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Research Paper

Nanofiltration of synthetic and industrial dye baths: Influence of temperature on rejection and membrane fouling

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HIGHLIGHTS

- Low and high rejections for salt and color allows for reuse of water.
- Fouling is more severe at higher temperatures.

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ABSTRACT

Nanofiltration (NF) has become a widely accepted process not only for producing drinking water but also for recovering wastewater in industrial processes or removing pollutants from industrial wastewater effluent. In the textile industry, the treatment of various dye baths with NF at room temperature have already been studied and was found feasible at lab-scale and pilot scale. The aim of this study was to investigate the effect of temperature on permeate quality and membrane fouling in NF of textile effluents using a range of commercial membranes (Desal 5 DK, Desal 5 DL, N30F, NF PES 10) in a temperature range from 20 ºC to 70 ºC. Synthetic dye baths at different salt and/or dye concentrations and real dye baths were used. The performance of the NF membranes was evaluated by measuring the water flux, salt and color rejection. Na_2SO_4 rejection of 15% and color rejection of more than 80% were achieved through the experiments at elevated temperature. Permeate quality was satisfactory enough to recycle these effluents in reactive dyeing for water and energy savings. The fouling effect at elevated temperature on NF membrane increases the Na_2SO_4 and color rejection slightly, but membrane damage was observed for some membranes. There was a correlation between the results of experiments with synthetic solutions and with real wastewater.

1. Introduction

Polymeric thin-film composite nanofiltration (NF) membranes are increasingly implemented in the fields of water purification, and industrial wastewater treatment processes for removing hardness, synthetic organic compounds, natural organic matter and also mono- or multivalent ions, etc. [1,2]. Nowadays, NF is applied in many industrial areas, especially in the textile industry for effluent treatment. NF experiments on dye baths have been carried out since 1990 and these kind of membranes are used to remove ions and dyes from dye bath wastewater [3,4]. Aouni et al. [5] used ultrafiltration (UF) and NF processes to treat synthetic reactive dyes aqueous solutions and a raw textile effluent supplied from rinsing baths of Spanish textile industry, and obtained high retentions for COD and color (>90%) for NE 200 and NF 270 membranes.

The textile industry is characterized by using a large quantity of chemicals and huge quantities of water. Detergent and caustic are used to remove dirt, grit, oils and waxes; bleach is used to improve whiteness and brightness. For that reason, effluents from the textile industry contain a high concentration of organic and inorganic chemicals and are characterized with residual COD and strong color [6]. The dye baths together with the rinsing and post-treatment baths constitute the largest fraction of the wastewater in a textile factory. Therefore, a technology that allows obtaining a water quality acceptable for reuse as process water would make significant savings in water qualities possible. However, in the textile industry the bleaching and dyeing water temperature may be as high as 90 ºC [7]. This kind of water cannot be treated directly through biological treatment due to recalcitrant chemicals and high temperature. Treatment of various dye baths with NF at room temperature has already been studied and was found feasible at lab-scale and at pilot-scale [8,9]. Different aspects have been described, such as the salt rejection (in view of reuse), the permeate quality and the importance of scaling on a short timescale [10,11]. Membrane synthesis has been studied extensively for the removal of dyes from wastewater, resulting in several novel membrane types, including self-assembled positively charged NF

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membranes [12], new thin-film-composite NF membranes developed through interfacial polymerization [13], and positively charged NF membranes on sulfonated polyphenylenesulfone support [14]. Lau and Ismail [15] reviewed all different membrane materials for textile effluents, with a focus on NF membranes.

Treatment of textile effluents at room temperature has been found feasible at room temperature, often after biological treatment [16], which can be even integrated in a hybrid bioreactor [17]. However, nanofiltration is in this case used as an end-of-pipe technology, while it may also be used in the process itself.

In view of integration of nanofiltration in the process, a further aspect to be studied is the application of nanofiltration at elevated temperatures. The aim is then to combine water savings and energy savings by obtaining treated water with process water quality at a temperature comparable to the temperature used in the process. Membrane manufacturers usually give the maximum temperature where their membranes can be used; however, it is not clear whether this value is the temperature resistance of the membrane itself [18]. There is a need to study the filtration properties of NF membranes at elevated temperatures (above 50 ºC) for their capacity to remove salts, color, organic or inorganic compounds, since this would allow reusing process water with a minimum energy loss for reheating. An additional positive effect is the higher fluxes expected at elevated temperatures, due to the lower viscosity of the feed water according to Hagen-Poiseuille's law. Hildebrand et al. [19] studied different dye solutions at different temperatures and at different pH conditions and obtained almost 100 % color removal in all cases, using NF90 and Desal DK membranes for the removal of Remazol Turquoise Blue G, Remazol Yellow GR and Lanaset Blue 2R. However, in a series of preliminary experiments prior to the experiments described in the underlying paper, it was observed that for some dye baths the permeate was colorless at room temperature while the rejection of color is lower at higher temperatures. Thus, it was questioned whether the membrane itself can withstand elevated temperatures (above 50 ºC). This manuscript describes some potential effects at elevated temperatures in such conditions for a range of NF membranes.

