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**NANOFILTRATION OF IONIC LIQUID AQUEOUS
SOLUTIONS**

MASTER'S DEGREE FINAL PROJECT

Supervised by Josep Font

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NANOFILTRATION OF IONIC LIQUID AQUEOUS SOLUTIONS

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Abstract. Ionic liquids (ILs) are a promising alternative to replace conventional organic solvents in a wide range of applications, yet recycling and reusing them still remain a challenge. In this context, nanofiltration (NF) can be used to separate and concentrate IL solutions. In this work, we evaluated the use of two commercially available NF membranes (NF270 and NFD) in order to separate Tetrakis(hydroxymethyl)phosphonium chloride solutions with content below 10 wt% using a crossflow nanofiltration unit. The effect of the transmembrane pressure (TMP) and the IL concentration of the feed solution were studied. The experiments showed that NF270 membranes offer higher recovery values and suffer less fouling although they exhibited slightly lower IL rejection than NFD membranes. By using NF270 membranes, it was possible to concentrate IL solutions from 2.2 wt% to 4.5wt% with rejection values over 80%. However, for solutions with higher IL content, the recovery values decreased rapidly due to irreversible fouling effects. On the other hand, we have also demonstrated that is possible to remove the fouling effects by using a 1 wt% EDTA solution and fully restore membrane initial performance.

1. INTRODUCTION

Ionic liquids (ILs), also known as molten salts, are synthetic electrolytes with low melting point (<100°C) and low volatility. They are composed by a large organic cation and a polyatomic inorganic anion. The shape and size difference between the asymmetric organic cation and the small inorganic counterpart causes an irregular ionic packing, which causes their low melting point [1,2].

ILs show a wide range of interesting properties caused by their special composition. They usually possess high thermal stability, good electrical conductivity, wide electrochemical window, non-flammability and favourable solvating properties for a high number of polar and non-polar compounds.

Furthermore, it is possible to tailor certain specific properties of an IL, such as density, viscosity or miscibility, by slightly modifying the alkyl chain of the organic cation. This allows designing ILs with specific properties to satisfy the requirements of a certain application [3,4]. ILs are mainly used to replace conventional organic solvents. Their excellent solvating capacity usually exceeds by far those from most organic solvents. In addition, the low volatility of ILs reduces possible problems regarding vapour emissions [5]. Therefore, ILs can be used to dissolve a wide range of natural polymers, including cellulose [6], silk [7], and wool chitin [8].

For these reasons, ILs can be used during the biodiesel production process in order to extract lipids from raw biomass. Imidazolium and

Phosponium-based ILs have already been successfully used to extract lipids from both sewage sludge and microalgae [9,10]. ILs have also applications in other fields such as electrolytes for batteries [11], highly versatile lubricants [12] and in the biocatalytic production of chiral alcohols [13].

Even though ILs are considered as green solvents due to their low volatility, they are extremely eco-toxic and still expensive compared to most organic solvents. Therefore, recycling of IL is highly necessary from the points of view of IL disposal and toxicity. At the same time, a recycling process is also economically convenient because ionic liquids are still costly in comparison to most classic organic solvents [14].

Recycling processes might notably differ according to the process where the IL is used, yet there are normally two basic steps: purification or separation of the IL and concentration of the IL [15]. Purification is necessary in order to remove or separate the IL from all the possible remaining compounds. Concentration stage is necessary prior to the reuse of the IL when it is diluted during the process. There are different alternatives that have been already studied to separate ILs mixtures such as the CO₂-induced separation [16], charge exclusive electro-dialysis [17], nanofiltration processes [18], and the use of water-structuring salts (K₃PO₄) to form an aqueous biphasic system (ABS) [19].

Nanofiltration (NF) shows several advantages in comparison with other separation techniques. Like all the membrane separation operations, they have low energy consumption and there is no need to add extra compounds to perform the separation. Moreover, NF membranes are able to separate products not only by their size, but also by their electrical charge. Commercially available NF membranes have been used to separate bromophenol blue/IL and lactose/IL mixtures [18] and to recover

ILs used in process such as the ionic liquid-assisted biorefining of lignocellulosic substrates [20].

Regarding the concentration of ionic liquids, evaporation and pervaporation can be used to concentrate ILs solutions [22]. However, it is a process that requires high energetic costs which makes it not viable for large scale applications. Once again, NF processes are a suitable option for recovering IL diluted solution. Han et al. [23] studied the concentration of ILs from diverse organic solutions such as methanol, toluene and ethyl acetate by commercially available STARMEMTM NF membranes. Similarly, it has also been possible to concentrate Imidazolium-based ILs, used to dissolve cellulose, aqueous solutions used for cellulose dissolution by NF using FILMTECTM membranes [15]. IL aqueous solutions usually show a high osmotic pressure which makes necessary to differentiate between concentrated and diluted aqueous solutions. Concentrating a solution with low IL content might require a different approach than removing/eliminating water from an aqueous solution with high IL content [15].

