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Drinking water ultrafiltration: state of the art and experimental designs approach

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ABSTRACT

During cleaning steps, ultrafiltration membranes are mechanically and chemically stressed. This can result in membrane degradations, failures, and be shut down for membrane replacement and therefore affect the production rate of the process and its sustainability. These phenomena raise the problem of necessary optimization of the cleaning procedures that have to tackle simultaneously, the best cleaning efficiency and the less detrimental procedures for the membranes. Despite the fact that aging is becoming a major issue between end-users, membrane manufacturers, and chemical product suppliers, there is considerably less literature dedicated to membrane aging than to cleaning. First, this study briefly reviews articles dedicated to aging damages involved by NaOCl and commercial detergents (especially on polysulfone ultrafiltration membrane). Then, the present study details the innovative way setup: "Designs of experiments" is used to provide additional data that help with a thorough understanding of membrane aging. Thus, contrary to the accelerated aging approach that is commonly used in membrane-aging researches (concentration per time of contact: "$c \times t$ parameter"), designs of experiments were used to organize at best the aging experiments in order to achieve a relevant establishment of an aging pattern. Results show that this scientific approach provides a satisfying and reliable pattern to simulate membrane aging in function of the chosen chemical parameters.

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1. Introduction

Membranes periodically undergo chemical cleanings. Regardless of the industrial fields in which organic UF membranes are applied, membrane fouling remains a persistent problem. As a consequence, since 1980, reduction of fouling and cleaning of fouled membrane have been approached in a number of ways. Besides, as membrane replacement generally accounts for 25–40% of the total membrane plant cost, aging have been studied deeper since the 2000s in order to increase the lifetime of the membrane. Membrane aging is currently at the heart of the industrial membrane applications issues. This is obvious in Fig. 1, where studies concerning membrane aging have increased by a factor 10 in the last decade. Contact with cleaning chemicals plays an important role in membrane aging and, as a result, on its lifetime. However, the processes by which a membrane is deteriorated are even more poorly understood than cleaning. For a better understanding of the aging mechanisms, studies are realized for NaOCl known not only as one of the most efficient cleaning chemical, but also as one of the most detrimental for membranes. However, the ways and approaches used may be sometimes questionable and remain hazy.

Among the number of publications satisfying the research criteria "membrane and aging" in the title of the articles published since 2000s, the major part of the studies dedicated to ultrafiltration membranes aging are focused on polysulfone (PSf) or polyethersulfone (PES) membranes. Because of their high chemical and thermal stability ($1 < pH < 13$, temperature until 80°C), these polymeric membranes are commonly used on industrial plants. For this reason, PSf membrane was finally chosen for this study.

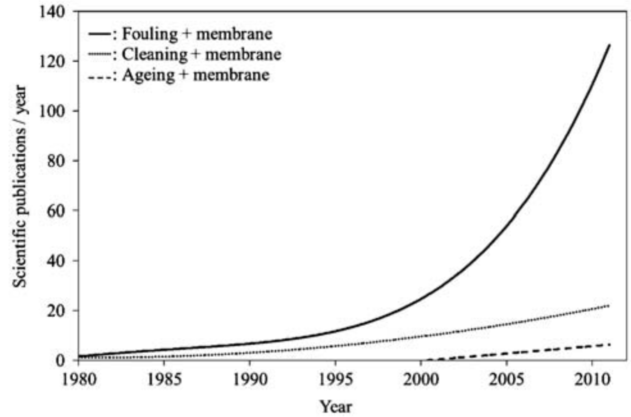


Fig. 1. The literature dedicated to membrane fouling, membrane cleaning, and membrane aging from 1980 until now [Number of publications in journals satisfying the research criteria "Membrane and (fouling or cleaning or aging)" in the title. Data were taken from www.sciencedirect.com in March 2012].

Within the framework of PSf aging, several knowledge gaps can be addressed. First, the most important part of the scientific researches on the membrane aging has been focused on the use of NaOCl, known as the most harmful chemical for the membrane [1]. A lot of parameters have been studied concerning the chlorine aging, and the aging mechanisms involved with hypochlorite as can be seen from Table 1.

