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CONSEQUENCES OF MEMBRANE AGEING ON REAL OR MISLEADING EVALUATION OF MEMBRANE CLEANING BY FLUX MEASUREMENTS.

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ABSTRACT

Skim milk ultrafiltration is worldwide used in dairy. Its management at industrial scale is based on the permeate flux mastering, the first bottleneck, and consequently on the nature of the overall fouling which is not yet fully understood with respect to the membrane lifespan. The second bottleneck is the mastering and control of the cleaning efficiency aiming at the full removal of the initial irreversible fouling mainly made of proteins. In this study, we have deliberately chemically aged several spiral wound membrane elements by filtering NaOCl solution (400 ppm in total free chlorine at pH 8.0 and 50°C) up to a cumulative chlorine dose of 2,800 ppm.d. The critical/threshold and limiting fluxes have been proven to increase with the membrane ageing together with a decrease in their related transmembrane pressure. This suggest that, at industrial scale, UF might be managed with respect to the chlorine dose received by the membrane during its service life. SEM and Raman spectroscopy have been used to localise the initial irreversible fouling whereas ATR-FTIR was the tool to quantify proteins on membrane. Membrane cleaning was achieved by a non-oxidative alkaline detergent removing the hereafter called “removable fouling” whereas a “residual fouling” remained on/in the membrane. However, the following NaOCl treatment (achieved for disinfection purpose at industrial scale) also acts both as cleaner (polishing the alkaline step by removing part of the residual fouling) and as degradation agent toward the membrane. Unambiguously NaOCl induced a significant decrease in the membrane intrinsic hydraulic resistance associated with an increase of the irreversible fouling, either initial or residual, build during the following skim milk UF. This paper shows how degradation and fouling can transiently compensate each other and lead to the impression of an initial water flux recovery. This phenomenon can lead to misinterpretation of the membrane cleanliness in the specific case of aged membranes. Indeed,

for a received chlorine dose close to 400 ppm.d at pH= 8.0, an irreversible residual fouling can remain, strongly anchored in/on the membrane with a water flux recovery after cleaning only 15% less than that of the pristine membrane. This residual fouling favours the rapid build-up of more and more irreversible fouling during the next skim milk filtration steps. However, with respect to the accuracy on flux measurement, the amplitude of the problem will be underestimated, preventing from getting rid of the first and crucial accumulated layers and consequently leading to an irreversible accelerated degrading process. Relationships have been found between the received chlorine dose and the aged membrane resistance and the residual irreversible fouling that could be used for management at industrial scale.

KEYWORDS: skim milk ultrafiltration ; critical flux ; threshold flux; limiting flux ; fouling; cleaning ; ageing ; sodium hypochlorite ;

1. INTRODUCTION

Ultrafiltration (UF) of skim milk is widely used in dairy industry for the standardization of proteins before the cheese making process. The process mastering at industrial scale is mostly based on flux measurements during skim milk filtration. However, the membrane material evolves during its use at industrial scale and membrane degradation is an identified bottleneck as it induces a membranes' turn-over each 2 years. This turn-over decreases strongly the sustainability and economy of the overall process because of (1) the productivity decrease due to the flux decline overtime and (2) the leakage of protein in the permeate (about 15% transmission compared to less than 5% with a new membrane) decreasing the quality of the valuable retentate fraction [1-3]. The decision of membrane element replacement is mainly based on economic considerations related with an equilibrium between the membrane cost, the protein loss and the productivity affected by the flux decrease.

The membrane replacement is generally made in emergency because of a lack of efficient tools to monitor on-line the change in membrane performances (except the skim milk flux monitoring). The current industrial practices consist in filtration at constant permeate flux by increasing the transmembrane pressure (TMP). Thus, users observed the reduction of the filtration duration before cleaning due to a too rapid increase in the TMP with the membrane lifespan. The consequence is the acceleration of the number of cleaning/disinfection steps with the membrane service life.

Except the flux in skim milk, the only other parameter monitored at industrial scale, is the water flux after the cleaning/disinfection step achieved twice a day in dairy. The water flux recovery, compared with the one obtained after the first production/cleaning+disinfection cycle is used as reference. Note that it is not the water flux of the pristine membrane that is never recovered, according all the industrials we have interviewed. Progressively, the cleaning efficiency seems to decrease and the cleaning/disinfection cycle duration increases.

It is a current idea that the problem is the cleaning efficiency and industrial practitioners always look for better detergents. However, the time at which cleaning difficulties occurs at industrial

scale still look like erratic. According to our own experience, industrial partners often attribute the performance loss to a failure in the cleaning process, even when this step is mostly automated. It is noteworthy to point out that such situations generally occur during the second part of the membrane industrial life. Our own assumption is that the problem is not due to a cleaning process failure but a consequence of the membrane ageing. Thus, from a fundamental point of view, membrane ageing can provoke a decrease of its hydraulic resistance, for instance due to the pore size increase. Consequently, if the membrane is efficiently clean (no residual fouling at all), the water flux is supposed to be higher than the one of the pristine membrane. Thus, considering the water flux of the pristine membrane as the target to reach, the recovery of water flux with the aged membrane will be misleading and will fail at evidencing the real membrane cleanliness. On the contrary, it will hide the accumulation of fouling in/on the membrane that could provoke an increased fouling during the subsequent skim milk filtration.

To better master the skim milk UF, it is thus necessary to have a fundamental understanding of the origin of flux variation during a membrane life at industrial scale. It required both a better comprehension of the chemical evolution of the membrane: membrane material, fouling nature and quantity, fouling localization and their impacts on fluxes either in skim milk or in water after water rinsing and cleaning/disinfection.

1.1. Overview of membrane fouling during skim milk ultrafiltration

Skim milk is a complex mixture made of an average of [1]:

- 45-48 g.L⁻¹ lactose and 8 g.L⁻¹ of various salts.
- 32 g.L⁻¹ proteins: that are mainly caseins in colloidal form (≈ 27 g.L⁻¹) and soluble proteins. β -lactoglobulin (36 kg.mol⁻¹ in dimer form at milk natural pH) is the main soluble protein (≈ 3 g.L⁻¹) and α -lactalbumin (14 kg.mol⁻¹, ≈ 1 g.L⁻¹) the smallest one.

UF is classically performed with spiral wound membrane elements, with a molecular weight cut-off close to MWCO= 5-10 kg.mol⁻¹. The membranes used are generally based on polyethersulfone (PES) in physical blend with small quantities of polyvinylpyrrolidone (PVP). PVP allows increasing the membrane hydrophilicity and thus the flux in aqueous media when compared to pure PES membranes.

The overall fouling obtained during UF of skim milk can be described as a multilayers' deposit. Moving from the bulk fluid to the membrane wall, the fouling is:

- (1) first made of a complex reversible layer including the concentration polarization and a gel deposit. This gel is mainly made of caseins, the colloidal fraction of the milk proteins, and is intrinsically a self-cohesive layer. However, it can be relatively easily removed by a careful water rinsing [4-5].
- (2) second an irreversible layer strongly attached to the membrane and on which the reversible complex layer described above is built-up.

This irreversible fouling is either external or internal. The external part is also a multilayers' one. β -lactoglobulin, was reported as the single or at least the main component entering in the composition of the irreversible fouling on the membrane surface [4-6]. Moreover, from contact angle measurements on both the pristine and fouled membranes using 3 different solvents, it

was drawn that hydrophobic interactions are the main forces responsible in the proteins-membrane interactions [7-8]. This is in good agreement with current knowledge about protein adsorption on surfaces. The existence of external irreversible fouling due to β -lactoglobulin was evidenced using tangential streaming potential measurements (i.e. along the membrane surface, before the pore entrance). It was found that the isoelectric pH of the fouled membrane matched well with that of the protein [6].

Moreover, existence of slight internal irreversible fouling was also evidenced using the same technique, but in this case, streaming potential was measured across the membrane thickness (i.e. into the pore) and showed that the isoelectric pH of the fouled membrane matched well with that of α -lactalbumin the only protein able to go into the permeate fraction with respect to its size and rejection [6].

This overall irreversible fouling, hereafter called “initial irreversible fouling”, is the target of the cleaning/disinfection steps which might represent up to 30 % of the total operating time. In addition, these steps originate, at least, one third of the environmental negative impacts of the overall UF process [9]. Consequently to match with requirements of a sustainable production, a better control of both the fouling and the cleaning steps is a real need.

For given hydrodynamic conditions (constant cross-flow velocity), the negative impacts of the overall fouling can be limited by filtering at, or below, the critical flux (J_{critical}) [10-18] (see Theoretical section).

1.2. Overview of membrane degradation during disinfection step

Besides the filtration conditions, the membrane material itself has to be taken into consideration as it drives the adsorption of the first irreversible fouling layer that favor the subsequent fouling anchoring. In the case of PES/PVP membranes, ageing was evidenced to be mainly due to the disinfection step involving alkaline solutions containing NaOCl oxidative agent [19-36]. However, the disinfection by chlorine agents remains widely use at industrial scale.

Material ageing ineluctably leads to changes in the membrane hydrophobicity. The first responsible is the oxidation of the hydrophilic PVP provoking its release from the composite membrane [23, 24, 27-29]. The PVP degradation is complex and depends on the chlorine dose received by the membrane, the pH and the temperature. PVP can sometimes evolves in the formation of succinimide groups (addition of an oxygen atom) and/or generates the formation of negatively charged carboxylates. The presence of these decomposition by-products, which are more hydrophilic than the initial PVP, can transiently increase the membrane hydrophilicity. Then the leakage of either PVP or its decomposition by-products can occur up to total disappearance. This last one has been showed for industrial applications at the end of the membranes' service life [22, 37] (see also **Appendix 2**). In addition, the PES backbone, even if much more stable than the PVP, can also be attacked. Once again, depending on the pH and the chlorine dose, negatively charged sulfonate groups and/or hydroxylation of phenyl rings can be produced. Both of them increase the membrane hydrophilicity [23, 24, 26-29, 37, 38] (see also **Appendix 2**).

Moreover, an increase of the membrane pore size has sometimes been evidenced [24, 25, 33, 39] having consequences either on the rejection/selectivity or on the fouling behavior.

Finally, on a phenomenological point of view, on one hand, the increase of the pore size and the appearance of surface charges (hydrophilicity increase) might induce a permeate flux increase. Whereas, on the other hand, the decrease in hydrophilicity due to the release of PVP and its degradation products (hydrophilicity decrease) might induce the flux decrease and make the membrane more prone to fouling by organics. Because of these contradictory trends, accurate analysis of permeate flux variation during a membrane life is probably more difficult to achieve than currently thought.

Results in good accordance with these comments have been reported in literature in several cases. Especially the fouling increase for pristine and aged membranes, such as (1) polysulfone (PSf) fouled by humic acids [40], (2) microfiltration (MF) membranes (PSf, PVDF, Polyethylene) fouled by micro-organisms and exopolysaccharides [41], (3) PVDF MF fouled by mixtures of bovine serum albumin (BSA) and alginate [39], or (4) fouling in submerged membrane bioreactor (MBR) treating wastewater [42].

Few authors have reported on the decrease in membrane cleanability associated with membrane ageing, often based on experimental fluxes and membrane resistance calculations with respect to the resistance in series' model; see for instance Puspitasari *et al.* [39] for PVDF membranes, Fenu *et al.* [42] for MBR waste water application. Our own preliminary work reported in [43] dealing with PES/PVP membrane used in skim milk UF was based on fouling quantification by ATR-FTIR as a complementary tool to flux measurements. In our opinion, due to a lack of fundamental understanding of consequence of ageing on membrane cleanability, mistakes are frequent.

Thus, the questions addressed in this paper are the two following ones: (1) Is the misleading interpretation of water flux recovery possible or not in the case of skim milk UF? (2) if any misleading interpretation is possible how to make correction to better master the membrane lifespan at industrial scale?

To answer, this study provides complements to our previous systematic studies devoted to: (1) the cleanability of a pristine PES/PVP UF membrane [18] and (2) reporting on the cleanability decrease due to NaOCl exposure [43, 44]. Especially, this paper reports on the misleading interpretation that can be drawn from water flux recovery during the membrane life, provoking the entrance into a cycle of fouling accumulation only evidenced when irreversible damage is done and service lifetime considerably shorten.

2. THEORY

This part exposes several aspects of the analysis of flux behavior.

2.1. Critical/threshold and limiting fluxes

In a given membrane/fluid system for which UF is performed at a constant cross-flow velocity, two particular fluxes can be defined: the limiting flux (J_{limiting} , maximum reachable flux) and the critical flux ($J_{\text{critical}} < J_{\text{limiting}}$), flux over which the fouling significantly increases.

Initially, the critical flux was defined as the maximum flux without any irreversible fouling on the membrane [10-12, 14]. However, two kinds of critical flux were distinguished: (1) the strong form and (2) the weak form. In the case of the strong form, no concentration polarisation exists below the critical flux, whereas with the weak form concentration polarisation exists.

