

Evaluation of High Pressure Effects on Ultrafiltration Process Applied to Aqueous Inkjet Colorant

Zambujo Pé-Leve, I. S.

Instituto Superior Técnico, Avenida Rovisco Pais, 1, 1049-001 Lisboa, Portugal

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Abstract

An aqueous inkjet colorant is purified and concentrated by an ultrafiltration process with diafiltration, using tubular membrane modules. The purity of the colorant is determinant in the final product quality, to meet the final target specifications.

Aiming to improve the product quality and the process yield, it was proposed to evaluate the increased pressure effects on the main parameters of the product and the process. Samples were processed on a pilot membrane unit at 30 bar pressure, which corresponds to the pressure applied in the large scale production, and at 40 bar pressure. The permeate flux rates, impurities rejection, process yield, cycle time and number of wash volumes during diafiltration were compared and discussed.

The results show that the increase of the pressure led to an increase of the permeate flux, on average, of 6%. The results suggest that, operating at 40 bar offers no benefits on the impurities removal. In general, it was observed a lower impurities removal rate at 40 bar pressure. In particular, the metal ion rejection increased, on average, by 3%. The polarisation concentration phenomenon and the molecular aggregates, formed by the dye molecule on the membrane surface, contribute to the results observed. At 40 bar, the process yield obtained was lower, with an increase of 25% on the permeate colour losses. Under these conditions, the water consumption during diafiltration is higher. It was concluded that the results indicate the increased pressure does not bring significant benefits to the process.

Keywords: Ultrafiltration, Diafiltration, Pressure, Concentration Polarisation, Rejection, Inkjet Colorant.

1 Introduction

The application of membrane technology in the dye industry is growing as dye manufacturers discover that it is a reliable and cost effective mean of improving yield and product quality, where repeatable purification and concentration are required [1]. The largest application in the dye industry is dye desalting and concentration of the finished product, which is most commonly applied to reactive dyes, but can also be used on other products. Membranes are also used with the many types of aqueous dyes. In this case, the membrane technology is utilised for concentration and purification. UF has been evaluated as a method for purification of aqueous dyes, separating particles of a size range of between 0.05 μm and 0.15 μm .

In particular, it has been found that when an aqueous colorant feed solution, of molecular weight above 1000 Daltons, is contacted with a semipermeable membrane under ultrafiltration conditions in a diafiltration mode, it is obtained: a permeate enriched in salts and impurities and a retentate enriched in colorant of MW above 1000 Daltons [2].

Diafiltration is a tangential flow filtration that can be performed in combination with any of the other categories of separation, namely ultrafiltration, to enhance both product yield and purity [3]. The combination of UF and DF is known as a fast and effective technique especially for concentrating and desalting or buffer exchange of protein solutions. Some of the important applications in this field include antigen purification, fractionation of whey protein isolate, albumin production from human

blood plasma for medical use and recovery of animal blood proteins from slaughterhouse effluents, separation of protease from tuna spleen extract, production of recombinant DNA derived human protein pharmaceuticals and antibody preparation, purification of soybean lecithin and leaf proteins, or concentration and desalination of gelatin [4].

Membrane diafiltration is a well established technique and has found many applications, including desalting of dyes and pigments[5].

Diafiltration results in the dilution of the retentate and, hereby, alleviates the problems associated with the built-up concentration boundary layer on the membrane surface. It has been reported that diafiltration combined with membrane separation could be an efficient tool to enhance the purity of the retained stream [6]. Also, the addition of pure solvent avoids an excessive concentration of the retentate, which would cause an increase in the effects of concentration polarisation and fouling, leading to a decrease in the permeate flux. This process can also provoke a positive effect due to the reduction in viscosity of the retentate, facilitating its pumping through the system.

UF/DF systems are used also for protein concentration. A study developed in order to optimise a UF/DF system applied to protein concentration [3], defines the optimal transmembrane pressure as described in Figure 1.