In this project, we aim to study the use of NF membranes for concentrating aqueous solutions of a Phosponium-based IL which is used in the extraction of lipid from wet sewage sludge for biodiesel production [10]. During this process, the IL is mixed and diluted with water due to their miscibility and needs to be recovered in order to be reused.

This work focuses on the concentration of diluted IL solutions with IL content below 10%. We will test different commercially available NF membranes using a crossflow operation mode. We will carry out experiments in continuous mode to study the performance of the NF filtration system under different conditions. Additionally, we will conduct batch mode experiments to evaluate how much is it possible to concentrate the IL.

2. EXPERIMENTAL SECTION

2.1 Chemicals and materials

The IL employed in this studied was Tetrakis(hydroxymethyl)phosphonium chloride ((HOCH₂)₄PCl) solution (80% wt. in H₂O, MW(g/mol): 190.56) purchased from Sigma-Aldrich (detailed information about the IL can be found in Table S1 on the supplementary information). Sodium hydroxide (purity >97%) and methanol (purity >99.8%) were purchased from Sigma-Aldrich. EDTA (purity >99%) was supplied by Panreac. Two commercially available polymeric flat sheet membranes (NF and NF270) purchased from DOW-Filmtec were tested. NF membranes will be named NFD from now thereafter in order to avoid confusions with the acronym for nanofiltration, NF. Both membranes are made of a semi-aromatic polyamide thin film composite (tfc) active layer supported on polysulphone. The main characteristics of both membranes are summarized in Table 1.

2.2 Experimental filtration set up

NF experiments were conducted using a home-made cross-flow nanofiltration laboratory unit. The available effective membrane area was 42 cm². The membranes were hosted using a membrane cell module (CF042 Sterlitech Corporation).

The system also included a membrane pump (ProMinent) and 1 L glass water-jacketed feed tank. A pressure dampener was incorporated after the pump to mitigate the pulses from the pump and achieve a constant regular flow. Several pressure gauges and back pressure valves were used to control the pressure during the experiment and to purge the system after the filtration runs. The equipment could be operated either in continuous mode (by returning the permeate flow to the feed tank) or in batch mode (if the permeate is not recirculated back). The pump allows for a maximum flowrate of 25 L·h⁻¹ and the maximum operation pressure is 10 bar. Figure 1 depicts a scheme of the system.

Table 1. Polymeric membranes tested

Membrane	NFD	NF270
Supplier	Dow-filmtec™	Dow-filmtec™
MWCO (Da) ^a	200	300
PWP (L·m ⁻² ·h ⁻¹ ·bar ⁻¹) ^b	8.11 ± 0.37	13.56 ± 0.62
Roughness (nm) ^c	0.16	4.47
Thickness (μm) ^c	139 ± 10	128 ± 24
Isoelectric point (pH) ^c	5.1	3.5
Max. Temperature (°C) ^d	45	45
Max. Pressure (bar) ^d	41	41
pH range ^d	3-10	3-10

(a) Molecular weight cut off. From Balanec et al [24]

(b) Pure water permeability at 30 °C. Determined in this work

(c) Ivonne et al 2014 [25]

(d) Values provided by the supplier

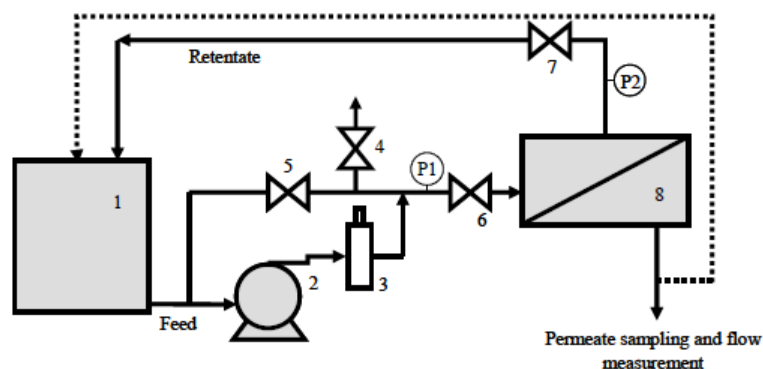


Figure 1. Experimental nanofiltration set-up. (1) Feed tank, (2) pump, (3) pulse dampener, (4) relief valve, (5) bypass valve, (6) and (7) backpressure valves, (8) membrane module, (P1) and (P2) pressure gauges [25]

2.3 Membrane pre-treatment and conditioning

All Membranes were initially dipped in a 50% wt. ethanol solution for 5 s and then soaked in deionized water during at least 24 h in order to remove possible manufacturing residues from the membrane surface. Prior to every experiment, each membrane was pressurized to 6 bar using deionized water for 1 h at 30 °C. This was necessary in order to eliminate any possible posterior compression effects. At the end of the compaction process, the initial water flux permeate (J_{w0}) was measured from 2 to 6 bar of transmembrane pressure (TMP) in order to obtain the membrane pure water permeability (PWP).