2. Methods and Materials

In a first step, synthetic solutions prepared according to dye baths recipes were used for NF experiments. An acid dye of Victoria blue was chosen in the feed solution with or without addition of salts. The different components were added subsequently to the synthetic dye baths so that the influence of each component can be evaluated separately. In a second step, real dye baths with known composition were used to verify the conclusions from the experiments with synthetic solutions.

2.1. Membrane types

The membranes that were used for the experiments are commercially available NF membranes. The most important characteristics of these membranes are summarized in Table 1. All membranes are specified to be operational at elevated temperature, up to 90 ºC and are thin film polymeric NF membranes.

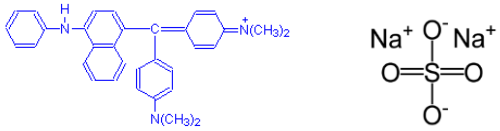
Table 1
Properties of selected membranes.

Membrane	Desal 5 DK	Desal-5-DL	N30F	NF-PES-010
Manufacturer	Osmonics, Vista USA	Osmonics, Vista USA	Nadir, Wiesbaden Germany	Nadir, Wiesbaden Germany
Material	PA	PA	PES	PES
MWCO (Da)	150-300	150-300	400	1000
Flux ($L.m^{-2}h^{-1}$)	5.4 at 1 bar	9.0 l/m²h bar	40-70 at 40 bar*	200-400 40 bar*
Max. temp. (°C)	90	90	95	95
Max. pressure(bar)	15	40	-	-
Charge at pH 7	-	-	-	-
pH	2-11.5	2-11.5	0-14	0-14

** measured at 40 bar, 20°C, stirred cell (700 rpm)*
PA: polyamide
PES: polyethersulfone

2.2. Feed solutions

A synthetic solution used for nanofiltration experiments in the first step was prepared in the laboratory according to real dye bath recipes. Furthermore, additives and salts were added to the solution to make different experiment formulas. Chemicals that are used to make dye solution feeds are Victoria blue ($C_{33}H_{32}ClN_3$ – triarylmethane) and sodium sulphate (white crystalline solid - Na_2SO_4) by single component or mixed component formulas. These chemical structures are shown in Figure 1. Distilled water was also used for preparation of synthetic solutions.



Triarylmethane (Victoria Blue) Sodium sulfate

Fig. 1. Chemical structure of Victoria Blue and sodium sulfate.

Victoria Blue was determined by spectrophotometry, using a Shimadzu UV-210A spectrophotometer at a wavelength of 638 nm. In addition, a conductivity and pH meter are also used to measure conductivity of salt solution and pH respectively.

After a preliminary test, a real dye bath collected at a textile factory in Belgium was applied to the next series of experiments, to confirm the conclusions from NF of the synthetic feed solutions. These experiments were carried out using the same temperature range as above.

2.2. Calculation of osmotic pressure

The osmotic pressure has to be counterbalanced by the applied trans-membrane pressure. Therefore, the pressure need to obtain a given water flux will be higher, or, the water flux at a given trans-membrane pressure will be lower. This can be expressed by the phenomenological equation for the water flux, originally introduced by Kedem and Ketchalsky.

$$J_v = L_p(\Delta P - \sigma.\Delta\pi) \tag{1}$$

where L_p is water permeability (l/m².h.bar); $\Delta\pi$ is osmotic pressure; ΔP is trans membrane pressure (bar) and σ is rejection coefficient.

For high salt concentrations this equation is inadequate and the Pitzer equation can be applied. This approach has been used for a nanofiltration application by Van der Bruggen et al. [9]. The osmotic pressure of an organic solute can be calculated as

$$\Delta\Pi org = A_1 c + A_2 c^2 + A_3 c^3 \tag{2}$$

and

$$A_1 = \frac{R.T}{M} \tag{3}$$

where A_i is the viral coefficients with A_2 and A_3 considered as negligible for concentrations up to 100 g/L. R is the ideal gas constant, M is the average molar mass of the organic/polymer and T is the absolute temperature of the solution.