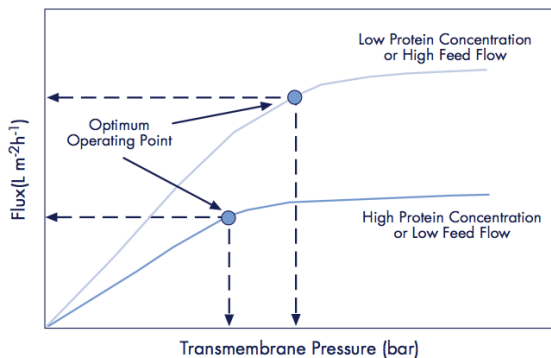


Figure 1 - A typical trend of flux versus TMP for a tangential flow filtration process.

The optimum pressure at which to run a process is at the knee of the curve, where nearly the highest flux is achieved without exerting excessive pressure or reaching exceedingly high solute wall concentration.

Inkjet colorants are high value products, thus it is important to understand and optimise the purification and concentration stage.

The main objective of this thesis is to study the overall high pressure effects on ultrafiltration/diafiltration process applied to an aqueous inkjet colorant. This study sets out to determine and test if the actual pressure applied to the process is at an optimum, or if it can be further improved.

The aqueous colorant, Cyan-X, is purified and concentrated by ultrafiltration with diafiltration, at 30 bar pressure. The study aims to evaluate the effects of operating at 40 bar pressure on the product quality, on the process yield and on the process parameters.

Figure 2 shows the flow diagram of the UF/DF system used on the aqueous inkjet colorant purification and concentration.

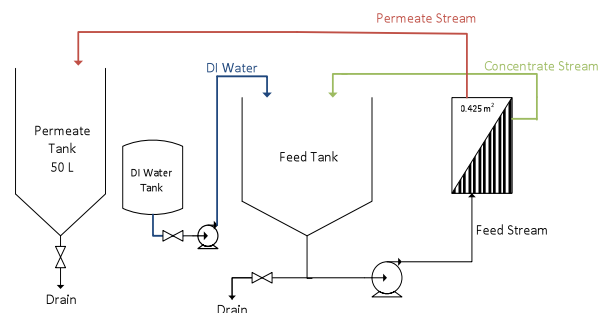


Figure 2 - Flow diagram of the UF/DF system used in the process.

2 Theory

2.1 Membrane Characterisation

The performance of ultrafiltration membranes is commonly quoted by manufacturers in terms of the pure water flux.

$$v_{p,w} = \frac{L_p \Delta P}{\mu_w} \quad (1)$$

Where $v_{p,w}$ is the pure water flux, L_p is the hydraulic permeability coefficient, ΔP is the pressure differential and μ_w is the water viscosity.

The standard permeability coefficient is characteristic of the system membrane/water and is independent of the pressure and temperature.

The retention coefficient R to the solute s is a parameter that depends only on the membrane and solute characteristics and it is defined as:

$$R_s = \left(1 - \frac{C_{p,s}}{C_{f,s}}\right) \times 100 \quad (2)$$

Where $C_{p,s}$ is the concentration of s in the permeate and $C_{f,s}$ is the concentration of s in the feed solution.

2.2 Permeation and Polarisation Concentration Phenomenon - Pressure Effects

The general membrane equation (3) is an attempt to state the factors that may be important in determining the membrane permeation rate for pressure driven processes.

$$J = \frac{\Delta P - \Delta \pi}{\mu(R_m + R_s)} \quad (3)$$

Where $\Delta \pi$ is the osmotic pressure difference, R_m is the membrane resistance and R_s is the resistance due to solute accumulation, forming a filter cake and gel foulants.

The separation of solute and solvent takes place at the membrane surface where the solvent passes through the membrane and the retained solute cause a local concentration increase. This effect is called concentration polarisation. Therefore a concentration profile is established within a boundary film generated by the hydrodynamic conditions.