2.4 NF experiments of IL aqueous solutions

We carried out NF experiments were conducted using the system mentioned above. During these experiments, both retentate and permeate were recirculated to the feed tank in order to keep the IL concentration of the feed (C_F) constant, simulating a continuous mode operation. The temperature was always kept constant at 30 °C and the feed flowrate provided by the pump was $21 \text{ L} \cdot \text{h}^{-1}$.

A typical NF experiment can be summarized as it follows. Firstly, the feed tank was filled with the IL solution and then set at the desired operation conditions. Permeate flux (J_p ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)) was followed for 180 minutes. Samples of permeate were taken every 10 minutes to measure the evolution of the IL concentration in the permeate (C_p). Once the filtration run was over, the ionic liquid solution was collected and the water flux after filtration (J_{wf}) was measured to evaluate the impact of fouling on the membrane. Finally, the system was cleaned by running deionized water for at least 1 hour. For every experiment, we analysed different parameters

to assess the performance of the NF process. We studied the capacity of the membrane to retain the IL is expressed with the rejection coefficient (R_{IL}). It was calculated using the following equation:

$$R_{IL}(\%) = \left(1 - \frac{C_p}{C_F}\right) \cdot 100 \quad (1)$$

The yield or recovery (γ) of the NF process is the relationship between the permeate flowrate (Q_p) and the feed flowrate and it was calculated with the following expression:

$$\gamma(\%) = \frac{Q_p}{Q_F} \cdot 100 \quad (2)$$

During membrane processes, concentration polarization and fouling phenomena eventually cause a decrease in the permeate flux, which implies a decrease of the membrane output [14, 15]. In order to evaluate this effect in our NF system, we followed the permeate flux decline throughout experiments using a normalized flux value. Normalized IL solution permeate flux decline is defined by the ratio between the permeate flux (J_p) and the permeate water flux of the clean membrane (J_{w0}) under the same conditions. The typical NF experimental protocol is shown in a schematic way on Figure 2.

2.5 Concentration of IL experiments

The same experimental NF equipment was used for concentrating ionic liquid solutions. This time, a batch operation mode was used, the permeate was collected and only the retentate was returned to the feed tank. Therefore, the feed volume was progressively reduced and the feed solution became concentrated.

The concentration experiment started by filling the feed tank with the desired solution, then the system was put under the desired operation conditions. The experiment was carried out for 7 hours.

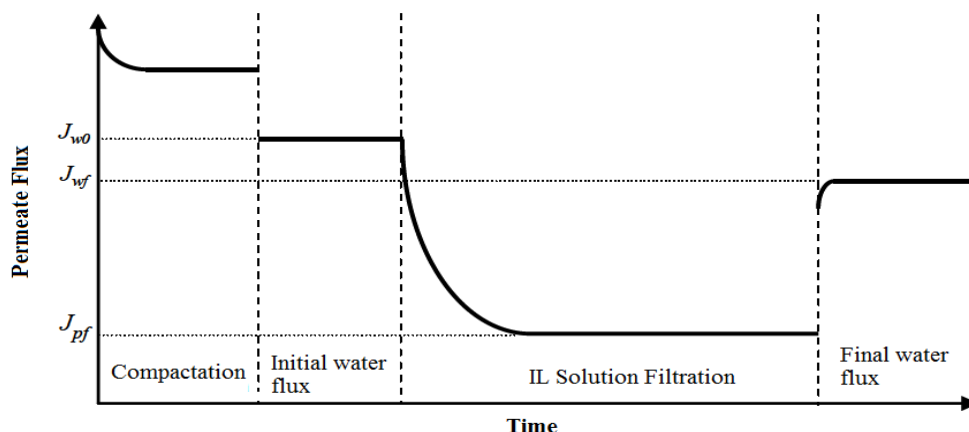


Figure 2. Nanofiltration test protocol scheme

The concentration experiment started by filling the feed tank with the desired solution, then the system was set under the desired operation conditions. The solution was filtered for 7 hours. Throughout the experiment, permeate and feed samples were collected at regular intervals to determine the evolution of the IL content in the permeate and the feed. In addition, the permeate flux was followed in order to obtain not only the flux decline, but also to know the feed volume reduction. As in former experiments, the system was cleaned by running deionized water for at least 1 hour through the system.

