



**HAL**  
open science

# Comprehensive study of supported PVDF membrane ageing in MBR: A direct comparison between changes at bench scale and full scale

Marcos Oliveira, Romain Mailler, Vincent Rocher, Yannick Fayolle, Christel Causserand

## ► To cite this version:

Marcos Oliveira, Romain Mailler, Vincent Rocher, Yannick Fayolle, Christel Causserand. Comprehensive study of supported PVDF membrane ageing in MBR: A direct comparison between changes at bench scale and full scale. *Separation and Purification Technology*, 2021, 279, pp.119695. 10.1016/j.seppur.2021.119695 . hal-03480189

**HAL Id: hal-03480189**

**<https://hal.inrae.fr/hal-03480189>**

Submitted on 1 Jun 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Comprehensive study of supported PVDF membrane ageing in MBR: a direct**  
2 **comparison between changes at bench scale and full scale**

3 OLIVEIRA FILHO, Marcos<sup>1</sup>; MAILLER, Romain<sup>2</sup>; ROCHER, Vincent<sup>2</sup>; FAYOLLE,  
4 Yannick<sup>3</sup>; CAUSSERAND, Christel<sup>1</sup>

5 <sup>1</sup> *Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Toulouse,*  
6 *France*

7 <sup>2</sup> *SIAAP, Direction Innovation, 92700, Colombes, France*

8 <sup>3</sup> *Université Paris-Saclay, INRAE, PROSE, 92761, Antony, France*

9

10 Corresponding author: OLIVEIRA FILHO, Marcos

11 E-mail: marcos.oliveira@siaap.fr

12 Phone: +33 1 41 19 52 12

13 Postal address : 82 Avenue Kléber, 92700 Colombes

14

## 1 **Abstract**

2 While membrane bioreactors (MBR) have been broadly applied to wastewater treatment,  
3 membrane ageing studies have focused mainly on: (i) understanding the chemical action of  
4 sodium hypochlorite or (ii) monitoring ageing in direct filtration facilities (drinking water,  
5 groundwater, etc.). Thus, a comprehensive investigation under full-scale MBR operating  
6 conditions is still required. In the present study, polyvinylidene difluoride (PVDF) hollow  
7 fibers were sampled from a full-scale MBR in northern Paris during 7 years of operation. In  
8 addition, pristine membranes were aged at bench scale by single soaking in hypochlorite  
9 solution at a concentration and pH similar to MBR cleaning protocols. Both bench-scale- and  
10 full-scale-aged hollow fibers were characterized using similar analytical methods to assess the  
11 contributions of chemical action and operating conditions to the ageing process. At bench  
12 scale, membranes experienced no changes in mechanical resistance, but intrinsic permeability  
13 (i) first increased as a result of the hydrophilic agent oxidation, i.e., polyvinyl pyrrolidone  
14 (PVP), increasing porosity with the appearance of small pores (diameter < 20 nm), and (ii)  
15 then the structure seemed to collapse and permeability decreased as a result. By contrast,  
16 membranes aged at full scale experienced a 46% decline in maximum tensile strength  
17 probably due to mechanical stress induced by aeration conditions in MBR. Besides,  
18 permeability increased for the whole period as a result of a more pronounced  
19 oxidation/dislodgement of PVP molecules leading to higher porosity and the appearance of  
20 bigger pores (diameter > 40 nm). These changes favored irreversible fouling in contrast to  
21 bench-scale ageing. Therefore, bench-scale ageing is not completely representative of full-  
22 scale ageing and membrane autopsies must be preferred to this end. However, permeability  
23 and PVP content measurements may be applied after cleaning as in situ nondestructive tools  
24 in full-scale MBR to monitor membrane ageing. Plant operators should be aware that a

1 continuous increase in intrinsic permeability may favor irreversible fouling accumulation  
2 demanding more frequent chemical cleanings.

3 **Keywords:** membrane bioreactor, ultrafiltration, hollow fiber, wastewater treatment,  
4 multiscale, long-term operation.

5

## 6 **1. Introduction**

7 Membrane bioreactors (MBR) have experienced an exponential growth during the past  
8 decade. The cumulative treatment capacity of large-scale facilities ( $>100,000 \text{ m}^3/\text{d}$ ), increased  
9 from  $500,000 \text{ m}^3/\text{d}$  in 2010 and is expected to reach over  $14,000,000 \text{ m}^3/\text{d}$  by 2025 [1]. The  
10 main drivers of this MBR expansion across the globe are stricter legislation concerning the  
11 reuse of the treated effluent, discharge to sensitive water bodies, space limitations, and  
12 retrofitting/upgrading wastewater treatment plants (WWTP) [2]. Membranes act as a reliable  
13 physical barrier, and thus MBR perform significantly better than classic processes. To  
14 illustrate, Bertanza et al. (2017) compared a full-scale MBR with a conventional activated  
15 sludge system (CAS) from a WWTP in Italy. Treating the same influent, MBR was able to  
16 remove 99.5% of chemical oxygen demand (COD) versus 90.6% for the CAS [3].

17 Despite the increasing interest in the application of MBR, membrane fouling is still a major  
18 concern. Several strategies are applied to reduce fouling such as aeration cycles, physical  
19 cleaning, i.e., relaxation or backwash, and chemical cleaning either by chemically enhanced  
20 backwash or cleaning-in-place (CIP) protocols [4]. However, these strategies may cause  
21 unrequired changes in membrane properties and are not able to eliminate fouling, instead  
22 residual fouling takes place over long-term use. The combined effect of residual fouling and  
23 changes in membrane properties in the long term results in membrane ageing, which is known

1 to hinder filtration capability and ultimately lead to membrane replacement [5]. Membrane  
2 lifespan is also a decisive factor in the economic efficiency of an MBR; a 19% reduction in  
3 the total costs of an installation was reported if membranes were replaced after 10 years  
4 instead of after 5 [6].

5 As a result, interest in understanding the ageing process of MBR has increased. Traditional  
6 studies focused on comprehending the changes in membrane properties due to exposure to  
7 chemicals often used in cleaning protocols, such as oxidants, bases, and acids. Among them,  
8 sodium hypochlorite (NaOCl) is the most commonly studied and widely used reagent in  
9 ultrafiltration processes thanks to its cleaning efficiency and associated low cost;  
10 unfortunately, however, NaOCl is also involved in the degradation of polymeric membranes.  
11 Polyvinylidene difluoride (PVDF), a chlorine-resistant polymer, has emerged as one of the  
12 most commonly used membrane materials for drinking water and wastewater treatment  
13 applications [7]. It has a high hydrophobic character and is usually mixed with hydrophilic  
14 and pore-forming additives, i.e., polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), in  
15 the manufacturing of ultrafiltration membranes.

16 Since 2010, at least 22 studies have been published on PVDF membrane ageing. The main  
17 approach used in these studies was to accelerate ageing by single soaking in a hypochlorite  
18 solution and to observe the changes in membrane properties [8–21]. Generally, the chlorine  
19 exposure dose, which is the product ( $C \times t$ ) between chlorine concentration (C) and soaking  
20 time (t), is used to monitor the ageing process. This parameter allows us to compare the  
21 ageing effects between bench scale and full scale. Other approaches included filtration of  
22 model fouling solutions and backwash hypochlorite cycles to include the impact of fouling  
23 [22–24]. Finally, one study investigated PVDF membrane ageing in full-scale direct filtration  
24 facilities [25].

1 The main conclusions drawn from these studies are: (i) the current understanding of PVDF  
2 membrane ageing is mainly based on chemical exposure at bench scale and (ii) contradictions  
3 can be found regarding permeability, pore size, and fouling reversibility changes with ageing,  
4 probably as a result of the differences in ageing conditions, in analytical methods, and in  
5 membrane type. Regarding these two points, the changes in PVDF membrane properties over  
6 time by direct filtration in drinking water facilities were elucidated in an initial study and the  
7 findings were later compared with changes observed in ageing of the same membranes at  
8 bench scale by single soaking and model fouling solution filtration/NaOCl backwash cycles  
9 [24,25]. By applying the same analytical methodology, the authors were able to conclude that  
10 single soaking is a reliable tool for predicting ageing changes in direct filtration facilities.

11 However, operating conditions in direct filtration and MBR are substantially different and a  
12 comprehensive study of changes in membrane properties over time under MBR operating  
13 conditions is still lacking. For direct filtration units, filtration cycles may take several hours at  
14 higher fluxes, i.e., over  $30 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  (LMH) before backwash, due to a low-charged influent in  
15 terms of dissolved organic carbon (DOC), i.e., approximately  $3.5 \text{ mgC/L}$  [26]. For MBR,  
16 membranes are expected to handle much more polluted water (DOC over  $100 \text{ mgC/L}$ ) with  
17 higher amounts of fouling agents and suspended solids, leading to smaller filtration fluxes  
18 ( $\sim 25 \text{ LMH}$ ) and more frequent relaxation/backwash (every 10–90 min) [2]. In addition, one of  
19 the major differences between applications is membrane aeration, i.e., constant or intermittent  
20 aeration cycles to control cake formation. As membranes are potted without tension into the  
21 modules, this enables them to oscillate, which results in friction between membranes and  
22 limits cake deposition, whereas in direct filtration, aeration is not applied for this purpose as  
23 membranes are compacted in the module. To withstand these high shear stress conditions, the  
24 hollow fiber PVDF membranes are supported with more resistant polymers, such as poly-  
25 ethylene terephthalate (PET) [19].

1 The dynamics of filtration and fouling in MBR are expected to play a major role in membrane  
2 ageing compared with direct filtration facilities. In the only study dealing with membrane  
3 ageing in full-scale MBR, membrane end-life was triggered by the decline in filtration  
4 capacity (or increase in operating pressure) instead of by the maximum chlorine exposure  
5 advised by membrane manufacturers; however, no membrane characterization was performed  
6 to identify changes in the physical–chemical properties and to quantify the accumulation of  
7 residual fouling [5]

8 Thus, the aim of this study is to better understand PVDF membrane ageing in full-scale MBR  
9 under long-term operating conditions. To assess separately the chemical contribution due to  
10 NaOCl exposure, new membranes from the same brand were single soaked in NaOCl solution  
11 at bench scale and the changes in membrane properties were compared with full-scale ageing  
12 via regular membrane sampling in a WWTP over a 7-year period. To the best of the authors’  
13 knowledge, this is the first study to present an autopsy characterization of PVDF membranes  
14 harvested from a full-scale MBR for such a long period.

15

## 16 **2. Materials and methods**

### 17 **2.1. Materials and ageing procedure**

#### 18 **2.1.1. Chemical ageing at bench scale**

19 For this study, virgin ZeeWeed® 500D (SUEZ Water Treatment Solutions, France)  
20 membranes were sampled from virgin ultrafiltration modules produced in 2018 equivalent to  
21 those installed in the WWTP facility (see section 2.1.2). These are supported PVDF hollow  
22 fibers with a nominal pore diameter of 0.04  $\mu\text{m}$ .