The phenomenon of concentration polarisation has influence in how pressure affects retention. It may cause the rejection to decrease with increasing pressure [7]. The reason is that, increasing the pressure, the concentration of solute at the surface of the membrane increases over that in bulk stream. As the pressure is increased, the permeate flux is increased and the convective transport of solute to the membrane is increased. If the solute is retained by the membrane, it accumulates at the surface of the membrane until the back diffusive mass transport, is equal to the forward convective transport. There is a concentration gradient that removes solute from the membrane, resulting in a decrease of solute retention.

The polarisation module also has influence on the flux, because it increases with increased pressure. When applied pressure is increased, the permeate flux also increases, within a certain range of pressure. Taking account of the concentration polarisation effect, the flux can be calculated by equation (4)

$$J = k_s \ln \left(\frac{C_m - C_p}{C_b - C_p} \right) \quad (4)$$

Where k_s is the mass transfer coefficient, C_m is the concentration on membrane surface, C_p is the concentration of permeate and C_b is the bulk concentration.

However, the accumulation of the solute at the membrane interface can limit the flux. The concentration on the membrane surface increase with pressure, until a point where it reaches a maximum value, and the back diffusive transport is fixed. From this point on, the solute only accumulates on membrane surface. According to the gel polarisation model, in the "gel polarized regime" the flux becomes independent of the pressure, and is described by equation (5).

$$J_v = k \ln \left(\frac{C_g}{C_b} \right) \quad (5)$$

Where C_g is the concentration of the gel formed on the membrane surface.

3 Experimental Apparatus and Procedure

3.1 Material Processed

The material processed was an aqueous inkjet dye, named Cyan - X, based on copper phthalocyanine.

3.2 Membranes and Module

The membranes used on the experiments are cross flow tubular membranes, made from polyethersulphone, with retention of 9000 MWCO. The module has 18 membranes with a total area of 0.425 m². This kind of membrane is suited to fluids with high viscosity, which is the case with the samples processed, as there are suspended solids. The samples were processed on a PCI tubular unit.

3.3 Membrane Unit

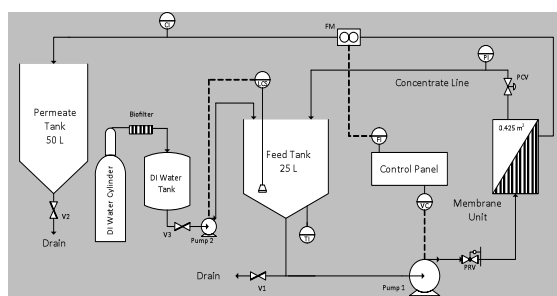


Figure 3 - Flow diagram of membrane filtration process in the PCI unit.

3.4 Experiments

The membrane characterisation experiment was carried out by running DI water in the unit, in recirculation mode. The trial was repeated at three different pressures – 30, 35 and 40 bar – and the readings of the flow rate were made at several temperatures. This procedure was carried out before and after a run of Cyan in order to evaluate the membrane performance.

The Cyan runs involved the following steps: initial CWF measurement, ultrafiltration/diafiltration process, final CWF measurement and cleaning.

In order to study the pressure effects on the cyan quality and process parameters, runs of the same initial feed were carried out at 30 bar (which is the pressure applied on the plant production) and at the increased pressure of 40 bar.

The UF/DF of Cyan includes the following steps: concentration from 3.37% to 5%, first diafiltration stage, concentration from 5% to 8%, second diafiltration stage and final concentration from 8% to 15%.

During the processing at both pressures, samples of concentrate and permeate were taken in order to track the content of metal ion, solvent and EDTA. The other parameters monitored were: time, flow rate, permeate conductivity, temperature, pH, permeate volume and wash volumes.

3.5 Analytical Methods

The strength of the samples (in g/L) was determined by measuring the optical densities (OD), using a spectrophotometer.

The measurements of EDTA and metal content were carried out by HPLC.

4 Results and Discussion

4.1 Membrane Characterisation

The trials for the membrane characterisation were carried out with DI water, in recirculation mode, at 30, 35 and 40 bar pressure. This procedure was carried out before the run, after the run and after the cleaning in order to determine the membrane performance.

