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Influence of commercial detergents on UF membrane ageing: Case of drinking water

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Abstract. During cleaning steps, ultrafiltration membranes are mechanically and chemically stressed. This may result in membrane degradations and failures. In this paper, polysulfone membranes were used to evaluate membrane deteriorations by commercial detergents in static conditions. Ageing of the membrane was simulated by immersing samples in solutions containing commercial detergents with various concentrations, temperatures and times defined by experimental designs. Indeed, an innovative approach in the chemical membranes ageing researches, based on methodological tools, was used in order to achieve significant ageing experiments without using an accelerated ageing protocol. The macroscopic changes were monitored by permeability measurements and mechanical strength tests coupled with a microscopic characterization by ATR-FTIR and HRSEM. The present work details results obtained for three commercial detergents: an alkaline, an acidic and an enzymatic detergent. It was found that the detergents used in the industrial advised conditions (concentration, temperature and time of contact) were not detrimental for membrane properties (permeability and elongation at break) and so for the quality of the produced water. Over the industrial cumulated time of contact, different ageing effects can be observed and compared with the ones induced by NaOCl.

Keywords: polysulfone; ageing; ultrafiltration; hypochlorite; commercial detergents; experimental designs; macroscopic characterization; microscopic characterization.

1. Introduction

For applications in drinking water production by ultrafiltration, the most frequent procedure for cleaning membranes is short back flushing with chlorine at low concentration each day. A chemical cleaning step with detergents or chlorine is also set up each month, more or less,

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depending on the irreversible fouling (Causserand *et al.* 2008). The cleaning products react relatively rapidly and unselectively with a wide variety of organic substrates and as a consequence they could also attack the polymeric materials constitutive of the membrane (Gaudichet-Maurin and Thominette 2006). Indeed, although chemical solutions are widely used to clean membranes, they can also be responsible for changes in membrane properties. The two major drawbacks are (i) the gradual change in membrane functional properties so that the production can no longer meet requirements in terms of volume or quality and the hollow fibers breaks up; (ii) the system has to be shut down for maintenance. So contact with these chemical products (oxidants, high pH, high temperature) plays an important role in the deterioration of the membrane (Causserand *et al.* 2006, Puspitasari *et al.* 2010, Wang *et al.* 2010, Awanis Hashim *et al.* 2011). This raises the problem of the anticipation of such changes in membrane properties (also called ageing), so as to be able to account for them in optimizing cleaning procedures. It is further complicated by the use of complex detergents (chelatants, surfactants, dispersion agents) in cleaning procedures. Moreover, formulation is generally a proprietary composition of detergent providers. The users at industrial scale do not know the exact composition of the cleaning solutions except for main components type.

Despite the numerous studies performed on cleaning performances of commercial detergents (Lindau and Jönsson 1994, Shorrock and Bird 1998, Liikanen *et al*, 2002, Väisanen *et al.* 2002, Li *et al*. 2005, Zondervan and Roffel 2007, Field *et al.* 2008, Porcelli and Judd 2010, Ettori *et al.* 2011), very few works have been focused on the membrane ageing resulting from the use of commercial detergents (Rabiller-Baudry *et al.* 2002, Bégoin *et al.* 2006 and Delaunay *et al.* 2006).

So, the aim of this study is to identify, evaluate and compare the effects of commercial chemical cleaning solutions on the degradation of hollow fiber ultrafiltration membranes (polysulfone, PSf) used in drinking water production. For that, this work is focused on three industrial detergents: two detergents usually used in classical industrial cleaning step (a complex acidic detergent commonly used to eliminate inorganic fouling and a complex alkaline detergent commonly used to eliminate organic fouling) and an enzymatic detergent (for curative use). These cleaning chemicals are expected to be more and more used in cleaning procedures in order to reduce the use of harmful cleaning/disinfecting solution such as NaOCl (and also to answer to the new membrane requirements and/or to the more and more restrictive sanitary and environmental regulations (Zondervan *et al.* 2007)). So the impact of these detergents on membrane ageing will be compared. Correlating these ageing data with the previously published ones on cleaning (Table 1), the reader will be able to evaluate by himself the balance between the cleaning efficiency and the ageing damages. As a consequence, in function of industrial configuration, the reader would be able to identify which cleaning parameters would be avoided to reduce membrane damages. For this purpose an experimental designs approach was chosen in order to evaluate, compare and quantify the ageing effects of chemical parameters of commercial detergents with an optimized number of experiments.

2. Materials and methods

2.1 Membranes

Studies have been carried out using in/out ultrafiltration hollow fibers polysulfone membranes (Aquasource, France, 0.02 µm nominal pore size). The industrial module (7 m²) was supplied in

Table 1 Summary of the studies realized using commonly used commercial detergents in membrane ultrafiltration cleaning

Application	Detergents	Membrane type	References
Skim milk (Lait de Montagne, UHT, Carrefour, France)	P3-Ultrasil 10 (0.1 wt.%) Ultraclean II (0.3 vol.%)	UF PES	Delaunay *et al*. 2006
Skim milk (Lait de Montagne, UHT, Carrefour, France)	P3-Ultrasil 10 (-) Ultraclean II (-)	UF PES	Rabiller-Baudry *et al*. 2006a
Skim milk (Lait de Montagne, UHT, Carrefour, France)	P3-Ultrasil 10 (0.1 or 0.4 wt.%) Ultraclean II (0.3 vol.%)	UF PES	Rabiller-Baudry *et al*. 2006b
Skim milk (Lait de Montagne, UHT, Carrefour, France)	P3-Ultrasil 10 (0.1 or 0.4 wt.%) Ultraclean II (0.3 vol.%)	UF PES	Rabiller-Baudry *et al*. 2008
Skim milk (Lait de Montagne, UHT, Carrefour, France)	P3-Ultrasil 10 (0.4 % w/w) P3-Oxonia (1 % or 10 % w/w) P3-Oxonia Active (1 % or 10 % w/w)	UF PES	Paugam *et al*. 2010
BSA (80 ppm)	P3-Ultrasil 10 (from 0.1 to 1 wt.%)	UF PSf UF PVDF	Nyström and Zhu 1997
BSA (1 g.L^{-1}, pH = 5)	F80 FILTER HE (1 %) F83 FILTER E (1 %) F86 FILTER VE (1 %) F89 FILTER HH (1 %) F91 FILTER VH (0.5 %)	UF PSf	Platt and Nyström 2007
WPC (reconstituted 3.5 wt.%) Pulp and paper mill	P3-Ultrasil 11 (0.5 wt.%) Libranone 960 (0.1 wt.%)	UF PES UF PA UF CE	Väisänen *et al*. 2002
WPC (WPC80 reconstituted with DIW)	P3-Ultrasil 75 (0.14% w/w) P3-Ultrasil 91 (0.45% w/w)	UF PSf / PP UF PVDF UF PES	Lawrence *et al*. 2006
Glutamic acid	P3-Ultrasil 11 (pH = 12.0)	UF PSf	Li *et al*. 2005
Spent sulphite liquor	P3-Ultrasil 11 (0.5 wt.%)	UF PES UF PSf	Weis *et al*. 2003
Spent sulphite liquor	P3-Ultrasil 11 (from 0.05 to 0.5 wt.%)	UF PES UF PSf UF R-CE	Weis *et al*. 2005
Lignosulphates	P3-Ultrasil 11 (0.1 wt.%)	UF PES	Weis and Bird 2001
Sulphite pulp mill	P3-Ultrasil 96 (0.6 vol.%) P3-Ultrasil 75 (0.5 vol.%) Berocell 537 (0.25 vol.%)	UF PES-PlyA	Wallberg *et al*. 2001
Goat milk Beetroot juice Cow milk	P3-Ultrasil 10 (0.25 % w/v) P3-Ultrasil 11 (1 % w/v)	Ceramic NF PE	Astudillo *et al*. 2010
Wastewater	Triclean 212F (High pH cleaner)	UF PES RO PA	Chen *et al*. 2003
Wastewater	Divos 110 (pH = 9.3) Divos 2 (pH = 1.5) Divos 25 (pH = 2.0)	UF	Te Poele *et al*. 2005
Oily waste water	P3-Ultrasil 70, P3-Ultrasil 75, P3-Ultrasil 11, P3-Ultrasil 91 (1 %)	UF PSf	Lindau and Jönsson 1994
Surface water	4Aquaclean Fer 12, P3-Ultrasil 70, Kleen MTC 411, P3-Aquaclean Sal, P3-Ultrasil 115 (0.05 mol.L^{-1})	UF	Zondervan and Roffel 2007
Surface water	Auxiclean B.13 (0.5–2 % w/v)	UF PSf	Arnal *et al*. 2008

preservative solution (glycerin) and before usage, it was rinsed with distilled water and then, washed with NaOH (pH 8.5; 1 hour; transmembrane pressure (TMP) = 0.1 bar) and citric acid (pH 4.0; 1 hour; TMP = 0.1 bar), with distilled water flushing between the alkaline and the acidic step and after the acidic step. The initial permeability of the module was measured in order to have a reference value of the native membrane. This module was then destroyed; some hollow fibers were initially characterized (permeability (measurement accuracy of 8%), mechanical properties (measurement accuracy of 3 - 4%) and microscopic characterization), the others were sampled.