First of all, almost all aging experiments realized until now are realized in static conditions. Some studies have used accelerated aging conditions [14,15]; others used the "$c \times t$ parameter" [12,13,16,17]; others have corrected pH [3–7] and studied the influence of the different active species; others studied, in more detail, the role of radical oxidation and the role of some dissolved metal ions [3]. Then, others identify polymer modifications using infrared spectroscopy and propose several aging mechanisms involved by NaOCl [3–6,10,12,16,17].

Concerning the commercial cleaning detergents, only one study was conducted on the aging modifications involved by the use of a formulated alkaline detergent on polymeric membranes. These studies found PES modifications when aged at 50°C in P3-Ultrasil 10 for 4 months [19,20]. New band appears at 1035 cm^{-1} due to aging. No study has been realized on the aging effects involved by acidic, enzymatic or oxidizing detergents on polymeric membranes of ultrafiltration.

In light of this brief review, two points can be emphasized: (i) there is an obvious lack of data dealing with membrane aging effects of commercial detergents compared with NaOCl ones. For this reason, the present work simultaneously studies membrane aging involved by NaOCl and by commercial detergents, (ii) all the results developed in previous studies have been achieved by using different aging protocols and approaches that are difficult to compare with each others'. The method used in this study is the same for all the tested commercial detergents, and it is an innovative method based on designs of experiments. In the present study, the approach is based on 4 choices: (i) experiments have been conducted using designs of experiments while

Table 1
Summary of published works on static aging induced by hypochlorite on UF PSf and PES membranes (adapted from Wang et al. [2])

Papers	Membrane	[NaOCl] (ppm)	pH	Time of aging
Causserand et al. [3]	PSf/PVP	100	5–8	–
Gaudichet-Maurin and Thominette [4]	PSf/PVP/PEG	400	8	–
Causserand et al. [5]	PSf/PVP	100	5–10	–
Gaudichet-Maurin [6]	PSf/PVP	100	5–10	–
Rouaix et al. [7]	PSf/PVP/PEG	–	–	–
Qin et al. [8]	PSf/PVP	2,000–6,000	11.5	–
Wolff and Zydney [9]	PSf/PVP	.1–1.0%	–	40 min
Wolff and Zydney [9]	PSf/PVP	2,400	7.4	–
Thominette et al. [10]	PSf	–	8	–
Bégoin et al. [11]	PES	200–7,600	9–11.7	–
Arkhangelsky et al. [12]	PES	150 mg L^{-1}	7.2	10 g h L^{-1} (3 days); 100 g h L^{-1} (28 days) and
Yadav et al. [13]	PES	700	9–12	10,000 ppm day; 25,000 ppm day
Thominette et al. [10]	PES	–	8	–
Wienk [14]	PES/PVP	3,000	3.9–6.9–11.5	2 days
Qin et al. [15]	PES/PVP	4,000	–	–
Yadav et al. [16]	PES	–	9–12	10,000 ppm day
Arkhangelsky et al. [17]	PES	.1 g L^{-1}	7.2	5 g h L^{-1} (2 days); 10 g h L^{-1} (4 days); 18 g h L^{-1} (8 days); 50 g h L^{-1} (21 days)
Delaunay [18]	PES/PVP/NMP ($CHCl_3$)	8.5 g Cl_2	9–12	8 months

accelerated aging conditions ("$c \times t$" parameter) are commonly used, (ii) as in previous studies, experiments have been conducted in a continuous manner (more practical implementation than dynamic aging), whereas in an industrial plant, membranes are in contact with water most of the time and with cleaning agents for short, periodic times, (iii) membrane aging was performed in static conditions, (iv) pH has not been corrected contrary to what it may be in some industrial cleaning protocols (in function of the used water for instance). In the present study, only the results obtained during experiments realized in static conditions (soaking and no mechanical effects) are presented. Aging conditions were determined with the designs of experiments, according to the desired requirements (broad experimental field including relevant industrial conditions). Quantitative changes in membrane properties were monitored by permeability measurement and mechanical strength tests. Qualitative and microscopic changes were monitored by attenuated total reflexion—Fourier transformed infra-red (ATR-FTIR) and high-resolution scanning electron microscopy (HRSEM). Only permeability and mechanical properties have been used in the evaluation of the constants of the designs of experiments. The aim is to determine whether designs of experiments could be used, and in the future, as a relevant and predictable aging pattern according to the chosen parameters and the cleaning detergent.

