 125-173.

[4] M. Kopke, C. Mihalcea, F. Liew, J.H. Tizard, M.S. Ali, J.J. Conolly, B. Al-Sinawi, S.D. Simpson, 2,3-butanediol production by acetogenic bacteria, an alternative route to chemical synthesis, using industrial waste gas, Appl Environ Microbiol, 77 (2011) 5467-5475.

[5] P.N.R. Vennestrøm, C.M. Osmundsen, C.H. Christensen, E. Taarning, Beyond Petrochemicals: The Renewable Chemicals Industry, Angew. Chem. Int. Ed., 50 (2011) 10502-10509.

[6] Z.L. Xiu, A.P. Zeng, Present state and perspective of downstream processing of biologically produced 1,3-propanediol and 2,3-butanediol, Appl. Microbiol. Biotechnol., 78 (2008) 917-926.

[7] S.K. Garg, A. Jain, Fermentative Production of 2,3-Butanediol: A Review, Bioresour. Technol., 51 (1995) 103-109.

[8] X.-J. Ji, H. Huang, P.-K. Ouyang, Microbial 2,3-butanediol production: A state-of-the-art review, Biotechnol. Adv., 29 (2011) 351-364.

[9] M.J. Syu, Biological production of 2,3-butanediol, Appl. Microbiol. Biotechnol., 55 (2001) 10-18.

[10] H.-J. Huang, S. Ramaswamy, U.W. Tschirner, B.V. Ramarao, A review of separation technologies in current and future biorefineries, Sep. Purif. Technol., 62 (2008) 1-21.

[11] L.M. Vane, Separation technologies for the recovery and dehydration of alcohols from fermentation broths, Biofuels, Bioprod. Biorefin., 2 (2008) 553-588.

[12] D.F. Othmer, W.S. Bergen, N. Shlechter, P.F. Bruins, Liquid-Liquid Extraction Data, Ind. Eng. Chem., 37 (1945) 890-894.

[13] M. Anvari, H. Pahlavanzadeh, E. Vasheghani-Farahani, G. Khayati, In situ recovery of 2,3-butanediol from fermentation by liquid-liquid extraction, J. Ind. Microbiol. Biotechnol., 36 (2009) 313-317.

[14] M. Senkus, Recovery of 2,3-Butanediol Produced by Fermentation, Ind. Eng. Chem., 38 (1946) 913-916.

[15] Y. Li, Y. Wu, J. Zhu, J. Liu, Separation of 2,3-butanediol from fermentation broth by reactive-extraction using acetaldehyde-cyclohexane system, Biotechnol. Bioproc. E., 17 (2012) 337-345.

[16] A.S. Afschar, C.E. Vaz Rossell, R. Jonas, A. Quesada Chanto, K. Schaller, Microbial production and downstream processing of 2,3-butanediol, J. Biotechnol., 27 (1993) 317-329.

[17] L.-H. Sun, B. Jiang, Z.-L. Xiu, Aqueous two-phase extraction of 2,3-butanediol from fermentation broths by isopropanol/ammonium sulfate system, Biotechnol. Lett., 31 (2009) 371-376.

[18] B. Jiang, Z.-G. Li, J.-Y. Dai, D.-J. Zhang, Z.-L. Xiu, Aqueous two-phase extraction of 2,3-butanediol from fermentation broths using an ethanol/phosphate system, Process Biochem., 44 (2009) 112-117.

[19] Z. Li, H. Teng, Z. Xiu, Aqueous two-phase extraction of 2,3-butanediol from fermentation broths using an ethanol/ammonium sulfate system, Process Biochem., 45 (2010) 731-737.

[20] D.A. Patterson, C.J. Davey, R. Rohani, Membrane Separations: from Purifications, Minimisation, Reuse and Recycling to Process Intensification, in: T. Letcher, J. Scott, D. Patterson (Eds.) Chemical Processes for a Sustainable Future, RSC, 2014, pp. 469 - 504.

[21] C. Davey, D. Leak, D. Patterson, Hybrid and Mixed Matrix Membranes for Separations from Fermentations, Membranes, 6 (2016) 17.

[22] J.M.K. Timmer, H.C. van der Horst, T. Robbertsen, Transport of lactic acid through reverse osmosis and nanofiltration membranes, J. Membr. Sci., 85 (1993) 205-216.