2.6 Membrane cleaning and reusing assessment

Permeate flux loss caused by fouling effects eventually reduces membrane performance. For this reason, it is interesting to study the possibility of cleaning the membranes and reusing them several times. Membranes with higher permeate flux decline were cleaned and reused in two subsequent filtration tests under the same conditions as the initial experiment. The cleaning solution was selected following the membrane manufacturer recommendations (FILMTEC Reverse Osmosis Membranes Technical Manual).

Fouled membranes were cleaned with 1 wt% EDTA solution adjusted at pH 12 using NaOH. The cleaning solution was applied for one hour. Finally, the system was run with distilled water until a neutral pH was achieved both in the permeate and the retentate.

2.7 Determination of the IL content

The refractive index of IL solutions varies linearly with the IL content [26]. Therefore, a linear calibration was performed in order to obtain the IL content of a given sample based on its refractive index. The refractive index of the samples was determined using an ABBE refractometer (Shibuya optical, model NO.196). The calibration plot is shown in the supplementary Figure S1.

2.8 Membrane characterization

JEOL SEM microscopy (model JSM-6400) was used to characterize the surface of the polymeric membranes. By using SEM, it was possible to accurately compare the surface of virgin and used membranes. SEM images of the membrane surface and the transversal cross-section were obtained.

3. RESULTS AND DISCUSION

3.1 Pure water permeability of the membranes

Figure S2 shows the initial distilled water fluxes (J_{w0}) for NFD and NF270 membranes as a function of the transmembrane pressure (TMP). As can be seen, initial water flux increases linearly with the applied TMP. It can be appreciated as well that NF270 shows a higher water flux, probably due to its larger pore size. Pure water permeability of the membranes obtained from the experimental data were 8.11 ± 0.37 and 13.56 ± 0.62 ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) for the NFD and the NF270, respectively. These values were similar to those found in the literature [15], which indicates that the membranes selected were reliable and in proper conditions.

3.2 Effect of TMP on Nanofiltration of IL aqueous solutions

Continuous mode experiments with a 2.5 wt% content of IL were carried out at different TMPs. Permeate flux decline as well as IL rejection were studied at 2, 4 and 6 bar for NF90 and NF270 membranes. Water permeate flux recovery after filtration (J_{wf}) was used as an indicator to study the concentration polarization (CP) and irreversible fouling effects. The portion of the flux that is recovered can be attributed to the reversible CP effects, whereas the flux not recovered is related to fouling [25]. IL rejection, normalized permeates fluxes of IL solution (J_p/J_{w0}) and deionized water after filtration (J_{wf}/J_{w0}) for both membranes are shown in Figure 3. According to the figure, CP effects are mainly responsible of the permeate flux decline since most of the water permeate flux is recovered (>80 %) in all cases. Recovery values are around 80%, being slightly higher for NDF membrane, which has a lower MWCO. Although it

is a relatively high value, it is still not high enough to be considered for practical applications. TMP appears not to have influence in the IL rejection of the membranes, yet working at higher pressures results in a higher IL normalized permeate flux (J_p/J_{w0}). The recovery (γ) values of these experiments can be found in Table 2. Experiments at higher pressure experiment show an enhancement in the permeate flux. Therefore, working at higher pressures improves the recovery of the process although it is necessary to keep in mind that it will require higher energetic input.

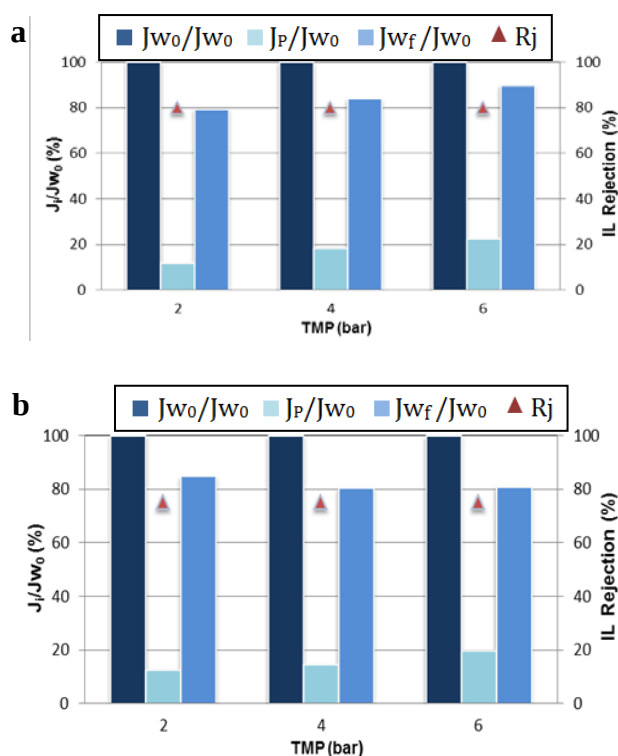


Figure 3. Normalized permeate fluxes at different pressures. Initial water flux (J_{w0}/J_{w0}), IL solution permeate flux (J_p/J_{w0}) and final water flux (J_{wf}/J_{w0}): (a) NFD; (b) NF270