With complex mixtures, especially when containing soluble organic polymers such as proteins, it is not possible to totally avoid the irreversible fouling because these organics tend to naturally adsorb on the polymer membrane. Thus, in these cases, the initial definition of the critical flux cannot be applied as no filtration conditions can be found without any irreversible fouling. However, one can determine the minimum irreversible fouling only due to adsorption of the fouling species without any pressure applied on the membrane and consider the fouling behaviour with respect to this minimum fouling. The critical flux concept was then adapted and, for the sake of precision, a new type of critical flux was proposed by Field and Pearce [13]: the threshold flux. This threshold flux is defined as the boundary between filtration conditions for which a low and constant irreversible fouling (due to adsorption) exists and conditions for which the irreversible fouling significantly increases. It has been previously demonstrated by our group [12] that, in the case of skim milk UF with the PES/PVP membrane used in the present study, the critical flux is of threshold type, (hereafter referred to as $J_{\text{critical/threshold}}$).

Both $J_{\text{critical/threshold}}$ and J_{limiting} are first reached for a minimum corresponding TMP as explained in [16] and shown for the sake of clarity in **Figure 1**. The critical/threshold point ($\text{TMP}_{\text{critical/threshold}}, J_{\text{critical/threshold}}$) delimits two membrane fouling behaviors: below this point the irreversible fouling is minimum and above it strongly increases. Note that this determination method of $J_{\text{critical/threshold}}$ can be done only if a hysteresis exists when decreasing the TMP after a first increase, that was previously checked for skim milk UF.

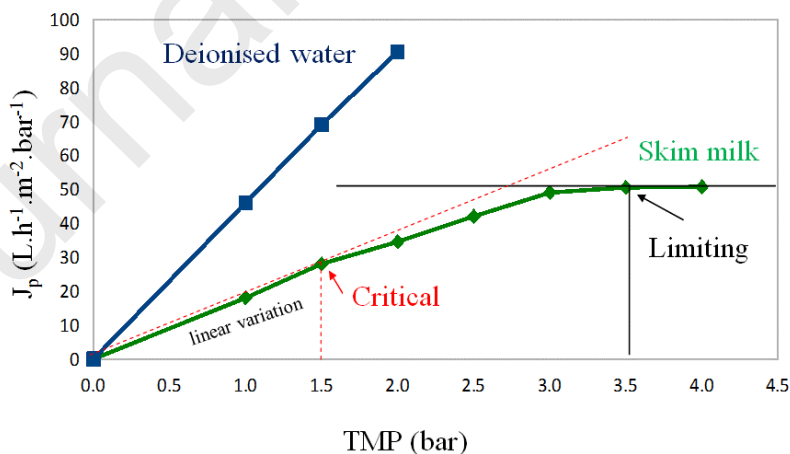


Figure 1: Permeate flux (J_p) vs transmembrane pressure (TMP) and determination of critical and limiting points during skim milk ultrafiltration.

2.2. Membrane resistance vs. membrane ageing (chlorine dose)

In the following, the membrane ageing will be referred as the cumulative chlorine dose received by the membrane, and calculated according to the following equation:

Cumulative chlorine dose (ppm.d)= concentration x number of exposition days (1)

With:

- Concentration: the concentration of the NaOCl solution expressed in ppm (mg.L^{-1}) of total free chlorine (TFC) that is the maximum amount of active chlorine (Cl_2) that can be produced by the solution.

It must be underlined that such definition of the cumulative chlorine dose, further called chlorine dose for the sake of simplicity, has to be coupled with the pH of the NaOCl solution to be an accurate data. Thus, the pH has an important impact on the membrane polymer degradation and huge differences were reported between pH= 8.0 (high and fast degradation) and pH=11.5-12.0 (lower and slow degradation) (see section 1.2).

As explained in the introduction, the membrane ageing may lead to several antagonist phenomena. Because of all these contradictory trends that may compensate each other, the analysis of permeate flux in skim milk with membrane exposure to chlorine has to be carefully perform to avoid misleading interpretations when using the “resistances’ in series’ model”.

The main idea of this work is that the membrane resistance varies with the received chlorine dose, whereas it remains constant for the same membrane only exposed to skim milk UF and alkaline cleaning without any chlorine contact. Accordingly, the membrane resistance was determined with respect to the received cumulative chlorine dose and hereafter noted $R_{m,dose}$. This assumption and its confirmation will be discussed later in this article.

The determination of $R_{m,dose}$ was based on the “resistances’ in series” model that was applied taking into account the received chlorine dose but also the fouling due to skim milk UF. Accordingly, several cases have to be considered. Details of the full method are given in **Appendix 3**.

The initial pristine membrane hydraulic resistance hereafter denoted $R_{m,0}$ was taken as reference (**Figure A3.1, Appendix 3**). It was determined from the water flux of the pristine membrane using the well-known Darcy’s law:

$$J_p = \frac{TMP}{\mu \cdot R_m} \quad (2)$$

With:

J_p : the permeate flux in water

μ : the permeate viscosity (close to that of water)

$R_m = R_{m,0}$: the hydraulic resistance of the pristine membrane

2.3. Hydraulic resistances due to fouling

The determination of the fouling resistances during skim milk UF was achieved using the Darcy’s law in combination with the well-known resistance in series model (**equation 3, equation 4**).

$$J_{UF} = \frac{TMP}{\mu \cdot R_{total}} \quad (3)$$

With:

J_{UF} : the permeate flux in skim milk

μ : the permeate viscosity (close to that of water)

R_{total} : the global resistance to mass transfer that can be defined according to:

$$R_{total} = R_{m,dose} + R_{f,total} \quad (4)$$

With:

$R_{m,dose}$ the membrane resistance taking into account the material ageing, and assuming that $R_{m,dose}$ would be constant during the skim milk UF.

$R_{f,total}$ the overall fouling resistance measured during skim milk UF. It can be calculated for each TMP. Hereafter only the value at the end of the filtration (higher TMP) will be shown and discussed.

This total fouling resistance actually accounts for both reversible and irreversible fouling (**equation 5**).

$$R_{f,total} = R_{reversible} + R_{irreversible,initial} \quad (5)$$

With:

$R_{irreversible,initial}$: the hydraulic resistance of the initial irreversible part of the fouling. It can be calculated from the water flux measured after the water rinsing immediately following skim milk UF. The calculated value only concerned the last applied TMP in skim milk. It was referred as “irreversible, initial” to avoid confusion with the irreversible resistance remaining during and/or at the end of the cleaning step (see below).

$R_{reversible}$: the resistance of the reversible part of the fouling, removable by a simple water rinsing that can be deduced from **equation 5**. The deduced value only concerned the last applied TMP in skim milk.

As it will be justified in the result section, the selected formulated alkaline detergent (P3-Ultrasil 10), was proven to be efficient to clean pristine and little aged membranes but not the severely aged membranes. To take into account the possible partial inefficiency of the alkaline cleaning, the irreversible initial fouling resistance was thus split in two components:

$$R_{irreversible,initial} = R_{irreversible,removable} + R_{irreversible,residual} \quad (6)$$

With:

$R_{irreversible,removable}$: the part of the initial irreversible fouling that can be removed by the chemical alkaline cleaning using the formulated alkaline detergent without any oxidative agent.

$R_{irreversible,residual}$: the part of the initial irreversible fouling not removable by the alkaline cleaning.

Thus, no resistance due to a final irreversible fouling (after alkaline cleaning + NaOCl exposition) can be detected when using the hypotheses of this study, indirectly assuming that NaOCl polished very efficiently the alkaline cleaning. Accordingly, $R_{m,dose}$ variation integrated the membrane variation minus an irreversible fouling remaining after NaOCl that is not detectable by this approach. This means that the impacts on $R_{m,dose}$ variation described below were probably lower than the real ones. Such assumption will be discussed at the end of the paper.

3. MATERIAL AND METHODS

3.1. Skim milk and solutions

The skim milk used was a commercial one (UHT, Lait de Montagne, Carrefour, France) containing an average of 32 g.L⁻¹ proteins and 48 g.L⁻¹ carbohydrates (mainly lactose) and only traces of lipids (< 0.5 wt %).

Water used either for solution preparation or membrane filtration was deionized and 1 μm filtered. Its conductivity was always lower than 1 μS.cm⁻¹.

A formulated cleaning-in-place (CIP) solution was prepared at 4 g.L⁻¹ in water from P3-Ultrasil 10 powder provided by Ecolab (France). Its natural pH was 12.0. This non-oxidative formulated detergent was previously shown to be efficient for the CIP of pristine PES/PVP membranes fouled by skim milk [18]. The water flux recovery was always better than 98% with the pristine membrane used in the present study after cleaning during 1 h at 50°C and 2 bar at the same cross-flow velocity than that use during the skim milk UF.

To deliberately chemically age the membranes, NaOCl solutions set at 400 ppm TFC were prepared from commercial bleach solution provided by Lacroix (“eau de Javel” (bleach) 96,000 ppm TFC, France). The pH was adjusted to 8.0 using HCl (analytical grade, Normapur, Prolabo, France). This value was previously found to correspond to the acceleration of the membrane chemical ageing, mainly due to the appropriate proportions of HClO and ClO⁻ allowing the formation of numerous OH[°] radicals [29].

3.2. Membranes and membrane analysis

Either membrane material or membrane spiral wound elements are described here together with the deliberate ageing made on certain spiral wound membrane elements.

○ *Membrane material*

A PES based UF membrane (MWCO= 5-10 kg mol⁻¹, HFK-131, Koch, USA) was selected as it is up to now the worldwide reference for the skim milk UF application at industrial scale. This membrane is mainly made of PES but also contains some PVP (see **Appendix 2** for structure of polymers).

According to its provider, this membrane is guaranteed up to a cumulative chlorine dose of 5,000 ppm.d. However, no clear information is given on the way to reach this maximum chlorine dose, especially when dealing with the pH of the NaOCl solution.

○ *Spiral wound membrane elements*

The spiral wound membrane used are made of the PES/PVP material described above. Four spiral wound membrane elements were used in this study. They are also called 4”(inch) elements or 4333 elements (Koch, USA) for 4.3” (109 mm) external diameter and 33” (838 mm) length, respectively. One single spiral membrane element is made of three or four double sheets of flat membranes, depending on the membrane element type (see below). Each double sheet is made of two flat membranes glued back to back on 3 of the 4 sides of the flat sheets, forming an opened pocket in which the permeate is collected and further recovered on the opened side itself glued on a central tube. All double sheets are wound around the permeate collector axis (central tube). The filtering area of one spiral membrane element was 6.5-6.8 m², according to the provider.

- *Negligible ageing by NaOCl.* A first spiral membrane element, hereafter called S-CIP-1 (3 double sheets, Koch reference KM8243083017V, F type spacers = 80 mil) was only used for skim milk filtration at 50°C. Over the 9 years’ life of the membrane element at laboratory scale, the permeance to water remained constant at $L_{p,water,50^{\circ}C} = 50 \pm 5 \text{ L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$ and that in skim milk at $L_{p,skim\ milk,50^{\circ}C} = 15 \pm 1 \text{ L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$ with a feed flow rate of 12.5 m³.h⁻¹. This membrane has been regularly cleaned at 50°C with alkaline detergents at pH 11.5-12.0. During the 9 years of its service life, the cumulative cleaning time by alkaline bleach at 200 ppm TFC and pH= 11.5 has been 330 min meaning that the chlorine dose received by the membrane was 46 ppm.d that was much less than those received by the other spiral membrane elements deliberately aged in this study (see below). In the following, S-CIP-1 was thus assumed to act as a “reference membrane” for which the natural, chemical, mechanical and physical ageing were not evidenced by flux measurements. Consequently, the evolution of the permeance, either in water or in skim milk, for the membrane elements deliberately aged, cannot be attributed to a pure mechanical & physical ageing when considering filtration experiments during less than 5 months (the maximum duration of experiments achieved with the other membrane elements, see below). However, in this study, when long NaOCl filtrations were achieved during the deliberate ageing, synergetic effects between chemical induced ageing and mechanical ones cannot be excluded. Note that even if S-CIP-1 was always correct to achieve filtration we have decided to autopsy it. After a final ultrafiltration of skim milk at an average TMP of 2.6 bar (3.7 at inlet, 1.5 bar outlet), 2h at 50°C and 0.3 m.s⁻¹, the entire spiral wound membrane element was autopsied after rinsing but without any chemical cleaning in order to map the initial irreversible fouling and the results have been reported in [45].

- *Deliberate ageing by NaOCl.* Two other spiral wound membrane elements were used (4333 K131 VYV module, 31 mil retentate spacers, Koch nomenclature); both were 4 double sheet membranes. They are hereafter referred to as S-CIP-2 (Koch reference KMS-K131-V-8983540008) and S-CIP-3 (Koch reference KMS-K131-V-8879759136), respectively. Before its first use, each pristine spiral membrane element was extensively rinsed by deionized water then cleaned by P3-Ultrasil 10 (4 g.L⁻¹, 50°C, 1 bar, 1 h). The membrane was then compacted by filtration of deionized water at 50°C, TMP= 4 bar for at least 2 h which was a sufficient time to reach a constant reference permeance. After compaction, the water permeance was $L_{p,0} = 50 \pm 5 \text{ L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$ (at 50°C) while the permeance in skim milk at 2 bar was $L_{p,UF} = 15 \pm 1 \text{ L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$ for both S-CIP-2 and S-CIP-3 with a feed flow rate of 9.5-10.0 m³.h⁻¹. These values

were in perfect accordance with those measured with S-CIP-1, meaning that the 3 spiral membrane elements were similar when dealing with their flux behaviour.