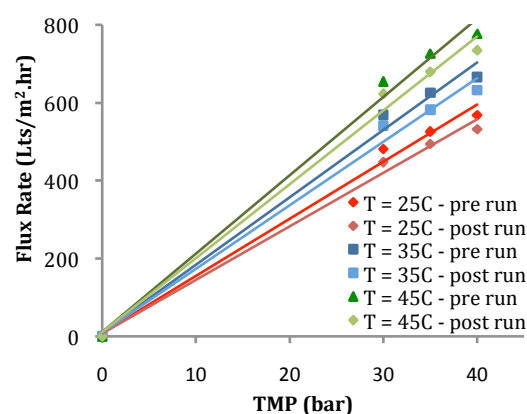


Figure 4 - Linear representation of the water flux rate versus pressure, at constant temperature, before and after the Cyan processing.

Table 1 - Hydraulic permeabilities at different temperatures. Slopes of the linear relations.

T (°C)	L _p (Lts/m ² .hr.bar)	
	Before Cyan-X run	After Cyan-X run
25	14.66	13.75
30	15.91	14.99
35	17.31	16.32
40	18.85	17.64
45	20.11	18.97

At constant temperature, the flux of pure water increases when the pressure is increased, in a linear way.

Regarding the membrane performance before and after the Cyan-X run, the results show that the performance decreases, as the hydraulic permeability values decrease after the run.

It was showed that the decrease of the flux after the run is more significant at higher pressures and consequently the recovery of the flux is less successful at higher pressures. Operating at 30 bar pressure, the flux rate almost return to the initial value.

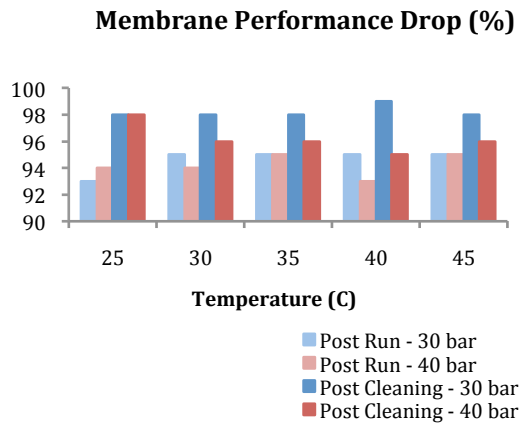


Figure 5 - Percentage of membrane performance obtained after the run and after the cleaning, at 30 and 40 bar.

It is observed at most temperatures, that the decrease of membrane performance is higher at 40 bar than at 30 bar pressure. While operating at 30 bar the chemical cleaning yields 98% recovery of the initial performance, at 40 bar, the recovery achieved is only 96%.

4.2 Cyan Trials at 30 and 40 bar

4.2.1 Permeate Conductivity Profile

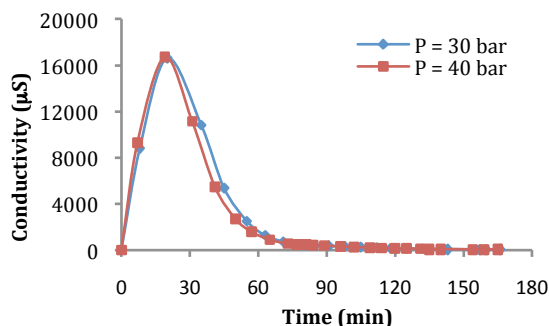


Figure 6 - Permeate conductivity profiles at 30 and 40 bar pressure.

Comparing the trials at 30 and 40 bar, a significant difference does not exist in respect to the permeate conductivity. Apparently, a higher pressure does not lead to a quicker decrease of conductivity, since it is necessary to allow the same time for the permeate conductivity achieve the desired values for both trials. The permeate conductivity is an indicator of ionic impurities presence.