2.3. Cylinder experimental procedure

In a lab-scale dead-end module (Sterlitech™ HP4750) stirred cell, the membrane piece was inserted into a bottom cell of the cylinder which was kept by a membrane disc and a stainless steel porous support disc. The active membrane area was 12.56 cm^2 with a cell height of 22.4 cm. The feed solution is poured in the inside body of cylinder where a stirring bar is installed to stir continuously avoiding sedimentation on the membrane surface at the bottom. The processing volume of cylinder is maximum 300 ml. A stable pressure of 10 bar is applied to the cell top of the cylinder. Distilled water is used to clean the module for each experiment to ensure the accuracy.

2.4. Crossflow filtration procedure

Crossflow filtration experiments (Amafilter Test Rig PSS1TZ) were conducted at a stable pressure of 10 bar for all experiments. Both permeate stream and retentate stream were recycled to the 10 liters feed-tank to keep the feed concentration constant and to limit the necessary feed water volume

[9]. For these studies, the feed solution is pumped to the membrane by a three-stage membrane pump. The filtration in a stainless steel pressurized cell – so-called the module (TZA 944) - occurs in cross-flow. Flat sheet membranes were used with a diameter of 0.09 m. The active surface of the membrane is 0.0044 m^2; the hydraulic diameter of the rectangular channel is 4.2 mm and the channel length is 293 mm.

The permeate flux J ($l/m^2.h$) was calculated from the time t (s) needed to obtain 4.0 ml of permeate:

$$J(l/m^2h) = \frac{4(ml)*3600(s/h)}{1000(ml/l)*t(s)*A(m^2)} \quad (4)$$

where A (m^2) is the effective membrane area (equal to active surface of membrane).

Samples of permeate and retentate were taken for each measurement; sampling was done in steady-state conditions (15 minutes after last change in parameter settings). In the experiments, a feed velocity of 40 l/min was maintained. The temperature is set with an electronic circuit (OMRON E5AJ) which can control automatically operational temperature. The temperature was varied from 20 to 70 ºC at different points with an increase step of 10 ºC for each experimental sample. The pressure was kept stable at 10 bars and the temperature was 25 ± 0.1 ºC in all experiments.

2.5. Experiments

Both dead-end cylinder tests and crossflow filtration tests were used. In a first stage, the membranes were tested in the dead-end cylinder with the feed solution of distilled water, salt solution and Victoria blue solution, respectively. These experiments were done at temperatures from 20 to 80 ºC with a stepwise increase of 10 ºC. The water flux at the outlet of the cylinder from the bottom is measured by a gauge glass. For the two last solutions, a feed and a permeate water sample is collected to measure its concentration and retention in each experiment. In a second stage, the same experiments for these solutions were applied in a crossflow unit (Amafilter, Test Rig PSS1TZ). The measurements of concentration and retention were done in the same way as mentioned above. An overview of all experiments is given in Table 2.

Table 2
Overview of experiments with different feed solutions (VB = Victoria Blue).

Feed solution	Membrane type			
	DK	DS 5 DL	N 30 F	NFPES10
Experiment with cyclinder				
Formula 1 (distilled water)	x	x	x	x
Formula 2 (salt, 10 g/L)	x	x	x	x
Formula 3a (VB, 50 mg/L)	x	x	x	x
Formula 3b (VB, 3.0 g/L)	x	o	o	x
Experiment with crossflow				
Formula 1 (distilled water)	x	x	x	x
Formula 2 (salt, 10 g/L)	x	x	x	x
Formula 3a (VB, 50 mg/L)	x	o	o	x
Formula 3b (VB, 3.0 g/L)	x			x
Formula 4a (10 g/L salt + 50 mg/L VB)	x	o	o	x
Formula 4b (10 g/L salt + 3.0 g/L VB)	x			x
Formula 5 (industrial wastewater)*	x			x

**: real wastewater samples.*
o: was rejected due to experimental problems (membranes were unstable)

3. Results and Discussion

3.1. Time and temperature dependence

3.1.1. Time dependence

Table 3 shows the extent of flux decline on a short timescale using dead-end filtration. The water flux was found stable at low temperatures (from 20 to 40 ºC). Some flux decline was observed at high temperature (from 50 to 70 ºC) (see Table 3), but the effect is limited to only a few percent, with only two values above 10%.

Table 3
Percentage of flux declines for DS 5 DK and NF PES 10 membranes.