2.2 Ageing solutions

Three cleaning solutions were studied throughout the experimental tests. All the solutions are commercial detergents of proprietary composition provided by Ecolab (Issy–les–Moulineaux, France).

- Acidic solution: P3-Ultrasil 75, a strong acidic detergent composed of nitric and phosphoric acid.
- Alkaline solution: P3-Ultrasil 110, an alkaline detergent containing emulsifying surfactants.
- Enzymatic solution: a combination of P3-Ultrasil 67 (mainly composed of proteolytic enzymes and alkylamine oxide components) and P3-Ultrasil 69New (mainly composed of alkaline components, potassium hydroxide and phosphonates) used to optimize the enzymatic activation.

The tested ageing conditions are detailed in Table 2(a). c° is the effective industrial concentration used during cleaning sequences on drinking water plants to reach the target of pH below. c° is respectively 0.3% wt (pH = 1.8), 0.7% wt (pH = 11.0) and 0.3% wt/0.8%wt (pH = 10.5) for P3-Ultrasil 75, P3-Ultrasil 110 and P3-Ultrasil 67/69N. They are commonly used at 40°C-50°C. pH has not been corrected (Table 2(a)).

In order to free from the broad diversity of the water used on plants during the cleaning steps (tap water, osmosed water, softened water), the water used for dilution or reagent preparations was Mont Roucous water (France, pH = 5.85, constant and known composition). This choice is explained by the lowest dry residue in Europe (25 mg.L^{-1}). In order to keep constant the ageing conditions (concentration and pH) over time, the solutions were changed each week. In the same time, fibers were also aged in water and water with bisulfite in the same ageing conditions (temperature and time duration) in order to quantify natural ageing.

2.3 Experimental approach based on experimental designs

Designs of experiments and especially response surface methodology (RSM) consist of a group of mathematical and statistical techniques that can be used to quantify the relationships between the response and the independent variables. In RSM, an empirical mathematical model is postulated and a suitable experimental design is performed to estimate the coefficients of the model and to predict the response in the whole domain with a good precision. Depending on the constraints on the experimental domain or on the possible values of the factors, different experimental designs can be performed. The most important parameters are the accuracy of the model equation and the quality of the prediction in the domain (Bas *et al.* 2007).

Thus, in the context of the chemical membrane ageing, RSM was used to cover a large experimental domain, to evaluate the influence of the parameters and to optimize the number of experiments. A mathematical empirical model was postulated and more precisely a second order polynomial model to capture the possible nonlinear effects and curvature in the domain:

$$Y = b_0 + \sum_{j=1}^{k} b_j X_j + \sum_{j=1}^{k} b_{j-j} X_j^2 + \sum_{i<j}\sum b_{i-j} X_i X_j$$

Table 2 Experimental field of ageing studies (a) and experimental designed conditions of ageing for P3-Ultrasil 110, P3-Ultrasil 75 and P3-Ultrasil 67/69New (b)

Table 2(a)

	Coded variable	**P3-Ultrasil 110**			**P3-Ultrasil 75**			**P3-Ultrasil 67/69New**		
		Low (-1)	(0)	High (+1)	Low (-1)	(0)	High (+1)	Low (-1)	(0)	High (+1)
Concentration	**X1**	0.35%wt	0.7%wt (pH = 11 à 40°C)	1.4%wt	0.15%wt	0.3%wt (pH = 1.8 à 40°C)	0.6%wt	**P3-Ultrasil 67:**		
								0.15 %wt	0.3%wt (pH = 10.8 à 40°C)	0.6 %wt
								P3-Ultrasil 69 New:		
								0.8%wt		
Time of contact (days)	**X2**	7	30	180	7	30	180	7	30	180
Temperature (°C)	**X3**	20	30	40	20	30	40	20	30	40
Number of experiments						13 (17 with 4 test points)				

Table 2(b)

N°Exp	**Concentration (*c°)**	**Time (days)**	**Temperature (°C)**
1	0.5	7	20.0
2	1.0	7	20.0
3	2.0	7	20.0
4	0.5	30	20.0
5	2.0	30	20.0
6	0.5	180	20.0
7	1.0	180	20.0
8	2.0	180	20.0
9	0.5	7	40.0
10	2.0	7	40.0
11	1.0	30	40.0
12	0.5	180	40.0
13	2.0	180	40.0
Test points			
14	2/3	14	20.0
15	1.5	90	20.0
16	2/3	90	40.0
17	1.5	14	40.0

with X_j (j = 1, 2, ... k) the undimensionnal variables.

To estimate at best the coefficients of this model, different experimental designs were established in function of the chemical agent and of the possible values of the factors.

The corresponding ageing factors used for this study are defined by the conditions detailed in Table 2(a). This table shows the values for high and low experimental settings. To have fairly spread experimental tests on the all experimental field, a log-scale was used in the construction of the experimental designs. This choice of the temperature was justified by a range between 20 and 40°C. Those temperatures let to study the commonly used industrial temperatures. The choice of the contact time and concentration were focused on the effective industrial concentration and cumulated time applied on the plants during the cleaning procedures all along the membrane life expectancy.

To take into account the different constraints on the possible values of the factors, specific experimental designs were necessary. D-optimal designs were established with certainty that the prediction in the whole experimental domain would be acceptable (variance function of the predicted response < 1).

Designs of experiments with 13 experiments (Table 2(b)) were respectively performed. To test the validity of the model inside the domain, 4 test-points were added to the designs (Table 2(b)).

From the results for each studied response Y (Y_1: permeability ($L.h^{-1}.m^{-2}.bar^{-1}$) and Y_2: elongation at break (%)), the estimates of the coefficients were calculated using multilinear regression. The calculations have been performed with the Nemrod-W software (LPRAI, Marseille, France), developed for building and processing designs of experiments. Those calculations have been realized for the designs of experiments with and without the test points. The results present in this paper are those achieved taking into account the test points.

For validation of the model adequacy, several techniques have been used: test points, residual analysis, ANOVA (ANalysis Of VAriance) and prediction error sum of squares residuals (especially the coefficient of determination R^2). After validation, this model could be used to predict the response all over the domain and the visualization of the predicted model equation can be obtained by the response surface plot (3D response) and contour plot (2D response). The response surface plot is the theoretical three-dimensional plot showing the relationship between the response and the independent variables. The two-dimensional display of the surface plot is called contour plot and in the contour plot, lines of constant response are drawn in the plane of the independent variables. The contour plot helps to visualize the shape of a response surface. When the contour plot displays ellipses or circles, the center of the system refers to a point of maximum or minimum response. These plots give useful information about the model fitted. However, one must not forget that the contours (or surfaces) represent contours of estimated response and the general nature of the system arises as a result of a fitted model, not the true structure (Bas *et al.*2007).

2.3.1 Adequation with the applied industrial conditions

Static ageing experiments have been conducted in a continuous manner (more practical implementation than dynamic ageing) whereas in an industrial plant, membranes are in contact with water most of the time and with cleaning agents for short, periodic times. So, from an industrial point of view, only results until 30 days of ageing are representative. Other ageing conditions have been realized in order to look deeply into long term ageing effects. Indeed, if a cleaning protocol is considered (20 to 30 minutes) every week at c° (the industrial concentration of each detergent) and a stronger cleaning protocol is considered (3 hours) every months at c°, in soaking conditions, it is possible to establish an equivalence between experimental time of ageing and the effective and cumulated industrial time of contact. 7 days of ageing (in soaking conditions, 168 hours) would correspond to a cumulative industrial time of contact of 2.8 years. 30 days of ageing (in soaking conditions, 672 hours) would correspond to an industrial cumulative time of contact of 11.2 years). 180 days of ageing (in soaking conditions, 4320 hours) would correspond to an industrial cumulative time of contact of 72 years).