1 Hypochlorite solutions used for the bench-scale ageing experiments were obtained by dilution  
2 of commercial sodium hypochlorite at 14 wt% (VWR chemicals, USA). In addition,  
3 concentrated sulfuric acid (analytical grade 95%, VWR chemicals, USA) for pH adjustment  
4 and sodium bisulfite (Honeywell Research Chemicals, USA) used for membrane storage were  
5 of analytical grade. Aqueous solutions were all prepared using pure water from Milli-Q™  
6 equipment (Thermo Fisher Scientific, USA).

7 Membranes were stored in 1 g/L sodium bisulfite solution at room temperature ( $21 \pm 2$  °C)  
8 before use. After rinsing in a large volume of pure water, laboratory ageing was performed by  
9 single soaking the pristine membranes in NaOCl solution at a total free chlorine concentration  
10 of 1000 ppm at room temperature; the intensity of ageing is presented as  $C \times t$  ranging from 0  
11 to 750,000 ppm.h. The volume of fibers did not exceed 1% of the soaking solution volume in  
12 order to avoid significant consumption of chlorine. Total chlorine concentration was checked  
13 three times a week via silver nitrate titration (Hach, USA). When a deviation of more than  
14 10% from the target concentration was measured, the concentration was corrected by adding  
15 NaOCl. Concentrated sulfuric acid was added to adjust the pH to 9.0 and was corrected  
16 whenever changes greater than 5% were observed over time. These conditions are usually  
17 found in MBR applied to municipal wastewater treatment, and are equivalent to those applied  
18 to the MBR facility considered in this study (see 2.1.2). The actual free chlorine  
19 concentrations and pH measured during the bench-scale ageing ranged from 950 to 1060 mg  
20 Cl/L (ppm) and from 8.98 to 9.09, respectively; thus, the conditions were considered to be  
21 very stable.

22 In addition, membranes were also soaked in solutions of sulfuric acid and citric acid,  
23 separately, at pH 2.7, but no changes in membrane physical-chemical properties were  
24 observed. Thus, only the effects of sodium hypochlorite are analyzed in the present study.



1

2           **2.1.2. Full-scale ageing**

3   Membranes in the full-scale operation were sampled over 7 years from the Seine-Morée  
4   WWTP in France (SIAAP). This facility was commissioned in 2014 and treats 50,000 m<sup>3</sup>/d  
5   wastewater (300,000-population equivalent) from the northern Paris urban area. This WWTP  
6   is composed of screening and grit and grease removal in its pretreatment unit, followed by a  
7   primary lamellar settler. The biological treatment and post-clarification are performed by  
8   MBR (Ultrafor®, Suez, France). Pretreated wastewater is divided equally into three biological  
9   basins (total volume of 39,500 m<sup>3</sup>) composed of anaerobic, anoxic, and aerated zones. Then,  
10   the mixed liquor is sent to eight membrane tanks of 300 m<sup>3</sup> each. Each membrane tank  
11   contains 10 immersed cassettes composed of ZeeWeed® 500D membrane modules. The total  
12   filtering surface of this MBR is 106,000 m<sup>2</sup> (13,250 m<sup>2</sup> per tank).

13   Membranes are operated under coarse bubble aeration during 10-s on/off intervals. Filtration  
14   cycles occur for 15 min followed by physical cleaning, i.e., 30 s relaxation and 30 s  
15   backwash. Mixed liquor suspended solids concentration (MLSS) is controlled between 5 and  
16   10 g/L by recirculation of mixed liquor from the membrane tanks to the biological basin and  
17   by sludge extraction periodically. Chemically enhanced backwashes (CEB) are performed  
18   once a week with NaOCl solution (200 ppm) and once every 2 weeks with citric acid solution  
19   (1000 ppm). Cleaning-in-place (CIP) is performed once a year. Ideally, membranes are  
20   submerged in a solution of 800 ppm NaOCl, and after rinsing they are then submerged in a  
21   solution of citric acid at a pH around 2.7. Each soaking is performed for 20 h with cyclic  
22   aeration every hour (giving a theoretical annual hypochlorite C × t of 16,000 ppm.h; however,  
23   deviations are not rare in full-scale operation). The influent and effluent characteristics along

1 with the precise membrane operating conditions are presented in the supplementary material  
 2 (Table S. 1).

3 Membranes were sampled from the same two cassettes in the center of membrane tank 3 from  
 4 2016 to 2021 right before CIP (from 2 to 7 years in operation). Fibers were cut on both potted  
 5 ends and stocked in sodium bisulfite solution at 1 g/L. Before characterization, membranes  
 6 were cleaned at bench scale according to the CIP protocol applied at full scale. The  $C \times t$   
 7 value for each sample is calculated using the concentration and exposure time given by the  
 8 operators for each CIP. The  $C \times t$  ascertained in the laboratory before measurements was also  
 9 added to these values. The  $C \times t$  value related to CEB was found to be negligible (500 ppm.h  
 10 annually) and only the  $C \times t$  related to CIP was considered. The  $C \times t$  values of each sample  
 11 are presented in Table 1.

12 Table 1: Exposure dose of study samples aged at bench scale and full scale.

Full scale		Bench scale
Operation time (months)	Estimated exposure dose $C \times t$ (ppm.h)	Exposure dose $C \times t$ (ppm.h)
		0
		12,000
		24,000
28	33,000	36,000
37	42,000	48,000
45	62,000	60,000
54	72,000	72,000
		78,000
		84,000
70	98,000	100,000
		125,000
		148,000

170,000
249,000
500,000
750,000

## 2.2. Characterization of membrane performance factors

### Tensile tests

Tensile tests were performed on an INSTRON 3340 series apparatus (INSTRON®, USA). The initial distance between grips was fixed at 100 mm and samples of wet membranes were extended at a constant elongation rate of 110 mm.min<sup>-1</sup>. Breaking force, elongation at break, and Young's modulus were calculated from the experimental stress–strain curves using Bluehill 3 software.

### Filtration properties

Intrinsic membrane permeability was measured by filtration of pure water at different permeate fluxes (J) in KrosFlo Research apparatus (SpectrumLab, USA). Permeability was then calculated and corrected to 20°C according to Pellegrin et al. (2013) [27]. The values obtained for each sample (L<sub>p</sub>) were then normalized with respect to the value of a pristine membrane (L<sub>p0</sub>) as the ratio L<sub>p</sub>/L<sub>p0</sub>.

To assess fouling reversibility, 11-cm-long modules composed of three fibers were constructed and submitted to three successive cycles of filtration and backwash of mixed liquor sample. The mixed liquor was collected from the MBR recirculation channel and filtered at 1.2 μm on the same day. This suspension was stored at 4°C for a maximum of 2 weeks before use. The procedure was performed to avoid high variations in the mixed liquor characteristics over the storage time and to focus on colloidal fouling. The resulting matrix is

1 mainly composed of the colloidal fraction typically present in an MBR mixed liquor (COD:  
2  $15.6 \pm 0.8$  mg O<sub>2</sub>/L; DOC:  $7.3 \pm 2.4$  mg C/L). These experiments were conducted with a  
3 Convergence Inspector Hydra device (Convergence Industry, The Netherlands). In this assay,  
4 membranes were submitted to two cycles of 60-min filtration with this matrix at a fixed  
5 transmembrane pressure (TMP) of 0.55 bar and 30 min of permeate backwash at TMP 0.8  
6 bar. The third filtration cycle was performed for 10 min prior to a final backwash of 30 min  
7 for practical reasons. Flowrate and pressure were automatically monitored every 2 s.

8 Membranes filtered pure water for 10 min prior to the mixed liquor filtration/backwash cycles  
9 at the same TMP, and pure water permeate flux ( $J_0$ ) was measured. The permeate fluxes in  
10 mixed liquor ( $J$ ) during filtration were then normalized by  $J_0$ , giving the curve  $J/J_0$  presented  
11 in the supplementary material (Figure S. 1). Cleaning recovery after a backwash could then be  
12 expressed as a percentage of the initial normalized flux  $(J/J_0)_{c1}$  according to Eq. 1. For  
13 instance, cleaning recovery presented in this study is obtained for the third filtration cycle  
14  $(J/J_0)_{c3}$ . The cleaning recovery results allow us to estimate reversible fouling in terms of  
15 recovered filtration flux after backwash. The remaining non-recovered flux is related to the  
16 physically irreversible fouling fraction.

$$\text{Cleaning recovery (\%)} = \frac{(J/J_0)_{c1} - (J/J_0)_{c3}}{(J/J_0)_{c1}} \times 100\% \quad \text{Eq. 1}$$

17 Evaluating how aged membranes would act when facing real fouling matrices (fouling  
18 propensity) is a key indicator to understanding the impact of ageing in a practical way. Some  
19 studies assessed these behaviors by using model solutions for filtration tests, usually  
20 composed of bovine serum albumin (BSA), sodium alginate, and/or polysaccharides to mimic  
21 real effluents [22,23]. Only one study performed tests with real mixed liquor, and although  
22 these matrices are not standardized, these protocols are expected to be more transposable to  
23 full-scale applications [8]. In the present study, both sets of samples (bench-scale- and full-

1 scale-aged membranes) were submitted to hydraulic cleaning recovery tests against foulants  
2 (mainly colloidal) from a real MBR mixed liquor in order to assess fouling reversibility.

3

### 4 **2.3. Characterization of membrane physical–chemical properties**

5 The physical–chemical properties of aged membranes were measured to identify the impact of  
6 NaOCl exposure at bench scale and the impact of operating conditions at full scale.

#### 7 Infrared spectrometry

8 Functional chemical groups present on the membrane surface were analyzed via attenuated  
9 total reflection-Fourier transform infrared (ATR-FTIR) using a Nicolet iS5 spectrometer with  
10 a germanium cell (Thermo Fisher Scientific, USA). Infrared (IR) spectra were recorded at  
11 wavelengths from  $600\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  (128 scans at  $4.0\text{ cm}^{-1}$ ). Spectral analyses were  
12 performed with OMNIC® software. Changes in the  $1674\text{-cm}^{-1}$  band (stretching vibration of  
13 carbonyl) were studied among other changes. This is a characteristic band associated with  
14 PVP used as hydrophilic agent by polymeric membrane manufacturers [28]. In order to  
15 normalize the values from each spectrum, PVP content was determined by the ratio between  
16 the intensity of the PVP peak (at  $1674\text{ cm}^{-1}$ ) and the band at  $1403\text{ cm}^{-1}$ , related to C-F bonds  
17 from PVDF, known for its stability over sodium hypochlorite exposure [25]. In the present  
18 study, the PVP content of each aged sample is then expressed as a percentage of the value  
19 obtained for pristine membranes.