2. Experimental part

2.1. Membranes

Studies have been carried out using in/out ultrafiltration hollow-fiber PSf membranes (Aquasource, France, .02 μm nominal pore size). The industrial module (7 m^2) was stored wet as delivered in preservative solution (glycerin) and before usage, glycerin was removed according to manufacturer recommendations. Initial permeability of the module was measured to check whether it was in agreement with manufacturer's specifications. This module was dismantled. Some hollow fibers were characterized without aging step in order to obtain reference characterization (flux measurement, elongation at break, HRSEM and

ATR-FTIR) of native membranes. These were the measurements to be referred to as reference values. The other hollow fibers were sampled. They were soaked in the aging conditions (concentration, time, and temperature) defined by the experimental designs. Finally, after the aging step, flux and mechanical properties were measured and microscopic structure was characterized.

2.2. Detergents

Five commercial detergents were studied:

(1) *Two oxidizing solutions*: NaOCl (Jo-Pro-Chim, Vedène, France) and P3-Oxysan ZS (P3-OZS) (Ecolab, Issy-les-Moulineaux, France).
(2) *Acidic solution*: P3-Ultrasil 75 (P3-U75) (Ecolab, Issy-les-Moulineaux, France).
(3) *Alkaline solution*: P3-Ultrasil 110 (P3-U110) (Ecolab, Issy-les-Moulineaux, France).
(4) *Enzymatic solution*: a combination of P3-Ultrasil 67 (P3-U67) and P3-Ultrasil 69 New (P3-U69N) (Ecolab, Issy-les-Moulineaux, France).

In order to keep the aging conditions constant (concentration and pH) over time, the solutions were changed each week. Aging was performed according to the conditions detailed in Table 3.

2.3. Designs of experiments

Statistical analysis and modeling based on data collected by means of accelerated aging tests was carried out in different fields of science and engineering [21–26]. However, little has been published on aging tests of UF membranes [27].

In this study, three factors (temperature, concentration, time of contact) have been studied for five commercial detergents. Three temperature levels, two temperature levels, and one temperature level have been studied. The concentration values vary between half and double of the advised concentration on site. Times of contact vary between 7 and 180 days (including the industrial cumulative time of contact). To evaluate the influence of these parameters and to determine the best experimental conditions, the value of the responses over the whole experimental domain is desired. To get this information, an empirical mathematical model was used, which establishes the relationship between the variation of the responses and the variation of the three studied factors. This model is a quadratic model with linear, quadratic, and cross product terms. To estimate the coefficients of this model, an optimal experimental design was performed, and from the results for each studied response, 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. The influence of aging on the membrane properties is evaluated by means of tensile testing and permeability measuring.

An experimental design scheme is presented in Table 2. Fourteen experiments are necessary for the design building (1–14); five additional experiments are used for designs validation. C° is the concentration advised on industrial plants during cleaning procedure.

Table 2
Designs of experiments for membranes aged in NaOCl

Exp	Concentration (C°)	Time (*t*) (days)	Temperature (T) (℃)
1	0.50	7	5.0
2	2.00	7	5.0
3	1.00	30	5.0
4	0.50	180	5.0
5	2.00	180	5.0
6	1.00	7	20.0
7	0.50	30	20.0
8	2.00	30	20.0
9	1.00	180	20.0
10	0.50	7	40.0
11	2.00	7	40.0
12	1.00	30	40.0
13	0.50	180	40.0
14	2.00	180	40.0
15	2/3	14	5.0
16	1.50	90	5.0
17	1.00	45	20
18	2/3	90	40.0
19	1.50	14	40.0

2.4. Aging characterization

The membranes were characterized by complementary techniques: measurements of permeate flux, tensile strength at break, ATR-FTIR and HRSEM. However, only permeability and tensile tests measurements were quantitatively exploited in designs of experiments.