4.2.2 Temperature Profile

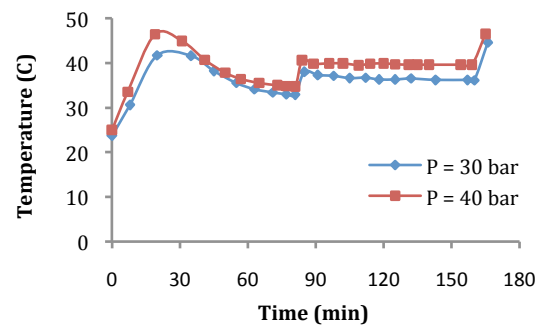


Figure 7 - Temperature profiles at 30 and 40 bar pressure.

Comparing the trials at 30 and 40 bar, it is observed that the temperature increases faster when the unit operates at 40 bar pressure, which is expected due to the higher cross flow velocity on the membrane.

4.2.3 Flux Rate Profile

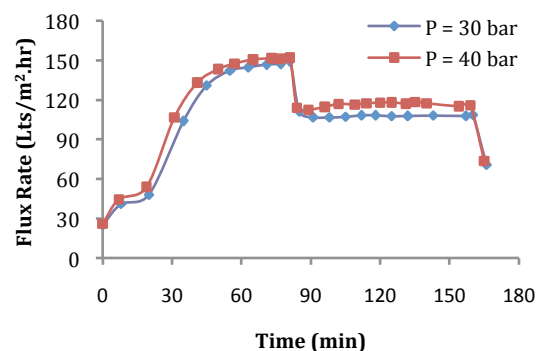


Figure 8 - Comparison of the flux rates at 30 and 40 bar pressure.

The comparison between both flux rates shows that the run at 40 bar pressure leads to flux rates slightly higher. It is observed that in both second and final concentrations, the

difference of the flux is very small, which suggest that at higher concentrations of the dye, the applied pressure does not have a significant effect on the flux. Taking the gel polarisation model into account, the results suggest that operating at 40 bar and higher concentrations, the limiting flux can be close to being achieved and the flux does not increase significantly with pressure.

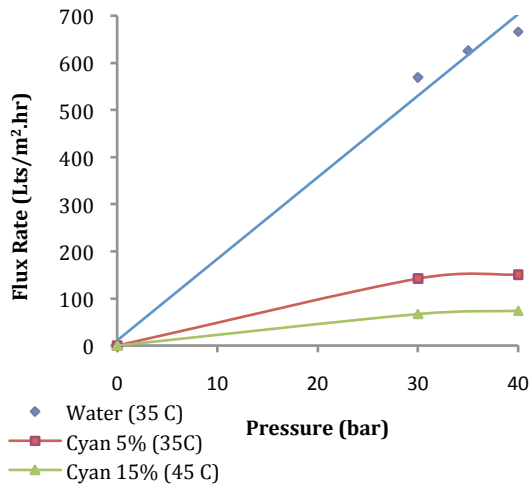


Figure 9 - Effect of pressure on Cyan UF/DF, at two different concentrations.

The solution has a completely different behaviour on pure water, when the pressure is increased.

4.2.4 Mass Balance

Table 2 - Mass balance to the dye at 30 and 40 bar.

	P = 30 bar		P = 40 bar	
	g	%	g	%
Feed	410	-	394	-
Permeate	0.126	0.031	0.167	0.042
Lost to Unit	6.56	1.60	17.5	4.45
Displacement	56.34	13.7	46.58	11.8
Product	347	84.6	329	83.7

Comparing the results, operating at 30 bar the percentage of product recovered is 84.6%, while at 40 bar it decreases to 83.7%. The permeate losses are higher when the increased pressure is applied.

4.2.5 Permeate Colour Losses

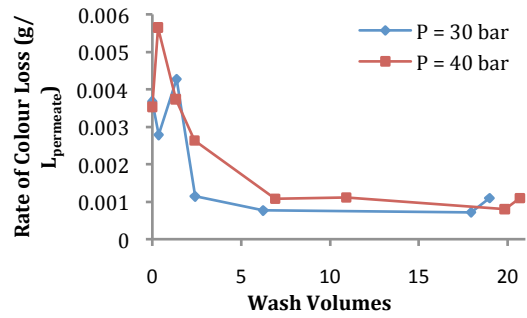


Figure 10 - Rate of colour loss the in permeate of the runs at 30 and 40 bar.