#### 20 Surface hydrophobicity

21 Membrane surface hydrophobicity was characterized indirectly by contact angle  
22 measurements using the captive bubble method, which was previously described by Pellegrin  
23 et al. (2013). This method is used instead of the sessile drop technique in the case of porous

1 materials since it provides a more realistic measure as the membrane surface is kept in wet  
2 conditions [27]. For these measurements, PVDF surface skin from samples was first peeled  
3 off from the support material and fixed on a microscope slide, then immersed in the  
4 measuring cell filled with water. This method was only applied to bench-scale samples as  
5 peeling off did not allow us to recover a piece of intact skin from the full-scale samples, and  
6 measurements on the whole hollow fiber led to large errors due to their concave surface.

### 7 Pore size and volume

8 Pore volume and pore size distributions were measured by nitrogen adsorption for both  
9 bench-scale- and full-scale-aged samples. Membrane samples of 0.2 g were oven dried at 40  
10 °C for 72 h and placed in the measurement chamber. Measurements were carried out at 77 K  
11 in a Belsorp apparatus (Microtrac MRN, Germany). The sorption isotherms can be used to  
12 determine pore volume and pore size distribution by the BJH model [29].

### 13 Microscopy

14 Scanning electron microscopy (SEM) was performed using a Hitachi TM3030. First, dried  
15 membranes were coated in 5 nm of gold. Then, images with an optical magnification of 60×  
16 and 500× were acquired in order to qualitatively evaluate the topographic aspects of the  
17 membranes.

18

## 19 **2.4. Statistical analysis**

20 Statistical analyses were conducted in R software [30]. In order to visualize the relationship  
21 among changes in membrane properties, a principal component analysis (PCA) was performed  
22 for each samples from bench-scale and full-scale ageing. Then, linear correlations were tested

1 for all properties and p-values relate to the null hypothesis that one property remains stable  
2 despite the other. All analysis were performed at 95% confidence level.

### 3 4 **3. Results**

5 First, the changes in performance factors, namely, mechanical and filtration properties, are  
6 presented for both chemical ageing at bench scale and at full scale (section 3.1). Then, the  
7 physical–chemical properties are evaluated in order to establish cause–effect relationships  
8 (section 3.2). Finally, these changes due to sodium hypochlorite contact and MBR operating  
9 conditions are discussed further in sections 4.1 and 4.2, respectively.

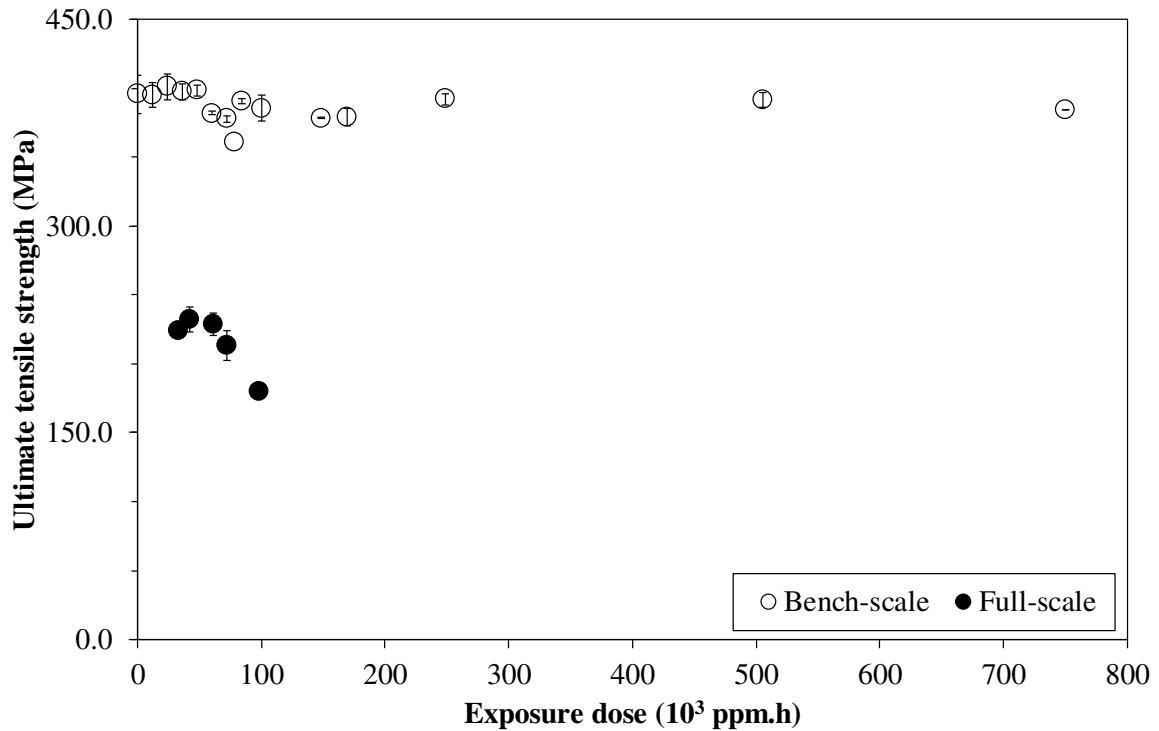
#### 10 11 **3.1. Impact of ageing on membrane performance factors at bench scale and full scale**

##### 12 **3.1.1. Mechanical properties**

13 The changes in ultimate tensile strength for bench-scale and full-scale samples as a function  
14 of exposure dose are presented in Figure 1.

15 At bench scale, single soaking in sodium hypochlorite did not cause statistically significant  
16 changes in the ultimate tensile strength of ZeeWeed® membranes (Kruskal test,  $p = 0.468$ ).  
17 This stability was also observed in percent elongation at break and Young’s modulus (data not  
18 shown).

19 Regarding membranes aged at full scale, the ultimate tensile strength showed a 45% decline  
20 over the study time. Nevertheless, operators did not report significant fiber breakage during  
21 the whole operation period.



1  
2 Figure 1: Ultimate tensile strength for bench-scale- and full-scale-aged membranes.

3  
4 **3.1.2. Filtration properties**

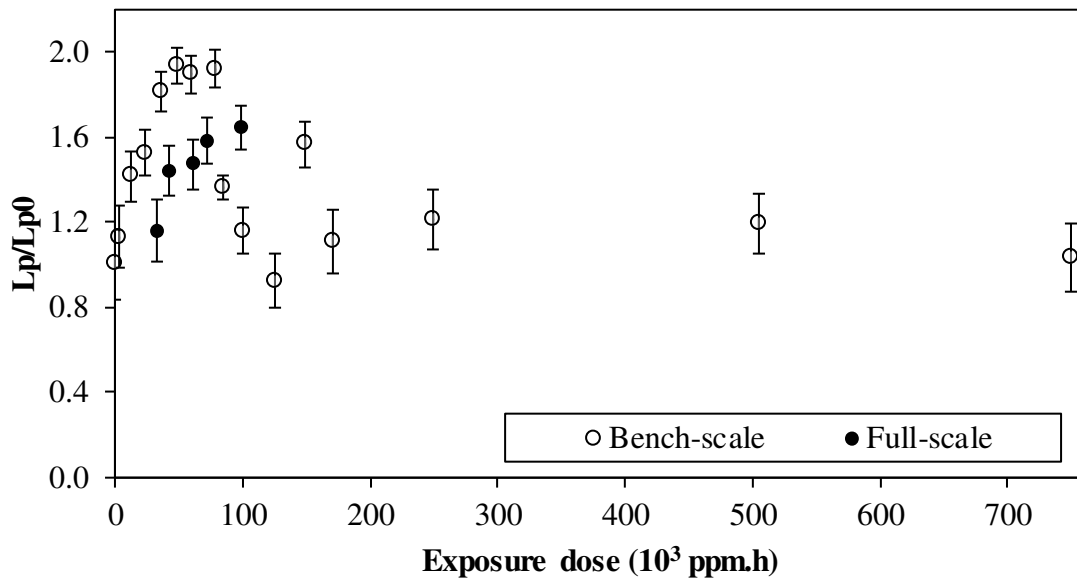
5 **3.1.2.1. Intrinsic membrane permeability**

6 Intrinsic membrane permeability is presented in Figure 2 as a ratio between the values of aged  
7 and pristine membrane ( $L_p/L_{p0}$ ) with respect to  $C \times t$ .

8 For ageing at bench scale, these results can be divided into three phases. The first phase,  
9 corresponding to membranes exposed to a  $C \times t$  of up to 78,000 ppm.h, showed an increasing  
10 trend until reaching 1.9 times the initial permeability. The second phase ( $C \times t = 78,000 -$   
11 150,000 ppm.h) of decreasing  $L_p/L_{p0}$  showed an increase in  $C \times t$ ; and in the third phase,  
12 after 150,000 ppm.h membranes reached a plateau at values comparable to a pristine  
13 membrane.



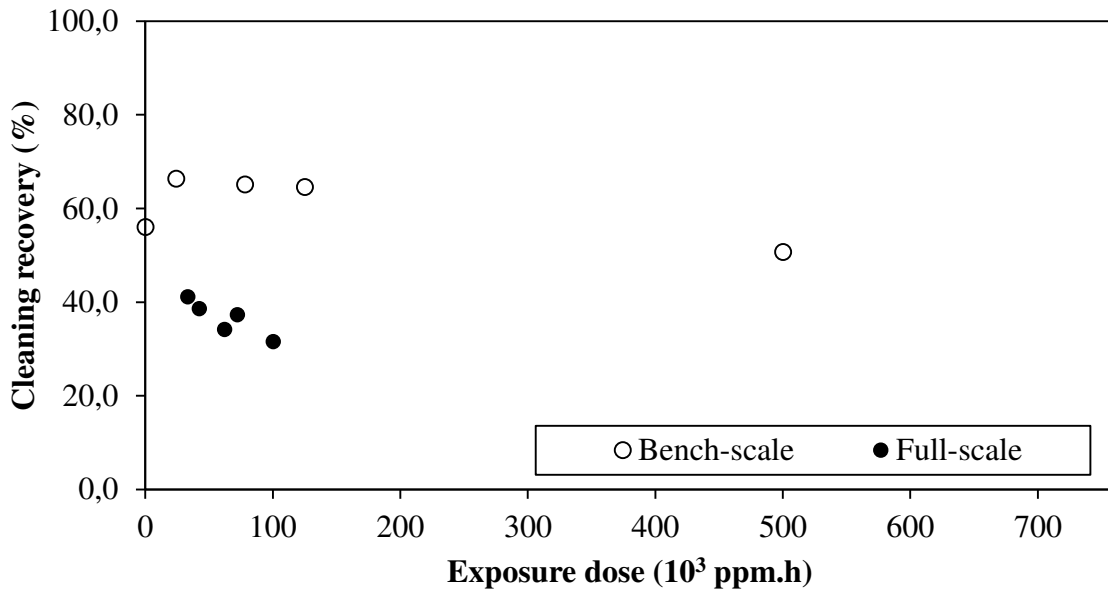
1 Moreover, the  $L_p/L_{p0}$  of membranes at full scale showed an increasing trend with  $C \times t$  (and  
 2 the associated time of operation), although to a lesser intensity than bench-scale-aged  
 3 samples, at least during the 7 years of data collection in the present research.