2.4 Methods of characterization

The membranes were characterized by conventional techniques: measurements of permeate flux, elongation and tensile strength at break, high resolution scanning electron microscopy (HRSEM) and Attenuated Total Reflectance Fourier Transform Infra-Red (ATR-FTIR). All protocols of measurements and sample preparation and conditioning are described with further details by Régula *et al.* (2012).

For the measurements of permeability, lab- scale modules were made using 5 fibers of 40 cm in length. Modules are made by potting the fibers in a PVC shell, with “epoxy” glue (Moulin et al, 2000). The permeability (at 20°C) of the hollow fibers was determined according to Darcy’s law by filtration of Mont Roucous water from 0 to 1.4 bar. Then, permeability of aged fibers is compared to the measured initial value.

The mechanical properties of the membrane (elongation and tensile strength at break) were measured on fibers under wet conditions using dynamic mechanical analysis (Zwicki-Line Testing Machines Z2.5). Previous studies underlined that elongation at break (E_l) was more sensitive to membrane degradation than tensile strength T_s (Gaudichet-Maurin et Thominette 2006). This point has been assessed in this study and for this reason, only elongation variation will be presented in the following experimental study.

The surface of the membrane was carefully examined by a high resolution scanning electron microscope (HRSEM) (JSM 6320F, Jeol Ltd., Japan). Only qualitative interpretations were realized on the images: crackles or changes in surface morphology. The results were compared with the images of the native membrane obtained after the preservative removal.

ATR-FTIR spectra were recorded on a Bruker spectrometer (Vertex 70). The detector is a DLaTGS (400–7000 cm^{-1}). The detected peaks and the exact wavenumber of each one are given in Table 3. Even if the exact composition of the polymer is not known, the initial membrane composition can be considered rather homogeneous. Apart the main polymeric material (Polysulfone), additives are most likely used in the studied fibers (PEG and PVP). As a consequence, the ATR-FTIR characterization will also cover these polymeric additives, especially PVP, even if it is present in small amounts (Gaudichet Maurin 2005). Indeed, even if those additives do not have influence on PSf degradation, they play a non-negligible role in the degradation of the fiber mechanical properties.

The spectra of each aged sample give only qualitative information and constitute a useful weapon to understand the influence of each chemical oxidant on membrane ageing. To be able to compare peak intensities of all the spectra, ratios H_x / H_{1243} were calculated and allow us to determine the peaks the most affected by the ageing conditions. An example is given on Figs. 1(a)-(c) Throughout the following work, results analysis was focused on the 4 peaks whose behavior was the most representative of the ageing:

- 1294 cm^{-1} / 1323 cm^{-1}: υ_{as} (SO_2) PSf
- 1365 cm^{-1}/ 1386 cm^{-1}: Not identified

Table 3 Identification of the main characteristically peaks from ATR-FTIR spectrum of the studied PSf hollow fibers

Data from literature Gaudichet-Maurin (2005)		**Experimental data**
Wavenumber (cm^{-1})	Characteristic bands of groups and compounds υ: vibration (υ_{as}: asymmetric; υ_s: symmetric) δ stretch	
3100 - 3000	$\boldsymbol{\upsilon}$ (= C-H) arene PSf	
2968	$\boldsymbol{\upsilon}_{as}$ (C-H) CH_3 PSf	
2873	$\boldsymbol{\upsilon}_s$ (C-H) CH_3 PSf	
1673	$\boldsymbol{\upsilon}$ (C-O) PVP amide	1663
1586	$\boldsymbol{\upsilon}$ (C-H) arene PSf (squaring stretch)	1586
1504 - 1410	$\boldsymbol{\upsilon}$ (C-H) arene PSf (semicircle stretch)	1504 1488 1464 1411
-	Not mentioned	1386
-	Not mentioned	1365
1324 - 1295	$\boldsymbol{\upsilon}_{as}$ (SO_2) PSf	1323 1294
1245	$\boldsymbol{\upsilon}$ (C-O) aryl-O-aryl PSf	1243
1170 - 1152	$\boldsymbol{\upsilon}_s$ (SO_2) PSf	1170 1151
1107 - 1014	δ (C-H) para arene (in plane) PSf	1014 1081 1106
835	δ (C-H) para arene (out of plane) PSf	874 854 834
692	δ (C-H) arene PSf	738 716 692

- 1411 cm^{-1} / 1464 cm^{-1}: $\boldsymbol{\upsilon}$(C-H) arene PSf (semicircle stretch)
- 1663 cm^{-1}: $\boldsymbol{\upsilon}$ (C-O) PVP amide

All these peaks present a homogeneous and decreasing evolution with ageing conditions. It can be noticed that new peaks can appear and other can completely disappear according to the ageing conditions. This would be detailed in greater details in the following parts.

3. Results and discussion

The experimental values (permeability and elongation at break) were used to calculate ageing models via Nemrod-W software (LPRAI, Marseille, France). As described above, several chniques have been used to validate the models: test points, residual analysis, ANOVA (ANalysis Of Ariance) and prediction error sum of squares residuals (coefficient of etermination R^2). The achieved results (the model coefficients and their respective significance, R^2 values and ANOVA)

(a)

(b)

(c)

Fig. 1 Ratios H_x / H_{1243} used for the identification of the chemical bonds the most affected by P3-Ultrasil 110 ageing (a), by P3-Ultrasil 75 ageing (b), and P3-Ultrasil 67/69N ageing (c)

Table 4 Model coefficients, their respective significance and R^2 values achieved with experimental designs (a) and ANOVA (b) results for permeability and elongation at break designs for ageing in P3-Ultrasil 110

Table 4(a)

	P3-Ultrasil 110			
	Y_1: Lp (L.h^{-1}.m^{-2}.bar^{-1})		**Y_2: E_l (%)**	
R^2	0.834		0.771	
	Coefficient	**Signif. %**	**Coefficient**	**Signif. %**
b_0	288.173	< 0.01 ***	48.345	< 0.01 ***
b_1	19.852	4.25 *	-2.320	0.660 **
b_2	34.477	0.309 **	0.139	83.4
b_3	17.352	3.26 *	-1.313	3.57 *
b_{1-1}	-12.522	47.9	-3.050	4.75 *
b_{2-2}	48.517	2.06 *	1.588	25.9
b_{1-2}	13.582	18.6	-0.394	60.2
b_{1-3}	14.580	11.5	-0.483	47.0
b_{2-3}	7.480	39.1	-0.975	16.5
***: significance > 99.9%; **: significance > 99.5%; *: significance > 95%				

Table 4(b)

P3-Ultrasil 110 – ANOVA					
Sum of squares (SS)	**Degrees of freedom (DF)**	**Mean square (MS)**	**F-test**	**Signif. %**	**Sum of squares (SS)**
Y_1: Lp (L.h^{-1}.m^{-2}.bar^{-1})					
Regression	$2.96101.10^4$	8	$3.70126.10^3$	5.0356	1.73 *
Residual	$5.88018.10^3$	8	$7.35022.10^2$		
Total	$3.54902.10^4$	16			
Y_2: E_l (%)					
Regression	118.7580	8	14.8447	3.3719	5.3
Residual	35.2197	8	4.4025		
Total	153.9776	16			
***: significance > 99.9%; **: significance > 99.5%; *: significance > 95%					

are gathered in Tables 4-6. All these tools lead to conclude that some regression models are significant: the changes in the selected response cannot occur by coincidence and those changes in the response are considered to be the effects of the influence factors. So those regression models can be considered reliable for the prediction of the changes of the permeability and the elongation at break in the range of operating conditions tested. All along the discussion, the reader can refer to Table 7 which sums up the ageing effect observed on permeability and mechanical properties.