The chart above shows that the trial carried out at 40 bar pressure leads to slightly higher colour losses in the permeate. This result is due to the fact that, at 40 bar, there is a higher convective flux to the membrane, resulting in a higher concentration of dye on the membrane surface. Thus, as the flux is higher, a bigger amount of dye can be pushed through the membrane, which increases the colour loss through the permeate.

4.2.6 Metal Ion Removal

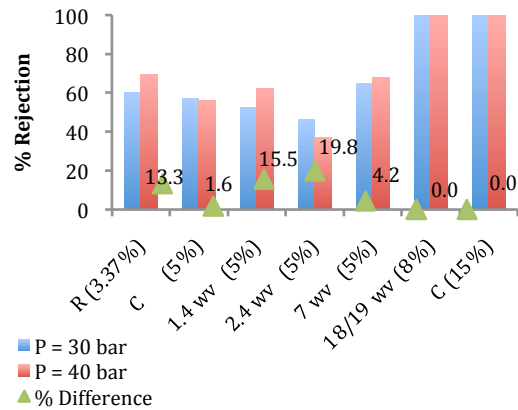


Figure 11 - Metal rejection at 30 and 40 bar as function of number of wash volumes (and indication of dye strength). R – recirculation, C – concentration, WV – wash volumes during diafiltration.

Remove the metal ion, in order to achieve the target specifications is one of the main objectives of this UF process, and therefore, the

metal ion rejection is one of the main parameters of this study.

Figure 11 shows that during the UF process, the increased applied pressure leads to an increase in the metal ion rejection.

It would be expected that an ultrafiltration membrane, in this case with 9000 MW cut-off, easily allowed the passage of a metal ion. However, the explanation of the increase of the metal rejection with increased pressure is related to the dye molecule itself. The cyan dye tends to aggregate, forming macromolecules. The higher rejection observed at 40 bar suggests that the aggregates formed can constitute a secondary barrier layer, blocking the passage of the metal ions.

4.2.7 Solvent Removal

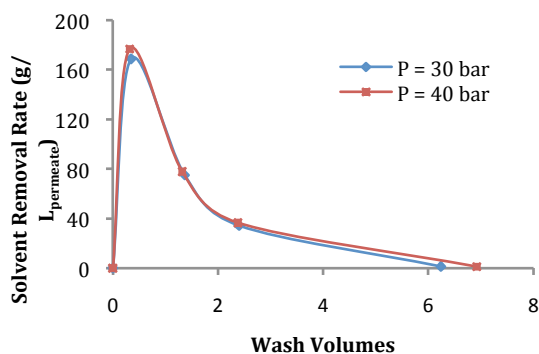


Figure 12 - Solvent removal rate, at 30 and 40 bar pressure.

The solvent is added to the samples during the chemical synthesis and it is intended to remove it completely during the membrane process.

The results show that both solvent removal rate profiles are identical. However, initially there is a slight difference, where the amount of solvent removed is higher in the run at 40 bar pressure. This is due to the fact that the flux is also higher at 40 bar. Between 6 and 7 wash volumes, the solvent content is very low for both trials.

4.2.8 EDTA Removal

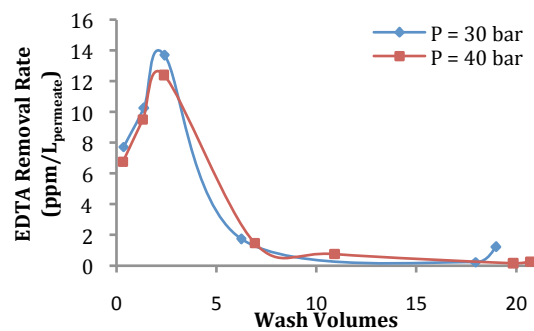


Figure 13 - Rate of EDTA removal at 30 and 40 bar pressure.