- *Stocked spiral membrane element to sample flat membranes.* A fourth spiral membrane element (denoted S-cut-CIP-1, 4 double sheet membrane, similar to S-CIP-2 and S-CIP-3) was used as a stocked material in which small flat membranes were sampled. These flat membranes were occasionally used for the determination of the irreversible fouling location by Raman spectroscopy and scanning electron microscopy pictures (see results section).

Images of fouled S-CIP-1 by FESEM

Field emission scanning electron microscopy (FESEM) was used to acquire images of the initial irreversible fouling of the S-CIP-1 membrane at the end of its service life, even if its performances remained satisfying. The sample was collected in a highly fouled zone as checked by ATR-FTIR quantification of proteins. Moreover, the dried membrane samples were put in liquid nitrogen and break in order to reveal the different layers of both the pristine membrane and the fouled ones. The consequence of the sample preparation was that some parts of the fouling were removed and the deposit was not homogeneous on the obtained pictures. The microscope was a JSM JEOL 6301 F (Japan) working at a low accelerating voltage of 7 kV.

○ *Analyses of fouled spiral wound membrane element by ATR-FTIR*

The two spiral wound membrane elements deliberately aged were autopsied after their final skim milk UF and a careful water rinsing (no cleaning, last TMP= 4.7 bar in skim milk).

The full autopsy of a single spiral membrane element required the registration of 336 ATR-FTIR spectra. Each one of the 8 flat sheets of a spiral membrane element (2 x 4 double sheets) was entirely cut in 42 coupons of 127 cm², and the location of each one was recorded, allowing a full mapping of the spiral membrane element. Before analysis the membrane samples have to be carefully dried few days under dynamic vacuum to totally remove traces of water. Each spectrum was collected at the center of the 127 cm² coupons.

ATR-FTIR spectra were registered on a Spectrum 1000 spectrometer (Perkin Elmer) using a ZnSe crystal at 45° allowing 12 reflexions. Each spectrum was the average of 20 scans with a 2 cm⁻¹ resolution. Data were processed by the mean of the Spectrum for Windows software (version 5.0).

Quantification of the protein amount (using the amide II band located at 1539 cm⁻¹, precision ± 1 µg.cm⁻²) directly on the PES/PVP membrane was achieved by ATR-FTIR according to a procedure previously described [4]. Simultaneously, the ageing states of the membranes were systematically checked by following the PVP removal (C=O band located at 1661 cm⁻¹) as well as the PES backbone attack (several mechanisms leading to different bands, all located at 1030 cm⁻¹) using a procedure reported in [34]. The final results for S-CIP-2 and S-CIP-3 were calculated as the average of the 336 spectra acquired for each one.

For small flat membranes, the same protocol was used except the number of registered spectra (see results section).

○ *Analyses of flat membrane by Raman scattering*

Raman spectroscopy was used to determine the location of the proteins of the initial irreversible fouling either on the membrane surface or in the membrane structure of a pristine flat membrane (127 cm² sampled in S-cut-CIP-1) after skim milk UF. Before analysis the samples were carefully dried under dynamic vacuum to remove water traces.

Measurements have been performed on a HR 800 (HORIBA, Jobin-Yvon) micro-Raman spectrometer with the following configuration: Helium-Neon laser (633 nm) coupled to a microscope with an x100 ulwd objective allowing a spatial resolution of about 1 μm. The spectrometer was coupled to a micro-translation table allowing control of the focusing distance (z).

The present study focused on the amide III bond of proteins (located close to 1450 cm⁻¹) and PES membrane signature (close to 1500 cm⁻¹). Spectra were collected between z = - 2.5 μm (outside membrane) and z = +10.1 μm (inside membrane) knowing that the membrane surface was located at z = - 0.7 μm. Measurements have been performed at room temperature and ambient air.

3.3. Ultrafiltration conditions

UF was achieved with small flat membrane for analytical purpose and with the 3 spiral wound membrane elements (S-CIP-1, S-CIP-2, S-CIP-3).

○ *UF with flat membrane used for Raman scattering*

A flat PES/PVP membrane (127 cm²) sampled in S-cut-CIP-1 was inserted in a plate and frame Rayflow X100 module. A 2 mm thickness spacer was inserted in the liquid channel on the feed/retentate side. A permeate spacer was also used in the permeate side to mimic as close as possible the sandwich spacer/membrane/spacer encountered in a spiral membrane element. The flat membrane was fouled by skim milk at 2 bar, 50°C, 0.3 m.s⁻¹ during 2 h then carefully rinsed by deionized water only allowing the removal of the reversible part of the fouling.

○ *UF with spiral membrane element and hydrodynamic standard conditions*

UF was carried out on a 100 L capacity-pilot scale filtration device provided by TIA (Bollène, France) equipped with one 4" spiral membrane element (see **Appendix 5** for scheme and pictures of the pilot).

Unless otherwise specified, UF at 50°C was achieved in standard conditions, processing 25 L of solution. The volume reduction ratio was VRR = 1, obtained by full recycling of both retentate and permeate in the feed tank. The feed flow rate was $Q_{\text{feed}} = 11.0 \pm 1.5 \text{ m}^3 \cdot \text{h}^{-1}$ leading to an average cross-flow velocity in free liquid channel estimated to be $v = 0.38 \pm 0.05 \text{ m} \cdot \text{s}^{-1}$. Depending on the experiment, the average TMP (mean value of the retentate pressure at inlet and outlet of the module) was varied in the 1-5 bar range. In these TMP range, the pressure drop along the module length was constant at $\Delta P = 2.2 \text{ bar}$.

○ *UF of skim milk, water rinsing and alkaline cleaning with spiral membrane element*

24 L of skim milk were processed for each filtration. The average TMP was progressively increased from 1.1 to 4.7 bar; critical and limiting fluxes were deduced from these filtrations.

After skim milk UF, water rinsing was carefully achieved at TMP= 2 bar in open circuit until whiteness has totally disappeared from the effluents, the pH of which were controlled to be neutral. After few minutes at TMP= 2 bar in water, the membrane permeance was measured again to evaluate the reversibility/irreversibility of the fouling.

Finally, the membrane was cleaned by P3-Ultrasil 10 at TMP= 2 bar, 50°C, 1 h. After alkaline cleaning, water rinsing was carefully achieved first in open circuit until pH of the retentate was neutral. Rinsing was then continued with retentate recycling (to minimize water consumption) until the permeate pH was neutral to guarantee the cleaning agent removal.

- *Spiral membrane element ageing by NaOCl in UF conditions*

The membranes were deliberately aged at 50°C by continuous filtration of NaOCl (25 L, 400 ppm at pH= 8.0) at TMP= 2 bar (UF standard conditions) during different time. Controlled chemical ageing of the two spiral wound membrane elements were achieved up to different cumulative chlorine dose: 2,000 ppm.d and 2,800 ppm.d, for S-CIP-2 and S-CIP-3, respectively. For each of the module, skim milk UF are sometimes intercalated between the filtrations of NaOCl to check the membrane behavior according to the received chlorine dose. The detailed protocol used for membrane ageing is given in **Appendix 1**.

3.4. Calculations

All these calculations were made for experiments achieved with S-CIP-2 and S-CIP-3 spiral wound membrane elements.

- *Determination of critical/threshold and limiting fluxes*

Permeate fluxes were measured during filtration of skim milk by increasing step by step the TMP from 1.1 to 4.7 bar. Each 0.5 bar increase of TMP was performed only after the plateau of permeate flux value was reached at the previous pressure. The duration of UF, at each TMP, was 25-40 min depending on the TMP. The accuracy on flux measurement was better than 3%. The critical and limiting points defined in the theory section were graphically determined (**Figure 1**).

- *Calculation of membrane resistance vs membrane ageing (NaOCl dose)*

In absence of any ageing due to chlorine, the hydraulic resistance of the membrane (R_m or $R_{m,0}$) remained the membrane resistance regardless of the fouling due to skim milk as no chemical degradation occurs. For instance, this is the case for the first filtration of skim milk with the pristine S-CIP-2 and for the 3 first ones (hereafter noted UF1, UF2, UF3 on figures) for the pristine S-CIP-3 and the two following duplicate, respectively.

During NaOCl filtration, experiences have depicted that the flux evolution with time was different depending on the presence of proteins on the membrane:

- **Case 1:** In absence of any residual fouling due to proteins the flux increased slowly vs time, following a monotone slope. The variation of the hydraulic resistance can unambiguously be attributed to the membrane progressive degradation (that can be due either to chemical degradation or to a combination of chemical and mechanical degradation if synergies existed between the two). This is the case of a membrane very efficiently cleaned after a fouling step (**Figure A3.2, Appendix 3**).

- **Case 2:** In presence of any residual fouling due to proteins, the flux increased rapidly during the first few minutes and then much more slowly. The first slope was attributed to the superimposition of the membrane degradation and the protein removal due to the cleaning effect of NaOCl polishing the previous alkaline cleaning when this last one was not efficient enough to remove all the proteins. The second slope can unambiguously be attributed to the membrane progressive degradation (similar trends as case 1). It was assumed that the second slope can model the impact of the membrane degradation due to NaOCl during the first minutes of NaOCl filtration, the sole cleaning impact being determined from the difference of the two slopes.

Case 1 was also that of little aged membranes; just after skim milk UF + alkaline cleaning, the water flux recovery was systematically close or better than 90%. After the NaOCl treatment up to a certain cumulative chlorine dose and water rinsing, the membrane resistance was easily calculated from the following water flux thanks to the Darcy's law, by substituting R_m for $R_{m,dose}$ in **equation 2**. This allowed the determination of the variation of $R_{m,dose}$ with contact time with NaOCl (and cumulative chlorine dose) (**Figure A3.2, Appendix 3**).

Case 2 was that of membranes having received "high" cumulative chlorine dose before skim milk UF and for which the flux recovery after the alkaline cleaning was lower than 90%. The flux increased following two distinct and consecutive slopes (high then low) meaning that two different phenomena occurred with different kinetics (**Figure A3.3, Appendix 3**).

4. RESULTS

The impact of the membrane chlorine exposure will now be shown, first on the global process parameters as critical/threshold and limiting fluxes, and second on the flux recovery after cleaning and its possible interpretations.

4.1. Initial irreversible fouling location

Complementary FESEM pictures and Raman analysis were achieved to evidence the location of the initial irreversible fouling due to proteins.

FESEM pictures of the initial fouling of the S-CIP-1 membrane in a region fouled by 125 $\mu\text{g}\cdot\text{cm}^{-2}$ proteins as quantified from ATR-FTIR are depicted **Figure 2 b-e**. In dried state, the external fouling layer can be estimated as 1-2 μm thickness. However, FESEM is not a tool able to highlight the pore size of the pristine membrane (**Figure 2a**) and consequently that of the fouled one. Similarly, FESEM failed at evidencing any internal fouling.

On the contrary, Raman spectroscopy achieved on a flat membrane fouled at 2 bar allowed to evidence the presence of both external and internal fouling due to proteins (**Figure 3**).

The fouling was mainly located on the membrane surface with a micron order thickness in very good agreement with SEM pictures obtained on the dried membrane after cryo-fracture in liquid nitrogen (**Figure 2e**). However, Raman spectroscopy also allowed to localise proteins inside the membrane in a layer of few microns thickness. Knowing from FESEM pictures that the active layer of the pristine membrane was about 1 μm thickness (higher magnification, **Figure 2a**), Raman spectroscopy clearly showed the fouling penetration in the whole membrane

structure including the active layer but also in the intermediate layer, both being made of a blend of PES and PVP. The fouling occurrence, on top of and inside the membrane, revealed by Raman spectroscopy was in good agreement with our previous results obtained from streaming potential measurements [6].