3.1 Caustic detergent: P3-Ultrasil 110

For this caustic detergent, c° is equal to 0.7%wt (pH = 11.0, 40°C). Permeability results obtained at 20°C and 40°C are shown in Figs. 2(a)-(b). The coefficients of the models, R² values and ANOVA results are summarized in Table 4. Taking into account the measurement accuracy (± 8%), the behaviors of permeability at 20°C and 40°C do not present the same trends. Indeed, at

Table 5 Model coefficients, their respective significance and R^2 values achieved with experimental designs (a) and ANOVA (b) results for permeability and elongation at break designs for ageing in P3-Ultrasil 75

Table 5(a)

		P3-Ultrasil 75		
	Y_1: Lp (L.h^{-1}.m^{-2}.bar^{-1})		**Y_2: E$_l$ (%)**	
R^2	0.665		0.845	
	Coefficient	**Signif. %**	**Coefficient**	**Signif. %**
b_0	326.486	< 0.01 ***	45.025	< 0.01 ***
b_1	-5.882	56.7	-2.052	1.03 *
b_2	-7.398	47.5	-1.772	2.02 *
b_3	21.403	2.89 *	-1.766	0.855 **
b_{1-1}	9.222	66.0	-1.135	37.8
b_{2-2}	29.101	18.8	0.984	44.5
b_{1-2}	-15.885	19.5	-1.234	10.8
b_{1-3}	9.817	34.9	-0.256	67.8
b_{2-3}	6.265	54.4	-1.007	13.2
***: significance > 99.9%; **: significance > 99.5%; *: significance > 95%				

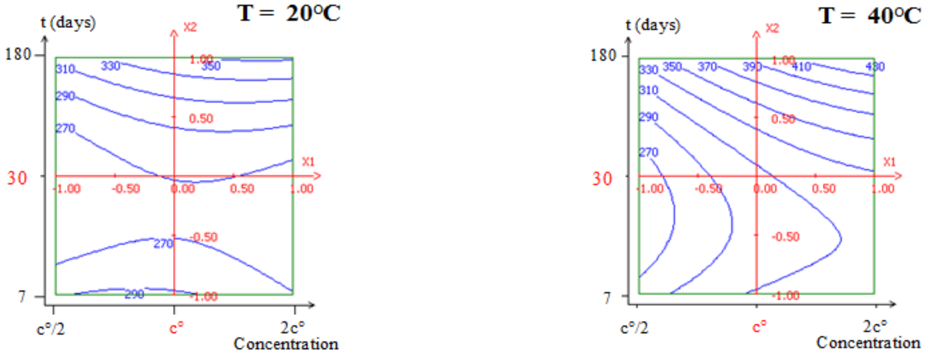
Table 5(b)

		P3-Ultrasil 75 - ANOVA			
Sum of squares (SS)	**Degrees of freedom (DF)**	**Mean square (MS)**	**F-test**	**Signif. %**	**Sum of squares (SS)**
		Y_1: Lp (L.h^{-1}.m^{-2}.bar^{-1})			
Regression	1.66964. 10^4	8	2.08705.10^3	1.9811	17.7
Residual	8.42781.10^3	8	1.05348.10^3		
Total	2.51242.10^4	16			
		Y_2: E_l (%)			
Regression	140.5442	8	17.5680	4.7641	2.69 *
Residual	25.8133	7	3.6876		
Total	166.3575	15			
***: significance > 99.9%; **: significance > 99.5%; *: significance > 95%					

20°C, membrane permeability is not influenced by a variation of detergent concentration. On a first stage (from 7 days to 30 days), permeability decreases with contact time from 337 ± 27 L.h^{-1}.m^{-2}.bar^{-1} for the initial membrane to 268 ± 21 L.h^{-1}.m^{-2}.bar^{-1} at 2c° (1.4%wt, pH = 11.6) over 7 days (308 ± 25 L.h^{-1}.m^{-2}.bar^{-1} at c°/2 (0.35%wt, pH = 10.9)) and to 255 ± L.h^{-1}.m^{-2}.bar^{-1} at 2c° over 30 days (247 ± 20 L.h^{-1}.m^{-2}.bar^{-1} at c°/2). For a second step (from 30 days to 180 days), permeability increases to 347 ± 28 L.h^{-1}.m^{-2}.bar^{-1} at 2c°, 323 ± 26 L.h^{-1}.m^{-2}.bar^{-1} at c° and 330 ± 26 L.h^{-1}.m^{-2}.bar^{-1} at c°/2 (especially stressed at high concentration). At 40°C, on the first hand, permeability decreases or stays stable according to concentration (at 7 days, 275 ± 22 L.h^{-1}.m^{-2}.bar^{-1} at c°/2 (0.35%wt, pH = 10.9), 326 ± 26 L.h^{-1}.m^{-2}.bar^{-1} at 2c° (1.4%wt, pH = 11.6)). Over 180 days, the increase in permeability especially occurs at high concentration (at 180 days, 316 ± 25 L.h^{-1}.m^{-2}.bar^{-1} at c°/2 and 428 ± 34 L.h^{-1}.m^{-2}.bar^{-1} at 2c°). Those two behaviors are more stressed and faster at 40°C than at 20°C.

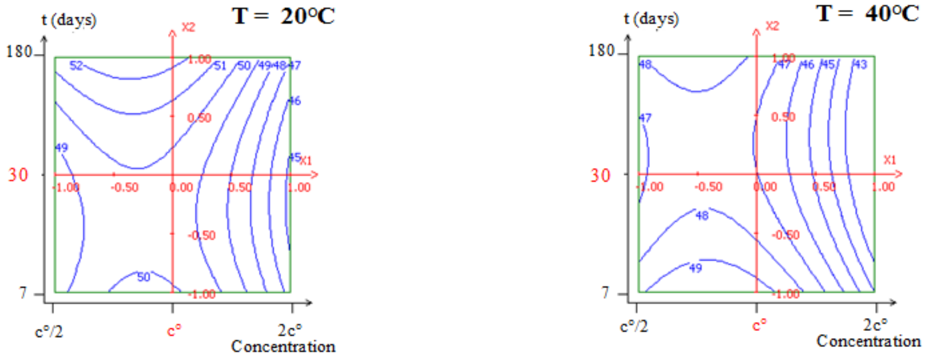
Mechanical results obtained at 20°C and 40°C are shown in Figs. 2(c)-(d). The achieved model

Y_1: Permeability Lp (L.h^{-1}.m^{-2}.bar^{-1})



(a) (b)

Y_2: Elongation at break E$_l$ (%)



(c) (d)

Fig. 2 2D-experimental designed permeability responses at 20°C (a) and 40°C (b) and elongation responses at 20°C (c) and 40°C (d) for hollow fiber membrane aged in P3-Ultrasil 110

Table 6 Model coefficients, their respective significance and R^2 values achieved with experimental designs (a) and ANOVA (b) results for permeability and elongation at break designs for ageing in P3-Ultrasil 67/69New

Table 6(a)

	P3-Ultrasil 67/69New			
	Y_1: Lp (L.h^{-1}.m^{-2}.bar^{-1})		**Y_2: E_l (%)**	
R^2	0.857		0.768	
	Coefficient	**Signif. %**	**Coefficient**	**Signif. %**
b_0	404.102	< 0.01 ***	51.957	< 0.01 ***
b_1	9.093	34.7	3.560	2.49 *
b_2	53.189	0.0589 ***	-1.064	38.5
b_3	-2.451	74.4	1.778	12.9
b_{1-1}	-11.556	52.4	-3.978	12.3
b_{2-2}	26.241	16.8	-0.460	83.8
b_{1-2}	-12.746	28.5	0.782	58.3
b_{1-3}	19.760	6.4	-1.635	20.6
b_{2-3}	-0.904	92.3	0.275	81.7

***: significance > 99.9%; **: significance > 99.5%; *: significance > 95%

Table 6(b)

P3-Ultrasil 67/69 New - ANOVA					
Sum of squares (SS)	**Degrees of freedom (DF)**	**Mean square (MS)**	**F-test**	**Signif. %**	**Sum of squares (SS)**
		Y_1: Lp (L.h^{-1}.m^{-2}.bar^{-1})			
Regression	$3.01109.10^4$	8	$3.76386.10^3$	5.2243	2.11 *
Residual	$5.04313.10^3$	7	$7.20447.10^2$		
Total	$3.51540.10^4$	15			
		Y_2: E_l (%)			
Regression	172.9364	8	21.6171	2.0652	22.0
Residual	52.3357	5	10.4671		
Total	225.2721	13			