4  
 5 Figure 2: Changes in intrinsic permeability with respect to virgin membranes ( $L_p/L_{p0}$  ratio)  
 6 at bench-scale and full-scale ageing.

7  
 8 **3.1.2.2. Mixed liquor fouling reversibility**

9 Pristine membranes recovered 56% of their flux and samples aged up to 125,000 ppm.h  
 10 reached 65%; subsequently, samples exposed to 500,000 ppm.h experienced a decline to a  
 11 value of 51% (Figure 3). When comparing these values with those obtained for full-scale  
 12 samples (Figure 3), we found that cleaning recovery was always higher in samples aged at  
 13 bench scale, regardless of the  $C \times t$  value. In addition, full-scale harvested membranes showed  
 14 a decline from 39% to 32% in cleaning recovery when the  $C \times t$  increased from 33,000 to  
 15 100,000 ppm.h.



1

2 Figure 3: Cleaning recovery (%) after two cycles of filtration and hydraulic backwash on  
 3 fibers aged at bench scale and at full scale.

4

5 **3.2. Impact of ageing on membrane physical–chemical properties at bench scale and**  
 6 **full scale**

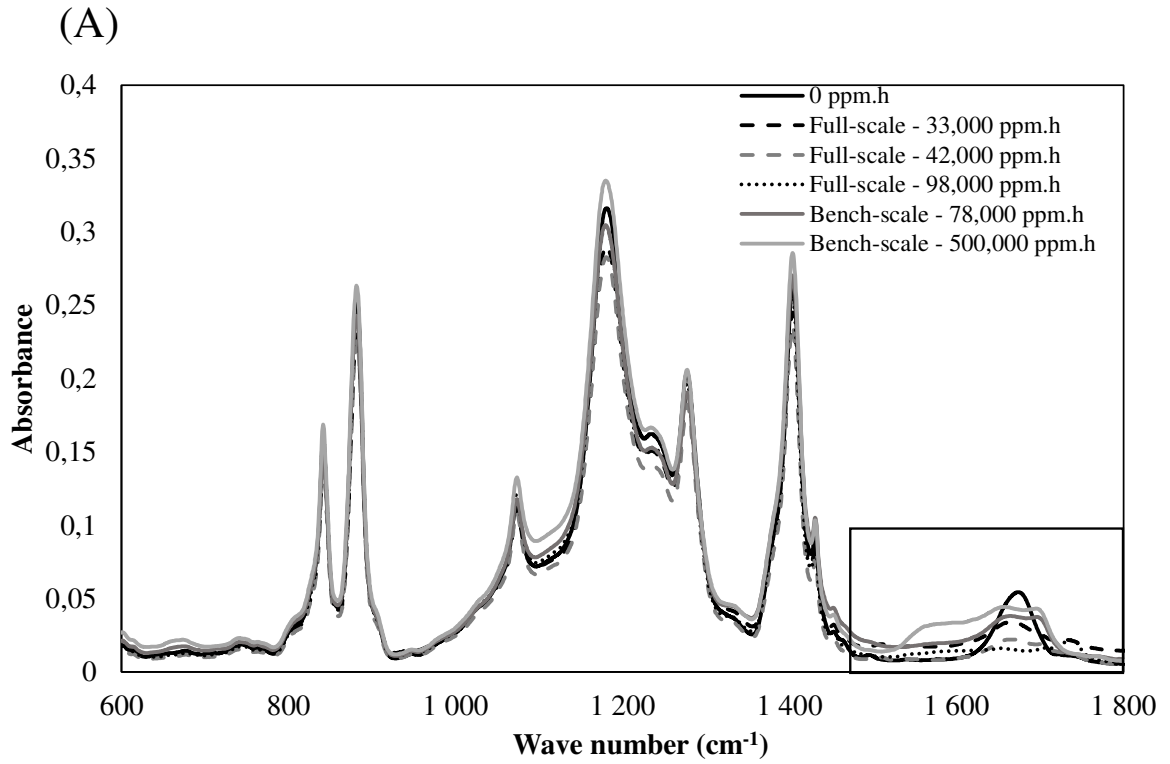
7 **3.2.1. Membrane surface chemistry**

8 **PVP degradation**

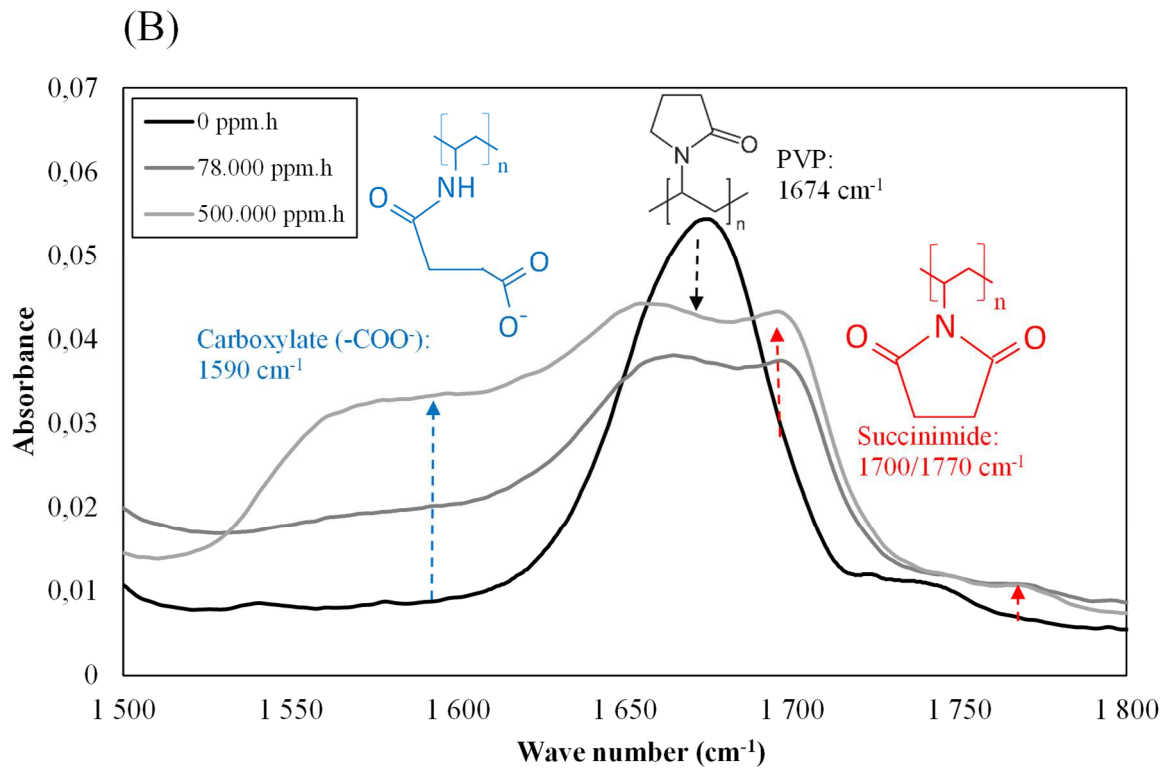
9 PVDF is a chlorine-resistant polymer and is relatively stable over long-term hypochlorite  
 10 exposure. By contrast, PVP is generally highly reactive in alkali conditions or in the presence  
 11 of oxidative radicals. The IR spectra presented in Figure 4.A confirmed the PVDF fingerprint  
 12 stability over NaOCl exposure (wavelengths considered: 1403, 1277, 1178, 1072, 880, and  
 13 841 cm<sup>-1</sup>). The band at 1674 cm<sup>-1</sup> indicated the presence of a hydrophilic agent. This band is  
 14 related to carbonyl stretches bonded to the amide group in the PVP chain. Moreover, it is  
 15 known that the area between 1500 and 1800 cm<sup>-1</sup> concentrates most of the PVP degradation  
 16 products [28]. Therefore, this zone is enlarged in Figure 4.B and C for both bench-scale and  
 17 full-scale ageing, respectively. The PVP content of aged membranes with respect to pristine

1 membranes among bench-scale- and full-scale-aged membranes as a function of  $C \times t$  is  
2 presented in Figure 5. Both sets of membranes showed a decline in PVP content that can be  
3 associated with either its removal from the membrane structure and/or to its degradation into  
4 other by-products. However, no change in PVP content is observable above 78,000 ppm.h for  
5 bench-scale samples.

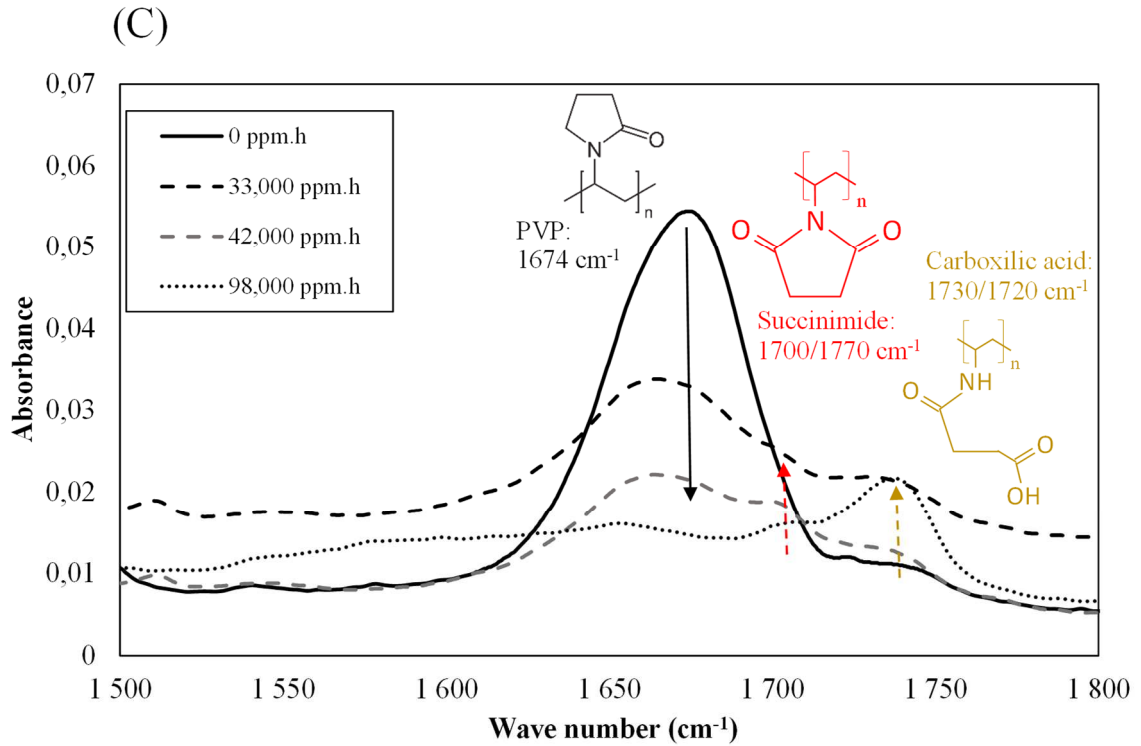
6 The decline in PVP content for full-scale-aged membranes seemed to follow the same trend  
7 observed at bench scale for  $C \times t$  values lower than 78,000 ppm.h. For higher  $C \times t$  values, the  
8 PVP content continued to decrease reaching 25% of the initial content (Figure 5).