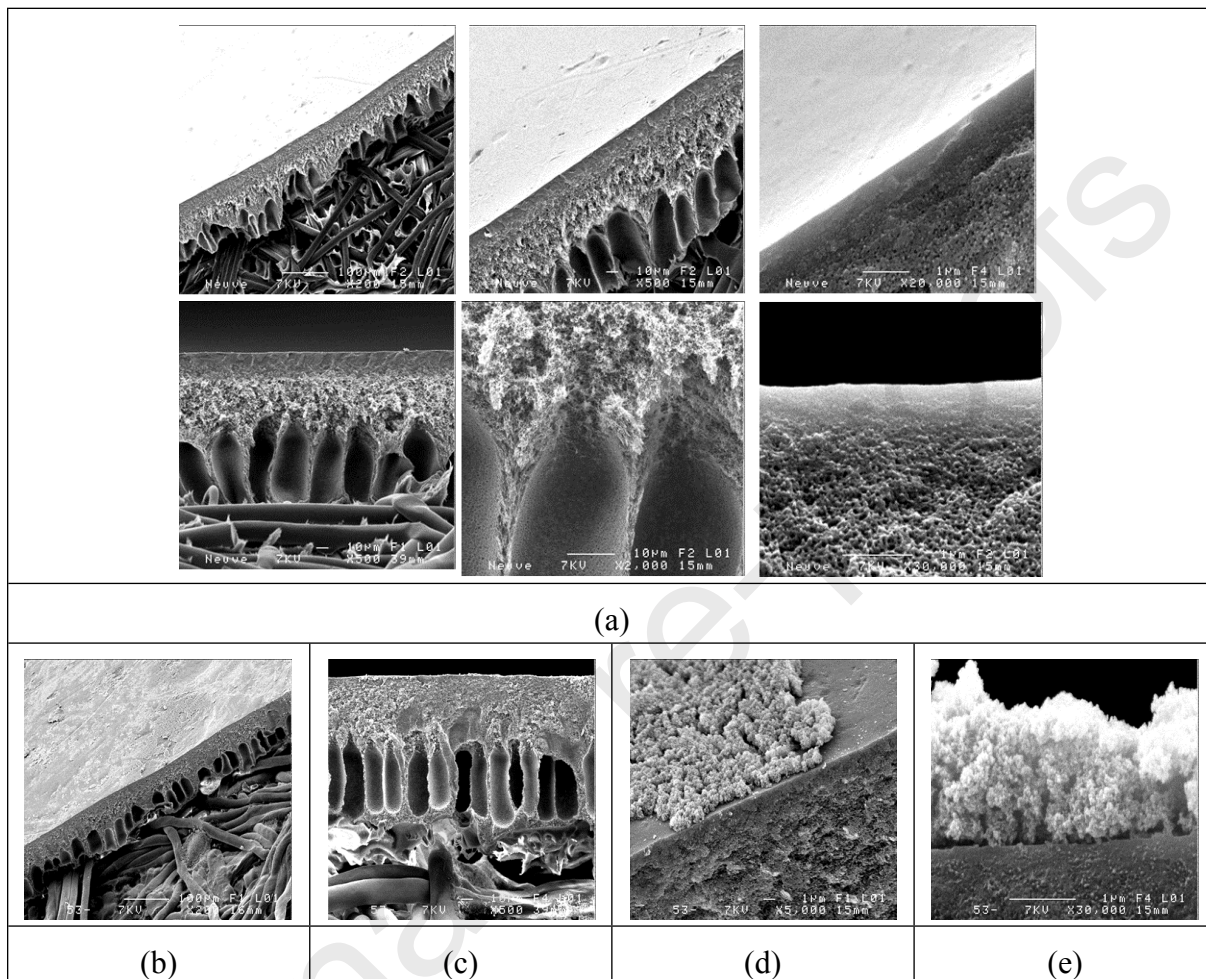


Figure 2: FESEM pictures - (a) PES/PVP HFK-131 pristine membrane evidencing a denser layer of less than 1 μm thickness assumed to be the active layer thickness in dried state.- (b-e) highly fouled zone observed near the permeate axis of the S-CIP-1 membrane after fouling and rinsing. (e) the white cloudy layer about 1-2 μm thick on the membrane surface is assumed to be the external initial irreversible fouling in dried state. The corresponding fouling amount was equal to 125 $\mu\text{g}\cdot\text{cm}^{-2}$ proteins as quantified by ATR-FTIR but is not representative of the entire autopsy reported in [45].

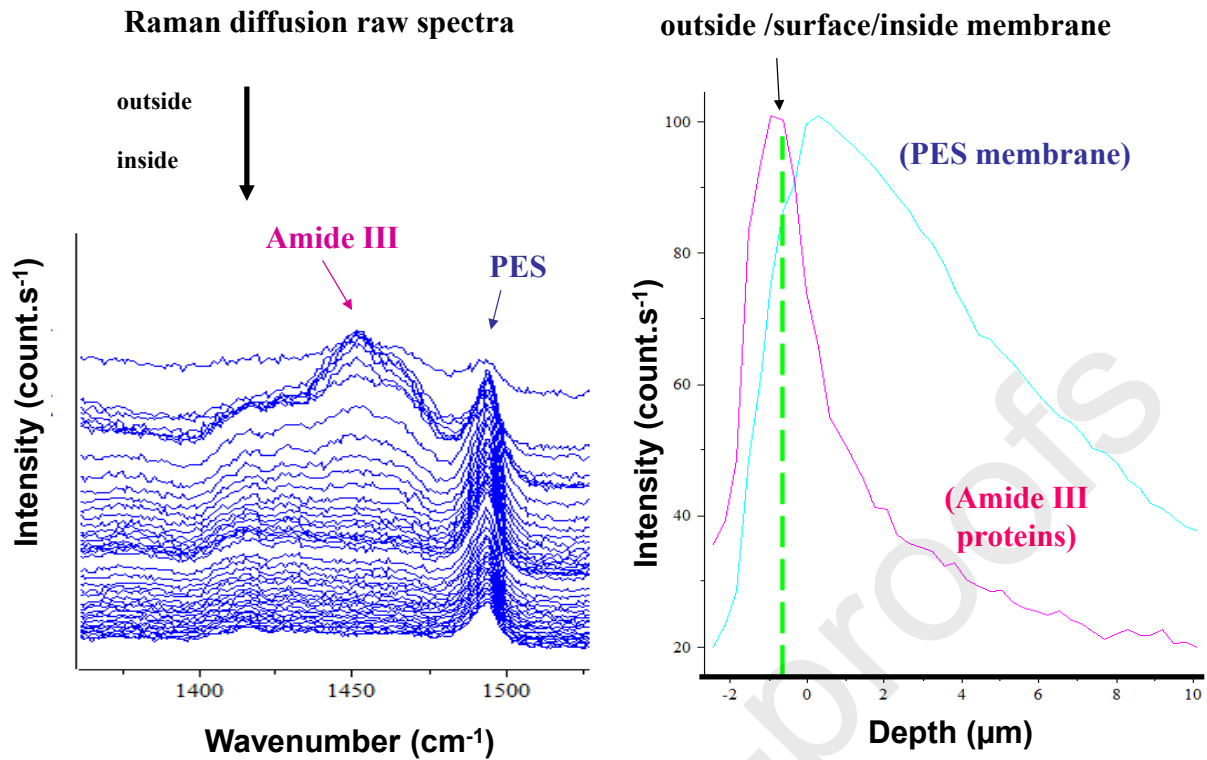


Figure 3: Raman spectroscopy analysis of a pristine PES/PVP (HFK-131) membrane fouled by skim milk at 2 bar, 50°C, $VRR=1$, 0.3 m.s^{-1} . Membrane surface is located at $z = -0.7 \text{ } \mu\text{m}$. Positive z values correspond to fouling inside the membrane. The corresponding fouling amount was equal to $30 \text{ } \mu\text{g.cm}^{-2}$ as quantified by ATR-FTIR.

4.2. Influence of membrane ageing on $J_{\text{critical/threshold}}$ and J_{limiting}

The variation of permeate flux with TMP in skim milk was studied for the two spiral wound membrane elements with respect to the received chlorine dose.

○ Pristine membranes

Before any ageing, one skim milk UF was achieved with the S-CIP-2 membrane whereas 3 successive filtrations were carried out with the S-CIP-3 membrane (with alkaline cleaning between each milk UF). Both $J_{\text{critical/threshold}}$ and J_{limiting} were deduced from **Figure 4**.

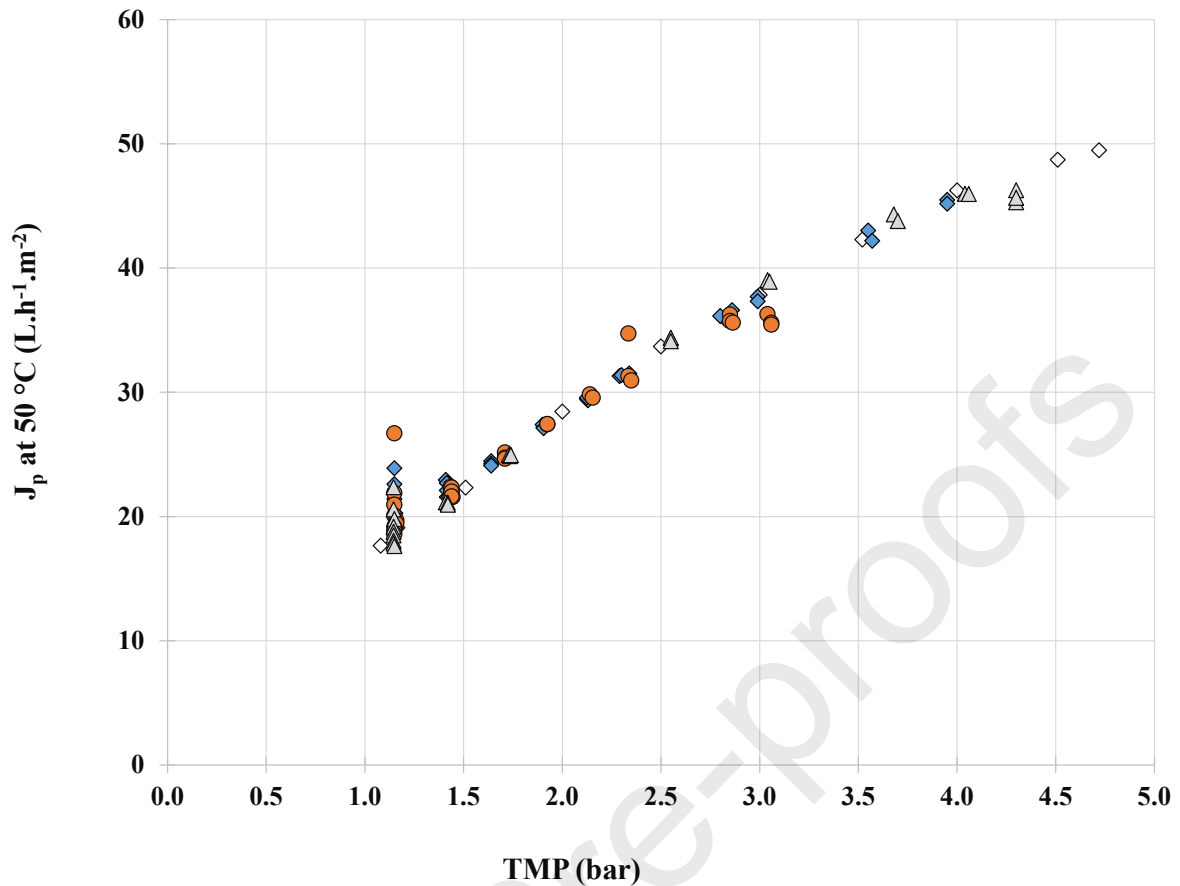


Figure 4: Variation of permeate flux with TMP during filtration of skim milk by spiral membrane elements S-CIP-2 and S-CIP-3. ◇: pristine S-CIP-2; ◆: pristine S-CIP-3, UF1; ●: S-CIP-3, UF2; ▲: S-CIP-3, UF3.

UF experiments showed a very good reproducibility and $J_{\text{critical/threshold}} = 29 \text{ L.h}^{-1}.\text{m}^{-2}$ while $J_{\text{limiting}} = 50 \text{ L.h}^{-1}.\text{m}^{-2}$. These values are in accordance with previous results obtained by Diagne *et al.* [18] for the same membrane type used in flat configuration in a plate-and-frame module with close hydrodynamic conditions.

After the alkaline cleaning, no residual fouling can be evidenced from water flux measurements. For the sake of comparison, it was checked over that the 9 years of service life of S-CIP-1 that the permeance to water remained equal to $L_p = 50 \pm 5 \text{ L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$ while its permeance in skim milk was constant and equal to $15 \pm 1 \text{ L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$. These results allowed to conclude that further evolution of the critical and limiting fluxes of S-CIP-2 and S-CIP-3 might be due to the membrane ageing induced by NaOCl and not to the polymer natural & physical & mechanical ageing.

○ *NaOCl aged membranes*

Figure 5 depicts the flux in skim milk for the same two membranes after membrane exposure to different chlorine dose. For a given pressure the permeate flux in skim milk tended to increase with membrane exposure to chlorine.