***: significance > 99.9%; **: significance > 99.5%; *: significance > 95%

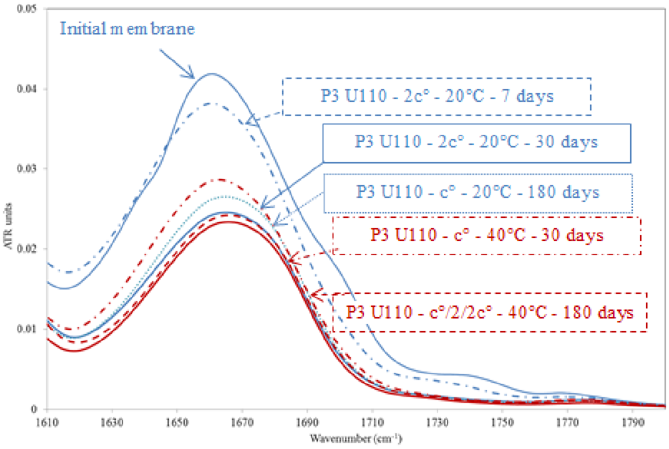
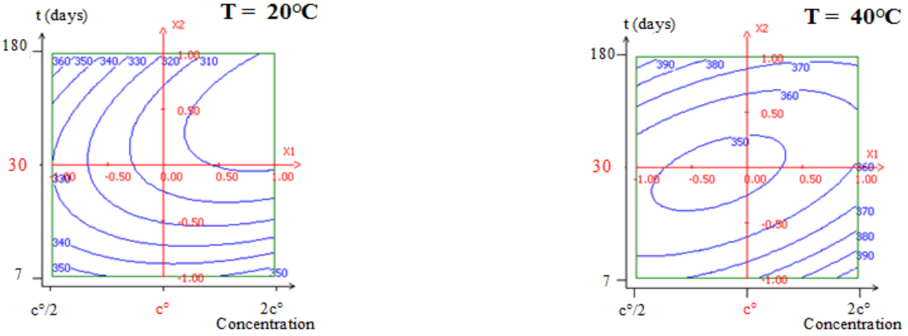


Fig. 3 Comparison of the changes of the amide bond of PVP by P3-Ultrasil 110 at 20°C (a) and 40°C (b)

is not significant ($R^2 = 0.77$). However, some ageing elongation at break modifications can be underlined and observed modifications are significant. At 20°C, no obvious deteriorations of the mechanical properties were observed at c°/2 over 180 days. Besides for a higher concentration (2 c° (1.4%wt)), the loss of elongation is 5% over 7 days and 12% over 30 days. Over 180 days of ageing, no more increase in the elongation loss occurs. Regardless of the temperature (20°C or 40°C) and for a concentration over the effective industrial concentration c° (0.7%wt), time of ageing is not yet a preponderant factor. Indeed, the elongations at break answers are parallel to the time axis. Concentration has a more severe impact on elongation at break decrease than time of contact. This trend is worsened at 40°C where the elongation at break decrease occurs for lower concentration than at 20°C (at c° at 40°C compared to 1.5c° at 20°). The trend in the elongation loss is worsened with a loss of 15% over 7 days at 2c° (1.4%wt). The same loss is observed over 180 days in the same ageing conditions.

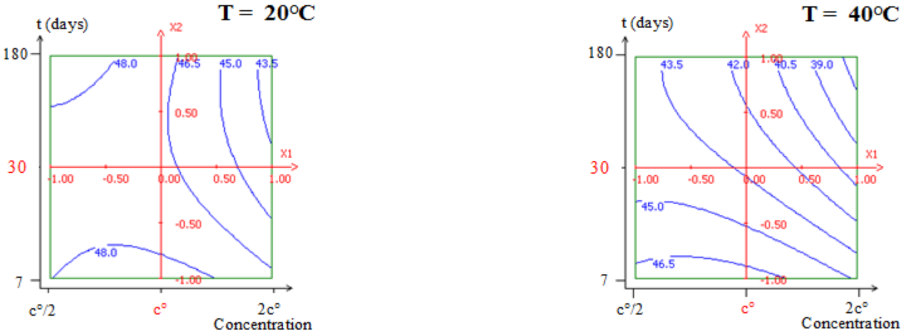
The HRSEM pictures of the membranes aged in alkaline conditions confirmed these results. The deteriorations of the macroscopic parameters (permeability and mechanical properties) are in agreement with the degradation of the microscopic morphology. In spite of the qualitative side of

Y_1: Permeability Lp (L.h^{-1}.m^{-2}.bar^{-1})



(a) (b)

Y_2: Elongation at break E_l (%)



(c) (d)

Fig. 4 2D-experimental designed permeability responses at 20°C (a) and 40°C (b) and 3D-experimental designed elongation at break responses at 20°C (c) and at 40°C (d) for hollow fiber membranes aged in P3-Ultrasil 75

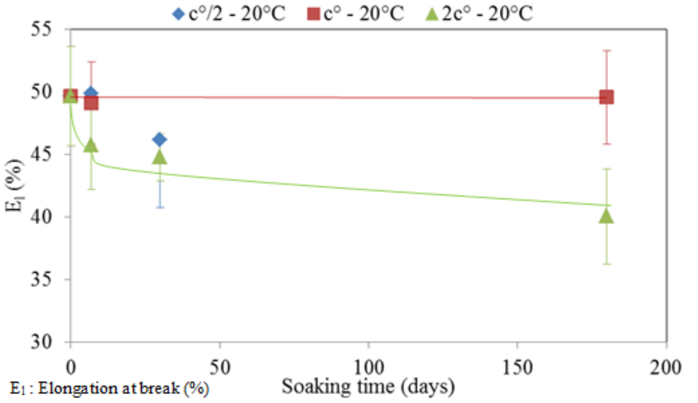


Fig. 5 Influence of c° on the variation in time of elongation at break of membranes aged in P3-Ultrasil 75

the HRSEM images interpretation, the morphology of the active layer undergoes the worst changes at high concentration and high temperature. The membrane surface becomes fuzzier. However, no crackle appears even on the samples aged in the harsher conditions. There was no

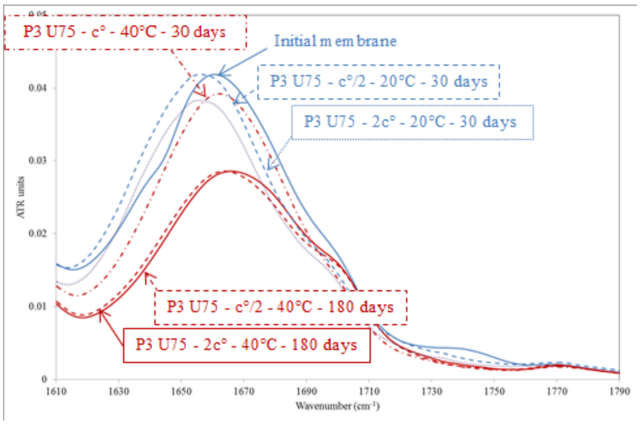


Fig. 6 ATR-FTIR spectra of PSf membrane aged in P3-Ultrasil 75 – Disappearance of the amide bonds of PVP at 20°C and 40°C

Table 7 Comparison of the macroscopic and microscopic qualitative and quantitative effects of the four tested detergents

	P3-Ultrasil 110	**P3-Ultrasil 75**	**P3-Ultrasil 67 / P3-Ultrasil 69New**	**NaOCl** (Régula *et al.* 2012)
Effect on Lp (Permeabiliy at 20°C)	- (from 7 to 30 days) + (from 30 days to 180 days)	0 (at 20°C) + (at 40°C)	+ +	+++
Effect on E_l (Elongation at break)	0 (at 20°C) - (at 40°C)	- (at 20°C) - - (at 40°C)	0	- - -
Surface deteriorations	No crackle	Crackles	No crackle	Crackles (instability of the polymer under the electronic beam)
Polymer modifications (peak displacement, decrease or increase in peak intensities)	- -	-	- - -	- - - (Final and complete disappearance of amide bond of Polyvinylpyrolidone (PVP) peak)
	After 7 days, disappearance of Polyethyleneglycol (PEG) peak whatever the ageing conditions			

- / - - : Decrease / High decrease compare to the initial membrane;
0: No modification compare to the initial membrane;
+ / ++: Increase / High increase compare to the initial membrane

problem to obtain HRSEM pictures which is a good telltale sign to know if the polymer is deteriorated or not.