The permeability test is a commonly used measure of the overall performance of a membrane. The permeability of the fibers is determined after each aging condition. For the measurements of permeability, laboratory-scale modules were fabricated using 5 fibers of 40 cm length. Modules are made by potting

Table 3
Aging conditions tested by the experimental designs

	$c°$*(pH at 20°C)	Tested concentrations' fields	Temperature	No. of experiments (Fibers)
NaOCl	200 ppm (pH = 9.5)	From 100 to 400 ppm	From 5 to 40°C	19 (475 fibers)
P3-OZS	%wt (pH = 3.5)	From 0.05 to 0.2%wt	20°C	13 (325 fibers)
P3-U110	0.7% wt (pH = 11.0)	From 0.35 to 1.4% wt	From 20 to 40°C	17 (1,275 fibers)
P3-U75	0.3% wt (pH = 1.8)	From 0.15 to 0.6% wt		
P3-U67/ P3-U69 N	0.3/0.8% wt (pH = 11.5)	From 0.15 /0.8% wt to 0.6/0.8% wt		

*$c°$: is the concentration advised on industrial plants during cleaning procedures.

the fibers in a PVC shell, with "epoxy" glue [7]. Modules were realized after the aging of the fibers in order to avoid a possible influence of the glue aging. The permeability (at 20°C) of the hollow fibers was determined by filtration of Mont Roucous water from 0 to 1.4 bars and compared with native fibers.

One of the most fundamental tests to determine the mechanical properties of a material is the tensile test. In this study, a tensile test apparatus of Zwick (Zwicki-Line Testing Machines Z2.5, Zwick/Roell, Ulm, Germany) is used. The samples were tested at 23 ± 2°C. At least 10 samples of 300 mm were tested for each aging condition.