Membrane type	Experimental formulas	Time (min.)	Flux decline (%) at different temperature (ºC)					
			20	30	40	50	60	70
Desal 5 DK	F2= Salt 10 g/L	*15/30*	0.00	0.00	0.00	0.22	1.68	9.14
		30/50	0.25	0.00	0.00	10.50	2.26	3.24
	F3a= 50mg/L VB	*15/30*	0.54	6.02	0.93	0.00	0.00	0.00
		30/50	0.84	2.91	0.77	0.00	0.00	0.00
	F3b= 3.0g/L VB	*15/30*	1.83	2.01	4.55	10.42	0.00	3.79
		30/50	0.57	0.00	6.26	5.81	5.81	1.15
	F4a= F1 + F2	*15/30*	0.00	3.73	3.26	3.34	4.52	3.45
		30/50	8.17	4.84	9.47	3.11	6.26	0.00
	F4b= F1 + F3	*15/30*	4.46	1.89	2.85	0.60	6.29	6.55
		30/50	5.80	6.42	1.40	0.06	6.80	1.45
NF PES 10	F2= Salt 10 g/L	*15/30*	0.76	3.87	3.84	3.49	9.31	19.80
		30/50	7.62	3.13	2.03	0.00	4.49	7.17
	F3a= 50mg/L VB	*15/30*	21.1	16.13	19.41	18.94	13.9	8.98
		30/50	5.89	9.22	6.20	13.92	7.51	7.35
	F3b= 3.0g/L VB	*15/30*	20.33	8.46	2.37	9.58	15.53	18.61
		30/50	11.16	2.66	0.34	9.55	6.88	13.07
	F4a= F1 + F2	*15/30*	7.83	8.85	19.40	11.61	4.74	21.09
		30/50	7.58	4.34	6.13	10.11	2.97	14.84
	F4b= F1 + F3	*15/30*	7.15	8.80	14.07	16.70	12.04	14.83
		30/50	4.67	7.09	9.48	10.46	11.11	10.20

15/30: flux decline at 30 minutes in comparison with the flux at 15 minutes
30/50: flux decline at 50 minutes in comparison with the flux at 30 minutes

Water fluxes were stable with time for F2 and F3a formulas with the Desal 5 DK membrane but fluxes tended to decrease as a function of time in most cases. The flux decline for NF PES 10 was more drastic than that of Desal 5 DK where a lower flux was observed. In addition, water fluxes fluctuated from 15 to 30 minutes in comparison to that in the later period of 30 to 50 minutes. In Table 3, it was not clear what the flux dependence on temperature is although there were obvious differences of flux decline at different temperatures.

3.1.2. Temperature dependence

To investigate the effect of temperature on nanofiltration, the system was operated at several temperatures (20, 30, 40, 50, 60, 70 ºC). After obtaining the first temperature, an equilibrium time of 15 minutes is respected before the water flux is measured. The temperature dependence on viscosity can be described by the following equation for the temperature range from 20 to 100 °C [20]:

$$Log\frac{\eta}{\eta_{20}} = \frac{1.3272(20-T) - 0.001053(T-20)^2}{T+105} \quad (5)$$

where η is the viscosity (poise) and T is the temperature (ºC).

The water flux was measured at different temperatures in which the

viscosity was calculated with this equation for both membranes. The calculated viscosity is given in Table 4 together with the water flux at different temperature. Figure 2 shows the relationship between the water flux and the inverse viscosity.

Table 4
The permeate flux (l/m2.h) at different temperatures and corresponding viscosity.

Temperature	20	30	40	50	60	70
η	1.002	0.7975	0.6529	0.5468	0.4665	0.4042
1/η	0.998	1.254	1.532	1.829	2.144	2.474
$Flux_{DS\ 5\ DK}$	54.09	91.53	131.42	154.57	188.49	231.27
$Flux_{NF\ PES\ 10}$	118.79	167.32	195.59	213.07	245.06	298.74
$\eta*Flux_{DS\ 5\ DK}$	54.2	73.0	85.8	84.5	87.9	93.5
$\eta*Flux_{NF\ PES\ 10}$	119.0	133.4	127.7	116.5	114.3	120.8

According to Table 4, the product of water flux and viscosity for NF PES 10: $\eta * Flux_{NF\ PES\ 10} \approx 120$ is nearly constant for any temperature. Thus, it can be concluded that the water flux is inversely proportional to viscosity for the NF PES 10 membrane.