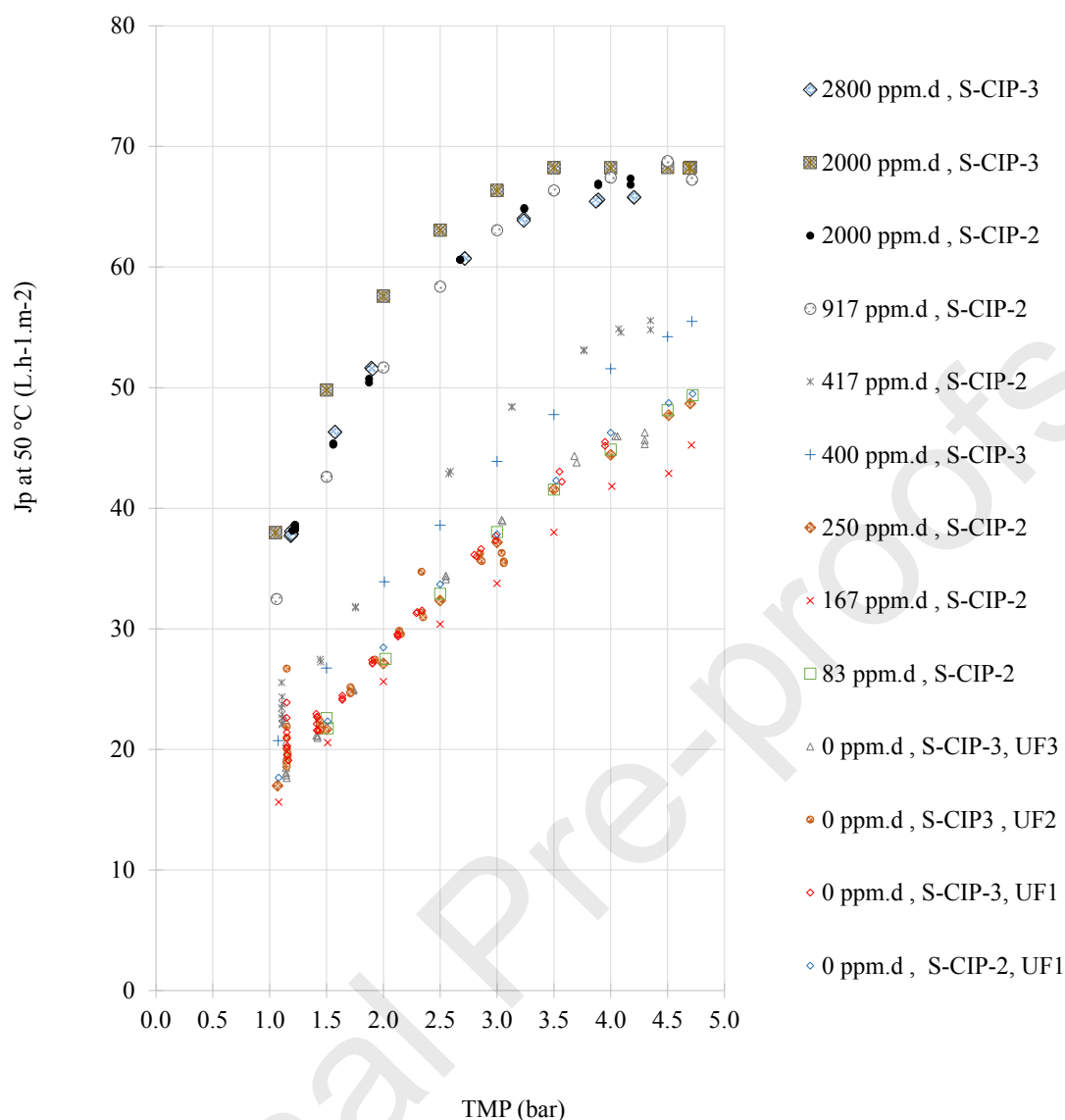


Figure 5: Variation of permeate flux with TMP during filtration of skim milk on the aged S-CIP-2 and S-CIP-3 spiral membrane elements. The values in ppm.d represent the cumulative chlorine dose received by each membrane before UF of skim milk.

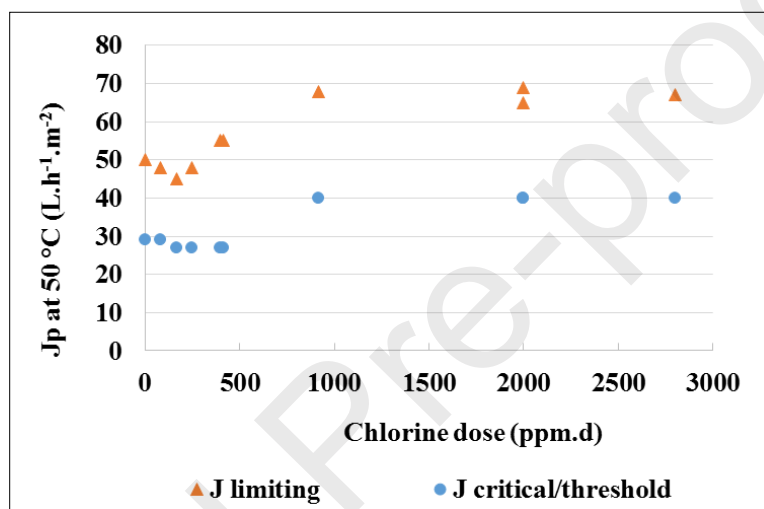
At first sight, these results could appear surprising as industrial partners regularly mentioned that fluxes in skim milk decrease with industrial lifetime of a membrane, generally inducing questions about the cleaning efficiency as already mentioned. However, these results are in good agreement with the several possible mechanisms explained in introduction, especially dealing with the complex variation of membrane hydrophobicity due to both PVP and PES oxidation which can in turn affect membrane filtration performances.

The PVP degradation was proven to induce two consecutive steps that have been observed for low MWCO PES/PVP membranes ($5-10 \text{ kg.mol}^{-1}$) [43] but not mentioned with membranes of higher MWCO such as $100-150 \text{ kg.mol}^{-1}$ [27, 28]. With the low MWCO membranes, first the PVP removal induced a decrease in water flux with respect to the increase in the membrane hydrophobicity. Second after a sufficient exposure to chlorine an increase in water flux was

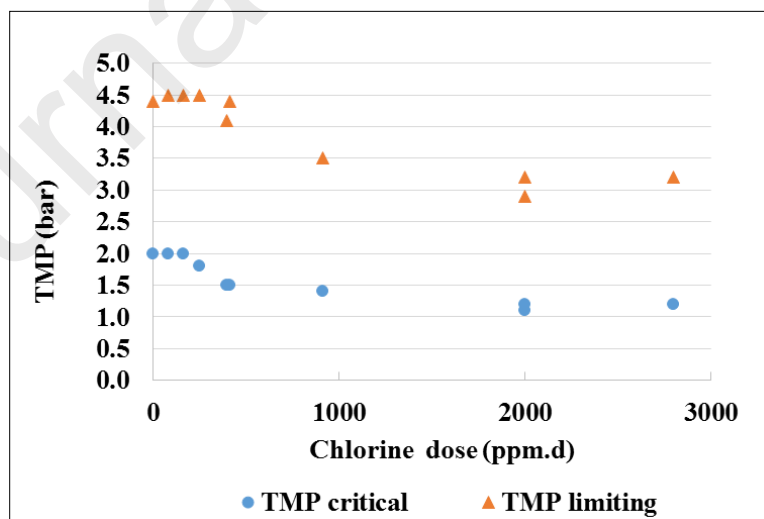
evidenced, due to a more important chemical degradation, also evidenced from contact angle measurements and drawn surface tensions, either polar or apolar ones [43].

Moreover, several studies have demonstrated the possible increase in membrane pore size due to the PVP dislodgment [24, 25, 27]. The pore size variation was not determined in the present work, and this variation is only an assumption here. However, if the pore size increases it could decrease the rejection of the smallest protein of milk (α -lactalbumin) and thus increase the internal fouling. Conditions of exact compensation of the two phenomenon, either pore size increase or fouling increase might exist.

Figure 6 depicts the variation of $J_{\text{critical/threshold}}$ and J_{limiting} , and the according $\text{TMP}_{\text{critical/threshold}}$ and $\text{TMP}_{\text{limiting}}$ against membrane chlorine dose exposition.



(a)



(b)

Figure 6: Evolution of (a) $J_{\text{critical/threshold}}$ and J_{limiting} and (b) $\text{TMP}_{\text{critical/threshold}}$ and $\text{TMP}_{\text{limiting}}$ with membrane chlorine dose exposition deduced from experimental data of Figure 5.

Both fluxes varied similarly with the membrane exposure to NaOCl. For chlorine doses below 250 ppm.d, fluxes were constant and equal to those measured with the pristine membranes. Further chlorine dose increase between 250 and 1,000 ppm.d led to an increase of both fluxes. Finally, for doses greater than 1,000 ppm.d and up to 2,800 ppm.d the fluxes level-off to reach plateau values of about 40 L.h⁻¹.m² and 70 L.h⁻¹.m² for J_{critical/threshold} and J_{limiting}, respectively. These plateau values correspond to 140 % of the initial respective values of the pristine membranes.

Variations of TMP_{critical/threshold} and TMP_{limiting} followed similar trends as fluxes, depicting constant values up to 50 ppm.d followed by a decrease between 250 and 1,000 ppm.d. Finally, a stabilization at 1.2 bar and 3.2 bar, respectively is observed for for greater doses.

Aiming at evidencing if such variations could be related to the gradual oxidation and the subsequent release of the PVP but also the PES backbone attack, the two membranes were autopsied at 2,000 ppm.d for S-CIP-2 and 2,800 ppm.d for S-CIP-3.

The quantitative evaluation of PVP amount in the membrane was determined from the relative absorbance at 1658 cm⁻¹ (H^{PVP}₁₆₅₈) with respect to an internal reference band of PES located at 1237 cm⁻¹ (H^{PES}₁₂₃₇). **Table 1** clearly confirms the reduction of PVP amount (H^{PVP}₁₆₅₈/H^{PES}₁₂₃₇ ratio decrease) compared to the pristine membrane but no total disappearance contrary to what was previously evidenced with a spiral wound membrane element at the end of its industrial life [34, 37]. ATR-FTIR showed also the increase in PES degradation determined from the relative absorbance at 1027 cm⁻¹ (H^{PES-backbone}₁₀₂₇) with respect to the internal reference band of PES (H^{PES-backbone}₁₀₂₇/H^{PES}₁₂₃₇ ratio increase).

The more advanced ageing state (S-CIP-3) corresponded approximately to about half of a membrane industrial lifespan, regarding the received chlorine dose that was equivalent to the half of the dose guaranteed by the membrane provider, but also to the half-decrease of the PVP band intensity. However, the PES degradation was also shown at these “early” stages.

Table 1: ATR-FTIR analysis of virgin and spiral aged membranes.

membrane	H ^{PVP} ₁₆₆₁ /H ^{PES} ₁₂₄₀	H ^{PES-backbone} ₁₀₃₀ /H ^{PES} ₁₂₄₀	reference
Virgin flat*	0.14 ± 0.01	0.04 ± 0.02	[34]
S-CIP-2** (2,000 ppm.d)	0.07 ± 0.02	0.13 ± 0.03	this study
S-CIP-3** (2,800 ppm.d)	0.08 ± 0.02	0.13 ± 0.06	[34]
Industrial membrane***	0.06 ± 0.03****	0.29 ± 0.08	[34]

*Average of 54 spectra acquired on different flat membranes collected in S-cut-CIP-1, ** average of 336 spectra acquired on the overall membrane element (4 double sheets = 8 flat sheets, 42 spectra per flat sheet) , ***8 inches spiral wound membrane element aged at industrial scale and at the end of its service life [37], **** raw band without removal of slight contribution due to proteins, knowing that applying roughly the treatment to remove amide II band led to a full disappearance of the PVP band.

4.3. Influence of membrane ageing on membrane fouling

In order to get further insight into membrane ageing consequences, the progressive influence of chlorine dose on membrane resistance and membrane fouling was evaluated for the spiral membrane elements.

Figure 7 shows the regular decrease of the membrane resistance ($R_{m,dose}$) with the received chlorine dose confirming the regular membrane degradation with exposure duration to NaOCl.

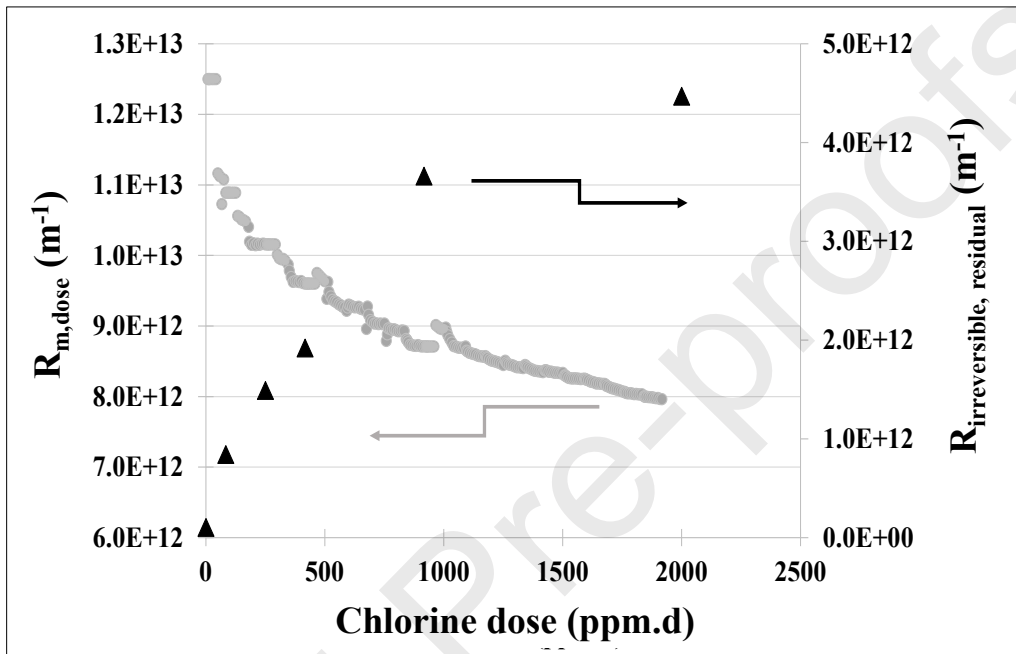


Figure 7: Variation of the membrane resistance (\bullet : $R_{m,dose}$) and of the residual irreversible fouling resistance (\blacktriangle : $R_{irreversible,residual}$) determined by the resistance in series' model after classical alkaline cleaning by formulated detergent against chlorine dose received by the membrane

Figure 8 shows the variation of the resistances determined at the end of each skim-milk filtration cycle (TMP= 4.7 bar) by the mean of the resistance in series' model. The total fouling resistance ($R_{f,total}$, **equation 5**) was significantly higher than the membrane resistance itself as $R_{m,dose}$ remained in the range $1.3 \cdot 10^{13}$ - $0.8 \cdot 10^{13} \text{ m}^{-1}$.