The ATR-FTIR results show major changes on the peak at 1663 cm^{-1} (Fig. 3) whatever concentration, temperature and time of contact. As seen on HRSEM pictures, no microbial development has occurred during the ageing tests, so the decrease of the peak intensities can be consider as representative of the ageing phenomenon (no “screening effect” coming from microbial development which would reduce peak intensities). At 20°C, samples aged at 2c° (1.4%wt, the higher tested pH) present the biggest variation of their spectra at 1663 cm^{-1}. This peak is reduced by a factor 1.1 over 7 days, 1.6 over 30 days and 1.7 over 180 days. No displacement of the peak is observed. These results are in agreement with the evolution of the mechanical properties: the major changes occur from 7 days to 30 days and then there is no more alteration. At 40°C and 30 days of ageing, the alkaline solution deteriorates the amide PVP in the same proportion as at 20°C (factor 1.5). Temperature does not have an impact on the deterioration of PVP in such alkaline conditions. Meantime, the peak decrease at c°/2 (0.35%wt) and 2c° (1.4%wt) over 180 days is the same (factor 1.6) whatever the concentration.

It can be concluded that in the case of membrane fouling, the concentration of P3-Ultrasil 110 can be increased and a temperature of 40°C can be applied for a curative cleaning without any damage on membranes (Table 7). Moreover, as cleaning efficiency is known to be better at 40°C than at 20°C for P3-Ultrasil 110, and c° = 0.7% wt being the preconized concentration, these cleaning conditions can be used for cleaning protocols.

3.2 Acidic detergent: P3-Ultrasil 75

For this acidic detergent, c° is equal to 0.3%wt (pH = 1.8, 40°C). Permeability results obtained at 20°C and 40°C are shown in Figs. 4(a)-(b). The coefficients of the models, R^2 values and ANOVA results are summarized in Table 5. The behavior of permeability at 20°C and 40°C present the same trend, but the deteriorations are more stressed at 40°C than at 20°C (only at high c° or high time of contact). The permeability is not significantly altered ($R^2 = 0.67$). Nevertheless, without considering the model, some ageing elongation at break modifications can be underlined. At 20°C, variations of permeability are included in the measurement accuracy (variation from 360 ± 29 $L.h^{-1}.m^{-2}.bar^{-1}$ to 310 ± 25 $L.h^{-1}.m^{-2}.bar^{-1}$) regardless of the parameters studied (concentration, ageing time). So the use of this acidic commercial detergent at the requested industrial concentration c° (0.3%wt) at 20°C would not affect the process performances since the permeability is not deteriorated in such conditions. At 40°C, over 7 days, permeability increases of 9% at c°/2 (pH = 2.1) and 19% at 2c° (pH = 1.7). This increase could be explained by the more important deteriorations of the membrane morphology at 40°C than at 20°C, with apparition of crackles on HRSEM images.

Mechanical results obtained at 20°C and 40°C are shown in Figs. 4(c)-(d). R^2 values (Table 5(a)) and ANOVA results (Table 5(b)) show the ageing model is significant. At 20°C, no significant alteration occurs over 180 days for a concentration corresponding to the industrial concentration of c° (0.3%wt). However, if concentration becomes superior to c°, there is a more important loss in the elongation at break (~10% at 2c°/30 days and ~12% at 2c°/180 days) which shortens the acceptable cumulated time of contact between the membrane and the detergent. It can be seen that cleaning at c°/2, in soaking conditions, would not affect membrane properties. On Fig. 5, a loss of elongation with an increasing soaking time and an increasing concentration is observed where the initial degradation rates is -0.21%/day at 2c°/20°C and -0.07%/day at c° /20°C (initial tangent calculated using the curves). Increasing the concentration by a factor 2 increases the initial degradation rate by a factor 3. Then, Fig. 5 underlines also that the concentration impact on the degradation rate is less and less important with an increasing time. Indeed, over 180 days, the degradation rate obtained at 0.6% (2c°) tends to the value obtained at c° (at c°/2 (0.15%wt): -0.05%/day for 30 days and -0.07%/day for 180 days; at 2c°(0.6%wt): -0.16%/day for 30 days and -

0.11%/day for 180 days). As regards the evolution of the elongation at break at 40°C (Fig. 4(d)), the loss of plasticity is more stressed at 40°C than at 20°C. The maximal loss observed at 20°C is ~ 12% at 2c° (0.6%wt) /180 days whereas it is ~ 28% in the same conditions but at 40°C.

The HRSEM pictures of membranes aged in acidic conditions were obtained and observations after 7 and 30 days of ageing do not present any morphological change. After 90 days, the membrane morphology begins to become hazier but no crackle is detected. The images after 180 days of ageing present heavy deteriorations of the active layer with crackles whatever the concentration. Those deteriorations are only visible at 40°C and are in agreement with the deteriorations of the macroscopic characteristics observed.

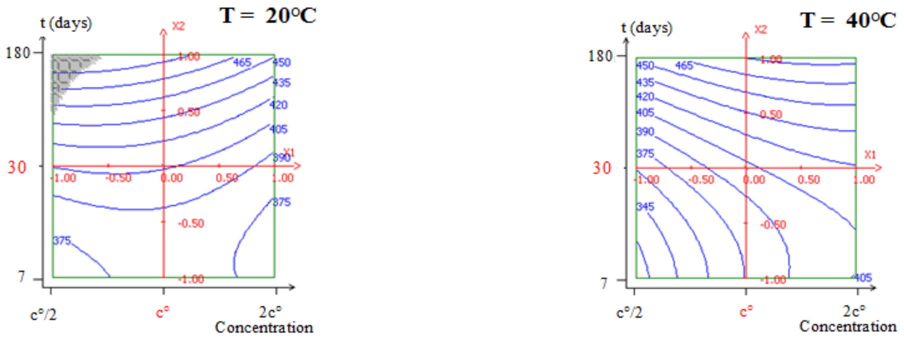
The ATR-FTIR spectra obtained at 20°C over 180 days do not present a significant evolution. That is why only results of industrial interest have been detailed (Fig. 6). Ageing data achieved at 40°C, for its part, present significant evolution. Whatever concentration, contact time and temperature, ATR-FTIR results show major changes on the peak at 1663 cm^{-1}. At 20°C, the peak at 1663 cm^{-1} is modified by a factor 1.1 at c°/2 (0.15%wt, pH = 1.7)/30 days and by a factor 1.2 at 2c° (0.6%wt, pH = 2.1)/180 days. At 40°C and 30 days of ageing (Fig. 6), the acidic solution deteriorates the amide PVP in the same proportion as at 20°C (factor 1.3). Temperature does not have an impact on the deterioration of PVP. Meantime, the peak decreases at c°/2 and 2c° over 180 days is the same (factor 1.5) whatever the concentration.

It can be concluded that at 0.3%wt P3-Ultrasil 75 at 20°C, the membrane properties are preserved also for a very long contact time (180 days). However, at 40°C (as normally used on sites), the oxidative power of nitric acid has a more negative impact on membranes than at low temperature (crackles detected on membrane surface at 40°C) over 180 days (Table 7). Besides, the considered time of contact (180 days) is far higher than industrial cumulative time of contact in such conditions. So, P3-Ultrasil 75 can be considered as not detrimental for membrane when it used respecting the cleaning conditions advised by the detergent manufacturer.