EDTA is present in the dye solution as a complexing agent, forming stable complexes with the metal ion. EDTA is used to sequester the metal ion in the aqueous dye solution, preventing metal ion impurities from contaminating the final product.

It is observed that the removal of EDTA is higher at 30 bar pressure during the process. Similar to what happens with the free metal removal, the results suggest that the increased pressure does not lead to a higher removal of EDTA. The explanation lies in the same phenomena described previously, the dye aggregates enlarge the effect of concentration polarisation on the membrane surface, which does not allow a higher removal with higher pressure.

4.2.9 Cycle Time and Wash Volumes

The cycle time is not the most relevant factor in a laboratory scale, but it becomes much more relevant in the large scale process.

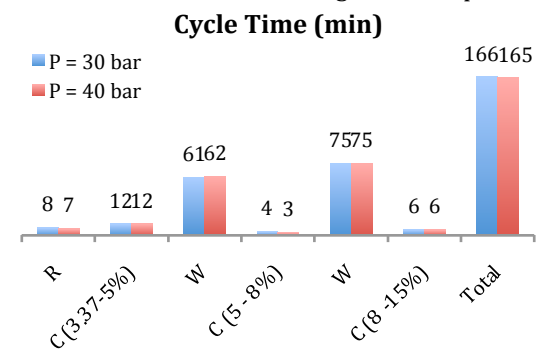


Figure 14 - Comparison of the cycle time, at 30 and 40 bar, differentiating the different filtration stages.

The chart above shows the actual times obtained during the recirculation (R), concentrations (C) and washing/diafiltration (W), at 30 and 40 bar. It is observed that, in all the stages, the times are equivalents for both pressures. Thus, the increase of applied pressure did not have a significant effect on the cycle time.

Wash volume is the volume of permeate removed equivalent to the total volume of the sample in the system, including the hold-up volume. As the system operates at constant volume, the volume of permeate collected is equal to the volume of DI water added to the system, thus wash volumes are the measure of the amount of DI water.

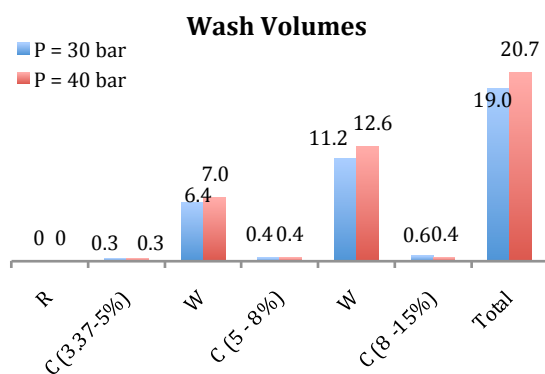


Figure 15 - Comparison of wash volumes required at 30 and 40 bar pressure, differentiating the filtration stages.

The results show that, the run at 40 bar pressure required more 1.7 wash volumes than the one at 30 bar. The major difference occurs during the second stage of diafiltration.

Relating the wash volumes with the cycle time and the permeate conductivity, the results suggest that, supplying more DI water to the system does not lead to a faster decrease of the conductivity (which means that does not increase the rate of impurities removal), and as result, the cycle time does not decrease significantly.

5 Conclusions

The membrane characterisation was carried out before and after a run of Cyan-X at 40 bar, and it was observed that the hydraulic permeability of the membrane decreased, on average, 6% after the run, of which only 3% was recovered with a chemical clean. It is concluded that the initial membrane performance is not restored to 100%, which is due to the membrane fouling and possible compaction of the membrane.

Regarding the Cyan trials at 30 and 40 bar:

- It is shown that the temperature of the feed solution increases faster operating the system at 40 bar, and consequently it gets closer to the 50 °C, limiting temperature, during the concentration stages than at 30 bar. This is an important parameter that contributes to the reduction in membrane performance.

- The combination of the increase of pressure with the higher temperature, that lowers the viscosity, leads to increase of the flux rate, on average, in 6% at 40 bar. This increase is noticeable during the diafiltration stages.