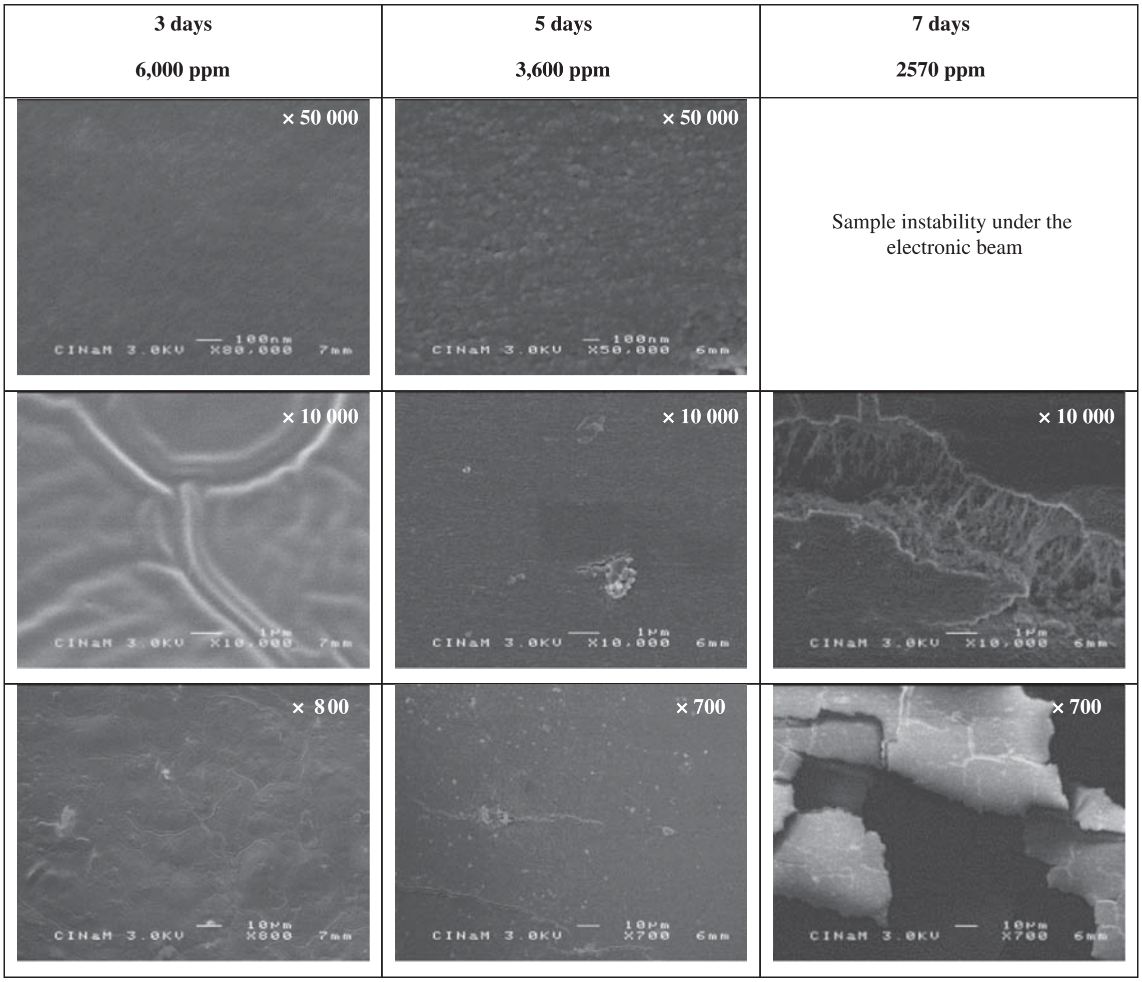


Fig. 2. HRSEM images of samples aged in NaOCl at 40°C for a same "$c \times t$" parameter (18,000 ppm days, with no pH correction 11.4 < pH < 11.9).

3. Results and discussion

First, preliminary experiments were carried out (only with NaOCl) for the same value of the $c \times t$ parameter, but with a simultaneous variation of concentration and time of exposure. For a same value of the $c \times t$ parameter, it was shown that the macroscopic and the microscopic aging were not equivalent for a high concentration/short time of exposure and low concentration/long time of exposure.

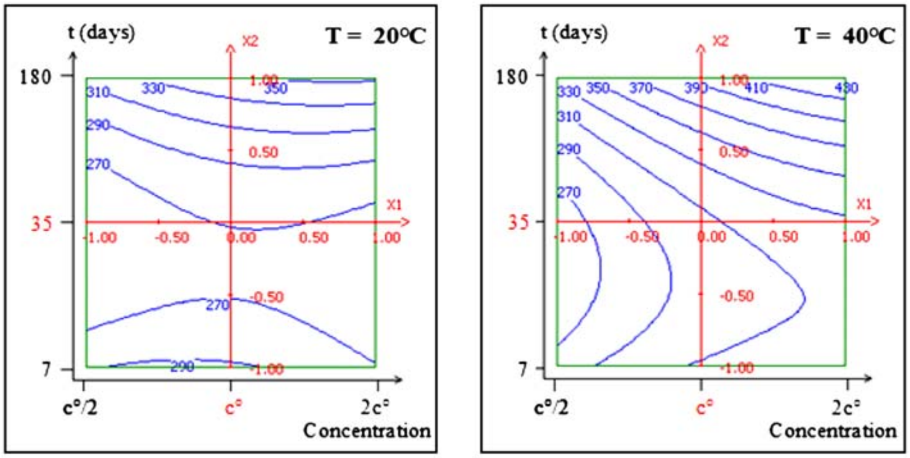
Table 4
Difference between experimental and designed values of Lp and E_l for samples aged in NaOCl

Exp.	Lp ($L\,h^{-1}\,m^{-2}\,bar^{-1}$)		E_l (%)	
	Experimental Lp_{exp}	Calculated Lp_{calc}	Experimental El_{exp}	Calculated El_{calc}
1	327	342	44.0	41.5
2	409	389	47.6	47.8
3	368	362	40.2	43.8
4	429	409	37.8	39.3
5	463	476	38.6	37.3
6	369	365	45.2	46.8
7	355	354	40.3	40.6
8	411	411	37.7	36.8
9	467	484	33.4	32.6
10	370	355	47.9	49.6
11	383	402	41.8	41.0
12	429	419	39.8	36.3
13	500	519	30.0	29.2
14	607	587	10.0	12.2
15	331	341	43.9	43.3
16	407	419	40.0	40.9
17	409	397	39.0	38.8
18	–	–	31.2	31.7
19	398	405	37.8	38.3

For the ultrafiltration membranes and for the experimental conditions tested, the permeability deterioration in function of $c \times t$ parameter has been shown to be not homogeneous according to the temperature. This is illustrated on HRSEM images on Fig. 2.