However, for Desal 5 DK, the product of water flux and viscosity: $\eta * Flux_{DS\ 5\ DK}$ was not constant. This means that the flux and inverse viscosity were not linearly correlated. The flux tends to increase more than expected from the viscosity decrease. The viscosity effect obviously plays a role, but an additional increase of water flux was observed. The literature suggests that this may be caused by plasticization of the pores allowing more flux through the membrane than expected [21]. The plasticization of membrane surfaces will be explained in section 3.3.

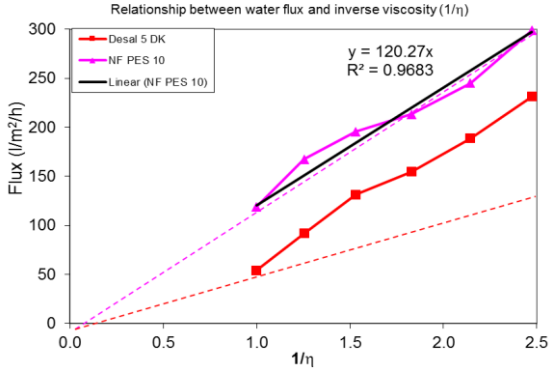


Fig. 2. Influence of temperature on fluxes: dependence of flux on inverse viscosity.

3.1.3. Osmotic pressure effects

The applied pressure was kept stable at 10 bar for all experiments, but the effective pressure is lower due to the effect of osmotic pressure. The effective pressure was calculated as (ΔP - $R*\Delta\pi$) with ΔP = 10 bar; R is the rejection of salt or dye. The corrected flux was calculated as $J_{corrected} = J * 10/(10 - R*\Delta\pi)$. These osmotic pressures were calculated for all experiments and given in Table 5.

Table 5
The osmotic pressure in all experimental formulas (Δπ, bar)

Osmotic pressure Δπ (bar)	Temperature (°C)					
	20	30	40	50	60	70
Δπ_F2=salt 10 g/L	5.15	5.32	5.50	5.67	5.85	6.02
Δπ_F3a= 50mg/L VB	0.02	0.02	0.03	0.03	0.03	0.03
Δπ_F3b= 3.0g/L VB	0.14	0.15	0.15	0.16	0.16	0.17
Δπ_F4a(=F1 + F2)	5.17	5.35	5.52	5.70	5.88	6.05
Δπ_F4b(=F1 + F3)	5.29	5.47	5.65	5.83	6.01	6.19

The osmotic pressures for the experimental formulas with only Victoria blue were very low. This means that water fluxes were not significantly affected by the osmotic pressure in the experiments where only this compound was added. However, the influence of osmotic pressure to water flux was taken into account for other experiment formulas where salts were added. All water fluxes were corrected for the osmotic pressure effect and are given in Figure 3 for both membranes.

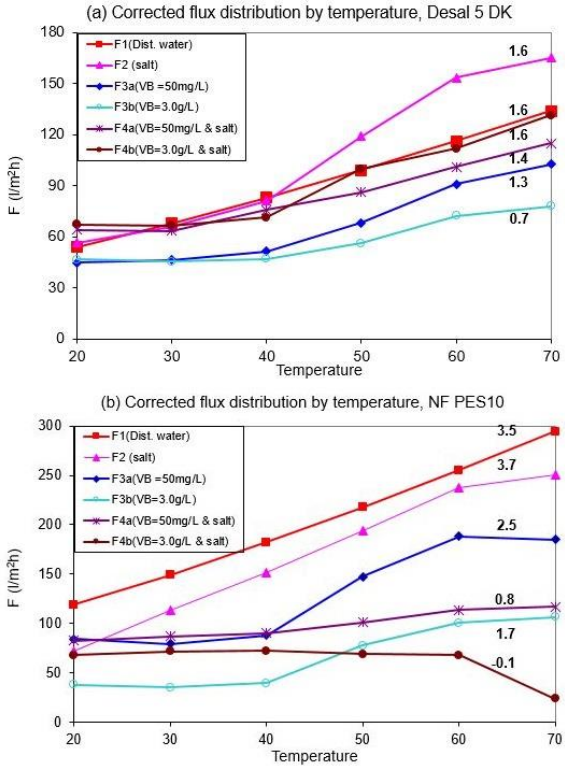


Fig. 3. Influence of temperature on fluxes: dependence of flux on inverse viscosity.