Table 2. Recovery (γ) of the experiments at different TMPs

TMP (bars)	NFD	NF270
	γ (%)	γ (%)
2	0,03	0,06
4	0,16	0,28
6	0,24	0,39

3.3 Effect of the IL content on Nanofiltration of IL aqueous solutions

Experiments using IL solutions with different IL content were conducted in order to study the performance of the NF membranes under different IL concentrations. Solutions of 2.5, 5, 7.5 and 10 wt% of IL were filtered using both membranes. The experiments were carried out at 6 bar in order to work with higher permeate fluxes and higher recovery values. Once again, permeate flux decline and IL rejection were followed throughout the experiment. The evolution of the permeate flow and the IL rejection during the NF tests is represented in Figure S3.

Figure 4 shows normalized permeate fluxes of IL solution (J_p/J_{w0}) and water after filtration (J_{wf}/J_{w0}) for both NFD and NF270 membranes as well as the corresponding IL rejections. As can be seen, it is clear that IL content has a strong effect in the rejection capacity of both types of membrane. When the IL content increases up to 10 %, the IL rejection value is drastically reduced (from 80 to 45 wt% and from 75 to 36 wt% for NFD and NF270 respectively). In addition, J_p decreases as the IL content increases. This trend is evidenced at the final recovery values shown on Table 3 and can be

explained because IL solutions with higher concentration show higher osmotic pressure between feed and permeate. Therefore, a higher driving force would be necessary to overcome the osmotic pressure in order to achieve the same permeate flux than solutions with lower percentage of IL.

Regarding the permeate flux decline; it can be appreciated that water flux after filtration recovered (J_{wf}/J_{w0}) decreases as we increase the concentration of IL. Therefore, it appears that CP effects are greater for solutions with low percentage of IL whereas irreversible fouling effects become more important as we increase the IL content.

If we compare the overall performance of the two membranes, we can discern that, despite showing slightly lower rejection capacity than NFD, NF270 membranes show higher permeate fluxes.

Table 2. Recovery (γ) of the experiments with different IL content.

	NFD	NF270
IL wt. (%)	γ (%)	γ (%)
2.5	0,24	0,39
5	0,11	0,15
7.5	0,07	0,08
10	0,04	0,06

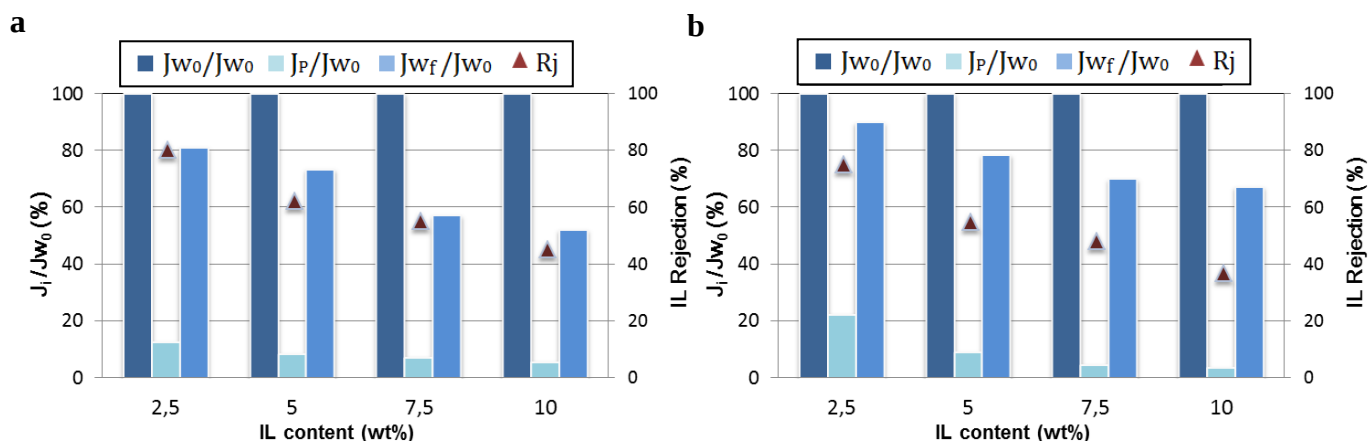


Figure 4. Normalized permeate fluxes for different IL solutions. Initial water flux (J_{w0}/J_{w0}), IL solution permeate flux (J_p/J_{w0}) and final water flux (J_{wf}/J_{w0}): (a) NFD; (b) NF270

What is more, it appears that NF270 membranes suffer less from fouling since they exhibit lower decline of water flux after filtration. This might be related to the fact that NF270 membranes possess higher pore size, which allows for higher flow of liquid and reduces the pore blockage.