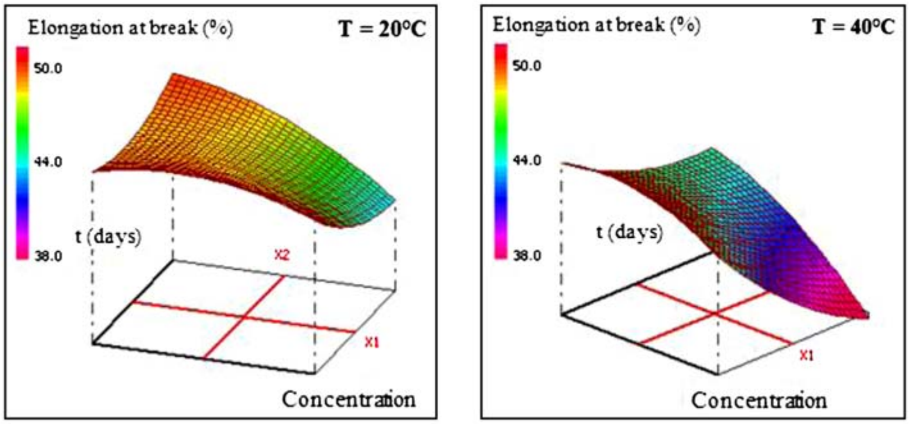
Secondly, further experiments were realized using an approach based on the experimental designs in order to achieve a relevant and predictive aging pattern without using an accelerated aging protocol. For all the tested detergents, permeability and elongation at break values obtained with the statistical model are simulated with an acceptable error (included in the measurement accuracy: 8% for Lp and 4% for E_l) (the case of results achieved for NaOCl aging are detailed in Table 4).

For all the studied detergents, differences between results from experiments (Lp_{exp} and El_{exp}) and values calculated by the model (Lp_{calc} and El_{calc}) are in such a way that the difference ΔLp ($Lp_{exp} - Lp_{calc}$) is always under 8% of Lp values and ΔE_l ($El_{exp} - El_{calc}$) is always under 4%. So, the pattern established for macroscopic membrane deteriorations can be considered satisfying and reliable, to simulate membrane aging in function of the tested parameters. For the 5 studied commercial detergents, 2D and 3D Lp and E_l responses can be provided for the complete field of the studied parameters (c°, t, and T). One example is given for 2D-designed responses of permeability Lp in case of P3-Ultrasil 110 aging (Fig. 3(a) and (b)) and 3D-designed responses of elongation at break El in case of P3-Ultrasil 75 aging (Fig. 4(a) and (b)).



(a) (b)

Fig. 3. 2D-experimental designed permeability responses at 20°C (a) and 40°C (b) and) for hollow fiber membrane aged in P3-Ultrasil 110.



(a) (b)

Fig. 4. 3D-experimental designed elongation at break responses at 20°C (a) and 40°C (b) for hollow fiber membrane aged in P3-Ultrasil 75 in function of concentration (X1) and time (X2).

At the same time, the obtained results confirmed that NaOCl is one of the most detrimental chemical for polymeric membranes. Results show high deteriorations induced by NaOCl as well in terms of mechanical properties and flux as in terms of macroscopic observations. The results at 20˚C of fibers aged in NaOCl and P3-Oxysan ZS at their respective industrial concentration show that degradations of membrane are far more detrimental with NaOCl than with P3-Oxysan ZS (Fig. 5). After seven days, the difference in Lp modification is obvious between NaOCl and P3-Oxysan ZS.

Concerning the other detergents tested (and considering the long aging duration applied in this study), it could be concluded that the industrial formulated detergents are quite harmless for the membrane for a time corresponding to the effective cumulated industrial time of contact.