3.2. Concentration dependence and membrane fouling

3.2.1. Concentration dependence

It was observed that the water flux decreases when salt was added and when Victoria blue was added. The former effect can possibly be explained by the increasing osmotic pressure, while the latter is possibly due to adsorption of Victoria blue on the membrane or pore blocking by this organic compound. This may be concentration dependent. However, a remarkable observation is that the effect on the water flux when salts are present in the mixture-feed solution seems to be quasi-independent of the Victoria blue concentration. Besides that, the slope of the temperature curves decreases when Victoria blue was added indicating that temperature has a smaller effect on the flux when a higher concentration of organics and/or inorganics was present. The presence of salt in a mixed feed solution where a dye was added did not increase the effect on the fluxes.

All water flux curves were lower than the water flux curve of the experiment with distilled water. Thus, there was a fouling effect on these membranes with different concentration of salt, or Victoria blue, or both. Fouling will be discussed using the observation with the formulas that have a difference concentration of only Victoria blue, or mixed compound of Victoria blue and salts. For NF PES 10 membrane, the slope of the curve obtained in the experiment with only salt in the solution was larger than that of distilled water; this can be explained by the change of the membrane surface at elevated temperature. This is the so-called plasticizing effect as mentioned before.

The corrected flux curves for Desal 5 DK (Figure 3-a) where both dye and salts were added, formulas F4a and F4b, nearly overlapped with the flux curve for distilled water, while there was a small difference for NF PES 10 (Figure 3-b). This indicates that there was not much fouling on Desal 5 DK compared to NF PES 10. In addition, there were effects of temperature and concentration on the water flux, so the influence of fouling on this membrane seems to be quasi negligible. In conclusion, there was no significant effect of fouling on Desal 5 DK membrane. However, for NF PES 10 a fouling effect was observed. Furthermore, the flux curves where only Victoria blue are used, formulas F3a and F3b, have different curve slopes; that value was 1.26 and 0.7 for Desal 5 DK, and 2.5 and 1.6 for NF PES 10, respectively. This means that there was an effect of concentration of Victoria blue to the water

flux and membrane fouling. This can be explained by the adsorption of Victoria blue on the membrane, which causes an obstacle for the transport of water.

Differences in the viscosity of the feed solution can be another effect to cause the slope of temperature curves decreases. The viscosity of sodium sulphate is higher than the viscosity of distilled water (at 20 ºC) [24]; thus, the total viscosity of salt solution, which includes salts and Victoria blue, is higher. A higher viscosity of solution causes a lower flux. However, the viscosity of the feed-salt solution at different temperatures was not measured.

3.2.2. Membrane fouling

Fouling will be discussed using the observations with the formulas that have a different concentration in formulas F3a (VB= 50 mg/l), F3b (VB= 3.0 g/l), F4a (VB= 50 mg/l and salt), and F4b (VB= 3.0 g/l and salt). This fouling effect is explained by the slopes of the curves in figure 3. The flux curves of F3a and F3b, where only Victoria blue are used, have different slopes: 1.26 and 0.7 for Desal 5 DK, and 2.5 and 1.6 for NF PES 10, respectively. This means that there is an effect of the concentration of Victoria blue to the water flux and membrane fouling. In the mixture solution of Victoria blue and salts, formulas F4a and F4b, the flux curves nearly overlapped for Desal 5 DK (Figure 3-a), while there was a small difference for NF PES 10 (Figure 3-b), showing again that Desal 5 DK is not influenced by fouling. However, for NF PES 10, a low flux and a lower slope of the curve was observed, in comparison with that of distilled water (formula F1), indicating a fouling effect for NF PES 10.

In comparison with the flux in formula 3, F3a and F3b, the fluxes in formula 4, F4a and F4b, where salts are added, are different. The presence of salts in the mixture seems to have decreased the dependence of flux on the concentration of dye. Thus, the water flux does not only depend on temperature but also depends on the concentration of dye and of the viscosity of the feed solution.

3.3. Rejection of salts and dyes

Rejection of salt and dyes is a critical aspect of the membrane performance for application on dye baths. The retention of salt (sodium sulphate) and dye (Victoria blue) for these membranes is shown in Figure 4 for the experimental formulas where salt (10 g/L Na_2SO_4) and/or dyes (50 mg/L or 3.0 g/L Victoria blue) or their mixtures were added.

3.3.1. Rejection of salts

According to Figure 4-a, the retention in the experiments with only salt, F2 formula at 10 g/L salt, for both membranes decreases when the temperature increases. The retention curve of F2 (salt) for Desal 5 DK membrane quickly decreases with temperature, from 95% at 20 ºC to 50% at 70 ºC, while it slightly decreased for membrane NF PES 10, from 37% at 20 ºC to nearly 30% at 70 ºC. This indicates that there is a dependence of temperature on the rejection of salt.