1

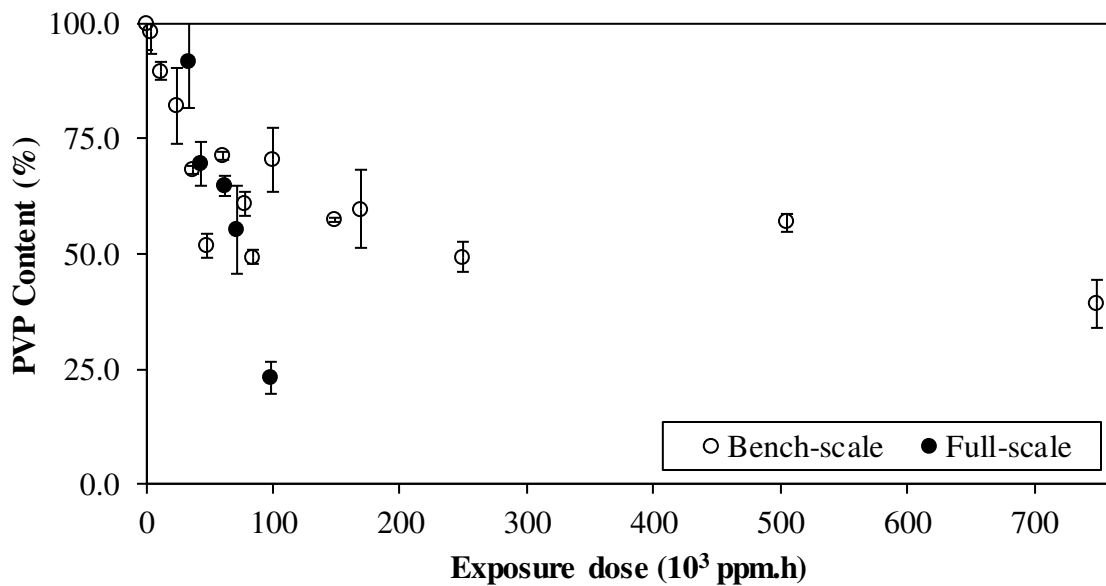


2



1

2 Figure 4: Full-range FTIR spectra ( $600\text{--}1800 \text{ cm}^{-1}$ ) of membranes aged at bench scale and full  
 3 scale (A) and enlarged view of the characteristic region of PVP and its degradation products  
 4 ( $1500\text{--}1800 \text{ cm}^{-1}$ ) for samples aged at bench scale (B) and at full scale (C).



5

6 Figure 5: Change in PVP content at bench-scale and full-scale ageing as a function of the  
 7 exposure dose.

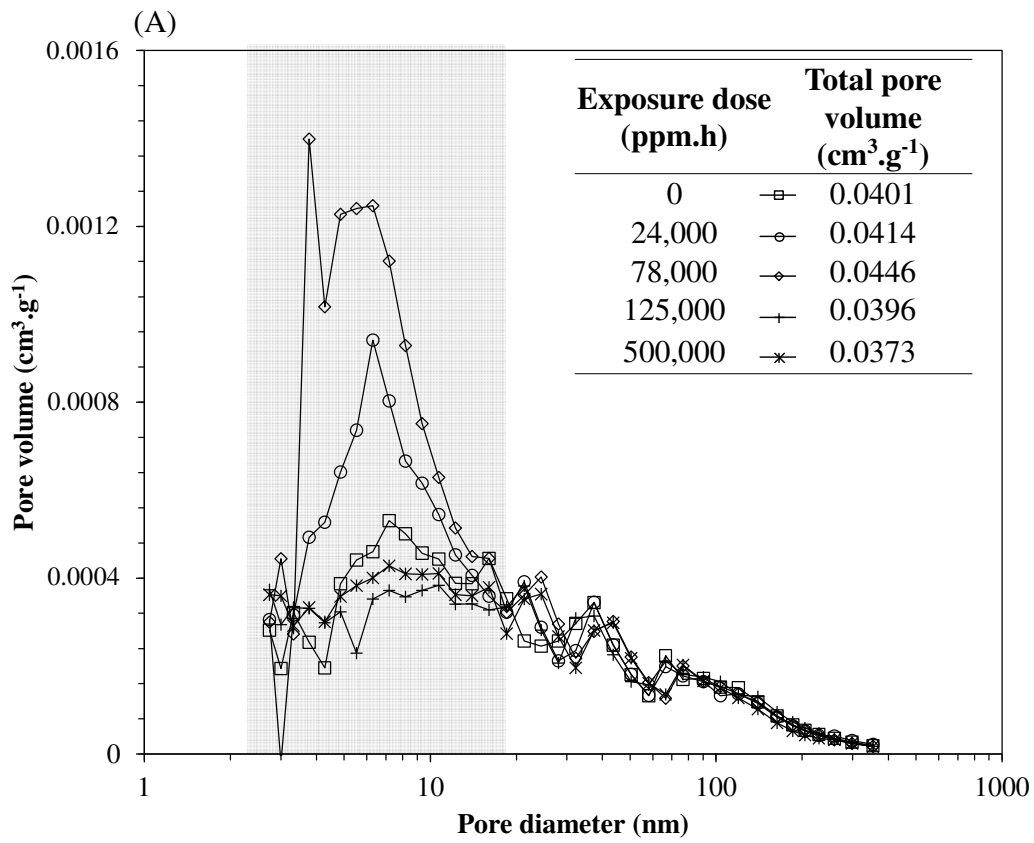
## 8 Hydrophobicity

1 Chemical ageing at bench scale had no significant influence on the contact angles as all values  
2 ranged from 38.7 to 44.9° within the experimental errors (Kruskal–Wallis test,  $p = 0.1041$ ).  
3 This result does not demonstrate that the membrane surface hydrophobicity is stable over  
4 hypochlorite exposure, but probably that the method is impacted by other phenomena (i.e.,  
5 electrical charges).

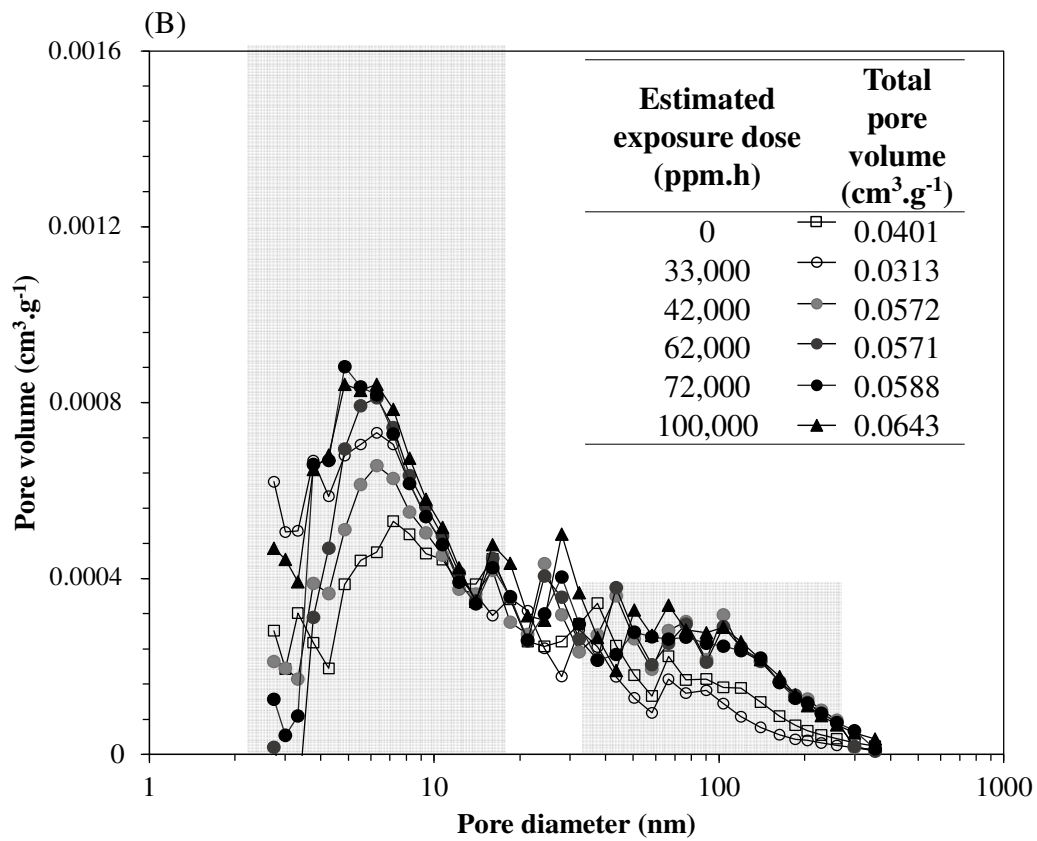
## 6 **Morphological properties**

7 The results of pore volume as a function of pore diameter ( $d_p$ ) are presented in Figure 6 for  
8 membranes aged at bench scale (A) and at full scale (B). Regarding the pore volume of  
9 bench-scale ageing (Figure 6.A), an increase in porosity is noted up to 78,000 ppm.h, after  
10 which it seems that a collapse on the structure promoted an intense decline in pore volume for  
11 samples exposed to 125,000 and 500,000 ppm.h of hypochlorite. Moreover, these changes in  
12 total pore volume seem to be governed by an initial increase followed by a decline in the zone  
13 of small pores ( $d_p < 20$  nm, gray zone).

14



1



2

1 Figure 6: Pore volume and size distribution of chemically aged membranes at bench scale (A)  
2 and at full scale (B).

3 For membranes ageing at full scale (Figure 6.B), although samples harvested in the early  
4 phase of ageing (33,000 ppm.h) had a slightly lower porous volume, the same trend of an  
5 increasing number of small pores was observed. In addition, samples aged for 42,000 ppm.h  
6 showed an increasing number of larger pores ( $d_p > 40$  nm), reinforcing the notion that the  
7 ageing mechanisms at full-scale operation are not exactly the same as chemically aged  
8 samples at bench scale. These two zones are highlighted in gray in the graph in Figure 6.

9 SEM images were acquired and qualitatively confirmed the presence of these larger pores in  
10 full-scale-aged membranes (supplementary material – Figure S. 2). In addition, an increase in  
11 surface roughness can be observed when comparing full-scale- with bench-scale-aged and  
12 pristine samples.