3.4 Concentration experiments

Due to the former reasons, we decided to concentrate ionic liquids using the NF270 membrane. IL solutions were concentrated using a batch mode operation for seven hours at a TMP of 6 bar. The results obtained for one IL solution with low IL content (2.2 wt%) and high content (7.5 wt%) are depicted in Figure 5.

Figure 5 shows the evolution of the permeate flux and the wt% IL content in the feed solution (IL_{FEED}) throughout time (t_F).

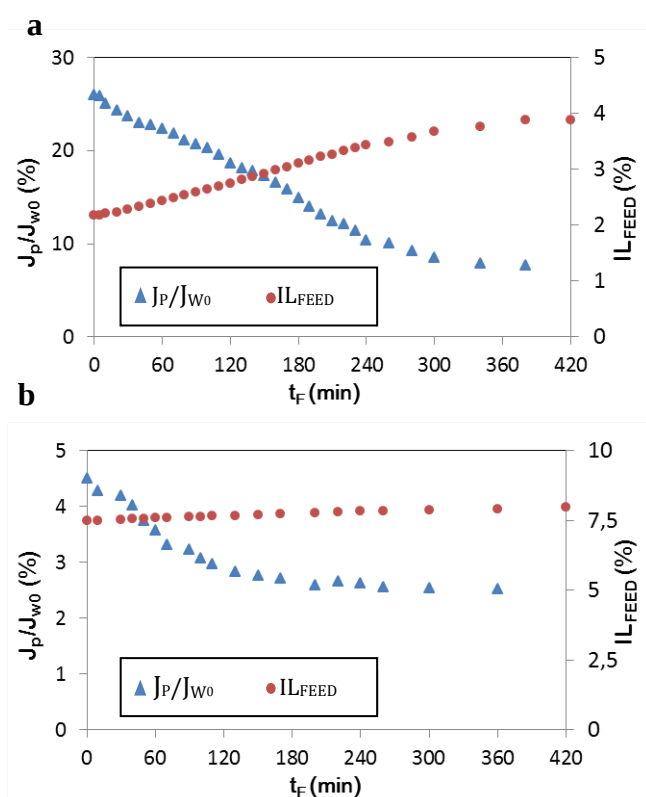


Figure 5. Normalized permeate flux decline and evolutions of the IL content in the feed (IL_{feed}) during concentration experiments: initial IL content (a) 2.2 wt%; (b) 7.5 wt%

Concentration experiments of low IL content solution (Figure 5a) show that it is possible to concentrate this solution from 2.2 wt% to almost 4 wt%. After 7 hours of experiments the feed volume was reduced from 1 L to 0.54 L. However, there is an important flux decline effect. As it can be observed in Figure 5, normalized permeate flux drops from 26 % to 10 % in four hours probably due to fouling. It is during this first period when most of the solution is concentrated. The IL content in the permeate flux never exceeded 0.63 wt% during the experiment. It was calculated that less than 1 % of the initial IL was lost in the permeate flux, hence almost all the IL was recovered.

With regards to the solution with higher IL content (Figure 5b), it was only possible to concentrate the feed solution from 7.5 wt% to 8 wt%. As shown in the Figure 5b, the normalized permeate flux decreases from 4.5 % to 2.5 % after two hours of experiment. Afterwards, the permeate flux is so low, that the solution is barely concentrated. After seven hours of experiment, the feed volume was only reduced from 1 L to 0.93 L. The low permeate flux together with the low IL rejection values of the 7.5 wt% IL solution, hindered the efficiency of the NF process.

3.5 Membrane reusing assessment

There results presented in previous sections indicate that there is an inevitably permeate flux fraction lost due to fouling effects. Fouling appears to be not significant for low IL concentrations but rapidly increases as the concentration becomes higher.

NFD membranes, which possess a smaller pore size, are those that suffer a higher fouling effect. Therefore, NDF membranes used in the experiments with 10 wt% of IL were cleaned according the

procedure explained in the experimental section and reused in two subsequent filtration cycles. The results are shown in Figure 6.

The Figure 6 displays the normalized permeate fluxes and the IL rejection coefficient of the initial NF experiment (cycle 0) and two more NF cycles after the corresponding cleaning step. As can be seen, cleaning procedure appears not only to be able to completely restore the initial membrane water flux, but also to increase the initial water permeate flux. Therefore, it seems that cleaning solution is able to clean possible not only manufacturing impurities, but also foulants accumulated on the membranes during their storage period. We can also note that IL rejection capacity of the membranes is not affected by the cleaning solutions. This fact is important, since cleaning solutions might alter membrane properties resulting in variations of their rejection capacity.