With the pristine membrane, skim milk UF in standard conditions led to a total fouling resistance $R_{f,total} = 4.0 \cdot 10^{13} \text{ m}^{-1}$. This value increased up to $4.8 \cdot 10^{13} \text{ m}^{-1}$ after the first 83 ppm.d dose (see also **Figure A4.1** in **Appendix 4**). However, further increase of the chlorine dose led to the decrease of the total fouling resistance in good agreement with flux increase, but surprisingly when compared to the industrial knowledge. Between 1,000 and 2,800 ppm.d, the total fouling resistance value seemed to reach a plateau value close to $R_{f,total} = 3.0 \cdot 10^{13} \text{ m}^{-1}$ which corresponds to chlorine dose above which $J_{critical/threshold}$ and $J_{limiting}$ leveled off. It must be checked in the future if this is a minimum level followed by a further increase or a real plateau.

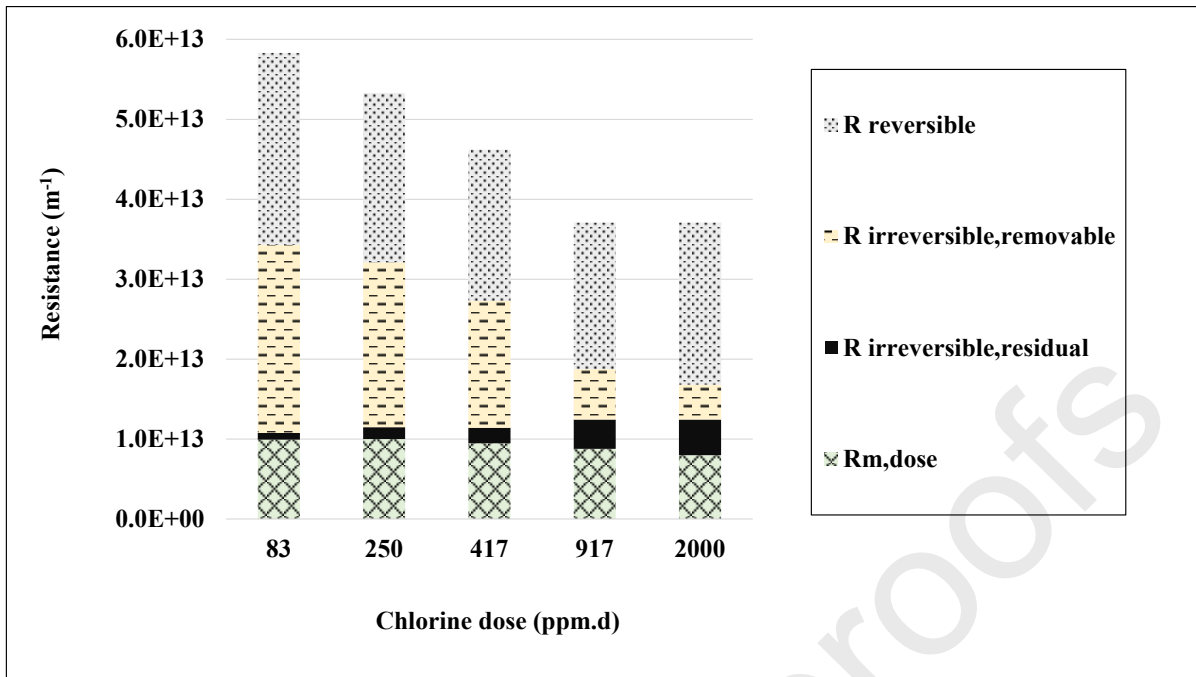


Figure 8: Decomposition of the different fouling types according to the resistance in series model for membrane having received different chlorine dose (all values correspond to S-CIP-2 membrane) with $R_{f,total} = R_{reversible} + R_{irreversible,initial}$ (equation 5) and $R_{irreversible,initial} = R_{irreversible,removable} + R_{irreversible,residual}$ (equation 6)

The reversible fouling contribution ($R_{reversible}$) could be considered more or less as roughly constant and independent of the membrane ageing (Figure 8, see also Figure A4.1 in Appendix 4). This behavior could be explained as follows. In the reversible part of the fouling, that was located far from the membrane surface, foulant-foulant (protein-protein) interactions acted rather than foulant-membrane interactions. Thus, once the first fouling layers were formed on the membrane, the build-up of the following layers becomes independent of the properties of the initial membrane material (charge, hydrophobicity).

The irreversible fouling resistance ($R_{irreversible,initial}$, Figure 8, see also Figure A4.1 of Appendix 4) strongly decreased with the chlorine dose received by the membrane. Furthermore, for chlorine dose greater than 1,000 ppm.d, a plateau was reached close to $R_{irreversible,initial} = 1.0 \cdot 10^{13} \text{ m}^{-1}$. This value is more than 2 times lower than the irreversible fouling resistance observed for a chlorine dose of 83 ppm.d. At first sight, this could appear in contradiction with the current idea of increase in problems due to fouling with membrane long term use.

For the sake of complement, the quantification of the proteins responsible for the initial irreversible fouling at 4.7 bar (final applied TMP during skim milk UF) was achieved by ATR-FTIR for the two spiral wound membrane elements (Table 2). The full autopsy of these two membrane elements suggested that the irreversible fouling remaining before the membrane final cleaning increased with the received chlorine dose. This increase of foulant protein amount is also in good agreement with quantification achieved on flat membrane deliberately aged by NaOCl under micro-wave conditions and reported in [44]. Such results appeared in better agreement with those expected contrary to the resistance calculations which gave relatively close results between 2,000 and 2,800 ppm.d dose.

Table 2: Quantification of proteins of the initial irreversible fouling on entire spiral membrane elements deliberately aged determined by ATR-FTIR

membrane	Final TMP during fouling (bar)	Proteins ($\mu\text{g}\cdot\text{cm}^{-2}$)	reference
S-CIP-2 (2,000 ppm.d)	4.7	39 ± 10 *	this study
S-CIP-3 (2,800 ppm.d)	4.7	50 ± 9 *	[34]

* average of 336 spectra acquired on the overall membrane element (4 double sheets = 8 flat sheets, 42 spectra per flat sheet)

4.4. Influence of membrane ageing on membrane cleaning

The water flux recovery is the only on-line determination to estimate the membrane cleaning efficiency. However, the pristine membrane (and its $R_{m,0}$) is always taken as the reference. According to the variation of $R_{m,dose}$ this reference appears as a “not well appropriate” one.

For the pristine membrane as well as for the membrane aged up to 83 ppm.d dose, $R_{irreversible,initial} = R_{irreversible,removable}$ and $R_{irreversible,residual}$ was null (see **equation 5** for definition). On the contrary, $R_{irreversible,residual}$ increased for more severely aged membrane. **Figure 8** (see also **Figure A4.2** in **Appendix 4**) shows the significant decrease of $R_{irreversible,removable}$ until a 1,000 ppm.d dose before reaching a plateau up to 2,000 ppm.d dose. A non-linear behavior was observed for $R_{irreversible,residual}$ with a sharp increase up to a chlorine dose of 1,000 ppm.d while it became lower above this value.

These results clearly evidenced that the irreversible fouling was more and more difficult to remove with membrane exposure to chlorine. This behavior might be the consequence of the membrane surface physico-chemical modifications leading to an increase in protein-membrane interactions. However, it could also be the consequence of the increase of the internal fouling amount for aged membranes compared to the pristine one, as already suggested in 4.2 section when dealing with possible pore size increase. Interestingly, and contrary to the decrease of the total and initial irreversible fouling resistances with membrane ageing that was commented above, difficulties in cleaning observed here were in fairly good agreement with industrial knowledge.

Figure 9 depicts the evolution of the flux in NaOCl following a cycle skim milk UF + alkaline cleaning. During the 150 first minutes, a rapid increase of the membrane permeance was observed mainly attributed to the oxidant cleaning (“cleaning polishing”). After that, the kinetics of the permeance increase was much lower and was attributed to the membrane degradation by chlorine. This assumption was reinforced as this second part looked like to the behavior in NaOCl for all treatment that did not immediately followed a skim milk UF + alkaline cleaning cycle. These observations confirmed the hypothesis of a cleaning action only during the first 150 min.

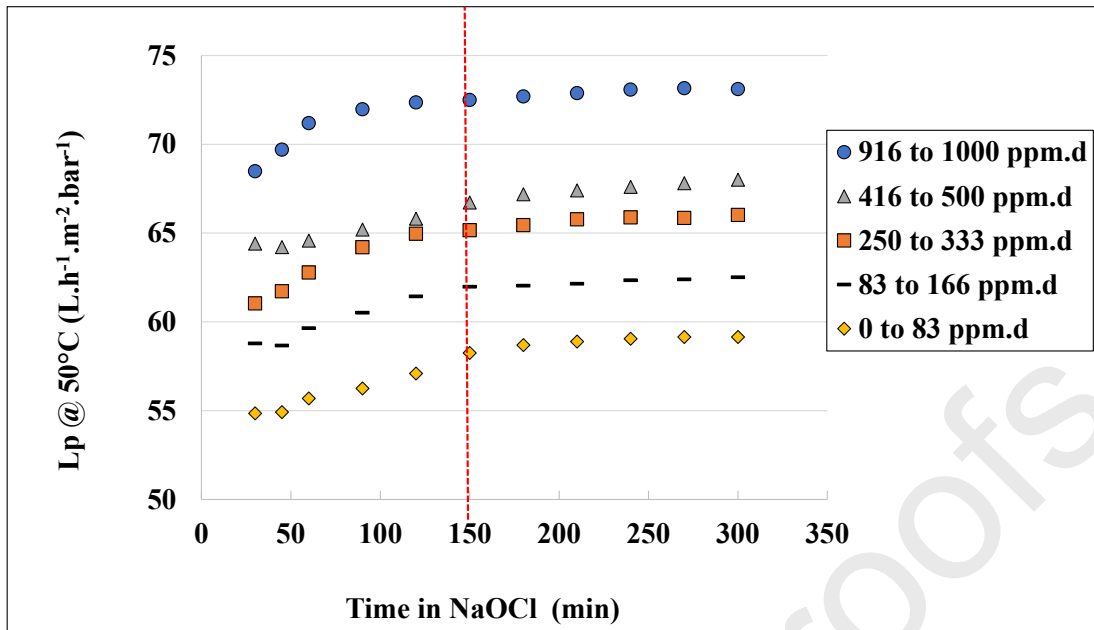


Figure 9: Membrane permeance variation during the NaOCl ageing steps immediately following each skim milk UF + alkaline cleaning + water rinsing

$R_{\text{irreversible, residual}}$ (equation 6) was negligible with the slightly aged membrane. However it was about 50% of the irreversible initial fouling for membrane having received a 2,000 ppm.d dose (Figure 8). It must be noticed that no residual irreversible fouling after NaOCl cleaning could be evidenced from such calculations, regardless of the membrane ageing up to a 2,000 ppm.d dose because of assumptions explained in the theoretical part.

Figure 7 highlights that during the first half-time life of the membrane (up to about 2,000 ppm.d dose) empirical correlation could be drawn between $R_{\text{m, dose}}$ and $R_{\text{irreversible, final}}$. Such relationship could be used as complementary data to the water flux recovery evidenced here as sometimes misleading when dealing with cleaning efficiency. Consequently, from an industrial point of view, monitoring the membrane cleanability/ageing by simple permeability measurements might not be feasible over a chlorine threshold dose that have not been determined yet.

5. DISCUSSION

The discussion aims first at the demonstration of the misleading interpretation that can be drawn from water flux recovery after cleaning of aged membranes when only using the pristine membrane as reference. The second part of the discussion is devoted at giving an explanation of the relative values of the fouling resistances depicted Figure 8 that could appeared counter-intuitive at first sight.

5.1. Is the water flux recovery relevant to control cleaning efficiency at industrial scale?

Figure 7 shows the variation of both $R_{\text{m, dose}}$ and $R_{\text{irreversible, residual}}$ (equation 4 & 5 & 6) against the received chlorine dose. The membrane chemical modifications induced by high chlorine

dose and evidenced by $R_{m,dose}$ variation have clearly a negative impact on both the fouling ability and the cleanability of PES/PVP UF membrane.

Figure 10 depicts the polynomial relationship between $R_{m,dose}$ and $R_{irreversible,residual}$. It clearly shows the acceleration in the irreversible fouling not removed by the alkaline cleaning with the membrane degradation ($R_{m,dose}$ decrease). This is in full agreement with the current intuitive understanding of increasing difficulty in membrane cleaning with ageing.