- Concerning the permeate conductivity, the results show that, despite the permeate flux bring slightly higher at 40 bar, it does not affects significantly the profile of the permeate conductivity. As the conductivity indicates the presence of ionic species, it means that there is not a big difference between impurities removed between 30 and 40 bar.

- On the process yield evaluation, the increased pressure does not improve the product recovery. At 30 bar the process yield is higher than at 40 bar.

- The pressure increase has a significant effect on the permeate colour losses. The run at 40 bar presents higher colour losses than the run at 30 bar, causing an increase of colour loss of 25%.

- It is shown that, an increase of pressure does not guarantee a higher removal of impurities. Due to the concentration polarisation phenomenon and to the fact that the dye molecules tend to form aggregates of macromolecules, higher fluxes does not lead to higher removal of impurities, because the resistance on the membrane surface increase.

- It is concluded that, running at higher pressure requires a higher number of wash volumes. This is expected, as the diafiltration is carried out at

constant volume. However, more wash volumes do not lead to higher impurities rate removal. Thus, despite higher fluxes, the cycle time of the operation does not change significantly.

The overall conclusion of the thesis, considering all the parameters, is that increasing the operation pressure from 30 to 40 bar does not provide clear benefits to the process, regarding the aim of improving the product quality and process yield.

5.1 Work Proposals

As the purity on the final product seems to depend strongly in the components that are initially present on the samples, it is important to study how the applied pressure affects the filtration of different production batches.

It is important to quantify long term, the membrane performance decay at 40 bar, as the membranes cost is a very important factor. It is also important to know how much it is possible to recover of the membrane performance, by applying a more aggressive chemical cleaning while tracking the CWF.

In order to have a wider range of data, which allows more reliable comparisons, more experiments at 30 and 40 bar pressure would be necessary, keeping strength and the initial volume constant.

An increase of 10 bar does not have a significant impact on the energy costs on laboratory scale, but it would be crucial to study the impact of a higher pressure on the costs related with the feed pumps and with the DI water consumption.

Nomenclature

List of symbols

$v_{p,w}$ – Pure water flux
 L_p – Hydraulic permeability coefficient
 J – Flux
 C_p – Permeate concentration
 C_f – Feed concentration

C_m – Membrane surface concentration

C_g – Gel concentration

C_b – Bulk concentration

k – Mass transfer coefficient

Abbreviations

UF – Ultrafiltration

DF – Diafiltration

MW – Molecular weight

DI – Deionised

CWF – Cold water flow

EDTA - Ethylenediamine tetraacetic acid

OD – Optical density

HPLC – High performance liquid chromatography

6 References

- [1] *How the Dye Industry is Benefiting from Membrane Technology*, Filtration + Separation, June 2002;
- [2] Dynapol, Palo Alto, Calif., *Salt Addition in Ultrafiltration Purification of Solutions of Polymeric Colorants*, Booth, R. G., Cooper, A. R., US 4,189,380, Feb. 19, 1980;
- [3] *Protein Concentration and Diafiltration by Tangential Flow Filtration*, Millipore, 2003;
- [4] R. Paulen, G Foley, M. Fikar, Z. Kovács, P. Czermak, Minimizing the process time for ultrafiltration/diafiltration under gel polarization conditions, *Journal of Membrane Science* 380, 148–154, 2011;
- [5] Z. Kovácsa, M. Discacciatib, W. Samhabera, Numerical simulation and optimization of multi-step batch membrane processes, *Journal of Membrane Science* 324, 50–58, July 2008;
- [6] D. Sen, A. Roy, A. Bhattacharya, D. Banerjee, C Bhattacharjee, Development of a knowledge based hybrid neural network (KBHNN) for studying the effect of diafiltration during ultrafiltration of whey, *Desalination* 273, 168–178, November 2010.
- [7] Porter, M. C., *Handbook of Industrial Membrane Technology*, Noyes Publications, New Jersey, 1990;