The retention decreases as a function of temperature, probably due to plasticizing. At high temperature, the membrane structure becomes more elastic so that the pore size of membrane is somewhat larger than at low temperature, causing a lower retention of salts.

3.3.2. Rejection of dyes

In order to compare the retention of color by each membrane when applying different formulas, Figure 4-b can be used for both membranes. Most retention curves were found to decrease when the temperature increases and the retention of dyes was nearly 100% at low temperature and then decreased at high temperature. This indicates that there is a dependency of temperature on the rejection of dyes. In Figure 4-b, it can be seen that the retention of Victoria blue is the highest in the presence of only Victoria blue for both membranes. The higher concentration of Victoria blue was used, the higher the retention. Moreover, the decrease of Victoria blue retention is the highest in the presence of salts. It was observed that the retention decreases somewhat for a higher concentration of Victoria blue, although the difference is negligible. However, for NF PES 10 membrane, a remarkably strong effect was obtained for the experiment with 50 mg/l Victoria blue without addition of salts (F3a).

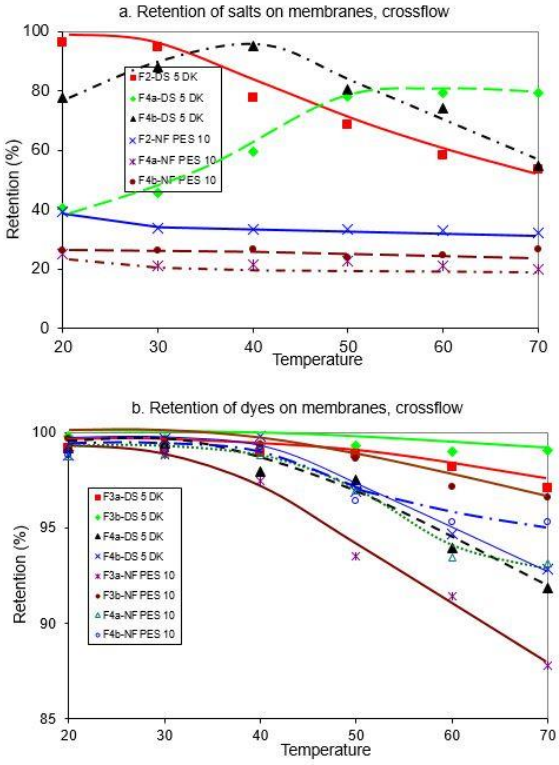


Fig. 4. Retention of salts and dyes for Desal 5 DK and NF-PES-10.

For the experiments with mixed solutions, F4a and F4b formulas, the retention curves were not much different, both for Desal 5 DK and NF PES 10. Thus, the concentration of Victoria blue has a smaller effect in the presence of salts. In other words, salts seem to have a negligible effect on the retention of dyes.

Thus, it can be concluded that the retention does not only depend on the temperature but also depends on the concentration of dyes and salts, and they have a reciprocal effect.

3.4. Experiments with real wastewater samples

3.4.1. Water flux and membrane fouling

The water fluxes for the experiments with real dye baths are given in Table 6. All fluxes increase with temperature (apart from the anomaly at 70 ºC for NF PES 10). In comparison to the flux with distilled water, the fluxes with real wastewater were found to be lower.

The water fluxes were corrected by Kedem and Katchalsky's equation and indicated in Table 6. These corrected fluxes are shown in Figure 6.

For Desal 5 DK (Figure 5-a), the fluxes for real wastewater were 32 l/m^2.h at 20 oC and 90 l/m^2.h at 70 ºC, compared to 55 l/m^2.h at 20 ºC and 135 l/m^2.h at 70 ºC for distilled water. This corresponds to 42% flux decline at 20 ºC, and 34% flux decline at 70 ºC. In addition, the slope of the curve for Desal 5 DK as a function of temperature was lower than that in the experiment with distilled water (1.3 and 1.6, respectively). Thus, there is an effect of temperature on membrane fouling: a higher temperature has more effect on fouling than a lower temperature.

For NF PES 10, similar observations were made, but the effect of flux decline was much larger. The water flux curve of real wastewater was very low: the flux was 4 l/m^2.h and increased to 12 l/m^2.h at 70 ºC, compared to a water flux of 120 l/m^2.h at 20 ºC and 295 l/m^2.h at 70 ºC for distilled water. This corresponds to 97 % flux decline at 20 ºC and 96 % flux decline at 70 ºC. The slope of the curve of flux as a function of temperature for NF PES 10, was smaller for real wastewater than for distilled water (0.17 and 3.52, respectively).