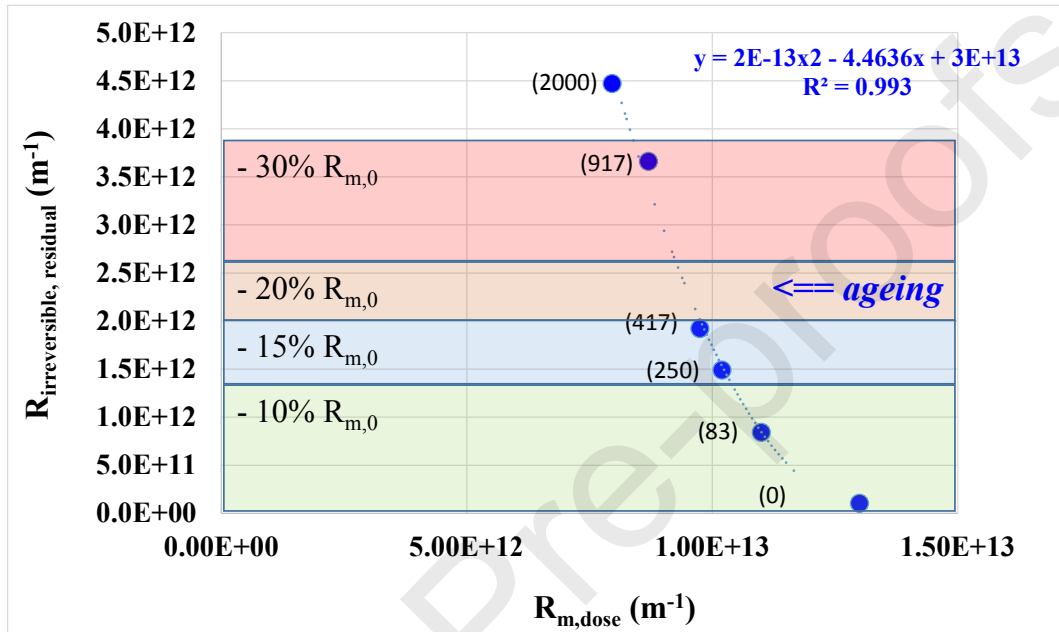


Figure 10: Correlation between $R_{irreversible,residual}$ and $R_{m,dose}$ compared to several variation of $R_{m,0}$ in the range 10%-30% highlighting how compensation between the membrane degradation decreasing $R_{m,dose}$ and the irreversible fouling increase can hide the build-up of fouling in a silent mode not detected by simple measurement of water flux. The number into the bracket is the chlorine dose received by the membrane for the given $R_{m,dose}$. with $R_{f,total} = R_{reversible} + R_{irreversible,initial}$ (equation 5) and $R_{irreversible,initial} = R_{irreversible,removable} + R_{irreversible,residual}$ (equation 6)

The $R_{irreversible,residual}$ was compared with fractions of $R_{m,0}$ and more especially 10%, 15%, 20% and 30% (rectangles in **Figure 10**). In this study, the accuracy on flux measurements was better than 3%. However, when dealing with industrial scale the current accuracy on permeate flux value is close to 10%. This value is thus used for the discussion. When the water flux recovery after the alkaline cleaning (compared to the pristine membrane) is better than 90%, the hydraulic cleanliness of the membrane is reached and the cleaning efficiency is considered as good.

Consequently, if $R_{irreversible,residual}$ remained lower than $0.10 \times R_{m,0}$ (chlorine dose close to 250 ppm.d at pH= 8.0) no problem would be detected and the next skim milk filtration would be achieved. Indeed, the membrane ageing has started, $R_{m,dose}$ was lower than $R_{m,0}$ and compensation between the two resistances can occur, leading to an acceptable misleading

interpretation of the water flux recovery. However, the irreversible fouling remaining on/inside the membrane after the alkaline cleaning was always existing and provided a place to anchor new foulants during the subsequent skim milk UF. This phenomenon can be called: an “irreversible fouling growing like in a silent mode”.

If $R_{\text{irreversible, residual}}$ increased in the range $0.15 \times R_{m,0}$ (chlorine dose close to 417 ppm.d at pH=8.0) – $0.20 \times R_{m,0}$, the water flux recovery after the alkaline cleaning will be better than 80% and the cleanability would be often considered as acceptable. However with respect to the accuracy on flux measurement, the amplitude of the problem will be underestimated; the growing of the irreversible fouling layer in a silent mode have significantly accelerated. It is already a strong structure that have resisted to cleaning and that allowed the anchoring of more and more proteins, moreover with a strong increasing rate.

It was drawn from these results that the misleading interpretation of water flux recovery when dealing with the membrane cleanliness can be within a 15-20 % accuracy. However, at this stage, the membrane is already entered in a vicious cycle with a power law relating the irreversible residual fouling and the membrane resistance. The strong evidence of irreversible fouling accumulation by flux measurements would be too late, preventing from getting rid of the first and crucial accumulated layers and consequently leading to an irreversible accelerated degrading process.

Relationship have been found between the received chlorine dose at pH=8.0, the aged membrane resistance and the post cleaning irreversible fouling that could be used for the skim milk process management. However for an efficient management at industrial scale results depicted **Figure 10** at pH=8.0 have to be validated/adapted at the exact pH of the industrial scale NaOCl disinfection.

5.2. Explanation of the apparent decrease of fouling resistances with membrane ageing

Whereas **Figure 10** allowed to explain the increasing difficulty in membrane cleaning in relation with the membrane ageing, the direct comparison of the hydraulic resistances (**Figure 8**) due to fouling failed at giving the good conclusion at first sight. Thus, they decreased with the chlorine dose increase. In the following, we provide a possible explanation based on two reasonable assumptions, in full agreement with experimental results:

- (1) $R_{m, \text{dose}}$ decrease with the chlorine dose (**Figure 7**) could reflect the pore size increase. Note that the increase of membrane hydrophobicity could be associated to that of the pore size and lead to an overall decrease of the hydraulic resistance by partial compensation of the two antagonist variations. The pore size was not measured in this study but the current industrial knowledge about α -lactalbumin increasing leakage with membrane ageing support this assumption (see **section 1.1**).
- (2) The fouling location either on the membrane surface (external) or in the pore (internal) was not similarly distributed for the pristine membrane and a sufficiently aged one.

First of all, let's consider the new (not chlorine aged) membrane. As seen on FESEM pictures (**Figure 2d & 2e**) and Raman analysis (**Figure 3**) the membrane was mainly fouled on the active top layer and only slightly inside the membrane structure. These results were in good

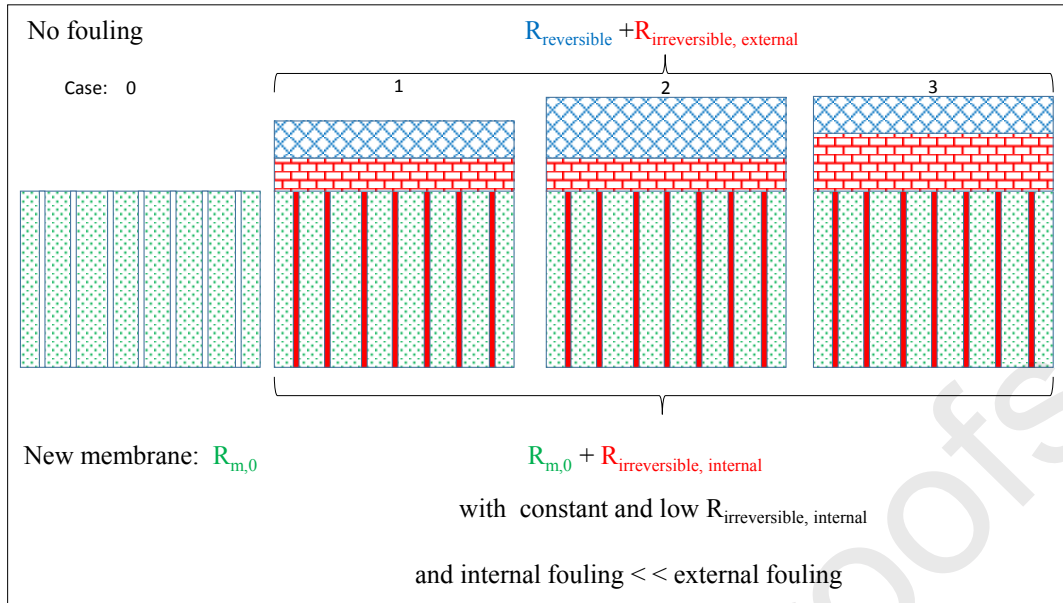
accordance with literature data (see **section 1.1**). When applying the resistance in series' model, a set of hydraulic resistances can be found (e.g.: $R_{m,0}$, $R_{f,total}$, $R_{reversible}$, $R_{irreversible, initial}$, **equation 4-6**, see also **Appendix 4**).

Figure 11a illustrates schematically the different states that can be encountered with a new membrane. Its pore size is low compared to the smallest protein of milk that is the only possible internal foulant.

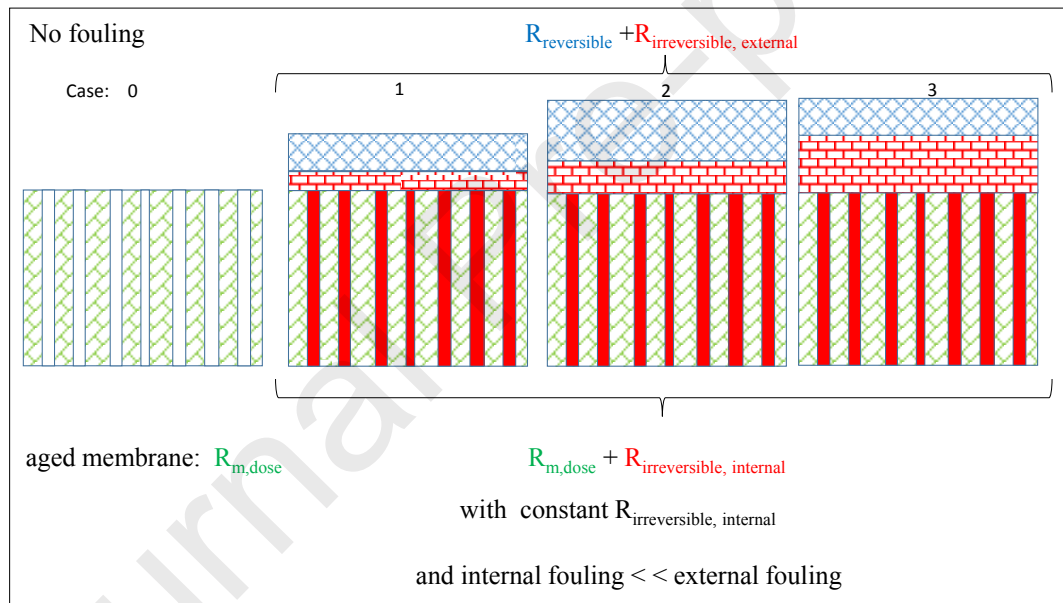
- Case 0: the new un-fouled membrane with a given pore size.
- Case 1: the new fouled membrane, with either reversible (blue) and irreversible fouling (red). The irreversible fouling can be divided in external fouling and internal fouling, this last one being low compared to the external fouling.
- Case 2: the overall description can be similar to that of case 1 but with more overall fouling (for instance due to a lower cross-flow velocity of the feed flow). The internal fouling is as low as in case 1. The external irreversible fouling is similar to that of case 1 whereas the external reversible fouling is lower than in case 1.
- Case 3: is similar to case 2 except the shear stress at the membrane wall.

All of the 3 cases dealing with the fouled membrane have the same hydraulic resistance ($R_{m,0}$) and the internal fouling exists but is negligible compared to the external fouling with respect to the very low transmission of the smallest protein ($\leq 5\%$). Applying the resistance in series' model for this 3 cases allowed to directly compare the fouling resistances. One can consider that the model will mainly reveal the increase in external fouling layers that are build up one on the other. In other words, using an analogy with current circuit, the additional resistances due to fouling are build-up in series (in good accordance with the name of the resistance in series' model).

Consider now a second new "membrane 2" with larger pores. These last ones can be selected to match with the pore size of the first membrane but after having received a certain chlorine dose. Thus, case 0 in **Figure 11b**, can illustrate that (except that the membrane resistance $R_{m,dose}$ has to be substituted by the hydraulic resistance of the new "membrane 2" in the caption). All comments written for the first membrane are still applicable for "membrane 2", except that the internal irreversible fouling can be higher. The two membranes filtering in similar hydrodynamic conditions will be fouled and the fouling resistances can be obtained from the resistance in series' model. However, the direct comparison of the absolute value of fouling resistances will not be appropriate and the ability of the two membranes toward fouling will be held by comparing the resistance relative ratio; for instance the $R_{irreversible}/R_{m,0}$ ratio of the two membranes.



(a) new membrane



(b) Aged membrane

Figure 11: Graphical explanation of the evolution of the fouling problem taking into account the membrane ageing.

(a) New membrane and its negligible internal fouling compared to external one and its variable external fouling modulated by hydrodynamics and shear stress.

(b) Aged membrane exhibiting greater pores and increased hydrophobicity compared to the pristine membrane leading to $R_{m,dose}$ lower than $R_{m,0}$. For given hydrodynamic conditions, the internal fouling is able to increase compared to that of the pristine membrane. Besides, the external fouling can be modulated by hydrodynamics and shear stress.

Figure 11b represents the membrane depicted **Figure 11a** but in a severely aged state. The pore size increase favored the internal fouling because the main foulant (α -lactalbumin) will be better transmitted in the permeate. It is also expected that the increase of membrane hydrophobicity would prone more fouling: hydrophobic interactions are well known to be involved in protein adsorption on polymer surface. However, the membrane resistance has significantly changed, decreasing from $R_{m,0}$ to $R_{m,dose}$ for the new and aged membranes, respectively. Filtration in similar hydrodynamic conditions will provoke fouling in both cases and the fouling resistances can be obtained from the resistance in series' model. The direct comparison of the calculated fouling resistances is no more valid as it would be similar to the direct comparison of the fouling of two new membranes of different pore size commented above. Indeed, the fouling increase of the aged membrane (e.g. case 1, **Figure 11b**) compared to the fouling of the new membrane (e.g. case 1, **Figure 11a**) is simultaneously external (additional resistance build-up in series) and internal (additional resistance build-up in parallel). Such comments could be repeated for different hydrodynamic conditions (case 2 and case 3 of **Figure 11a & 11b**) all degradation states of the membrane.