3.3 Enzymatic detergent: P3-Ultrasil 67/69New

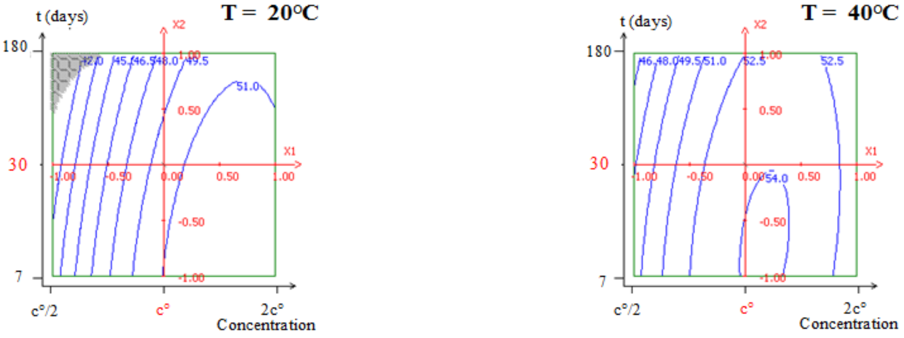
For the enzymatic detergent, the concentration of the alkaline buffer (P3-Ultrasil 69New) remained constant all along the ageing tests (c° = 0.8%wt) and only the enzymatic concentration (P3-Ultrasil 67) varied (c° = 0.3%wt, pH = 10.8, 40°C). Permeability results obtained at 20°C and 40°C are shown in Figs. 7(a)-(b). The coefficients of the models, R^2 values and ANOVA results are summarized in Table 6. Given the measurement accuracy, the behaviors of permeability at 20°C and 40°C present the same trends (especially for a time of ageing above 30 days). The permeability response become more and more independent from ageing concentration (the response is parallel to the concentration axis) and time of contact is the most significant ageing parameter, in agreement with the significance of the corresponding coefficient of the models (Table 6(a)). Temperature has not a significant impact on permeability increase. At 20°C, permeability increases from 377 ± 30 $L.h^{-1}.m^{-2}.bar^{-1}$ at 2c°/7 days to 478 ± 38 at 2c°/180 days. At 40°C, permeability increases from 416 ± 33 $L.h^{-1}.m^{-2}.bar^{-1}$ at 2c°/7 days to 477 ± 38 $L.h^{-1}.m^{-2}.bar^{-1}$ at 2c°/180 days. The increase in permeability observed at 20°C and 40°C cannot be explained by an eventual degradation of the active layer since no crackle was detected on HRSEM images. Mechanical results are shown in Figs. 7(c)-(d). Regarding the evolution of the mechanical properties of the aged fibers, at 20°C and 40°C, in the same ageing conditions (concentration and time of contact), no significant alteration occurs over 180 days (in agreement with R^2 values ANOVA study (Table 6(a)-(b)).

Y_1: Permeability Lp (L.h-1.m-2.bar-1)



(a) (b)

Y_2: Elongation at break *E*l (%)



(c) (d)

Fig. 7 3D-experimental designed permeability responses at 20°C (a) and 40°C (b) and 2D-experimental designed elongation at break responses at 20°C (c) and 40°C (d) for hollow fibers membranes aged in P3-Ultrasil 67/69New

The HRSEM pictures of the membranes aged in enzymatic conditions do not reveal any crackle even on the samples aged in the harsher conditions (40°C, 2c°, 180 days). There was no problem to obtain HRSEM pictures which is a good telltale sign to know if the polymer is deteriorated or not.

The ATR-FTIR results exhibit major changes on the peak at 1663 cm^{-1} whatever concentration, temperature and time of contact. At 20°C (Fig. 8), the peak at 1663 cm^{-1} is modified by a factor 1.7 at 2c°/7 days and 2.7 at 2c°/180 days. At 20°C, no displacement of the peak was observed. In the same conditions at 40°C, the amide bond of PVP is less deteriorated than at 20°C for 7 days (factor 1.3) and deteriorated in the same proportion than at 20°C for 180 days (factor 2.8). Temperature has not an impact on the deterioration of PVP for a long contact time. With regard to minor changes of the spectrum, contrary to what is happened with alkaline and acidic detergents, two other peaks (at 1425 cm^{-1} and 1445 cm^{-1}) are significantly modified at 20°C and 40°C. One peak at 1032 cm^{-1} (unidentified) appears at 7 days for high concentration whatever the ageing temperature. This peak has also been detected and studied on static or under microwaves ageing of PES membrane by Lepéroux *et al*. 2012.

It can be concluded that P3-Ultrasil 67 and 69 New soaking with high concentration during several hours at 40°C would not be detrimental for the membrane (Table 7). ATR-FTIR

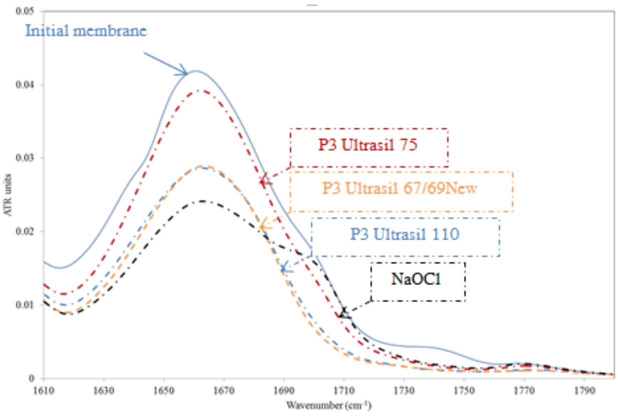


Fig. 9 Comparison of the changes of the amide bond of PVP by P3-Ultrasil 75, P3-Ultrasil 110, P3-Ultrasil 67/69New and NaOCl at c°/40°C for 30 days

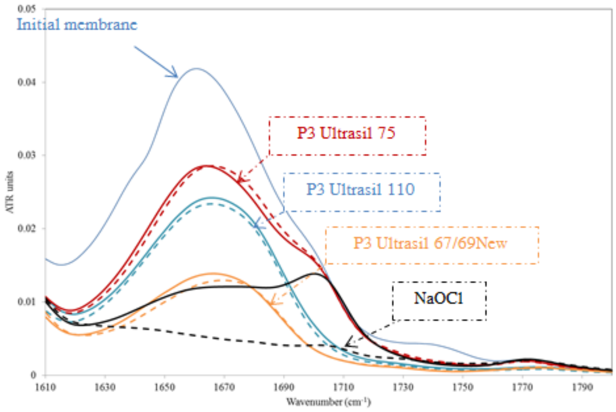


Fig. 10 Comparison of the changes of the amide bond of PVP by P3-Ultrasil 75, P3-Ultrasil 110, P3-Ultrasil 67/69N and NaOCl at 0.5c°/40°C and 2c°/40°C for 180 days

observations have to be considered cautiously because the static ageing realized in the present study have been conducted on “pristine” membranes (no foulants materials). Enzymatic action on industrial fouled membrane and pristine membrane could be different.

3.4 Discussion

In a previous study (Régula *et al*. 2012), NaOCl was tested in the same experimental conditions via the methodology of the experimental designs. As the most recently issued scientific publications concerning ageing, this study dealt with ageing effects of NaOCl, known as one of the most efficient cleaning chemical but also as one of the most detrimental for membranes. Indeed, NaOCl is commonly used in industrial cleaning protocols to recover the initial water flux and in production during short and daily backwashing in order to neutralize pathogen agents. Its use becomes questionable in regard to by-products production as chloroform or to the bio-degradability of the effluents. For this reason, optimizing cleaning protocols with presumably less detrimental cleaning detergents such as P3-Ultrasil 110, P3-Ultrasil75 or P3-Ultrasil 67/69New could let to reduce NaOCl quantities in cleaning protocols and, so far, increase membrane life time. Moreover, enzymatic detergents are also widely bio-degradable and lead to more digestible effluents. This can be interesting in the current environmental context. For this reason, the ageing effects of these cleaning detergents have been compared.

If ageing effects of P3-Ultrasil 110 and P3-Ultrasil 75 are considered, (even if cleaning performances cannot be compared, since they do not have the same cleaning applications- organic and inorganic fouling elimination), macroscopic (Lp and E_l) and microscopic (HRSEM) characterization underline a worse effect of the acidic commercial detergent than the alkaline commercial detergent, especially at 40°C. This is confirmed by the presence of crackles detected on fibers aged in acidic conditions (not on fibers aged in alkaline conditions). However, ATR-FTIR data are more controversial and the alkaline detergent is more detrimental for PVP than acidic detergent (Figs. 3 and 6). Indeed, the peak intensity of PVP of the sample aged at c° (0.7%wt, pH = 11.0)/40°C/30 days in alkaline detergent is equivalent to the one of the peak aged in acidic detergent at 2c° (0.6%wt, pH = 2.1)/40°C/180 days.

If ageing effects of P3-Ultrasil 110 and P3-Ultrasil 67/69New are considered, the degradations of permeability for 180 days of ageing are more stressed and significant than with P3-Ultrasil 75. At the same time, the PVP degradations are also more stressed. However, the permeability increases are of the same order of magnitude whereas PVP is far more deteriorated with P3-Ultrasil 67/69New than with P3-Ultrasil 110. So the correlation is not rigorously proportional and the deterioration of the polymer has not a significant and direct impact on permeability. No definitive correlation can be established between the permeability variation and the deterioration of the mechanical properties. Of course, permeability is mainly monitored by membrane skin properties whereas elongation at break point depends on the whole membrane structure.