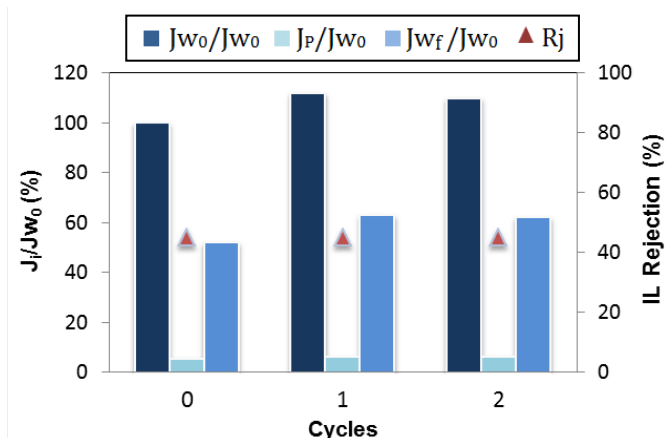


Figure 6. Normalized permeate flux decline and IL rejection for the membrane cleaning experiments after 2 cleaning cycles.

3.6 SEM membrane characterization

Figure 7 show some SEM images of the surface different virgin and used membranes. Typically, no morphological differences can be appreciated between virgin and used membranes. However, certain impurities are observed in some used

membranes as it is shown in figure 7b. The remaining micrographies can be found in Figure S4.

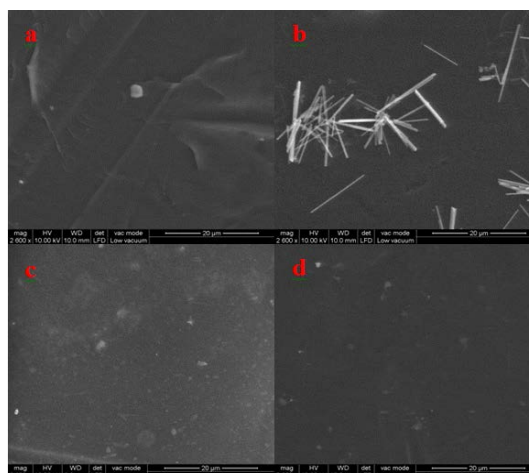


Figure 7. SEM images of the virgin membranes: (a) NFD (c) NF270. SEM images of the used membranes: (b) NFD (d) NF270

4. CONCLUSIONS

Concentration of $(\text{HOCH}_2)_4\text{PCl}$ aqueous solutions with IL content below 10% was investigated using commercial NF membranes (NF270 and NFD). Results indicated that membranes were indeed able to separate the IL and water for low IL concentrations with rejection values up to 80%. This value can be attributed to the fact that the molecular weight of the IL is slightly below the MWCO of the membranes. CP effects appeared to be predominant for solutions with low IL content whereas fouling became more important as the IL content increased. NF270 membranes showed slightly lower IL rejection capacity than NFD although they exhibited higher recovery values and suffered less fouling effects. Concentrating experiments showed that NF270 membranes were effective for concentrating solutions with lower IL content (from 2 to 4 wt%) despite having an important permeate flux drop after several hours of experiment.

We also proved that it was possible to completely remove fouling effects and restore

membrane's initial performance with the use of a 1 wt% EDTA (pH=12) cleaning solution.

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SUPPLEMENTARY INFORMATION

Table S1: Pure water permeability of the membranes

Table S1 shows the main properties of the ionic liquid used in this work.

Table S1. Main properties of the IL

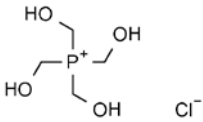
Ionic liquid	Tetrakis(hydroxymethyl)phosphonium chloride
Formula	(HOCH ₂) ₄ PCl
Molar mass (g·mol ⁻¹)	190.56
Density(g·cm ⁻³)	1.341
Concentration	80% in H ₂ O
Boiling point (°C)	150
Appearance	Crystalline
Structure	

Figure S1: IL content calibration curve plot

Figure S1 shows the correlation between the IL content of the solution (wt%) and its refractive index (n). The figure also shows the equation of the linear regression.

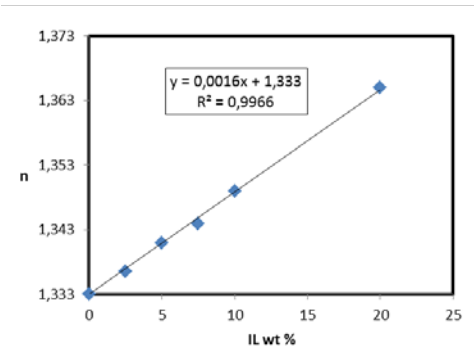


Figure S1. IL content determination calibration curve plot.

Figure S2: Pure water permeability of the membranes

Figure S2 show the distilled water flux (J_w) of the membranes as function of the TMP. It also includes the linear regression equation used to obtain the PWP.