13

## 14 **4. Discussion**

### 15 **4.1. Sodium hypochlorite impact on membrane performance factors**

#### 16 Impact of NaOCl chemical ageing on mechanical resistance

17 In the case of supported membranes, mechanical resistance is mainly linked to the material  
18 used to support PVDF. By ATR-FTIR analysis, it was found that the supporting material of  
19 these membranes had 68% accordance with PET. PET is often used as a support material for  
20 ultrafiltration membranes. However, only few studies of membrane ageing characterized its  
21 mechanical resistance. Pulido et al. (2019) evaluated the properties of recycled PET-based  
22 membranes and concluded that the material was chlorine resistant after a 2-h exposure to a  
23 5000-ppm solution [31]. However, the effects of long-term exposure were not determined.  
24 The results of bench-scale-aged samples in the present research indicate that the long-term



1 exposure to NaOCl does not impact the mechanical properties of these supported hollow  
2 fibers. Conversely, Wang et al. (2018) characterized hypochlorite aged membranes reinforced  
3 with PET nonwoven fabric and found a slight decline in ultimate tensile strength. It is worth  
4 noting that these membranes exhibited ultimate tensile strength in the range of 40 MPa, which  
5 is 10 times less resistant than fibers used in the present study.

#### 6 Impact of NaOCl chemical ageing on intrinsic permeability

7 Changes in permeability of bench-scale-aged membranes can be associated mainly with: (i)  
8 changes in the surface physical–chemical characteristics, especially hydrophobicity and  
9 electrical charges and (ii) modifications in skin porosity. The first phase of increasing  
10 permeability between 0 and 78,000 ppm.h (Figure 2) was found to be linked to the decline in  
11 PVP content (Figure 5). Statistical analysis confirmed a significant correlation in this dose  
12 range, giving a correlation coefficient ( $r$ ) of -0.951 ( $p = 0.0003$ , Pearson correlation test).  
13 Despite the decline in PVP, the contact angle values did not change significantly. However,  
14 changes in contact angle due to an increase in hydrophobicity may be counter-balanced by an  
15 increase in electrical surface charges, and this combined effect of the surface physical–  
16 chemical properties does not seem to significantly impact permeability [27].

17 Regarding the change in skin porosity, a formation of small pores ( $d_p < 20$  nm) is observed in  
18 Figure 6.A, enhancing overall membrane porosity. In fact, FTIR spectra (Figure 4.B) showed  
19 that PVP molecules are not fully dislodged from the membrane structure. They are instead  
20 oxidized into succinimide (at  $1700/1770$   $\text{cm}^{-1}$ ) and carboxylates ( $1590$   $\text{cm}^{-1}$ ) following the  
21 PVP degradation mechanism proposed by Prulho et al. (2013) [28]. These molecules  
22 remained (totally or partially) in the membrane structure, possibly leading only to the  
23 formation of small pores, whereas a full PVP dislodgement would lead to the formation of  
24 macro-voids. By contrast, there seems to be agreement in the literature that NaOCl exposure

1 causes PVDF membrane permeability to increase as a result of a pore enlargement due to the  
2 oxidation and dislodgement of PVP from the fiber structure [9,19,22,24]. However, Ravereau  
3 et al. (2016) similarly reported an increasing volume of pores smaller than 10 nm, only for  
4 PVDF membranes containing PVP when exposed to sodium hypochlorite, whereas PVDF  
5 membranes with no additive did not show any changes in pore size distribution [16].

6 After the exposure threshold of 78,000 ppm.h, the decline in  $L_p/L_{p0}$  was no longer correlated  
7 with PVP content. It seems that after the increasing porosity, the membrane structure  
8 collapsed ( $C \times t > 78,000$  ppm.h), decreasing pore volume and  $L_p/L_{p0}$  as a result. Based on  
9 Gao et al. (2016), PVP is degraded into new products and macromolecular chains in the  
10 PVDF matrix may rearrange by crosslinking, which might be the reason for the shrinkage in  
11 porosity [23]. A statistically significant correlation was found between  $L_p/L_{p0}$  and the volume  
12 of smaller pores for the whole range of  $C \times t$  studied ( $r= 0.966$ ,  $p = 0.008$ , Pearson correlation  
13 test).

#### 14 Impact of NaOCl chemical ageing on cleaning recovery

15 Cleaning recovery is also impacted by the physical–chemical properties of surface and  
16 porosity. Pore volume did not correlate well with cleaning recovery ( $p > 0.05$ ), indicating that  
17 the appearance of small pores did not change the fouling mechanisms. Nevertheless, cleaning  
18 recovery is related to the interactions between foulants and membrane surface as well. Firstly,  
19 cleaning recovery increased with ageing, indicating that foulants became less attached to the  
20 membrane surface, i.e., increasing fouling reversibility. Irreversible fouling is mainly related  
21 to organic matter adsorption on the membrane surface, which is explained by the extended  
22 Derjaquin–Landau–Verwey–Overbeek (DLVO) theory as a synergic work of Van der Waals  
23 force, polar force, and electrostatic interactions. Foulants in mixed liquor are mostly  
24 hydrophobic organic matter and negatively charged at neutral pH [32]. When in contact with

1 NaOCl, the PVP cyclic group, pyrrolidone, is opened forming carboxylates. As a result,  
2 membranes may increase their negative charges as they age, leading to higher electrostatic  
3 repulsion between the membrane surface and foulants, enhancing then cleaning recovery.  
4 Recently, Li et al. (2021) confirmed the increase in negative charges as PVDF membranes  
5 aged in contact with NaOCl [12].

6 For further exposed samples (500,000 ppm.h), cleaning recovery dropped to 51%. We  
7 hypothesize that topographic changes (increase in roughness) may be playing a bigger role  
8 favoring foulant adsorption, as reported by Levitsky et al. (2011), and correlated well with an  
9 increase in protein adsorption onto the membrane surface [11].

10

## 11 **4.2. Membrane ageing under MBR operating conditions at full scale**

### 12 Full-scale operation effects on mechanical resistance

13 Regarding mechanical resistance, membranes aged by single soaking in hypochlorite  
14 solutions did not experience the weakening observed in the membranes at full-scale operation  
15 (Figure 1). These findings suggest that a synergic effect of aeration and filtration conditions in  
16 MBR may be the reason for the decline in ultimate tensile strength. However, the precise  
17 mechanism behind these changes could not be assessed and further studies are needed. Even  
18 though the functional groups showed no changes on the PET fingerprint (1124 and 1240  $\text{cm}^{-1}$ )  
19 in the IR spectra (supplementary material – Figure S. 3), alterations in the support polymer  
20 crystalline structure, crosslinking/chain breakage, and material fatigue could be the reasons  
21 for this decline. This weakening could lead to fiber breakage, which could degrade the  
22 filtration quality. In addition, PVDF skin tearing was observed in SEM images of full-scale-  
23 aged samples (supplementary material – Figure S. 2 G and H) and can impact permeate

1 quality. Although FTIR spectra failed to confirm changes in the PVDF functional groups  
2 (Figure 4), other studies already reported embrittlement of PVDF due to dehydrofluorination  
3 and chain scission after exposure to NaOCl [15,16,22]. Nevertheless, operators reported no  
4 changes in the permeate quality over these 7 years of operation despite the decline in  
5 mechanical resistance.

#### 6 PVP degradation differences between ageing at bench scale and full scale

7 The mechanisms of PVP degradation between bench-scale and full-scale ageing are also  
8 different (Figure 4.B and C, respectively). At bench scale, the sole effect of hypochlorite (pH  
9 9.0) induces the production of carboxylate and succinimide from the chemical attacks to PVP  
10 molecules. These degradation products remained in the membrane structure. At full scale  
11 (Figure 4.C), the PVP peak ( $1674\text{ cm}^{-1}$ ) is strongly suppressed and the typical peaks  
12 associated with by-products did not seem to increase to the same extent, with only a slight  
13 increase in the succinimide peak ( $1700\text{ cm}^{-1}$ ) being observed, suggesting that PVP is oxidized  
14 into succinimide and then removed from the membrane structure. In addition, a peak at  $1730$   
15  $\text{cm}^{-1}$  (carboxylic acids) is formed, which can be assigned either to a PVP degradation product  
16 or to residual fouling. For the former, Prulho et al. (2013) reported that carboxylates ( $1590$   
17  $\text{cm}^{-1}$ ) are favored under alkali conditions, which is the case for the whole ageing process at  
18 bench scale [28]. At full scale, however, membranes are cleaned by sodium hypochlorite  
19 followed by citric acid solutions at a pH between 2.5 and 3.0, which might favor the  
20 formation of carboxylic acids versus carboxylates in the PVP degradation process. For the  
21 latter, it is worth noting that this carboxylic acid peak may also be assigned to residual  
22 fouling, as reported by Levitsky et al. (2011) [11].

23 Several studies compared PVP degradation in different ageing protocols. For instance,  
24 Causserand et al. (2015) found no significant differences in PVP degradation between single-

1 soaked membranes and performing filtration/backwash cycles in NaOCl solution at bench  
2 scale [33]. In addition, Robinson and Bérubé (2021) investigated the hydrophilic agent  
3 content of membranes single-soaked and cyclic NaOCl filtration at bench-scale and full-scale  
4 ageing in drinking water facilities and also reported no significant differences in hydrophilic  
5 agent removal [24]. However, the impacts of MBR operating conditions were not assessed in  
6 such ageing studies. While in direct filtration facilities, membranes are trapped inside their  
7 housing, in MBR modules, ZeeWeed® fibers are potted on both ends but not stretched under  
8 tension, thus being able to oscillate when aeration cycles are performed. These cycles occur  
9 every 10–30 s to detach foulants during filtration and cleaning protocols, by increasing shear  
10 stress at the membrane surface and convective forces. These operating conditions might also  
11 enhance hydrophilic agent dislodgement from the membrane structure.

12

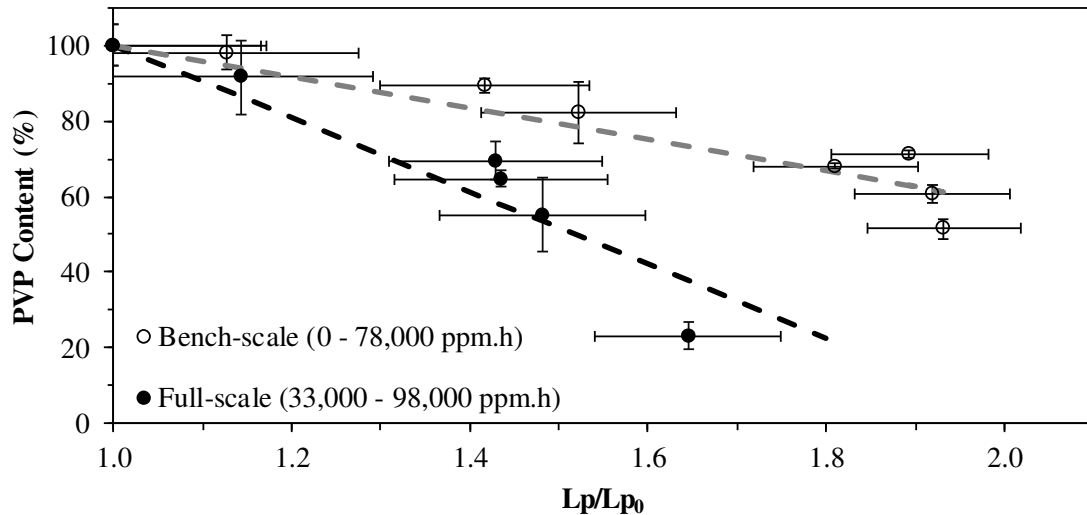
### 13 Full-scale operation impacts on intrinsic permeability

14 Fibers harvested from a full-scale MBR seemed to experience an increasing  $L_p/L_{p0}$  for the  
15 whole study period, highlighting two main differences when compared to the sole  
16 hypochlorite action at bench scale: (i) permeability increased to a lesser extent and (ii) no  
17 decline in  $L_p/L_{p0}$  was experienced in the range studied. Both residual fouling and the  
18 differences in porosity changes can be related to these results.