If ageing effects of P3-Ultrasil 67/69New and NaOCl are considered, the degradation of permeability at c°/40°C/30 days induced by P3-Ultrasil 67/69New (pH = 11.5) and by NaOCl (pH = 9.0) is in the same order of magnitude. Over 180 days, the permeability increase is still in the same order of magnitude at c°/2/40°C (460 ± 37 L.h^{-1}.m^{-2}.bar^{-1} for P3-Ultrasil 67/69New and 503 ± 48 L.h^{-1}.m^{-2}.bar^{-1} for NaOCl). The discrepancy is slightly emphasized at 2c°/40°C with a relative difference of 27% (477 ± 38 L.h^{-1}.m^{-2}.bar^{-1} for P3-Ultrasil 67/69New and 606 ± 40 L.h^{-1}.m^{-2}.bar^{-1} for NaOCl). If the deterioration of PVP is considered, modifications in enzymatic conditions at c°/2 or 2c° (pH = 10.9) at 40°C/180 days are equivalent to those in chlorine conditions at c°/2 (100 ppm, pH = 8.0) or 2c° (400 ppm, pH = 9.9) at 20°C/180 days (Fig. 10). It is obvious that the degradation mechanism is not the same since with NaOCl the peak is decomposed into two different peaks contrary to the case of enzymatic detergent. As enzymatic detergents are supposed to be less harmful than NaOCl (no crackles have been observed on HRSEM images of samples aged in enzymatic conditions contrary to in chlorine conditions), a possible explanation for such a PVP degradation could be found in a possible hydrolyze action of enzymes (enzymes contained in P3-Ultrasil 67 could interfere on lactam chemical function of PVP) on amide bond of PVP contained in the tested membrane (Rabiller-Baudry *et al.,* 2009). Indeed, on an industrial site, it has been encountered that enzymes were able to alter polyamide by hydrolyzing amide bonds. So, this result highlights the importance of the enzyme choice in industrial cleaning applications. Other study carried out on spiral-wound PES membranes in the same ageing conditions confirms this observation. Meanwhile, the use of another enzymatic mixture (of lipases and proteases) revealed a lesser decrease of the amide bond PVP peak intensity. In the same study, another alkaline buffer was used (P3-Ultrasil 160) in order to have a more appropriate pH (9.5 rather than 11.6 as with P3-Ultrasil 69 New). In terms of membrane modifications, ATR-FTIR spectra are not clearly different. So, ATR-FTIR modifications cannot be attributed to higher pH or to ageing effects of components included in P3-Ultrasil 69New.

To sum up and correlate the microscopic and macroscopic alterations for each detergent, the following outcomes can be noted to:

- If mechanical properties changes are linked with HRSEM images, it will be seen that the more the membrane surface is significantly damaged (crackles), the more elongation at break point decreases. Thus, Table 7 distinguishes two cases:
  - Membrane surfaces of samples aged in P3-Ultrasil 75 (and NaOCl) revealed crackles and a cumulative loss in mechanical properties at 40°C over along time of contact
  - Membrane surfaces of samples aged in P3-Ultrasil 110 or in P3-Ultrasil 67/69N did not revealed crackles or deteriorations of mechanical properties.
- If effects on PVP are compared, polymer ageing tendencies can be drawn too. Even if, it has been proved that whatever the conditions hydrolysis of PVP was inevitable (around 1% of opening ring whatever the pH (Gaudichet-Maurin, 2005)), the tested commercial detergents will be classified into two groups according Table 7:
  - P3-Ultrasil 75: no influence for 30 days, significant decrease over 180 days with decomposition of the peak into two peaks (this suggests that less opening of the amide ring would occur in acidic ageing conditions (pH = 1.8)).
  - P3-Ultrasil 110 and P3-Ultrasil 67/69New: decrease after 7 days without decomposition of the peak (this suggests that more opening of the amide ring would occur in alkaline ageing conditions (pH = 11.0–11.5)).

By comparing this classification, with the permeability deteriorations observed for 30 days of ageing, at c°/40°C (Fig. 9) and for 180 days of ageing at c°/2 or 2c°/40°C (Fig. 10), it can be observed that the less the PVP is deteriorated (P3-Ultrasil75) the less the permeability is modified and the more the PVP is deteriorated the more the permeability is modified (by one order of magnitude: P3-Ultrasil 75, P3-Ultrasil 110, P3-Ultrasil 67/69New and NaOCl).

4. Conclusions

The goals of this study were: to identify and compare the effects of commercial chemical cleaning solutions on the degradation of hollow fiber ultrafiltration membranes (polysulfone, PSf) and, so far, to gain access to new ageing data with commercial detergents which has not been studied until now.

Designs of experiments were used to organize at best the experiments in order to get a relevant establishment of an ageing pattern without using an accelerated ageing. For all the tested detergents, permeability and elongation at break values obtained with an empirical mathematical model are simulated with an error included in the measurement accuracy. So, the pattern established for the permeability of membranes and the mechanical properties aged regardless of the solution can be considered satisfying and reliable to simulate deteriorations in function of the chemical cleaning parameters. The results achieved in this study confirmed that it is necessary for an ageing membrane study to couple macroscopic and microscopic methods of characterization.

In comparison with previous works, the results of this study deals with the membrane ageing quantification induced by commercial detergent which had not been tested up to now. Considering the long ageing duration applied in this study, it could be concluded that the commercial detergents are quite harmless for the membrane for a time corresponding to the effective cumulated industrial time of contact. These results would help operators to optimize the cleaning conditions and to avoid the worst combinations concentration/temperature/time of contact in order to maintain the best performances of membranes in place. Moreover, combining this study based on ageing effects with other already completed studies on cleaning efficiencies (Zondervan and Roffel, 2007 for P3-Ultrasil 115; Lawrence *et al.* 2006, Wallberg *et al.* 2001, Lindau and Jönsson,1994 for P3-Ultrasil 75; Munoz-Aguado *et al,* 1996 for enzymes comparative cleaning efficiencies for instance), it will be possible to evaluate the economical balance of such a commercial detergent or not in function of its impact on process performances, on membrane cleanliness, on costs, on membrane renewal time…

Then, in order to get through this study and to fills the gaps in the understanding of the ageing mechanisms, complementary experiments are ongoing to further confirm the observation: dynamic ageing, in the same c°, T° and time as the static ones will allow to evaluate the impact of chemical and hydrodynamic parameters on membrane ageing.

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Appendix A. Nomenclature

ANOVA	ANalysis Of VAriance
ATR –FTIR	Attenuated Total Reflectance Fourier Transform Infra-Red
b_i	Coefficient of the quadratic model
c°	Effective industrial concentration (ppm)
CA	Cellulose Acetate
DF	Degrees of freedom
E_l	Elongation at break point (%)
E_{lo}	Elongation at break of native membrane (%)
F-Test	Fischer test
Lp	Hydraulic permeability of the membrane ($L.h^{-1}.m^{-2}.bar^{-1}$)
Lp_o	Hydraulic permeability of the native membrane ($L.h^{-1}.m^{-2}.bar^{-1}$)
MS	Mean square
PA	Polyamide
PAN	Polyacrylonitrile
PEG	Polyethylene glycol
PEI	Polyetherimide
PES	Polyethersulfon
pH	Hydrogen potential
PlyA	PolyAcrylate
PSf	Polysulphone
P3-U67	P3-Ultrasil 67, Ecolab, Fance
P3-U69N	P3-Iltrasil 69 New, Ecolab, France
P3-U75	P3-Ultrasil 75, Ecolab, France
P3-U110	P3-Ultrasil 110, Ecolab, France
PVDF	Polyvinyldifluoride
PVP	Poly(vinyl pyrrolidone)
R-CE	Regenerated Cellulose
RSM	Response surface methodology
σ_B	Ultimate strain (MPa)
Signif.	Significance (%)
SS	Sum of squares
t	Time (days)
T	Température (°C)
Ts	Tensile strength at break point (N)
HRSEM	High Resolution Scanning Electron Microscopy