[23] J.M.K. Timmer, J. Kromkamp, T. Robbertsen, Lactic acid separation from fermentation broths by reverse osmosis and nanofiltration, J. Membr. Sci., 92 (1994) 185-197.

[24] I.S. Han, M. Cheryan, Nanofiltration of model acetate solutions, J. Membr. Sci., 107 (1995) 107-113.

[25] I. Han, M. Cheryan, Downstream processing of acetate fermentation broths by nanofiltration, Appl. Biochem. Biotechnol., 57-58 (1996) 19-28.
[26] S.H. Kang, Y.K. Chang, Removal of organic acid salts from simulated fermentation broth containing succinate by nanofiltration, J. Membr. Sci., 246 (2005) 49-57.
[27] T. Brás, M.C. Fernandes, J.L.C. Santos, L.A. Neves, Recovering bioethanol from olive bagasse fermentation by nanofiltration, Desalin. Water Treat., 51 (2013) 4333-4342.
[28] J. Bastrzyk, M. Gryta, K. Karakulski, Fouling of nanofiltration membranes used for separation of fermented glycerol solutions, Chem. Pap., 68 (2014) 757-765.
[29] C. Sagne, C. Fargues, R. Lewandowski, M.-L. Lameloise, M. Decloux, Screening of reverse osmosis membranes for the treatment and reuse of distillery condensates into alcoholic fermentation, Desalination, 219 (2008) 335-347.
[30] C. Sagne, C. Fargues, R. Lewandowski, M.-L. Lameloise, M. Gavach, M. Decloux, A pilot scale study of reverse osmosis for the purification of condensate arising from distillery stillage concentration plant, Chem. Eng. Process. Process Intensif., 49 (2010) 331-339.
[31] C. Bellona, J.E. Drewes, P. Xu, G. Amy, Factors affecting the rejection of organic solutes during NF/RO treatment—a literature review, Water Res., 38 (2004) 2795-2809.
[32] S. Mondal, S.R. Wickramasinghe, Produced water treatment by nanofiltration and reverse osmosis membranes, J. Membr. Sci., 322 (2008) 162-170.
[33] A.R.D. Verliefde, E.R. Cornelissen, S.G.J. Heijman, I. Petrinic, T. Luxbacher, G.L. Amy, B. Van der Bruggen, J.C. van Dijk, Influence of membrane fouling by (pretreated) surface water on rejection of pharmaceutically active compounds (PhACs) by nanofiltration membranes, J. Membr. Sci., 330 (2009) 90-103.
[34] Y.H. See Toh, X.X. Loh, K. Li, A. Bismarck, A.G. Livingston, In search of a standard method for the characterisation of organic solvent nanofiltration membranes, J. Membr. Sci., 291 (2007) 120-125.
[35] R. Rohani, M. Hyland, D. Patterson, A refined one-filtration method for aqueous based nanofiltration and ultrafiltration membrane molecular weight cut-off determination using polyethylene glycols, J. Membr. Sci., 382 (2011) 278-290.
[36] C.Y. Tang, Y.-N. Kwon, J.O. Leckie, Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes: II. Membrane physiochemical properties and their dependence on polyamide and coating layers, Desalination, 242 (2009) 168-182.
[37] K. Košutić, D. Dolar, B. Kunst, On experimental parameters characterizing the reverse osmosis and nanofiltration membranes' active layer, J. Membr. Sci., 282 (2006) 109-114.
[38] C.Y. Tang, Y.-N. Kwon, J.O. Leckie, Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes: I. FTIR and XPS characterization of polyamide and coating layer chemistry, Desalination, 242 (2009) 149-167.
[39] J. Geens, K. Peeters, B. Van der Bruggen, C. Vandecasteele, Polymeric nanofiltration of binary water–alcohol mixtures: Influence of feed composition and membrane properties on permeability and rejection, J. Membr. Sci., 255 (2005) 255-264.
[40] J. Geens, B. Van der Bruggen, C. Vandecasteele, Characterisation of the solvent stability of polymeric nanofiltration membranes by measurement of contact angles and swelling, Chem. Eng. Sci., 59 (2004) 1161-1164.

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