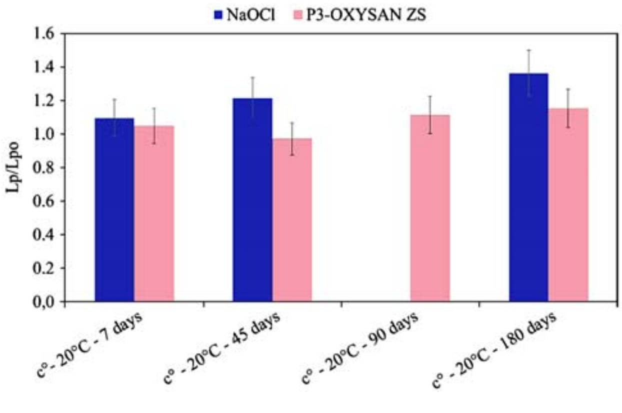


Fig. 5. Variation of permeability of hollow fibers soaked in NaOCl and P3-Oxysan ZS at 20˚C.

4. Conclusion

The goals of this study were the following: to establish a new relevant aging protocol in order to study commercial detergents that have not been studied until now. So experiments using accelerated conditions and designed conditions were realized and compared. The results revealed that the "$c \times t$" parameter (largely used in previous studies) is not a reliable parameter to simulate aging effects. High concentration for a short time is not representative of a significant industrial concentration for a significant cumulated contact time. On the contrary, the aging pattern established using experimental designs for permeability and mechanical properties can be considered satisfying and reliable, to simulate deteriorations in function of the chemical aging parameters. Moreover, aside the results detailed in this study, other aging data on commonly used commercial detergents have been achieved:

- Concerning oxidants, P3-Oxysan ZS presents, as for NaOCl, coupled permeability increase, loss of plasticity and decrease in PVP peak intensity but to a much lesser degree.
- Concerning other detergents, it can be concluded that P3-Ultrasil 110's concentration can be increased (<2c°) and a temperature of 40˚C can be applied for a curative cleaning without any damage on membranes. On the first hand, .3% wt of P3-Ultrasil 75 at 20˚C would not have damaging impacts on membranes even for a long time (180 days). On the other hand, an increase in temperature from 20 to 40˚C would have a negative impact on membrane integrity (crackles). Then, P3-Ultrasil 67/P3-Ultrasil

69 New at 40°C, no crackles on HRSEM images or degradations of mechanical properties has been observed. Increase in permeability could explain by a possible adsorption of surfactants contained in the detergent.

If P3-Ultrasil 110 and P3-Ultrasil 67/69 New are considered, the degradations of permeability for 180 days of aging are more stressed 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 67/69 New than with P3-Ultrasil 110. No definitive correlation can be established between 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. So, the results achieved in this study confirmed that it is necessary for an aging membrane study to couple macroscopic and microscopic methods of characterization.

Then, in order to get through and deepen this study, complementary experiments are ongoing to further confirm the observation (dynamic aging, aging of other membranes).

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List of symbols

ATR-FTIR — attenuated total reflectance Fourier transform infra-red
c° — effective industrial concentration (ppm)
ΔE_{l} — difference between calculated and experimental El values
$\Delta \mathrm{Lp}$ — difference between calculated and experimental Lp values
E_{l} — elongation at break point (%)
$\mathrm{El}_{\mathrm{calc}}$ — calculated elongation at break point (%)
$\mathrm{El}_{\mathrm{exp}}$ — experimental elongation at break point (%)
Lp — membrane hydraulic permeability ($\mathrm{L\,h^{-1}\,m^{-2}\,bar^{-1}}$)
$\mathrm{Lp}_{\mathrm{calc}}$ — calculated membrane hydraulic permeability ($\mathrm{L\,h^{-1}\,m^{-2}\,bar^{-1}}$)
$\mathrm{Lp}_{\mathrm{exp}}$ — experimental membrane hydraulic permeability ($\mathrm{L\,h^{-1}\,m^{-2}\,bar^{-1}}$)
PEG — polyethyleneglycol
PES — polyethersulfone
pH — hydrogenpotential
PSf — polysulfone
PVP — poly(vinyl pyrrolidone)
t — time (days)
T — temperature (°C)
HRSEM — high-resolution scanning electron microscopy

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