3.4.2. Removal of salts

From Figure 5-b, it can be seen that the salt retention decreases slightly when the temperature increases in both cases (Desal 5 DK-salt and NF PES

10-salt formulas). For Desal 5 DK, the retention of salt is about 60% at 20 ºC, and decreases to about 50% at 70 ºC; for NF PES 10, it is about 15% and 10%, at 20 ºC and 70 ºC, respectively. This indicates that the retention of salt depends on temperature, but the effect is small.

3.4.3. Removal of color

The removal of color by nanofiltration is the most important aspect for application of nanofiltration. A very high color rejection is necessary to reuse the treated water in the process. The experimental results are given in Figure 5-b as well.

It can be seen that the retention curves decrease with temperature for both membranes. The slope of the curve of Desal 5 DK is somewhat smaller than that of NF PES 10. Thus, the rejection of color by NF PES 10 membrane is more affected by temperature than the rejection of color by Desal 5 DK membrane. The retention of color with Desal 5 DK is nearly stable with temperature at a value of more than 90%, while for NF PES 10 the retention decreases from about 60% at 20 ºC to 50% at 70 ºC.

4. Conclusions

It can be concluded that Desal 5 DK membrane is better than NF PES 10 for the removal of color and salt. In addition, Desal 5 DK does not face a significant fouling problem in comparison to NF PES 10. In a real application for the treatment of wastewater from the textile industry, the treated water can be reused in the process. However, nanofiltration of dye baths from textile industry is very complex. The flux increases with temperature according to the Hagen-Poiseuille equation, but the influence of temperature depends on the composition of the dye baths. A concentration dependent fouling effect related to the dyes can be assumed.

Nanofiltration can be applied to reject color and salts from textile wastewater. With a low rejection of salt and a high rejection of color, reuse of water containing salts and energy savings can be combined. NF PES 10 appears to have suitable properties to achieve this. However, the performance of this membrane was found to be substantially affected by fouling, leading to a drastic flux decline.

A plasticizing effect leading to pore size enlargement at elevated temperatures (> 50 ºC) was assumed. As a consequence, the retention of salts and dyes slightly decreases with temperature. In addition, fouling is more expressed at high temperatures. This can lead to membrane damage, especially at elevated temperatures. These effects are the main causes of a poor performance of nanofiltration membranes at high temperature. Nevertheless, a smart choice of membranes allows to overcome these challenges.

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Table 6
Water flux (L/m².h) and osmotic pressure on the membranes with temperature.

Membrane types	Temperature (ºC)					
	20	30	40	50	60	70
Desal 5 DK	32.6	37.0	43.5	61.8	74.9	89.3
NF PES 10	4.1	6.1	7.5	14.3	14.6	9.4
Osmotic pressure (Δπ)						
Δπ-F5	2.06	2.13	2.20	2.27	2.34	2.41

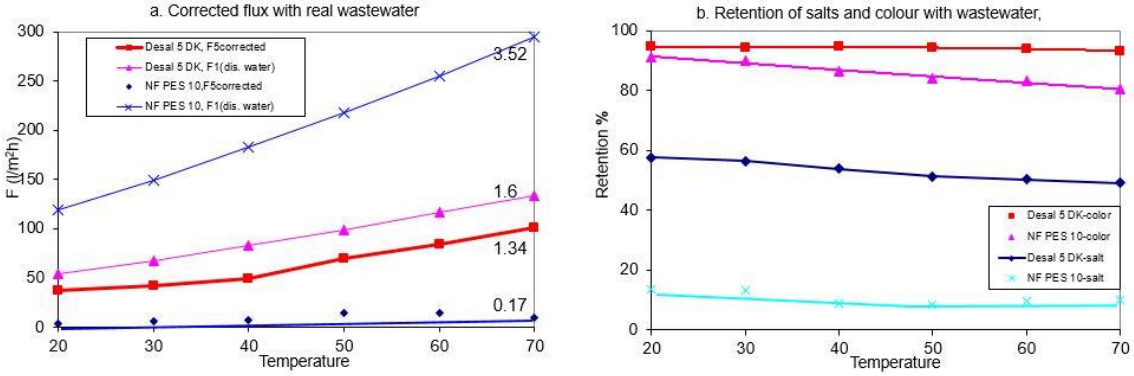

Fig. 5. Flux and retention on membrane with real wastewater.

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