19 For the first point, membranes operating at full scale still showed high amounts of PVP in the  
20 early stages, which was considered the main driver for permeability changes. Moreover, these  
21 membranes experience fouling, which is partially removed by chemical cleanings. However,  
22 the later appearance of bigger pores may enhance residual fouling in the long term as more  
23 organic matter is able to flow through and be adsorbed into the membranes (Figure 6). This  
24 may increase membrane hydrophobicity [22] and despite the increasing porosity, water is

1 hampered to flow through membranes, whereas membranes aged by single-soaking in NaOCl  
2 solution did not experience fouling, which enables the permeability to increase to higher  
3 values. By comparing the changes in permeability of membranes exposed only to sodium  
4 hypochlorite with membranes that went through cycles of a model fouling solution filtration  
5 and sodium hypochlorite cleaning at bench scale, Hajibabania et al. (2012) confirmed the  
6 smaller increases among the latter samples, assigning this difference to residual fouling [22].  
7 In addition, the  $C \times t$  value is used as a reference for comparison between these ageing  
8 methods, but it is worth noting that at full scale, NaOCl species are reacting not only with  
9 membrane polymers but also with the organic matter. In addition, plant operators reported  
10 declines in free chlorine concentrations of up to 30% over CIP soaking time. As the  $C \times t$  in  
11 this study was calculated considering a stable free chlorine concentration over the CIP  
12 soaking time, this may have led to an overestimation of the actual  $C \times t$  in direct contact to the  
13 membrane surface for full-scale samples. To avoid this probable overestimation in  $C \times t$  for  
14 full-scale samples, the relationship between PVP content and  $L_p/L_{p0}$  is plotted in Figure 7 for  
15 both sets. For the same PVP removal, the increase in  $L_p/L_{p0}$  in samples aged at bench scale is  
16 higher than full-scale-aged membranes. This illustrates the role of the different pore size  
17 distributions and residual fouling, which impairs the increase in  $L_p/L_{p0}$ , limiting the  
18 overestimation of exposure dose among full-scale samples.

19



1

2 Figure 7: Relationship between PVP content removal and the changes in  $L_p/L_{p0}$  for  
 3 membranes aged at bench scale and at full scale.

4

5 For the second point, the lack of a permeability-declining phase might be linked to the  
 6 cyclical backwashes that are known to increase pore size, contributing for a permeability  
 7 increase [34]. In addition, a difference in the ageing process might also play a role. At bench  
 8 scale, PVP was degraded until its content reached approximately 40% of the pristine fibers  
 9 (Figure 5), but these molecules seemed not to be fully dislodged from the polymer structure  
 10 (Figure 4.B), leading to the appearance of only smaller pores (Figure 6). On the other hand,  
 11 samples of full-scale-aged membranes continued to lose PVP, reaching 25% of the pristine  
 12 membrane (Figure 5). This change along with the FTIR spectra in the PVP and its degradation  
 13 product region (Figure 4.C) might indicate that PVP is not only degraded but also dislodged  
 14 from the membrane structure, leading to the appearance of bigger pores as presented in Figure  
 15 6. The relationships between (i) PVP content and total pore volume ( $r = -0.864$ ,  $p = 0.026$ ,  
 16 Pearson's test), (ii) total pore volume and  $L_p/L_{p0}$  ( $r = 0.904$ ,  $p = 0.014$ , Pearson's test), and  
 17 (iii) the direct relationship between PVP content and  $L_p/L_{p0}$  ( $r = -0.930$ ,  $p = 0.007$ , Pearson's  
 18 test) were confirmed to be statistically significant. These results highlight the importance of

1 the hydrophilic agent content in preserving the membrane filtration properties. Moreover, they  
2 illustrate that changes in  $L_p/L_{p0}$  are mostly governed by changes in pore size for either bench-  
3 scale or full-scale ageing.

#### 4 Impacts of full-scale operation on cleaning recovery

5 The lower overall values of cleaning recovery for full-scale-aged membranes and its declining  
6 trend (Figure 3) can be ascribed to: (i) stronger interactions between foulants in mixed liquor  
7 and residual fouling remaining on the membrane surface; (ii) SEM images (supplementary  
8 material – Figure S. 2) showed a much rougher surface, which enhances fouling adsorption  
9 [11]; (iii) and the appearance of larger pores that can lead to higher amounts of matter inside  
10 the pores causing more severe pore clogging, which is a less reversible form of fouling than  
11 floc adhesion or cake formation [35]. In this study, pore size might contribute to cleaning  
12 recovery. However, statistical analysis were performed for changes in bigger pore volumes  
13 ( $>40$  nm) and smaller pore volumes ( $<20$  nm), separately, and no significant linear  
14 correlations were found ( $p > 0.05$ ).

15 Ultimately, changes in cleaning recovery correlated well with the loss of hydrophilic agent  
16 and with the increase in  $L_p/L_{p0}$  ( $r = 0.819$ ,  $p = 0.046$  and  $r = -0.897$ ,  $p = 0.015$ , Pearson's test,  
17 respectively). Since permeability correlated well with all other parameters, MBR operators  
18 should apply these measurements after CIP as an in situ diagnostic tool for membrane ageing.  
19 For increasing values, operators should expect a build-up of hydraulic irreversible fouling,  
20 which would lead to an increasing requirement for chemical cleanings. For future studies, this  
21 parameter may be correlated with full-scale filtration capacity data in order to identify the  
22 period when filtration is no longer possible, leading to membrane replacement. In addition,  
23 hydrophilic agent degradation seems to be the primary cause for all the other changes and as



1 in situ FTIR measurements are becoming available, it can also provide important information  
2 on membrane ageing in MBR operation.

### 3 **5. Conclusions**

4 The main conclusions of this study can be summarized as:

- 5 • Differences in the membrane ageing process for membranes aged by single soaking in  
6 NaOCl solution and during a 7-year period in an MBR treating municipal wastewater  
7 are highlighted by applying the same methodological protocol. A non-negligible  
8 contribution of filtration conditions, mechanical stress due to aeration, and residual  
9 fouling, specific to full-scale operating conditions, may significantly change ageing  
10 mechanisms. This study showed that understanding the mechanisms behind the action  
11 of NaOCl on PVDF membranes may not represent what actually occurs at full-scale  
12 operation and does not replace continuous autopsies of harvested fibers over the years.
- 13 • At bench scale, NaOCl species caused PVP oxidation, which led to the formation of  
14 small pores causing an increase in  $L_p/L_{p0}$  in contrast to the generally accepted  
15 hypothesis of pore enlargement reported in the literature. For exposures higher than  
16 78,000 ppm.h, the membrane structure collapsed and  $L_p/L_{p0}$  decreased.
- 17 • In contrast to bench-scale ageing, full-scale-aged membranes experienced a decline in  
18 mechanical resistance due to MBR operating conditions, i.e., aeration. In addition,  
19 bigger pores are formed as a result of a more pronounced degradation of PVP when  
20 compared to bench-scale ageing, which ultimately led to an increasing  $L_p/L_{p0}$  during  
21 the study period.
- 22 • The increase in  $L_p/L_{p0}$  with age in full-scale samples is less intense than in bench-  
23 scale samples for the same PVP removal as a result of residual fouling on the  
24 membrane surface that also led to a decline in hydraulic cleaning recovery.

- 1 •  $L_p/L_{p0}$  and PVP content correlated well with all ageing changes among full-scale  
2 samples and can be applied for full-scale MBR operators as nondestructive in situ  
3 tools to monitor membrane ageing.
- 4 • Since the major changes seemed to be related to PVP oxidation, efforts are needed to  
5 change membrane formulations in order to achieve a stronger bond between PVP or  
6 other hydrophilic agents and the main polymer.
- 7 • Since bench-scale ageing protocols are not fully representative of full-scale MBR  
8 ageing, an accelerated ageing protocol at pilot-scale would be useful for validating  
9 long-term membrane performance.
- 10 • Changes in membrane properties from full-scale MBR are becoming available. Thus,  
11 efforts into membrane ageing modelling are needed to perform predictive calculations  
12 of the long-term ageing effects in MBR operation.

### 13 **CRedit AUTHOR STATEMENT**

14 Oliveira Filho Marcos: Conceptualization, Methodology, Visualization, Validation, Formal  
15 analysis, Investigation, Writing – Original Draft. Mailler Romain: Conceptualization,  
16 Validation, Supervision, Project administration, Writing – Review & Editing. Rocher  
17 Vincent: Conceptualization, Resources, Funding acquisition. Fayolle Yannick:  
18 Conceptualization, Validation, Supervision, Writing – Review & Editing. Causserand  
19 Christel: Conceptualization, Resources, Methodology, Validation, Supervision, Funding  
20 acquisition, Writing – Review & Editing.

### 21 **ACKNOWLEDGMENTS**

22 The authors would like to acknowledge Céline Briand, Julien Pouillaude (DI-SIAAP), and the  
23 DLE team (SIAAP) for their participation in mixed liquor analysis, membrane sampling, and

1 characterization. The technical contribution of Estelle Langlet and Ophélie Michot and their  
2 team (SEM-SIAAP) was also essential for this work. We are also grateful to Gwenaëlle  
3 Guitier and Emma Roubaud (LGC-Toulouse) for their readiness to meet special membrane  
4 characterization demands.

## 5 **FUNDING SOURCES**

6 This research did not receive any specific grant from funding agencies in the public,  
7 commercial, or not-for-profit sectors.

## 8 **REFERENCES**

- 9 [1] The MBR site, (2021). <https://www.thembrsite.com/> (accessed April 20, 2021).
- 10 [2] P. Krzeminski, L. Leverette, S. Malamis, E. Katsou, Membrane bioreactors – A review  
11 on recent developments in energy reduction, fouling control, novel configurations, LCA  
12 and market prospects, *J. Membr. Sci.* 527 (2017) 207–227.  
13 <https://doi.org/10.1016/j.memsci.2016.12.010>.
- 14 [3] G. Bertanza, M. Canato, G. Laera, M. Vaccari, M. Svanström, S. Heimersson, A  
15 comparison between two full-scale MBR and CAS municipal wastewater treatment  
16 plants: techno-economic-environmental assessment, *Environ. Sci. Pollut. Res.* 24 (2017)  
17 17383–17393. <https://doi.org/10.1007/s11356-017-9409-3>.
- 18 [4] M. Bagheri, S.A. Mirbagheri, Critical review of fouling mitigation strategies in  
19 membrane bioreactors treating water and wastewater, *Bioresour. Technol.* 258 (2018)  
20 318–334. <https://doi.org/10.1016/j.biortech.2018.03.026>.
- 21 [5] A. Fenu, W. De Wilde, M. Gaertner, M. Weemaes, G. de Gueldre, B. Van De Steene,  
22 Elaborating the membrane life concept in a full scale hollow-fibers MBR, *J. Membr. Sci.*  
23 421–422 (2012) 349–354. <https://doi.org/10.1016/j.memsci.2012.08.001>.