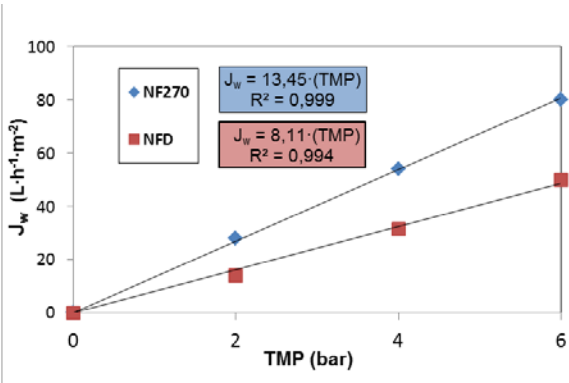


Figure S2. Distilled water flux (J_w) of the membranes at different TMP and PWP determination.

Figure S3: Pure water permeability of the membranes

Figure S3 shows the evolution of the normalized permeate flux decline (J_p/J_{w0}) during the NF tests with solutions with different IL content.

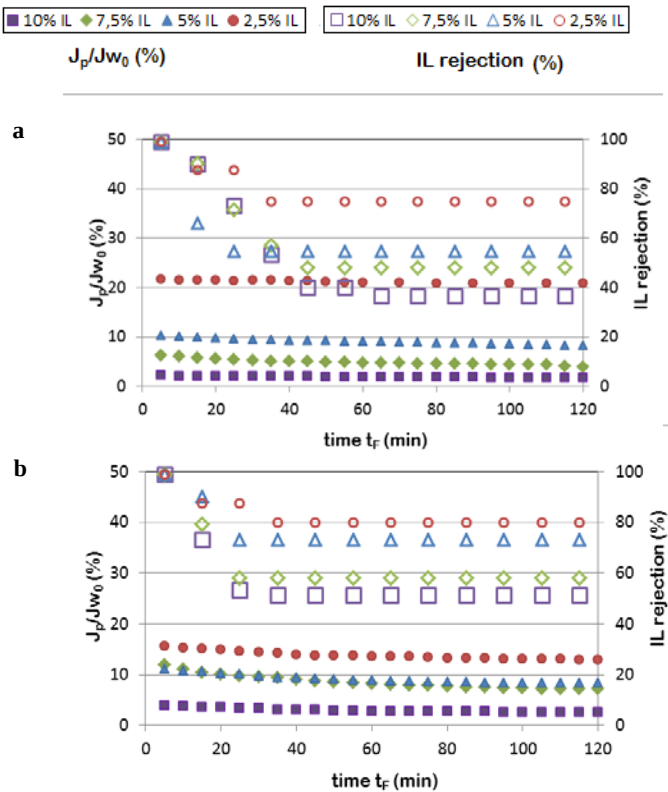


Figure S3. Permeate and IL content evolution of the NF experiment with different IL solutions: (a) NF270 (b) NFD

Figure S4: SEM membrane characterization

Figure S4 shows diverse SEM images, of dirty and virgin membranes. Images of the membrane's cross-section are also included.

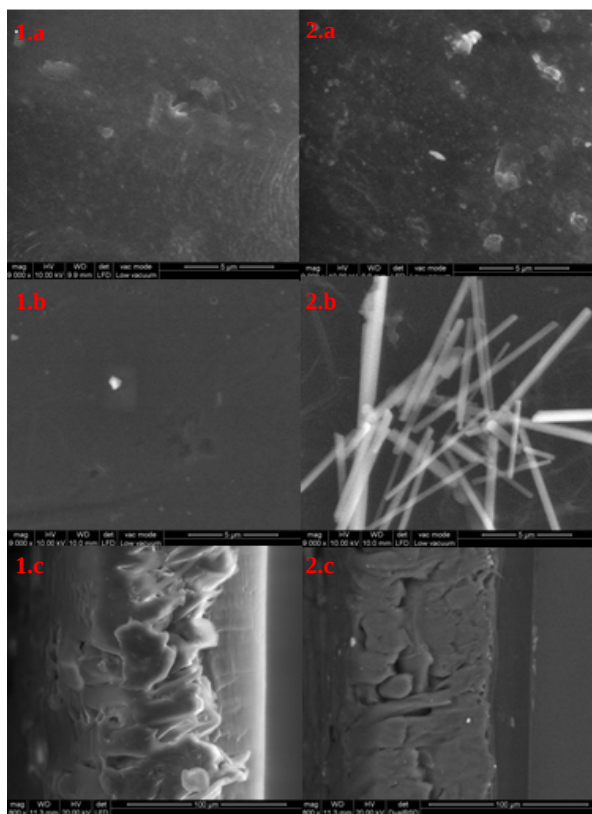


Figure 7. SEM images of the virgin membranes (a), used membranes (b) and cross-section images (c): (1) NF270 (2) NFD.