- 1 [6] B. Verrecht, T. Maere, I. Nopens, C. Brepols, S. Judd, The cost of a large-scale hollow  
2 fibre MBR, *Water Res.* 44 (2010) 5274–5283.  
3 <https://doi.org/10.1016/j.watres.2010.06.054>.
- 4 [7] S. Robinson, S.Z. Abdullah, P. Bérubé, P. Le-Clech, Ageing of membranes for water  
5 treatment: Linking changes to performance, *J. Membr. Sci.* 503 (2016) 177–187.  
6 <https://doi.org/10.1016/j.memsci.2015.12.033>.
- 7 [8] S.Z. Abdullah, P.R. Bérubé, Filtration and cleaning performances of PVDF membranes  
8 aged with exposure to sodium hypochlorite, *Sep. Purif. Technol.* 195 (2018) 253–259.  
9 <https://doi.org/10.1016/j.seppur.2017.12.004>.
- 10 [9] S.Z. Abdullah, P.R. Bérubé, Assessing the effects of sodium hypochlorite exposure on  
11 the characteristics of PVDF based membranes, *Water Res.* 47 (2013) 5392–5399.  
12 <https://doi.org/10.1016/j.watres.2013.06.018>.
- 13 [10] F. Gao, J. Wang, H. Zhang, M.A. Hang, Z. Cui, G. Yang, Interaction energy and  
14 competitive adsorption evaluation of different NOM fractions on aged membrane  
15 surfaces, *J. Membr. Sci.* 542 (2017) 195–207.  
16 <https://doi.org/10.1016/j.memsci.2017.08.020>.
- 17 [11] I. Levitsky, A. Duek, E. Arkhangelsky, D. Pinchev, T. Kadoshian, H. Shetrit, R. Naim,  
18 V. Gitis, Understanding the oxidative cleaning of UF membranes, *J. Membr. Sci.* 377  
19 (2011) 206–213. <https://doi.org/10.1016/j.memsci.2011.04.046>.
- 20 [12] K. Li, Q. Su, S. Li, G. Wen, T. Huang, Aging of PVDF and PES ultrafiltration  
21 membranes by sodium hypochlorite: Effect of solution pH, *J. Environ. Sci.* 104 (2021)  
22 444–455. <https://doi.org/10.1016/j.jes.2020.12.020>.
- 23 [13] V. Puspitasari, A. Granville, P. Le-Clech, V. Chen, Cleaning and ageing effect of  
24 sodium hypochlorite on polyvinylidene fluoride (PVDF) membrane, *Sep. Purif. Technol.*  
25 72 (2010) 301–308. <https://doi.org/10.1016/j.seppur.2010.03.001>.

- 1 [14] M.F. Rabuni, N.M.N. Sulaiman, N.A. Hashim, A systematic assessment method for the  
2 investigation of the PVDF membrane stability, *Desalination Water Treat.* 57 (2016) 1–  
3 12. <https://doi.org/10.1080/19443994.2015.1012336>.
- 4 [15] M.F. Rabuni, N.M. Nik Sulaiman, M.K. Aroua, C. Yern Chee, N. Awanis Hashim,  
5 Impact of in situ physical and chemical cleaning on PVDF membrane properties and  
6 performances, *Chem. Eng. Sci.* 122 (2015) 426–435.  
7 <https://doi.org/10.1016/j.ces.2014.09.053>.
- 8 [16] J. Ravereau, A. Fabre, A. Brehant, R. Bonnard, C. Sollogoub, J. Verdu, Ageing of  
9 polyvinylidene fluoride hollow fiber membranes in sodium hypochlorite solutions, *J.*  
10 *Membr. Sci.* 505 (2016) 174–184. <https://doi.org/10.1016/j.memsci.2015.12.063>.
- 11 [17] L. Ren, S. Yu, H. Yang, L. Li, L. Cai, Q. Xia, Z. Shi, G. Liu, Chemical cleaning reagent  
12 of sodium hypochlorite eroding polyvinylidene fluoride ultrafiltration membranes:  
13 Aging pathway, performance decay and molecular mechanism, *J. Membr. Sci.* 625  
14 (2021) 119141. <https://doi.org/10.1016/j.memsci.2021.119141>.
- 15 [18] L. Vanysacker, R. Bernshtein, I.F.J. Vankelecom, Effect of chemical cleaning and  
16 membrane aging on membrane biofouling using model organisms with increasing  
17 complexity, *J. Membr. Sci.* 457 (2014) 19–28.  
18 <https://doi.org/10.1016/j.memsci.2014.01.015>.
- 19 [19] Q. Wang, H. Zeng, Z. Wu, J. Cao, Impact of sodium hypochlorite cleaning on the  
20 surface properties and performance of PVDF membranes, *Appl. Surf. Sci.* 428 (2018)  
21 289–295. <https://doi.org/10.1016/j.apsusc.2017.09.056>.
- 22 [20] Q. Wu, X. Zhang, G. Cao, Impacts of sodium hydroxide and sodium hypochlorite aging  
23 on polyvinylidene fluoride membranes fabricated with different methods, *J. Environ.*  
24 *Sci.* 67 (2018) 294–308. <https://doi.org/10.1016/j.jes.2017.07.014>.

- 1 [21] Y. Zhang, J. Wang, F. Gao, Y. Chen, H. Zhang, A comparison study: The different  
2 impacts of sodium hypochlorite on PVDF and PSF ultrafiltration (UF) membranes,  
3 *Water Res.* 109 (2017) 227–236. <https://doi.org/10.1016/j.watres.2016.11.022>.
- 4 [22] S. Hajibabania, A. Antony, G. Leslie, P. Le-Clech, Relative impact of fouling and  
5 cleaning on PVDF membrane hydraulic performances, *Sep. Purif. Technol.* 90 (2012)  
6 204–212. <https://doi.org/10.1016/j.seppur.2012.03.001>.
- 7 [23] F. Gao, J. Wang, H. Zhang, Y. Zhang, M.A. Hang, Effects of sodium hypochlorite on  
8 structural/surface characteristics, filtration performance and fouling behaviors of PVDF  
9 membranes, *J. Membr. Sci.* 519 (2016) 22–31.  
10 <https://doi.org/10.1016/j.memsci.2016.07.024>.
- 11 [24] S.J. Robinson, P.R. Bérubé, Seeking realistic membrane ageing at bench-scale, *J.*  
12 *Membr. Sci.* 618 (2021) 118606. <https://doi.org/10.1016/j.memsci.2020.118606>.
- 13 [25] S. Robinson, P.R. Bérubé, Membrane ageing in full-scale water treatment plants, *Water*  
14 *Res.* 169 (2020) 115212. <https://doi.org/10.1016/j.watres.2019.115212>.
- 15 [26] H. Yu, X. Li, H. Chang, Z. Zhou, T. Zhang, Y. Yang, G. Li, H. Ji, C. Cai, H. Liang,  
16 Performance of hollow fiber ultrafiltration membrane in a full-scale drinking water  
17 treatment plant in China: A systematic evaluation during 7-year operation, *J. Membr.*  
18 *Sci.* 613 (2020) 118469. <https://doi.org/10.1016/j.memsci.2020.118469>.
- 19 [27] B. Pellegrin, R. Prulho, A. Rivaton, S. Thérias, J.-L. Gardette, E. Gaudichet-Maurin, C.  
20 Causserand, Multi-scale analysis of hypochlorite induced PES/PVP ultrafiltration  
21 membranes degradation, *J. Membr. Sci.* 447 (2013) 287–296.  
22 <https://doi.org/10.1016/j.memsci.2013.07.026>.
- 23 [28] R. Prulho, S. Therias, A. Rivaton, J.-L. Gardette, Ageing of  
24 polyethersulfone/polyvinylpyrrolidone blends in contact with bleach water, *Polym.*

- 1 Degrad. Stab. 98 (2013) 1164–1172.  
2 <https://doi.org/10.1016/j.polymdegradstab.2013.03.011>.
- 3 [29] E.P. Barrett, L.G. Joyner, P.P. Halenda, The Determination of Pore Volume and Area  
4 Distributions in Porous Substances. I. Computations from Nitrogen Isotherms, *J. Am.*  
5 *Chem. Soc.* 73 (1951) 373–380. <https://doi.org/10.1021/ja01145a126>.
- 6 [30] R Core Team, *R: A Language and Environment for Statistical Computing*, R Foundation  
7 for Statistical Computing, Vienna, Austria, 2019.
- 8 [31] B.A. Pulido, O.S. Habboub, S.L. Aristizabal, G. Szekely, S.P. Nunes, Recycled  
9 Poly(ethylene terephthalate) for High Temperature Solvent Resistant Membranes, *ACS*  
10 *Appl. Polym. Mater.* 1 (2019) 2379–2387. <https://doi.org/10.1021/acsapm.9b00493>.
- 11 [32] G. Matar, G. Gonzalez-Gil, H. Maab, S. Nunes, P. Le-Clech, J. Vrouwenvelder, P.E.  
12 Saikaly, Temporal changes in extracellular polymeric substances on hydrophobic and  
13 hydrophilic membrane surfaces in a submerged membrane bioreactor, *Water Res.* 95  
14 (2016) 27–38. <https://doi.org/10.1016/j.watres.2016.02.064>.
- 15 [33] C. Causserand, B. Pellegrin, J.-C. Rouch, Effects of sodium hypochlorite exposure mode  
16 on PES/PVP ultrafiltration membrane degradation, *Water Res.* 85 (2015) 316–326.  
17 <https://doi.org/10.1016/j.watres.2015.08.028>.
- 18 [34] E. Akhondi, F. Zamani, A. W.K. Law, W.B. Krantz, A. G. Fane, J. Wei Chew, Influence  
19 of backwashing on the pore size of hollow fiber ultrafiltration membranes, *J. Membr.*  
20 *Sci.* (521) 2017 33–42. <https://doi.org/10.1016/j.memsci.2016.08.070>
- 21 [35] H. Lin, M. Zhang, F. Wang, F. Meng, B.-Q. Liao, H. Hong, J. Chen, W. Gao, A critical  
22 review of extracellular polymeric substances (EPSs) in membrane bioreactors:  
23 Characteristics, roles in membrane fouling and control strategies, *J. Membr. Sci.* 460  
24 (2014) 110–125. <https://doi.org/10.1016/j.memsci.2014.02.034>.

25