Finally, the following summary can be done. The resistances in series' model is fundamentally able to describe the accumulation of layers of various resistances built-up on/in a given membrane. However direct comparison of the resistances' values can only be made for a membrane having a stable structure. This case is that of a new membrane. This is also the case of an aged membrane in a given aged state, even if this last one is different from that of the new membrane. However, the direct comparison of resistances calculated thanks to the model of resistances in series is not able to take into account the dynamic resulting from the membrane ageing. This is especially true when the membrane degradation is very different between the two states that have to be compared. Indeed, we thought that the direct comparison of the calculated resistances makes no sense on a physical point of view. Only considering the irreversible fouling, the total resistance to transfer through an aged membrane ($R_{m,aged} = R_{m,dose}$ if ageing is due to chlorine) is thus classically expressed as:

$$R_{total} = R_{m,aged} + R_{irreversible} \quad (7)$$

However, we propose to take into account that only a global resistance combining the membrane ageing and the internal fouling ($R_{m,aged \& \text{internally fouled}}$) is built-up in series with the external irreversible fouling ($R_{irreversible, external}$). By analogy with the resistances in an electrical circuit, **equation 7** might be change for:

$$R_{total} = R_{m,aged \& \text{internally fouled}} + R_{irreversible, external} \quad (8)$$

With:

$$1/R_{m,aged \& \text{internally fouled}} = 1/R_{m,aged} + 1/R_{irreversible, internal} \quad (9)$$

In order to be more realistic on a physical point of view as $R_{irreversible, internal}$ is built-up in parallel and not in series with the membrane hydraulic resistance at its given age state.

Note that $R_{m,dose}$ calculated in this study was determined from water flux on the membrane at different age states but supposed to be perfectly cleaned after the alkaline cleaning + NaOCl

treatment. If some fouling remained in the membrane (that cannot be totally excluded) calculated $R_{m,dose}$ have to be decomposed according the **equation 9**. However, up to now we failed at finding an experimental tool able to go ahead in such direction on a quantitative point of view. In the future, Raman spectroscopy would be able to help at evidencing the amplitude of the problem but complementary tools have to be found for a more accurate analysis. However, we think that the general trends and messages given in this paper will not be fundamentally changed.

Thus, conditions might exist for which the sum of resistance of the aged & fouled membrane ($R_{m,aged \& fouled}$, with a fouling either internal or external) can exactly match with the resistance of the pristine un-fouled membrane (**Figure 12, Figure 10**). In that case water flux measurement corresponding to a global hydraulic resistance equal to $R_{m,0}$ would be fortuitous, but however would not reveal an efficient cleaning, even on a pure hydraulic point of view of the cleanliness.

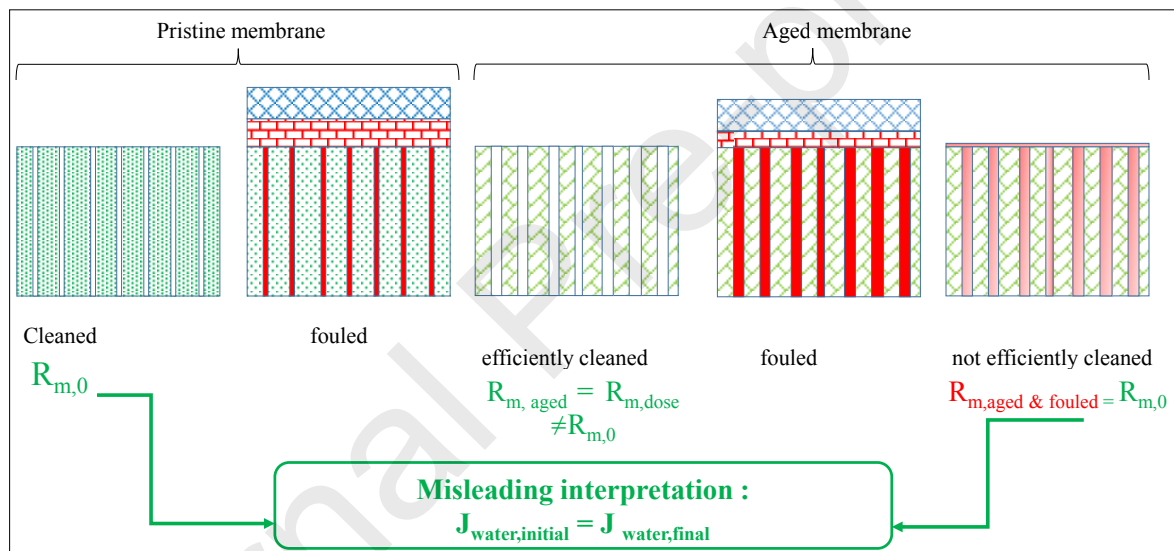


Figure 12: Schematic representation of the possible accordance of resistance of a pristine & cleaned membrane and that of an aged and un-completely cleaned membrane

6. CONCLUSION

According to the best of our knowledge, dealing with UF of skim milk, the main current industrial practice consists in achieving the filtration at constant permeate flux equal to the limiting flux. This is commonly achieved by increasing progressively the pressure according to membrane fouling. When the pressure becomes too high, a severe irreversible fouling of the membrane is observed. In dairy industry, engineers have capitalized on assay & errors trials and have progressively found a maximal pressure value that must not be exceeded. However, flux decline over the membrane lifespan remains the daily reality and induces a relatively frequent turn-over of membranes. This highlights that the maximal pressure is probably not

widely selected. The common idea, in dairy, is that this is mainly a problem of cleaning and industry always claimed for new detergents that must be more efficient.

According to us, by considering that the solution would not be only in the formulation of new detergents, sufficient focus is not made on the real origin of these behaviors and thus part of the necessary research to better master the process is not well oriented.

On the one hand are the ameliorations that could be obtained by using the recent concepts in membrane process. We refer particularly here, to the critical flux concept and the evolution of its definition to take into account the complexity of real fluids (critical flux of threshold type). Accordingly, UF of skim milk below the critical/threshold flux has to be favored to minimize membrane irreversible fouling by proteins and thus to reduce the overall energy consumption of the process. Indeed, according to the best of our knowledge, this concept has only been studied using pristine membranes. However, one important result of this paper is that either the limiting or the critical/threshold flux should be re-evaluated during the membrane life in conditions of use. Besides the change in their absolute value, they both appeared at lower pressure for aged membranes than for the pristine one. With respect to the filtration practice at constant flux, it means that the maximum pressure that can be used during the process management have to be decreased along the membrane lifetime. To go ahead, abacuses could be proposed relating the pressure and the cumulative chlorine dose received by the membrane to help in the process mastering at industrial scale.

On the other hand are the ameliorations that could be obtained from a better understanding of the fouling either dealing with the composition or location or the interactions with the membrane material along its lifespan. The present results have evidenced the correlation between the residual part of the irreversible fouling after alkaline cleaning and the decreasing membrane resistance due to its contact with NaOCl. The fouling removal becomes more and more difficult with membrane ageing. This is in good agreement with the increasing troubles during cleaning observed in the second part of the membrane life at industrial scale. This might probably be due to the combination of both (1) the possible increase of internal fouling with respect to the pore size increase and (2) the increasing attractive interactions between the foulant species and the aged membrane being more hydrophobic than the pristine one. Consequently, filtration and cleaning procedures should be established with respect to the membrane degradation state (age) and not only for the pristine membrane as it is currently done nowadays. Providers of detergents have to play a role to adapt their detergent formulations.

However, besides the better fundamental comprehension is the ability to give the good diagnostic about the membrane age and its related consequences. Up to now, except the change in α -lactalbumin rejection (the smallest soluble protein of milk), the *on-line* flux measurements remained the sole parameter to follow/master a process at industrial scale. Indeed, a major difficulty lies in the *real-time* evaluation of membrane ageing: following the cumulative chlorine dose received by the membrane is indeed only few informative.

What can be done now when waiting for methods that have to be developed to overcome this situation? To be more aware about the misleading interpretation that can be drawn from the water flux recovery after cleaning is a first step beyond. This study has proved that the

membrane ageing provoked by chlorine contact (during the disinfection step) induces a decrease in the membrane hydraulic resistance (in an ideal world chlorine disinfection would be more or less prohibited). Moreover, the overall irreversible fouling increases with ageing. With respect to possible compensation of these two phenomena, the same water flux can be obtained with a pristine un-fouled membrane and an aged & fouled one. Indeed, using the water flux of the pristine membrane as unique reference this situation could be interpreted as “everything works well” instead of “nothing works well” and each following production step would increase the difficulties. Finally, depending on the membrane ageing state, after skim milk UF and its consecutive alkaline cleaning, the membrane water flux of a perfectly cleaned membrane can be:

- lower (no variation of pore size but slight increase of hydrophobicity)
- equal (pristine or slightly aged membrane)
- or greater (middle or severely aged membrane with increase of pore size with/without slight variation of hydrophobicity)

than that measured on the pristine membrane. The strong message is thus that the reference cannot be the pristine membrane for the overall lifespan of the membrane.

The resistance in series' model can be used to estimate the hydraulic resistance of the membrane ($R_{m,dose}$) against the received chlorine dose as made here for a membrane in the first part of its service life (comparing the 2,000-2,800 ppm.d dose to 5,000 ppm.d guaranteed by the membrane provider). This study has clearly shown that $R_{m,dose}$ drastically decreased (roughly 40 %) along membrane first mid-life due to NaOCl exposure. Its non-linear variation with the chlorine dose might be related to the complex degradation mechanisms. However, the superimposition of $R_{m,dose}$ decrease and possible increase of residual internal fouling remains a possibility. The problem has been exposed by introducing the necessity of modifying the calculation mode to take into account either additional resistances in series or in parallel. However, an opened question concerns the evaluation of the real value of $R_{m,dose}$ when residual fouling, both internal & external, cannot be removed at all, which can probably happened during the second part of the membrane industrial life. This study, in progress, required new analytical tools.

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APPENDICES / SUPPLEMENTARY

Appendix 1: Membrane ageing detailed protocol

The membranes were aged in filtering conditions at TMP= 2 bar, 50°C during a various time. Controlled chemical ageing of the two spiral membrane elements were achieved up to different chlorine cumulative doses expressed, as classically, in ppm.d TFC:

$$\text{Cumulative chlorine dose} = 400 \text{ ppm} \times \text{number of days} \quad (1)$$

On a practical point of view, for local safety reasons, it was not possible to maintain the membrane in UF conditions during several days without any interruption in our lab. The ageing protocol was then applied all day long (5 h) during several days but has to be interrupted each evening during which the membrane was let to withstand in pure water after a careful rinsing. Accordingly, the membrane was then daily exposed to a chlorine dose of 83 ppm.d, hereafter called “one” ageing step. Thus the overall membrane ageing was the consequence of succession of 83 ppm.d doses with water inter-rinsing. However, from time to time, a skim milk UF was achieved, followed by an alkaline cleaning and rinsing before starting again the ageing protocol. **Table A1.1** and **Table A1.2** detail ageing procedures applied to the S-CIP-2 and S-CIP-3 spiral membrane elements, respectively. The cumulative doses were 2,000 ppm.d and 2,800 ppm.d, for S-CIP-2 and S-CIP-3, respectively. The flux behaviours were in full agreement up to 2,000 ppm.d, highlighting that the way to reach the cumulative chlorine dose was not an important parameter when following the chosen protocol. By inserting regular skim milk UF, the evolution of critical (threshold) and limiting fluxes of the membrane cleanability can be studied with respect to the membrane ageing (see below).

Table A1.1: Details of the filtration-cleaning-ageing cycles applied to S-CIP-2 membrane

Entry	Treatment	Cumulative number of ≈ 83 ppm.d ageing steps	Cumulative dose (ppm.d)
1	UF of skim milk + rinsing + cleaning	0	0
	1 ageing step \rightarrow 1x 83 ppm.d		
2	UF of skim milk + rinsing + cleaning	1	83
	1 ageing step \rightarrow 1x 83 ppm.d		
3	UF of skim milk + rinsing + cleaning	2	167
	1 ageing step \rightarrow 1x 83 ppm.d		
4	UF of skim milk + rinsing + cleaning	3	250
	2 ageing steps \rightarrow 2x 83 ppm.d		

5	UF of skim milk + rinsing + cleaning	5	417
6 ageing steps → 6x 83 ppm.d			
6	UF of skim milk + rinsing + cleaning	11	917
12 ageing steps → 12x 83 ppm.d			
7	UF of skim milk + rinsing	23	2,000

Table A1.2: Details of the filtration-cleaning-ageing cycles applied to S-CIP-3 membrane

Entry	Treatment	Cumulative number of \approx 83 ppm.d ageing steps	Cumulative dose (ppm.d)
1	UF of skim milk + rinsing + cleaning In triplicate*	0	0
5 ageing steps → 5 x 83 ppm.d			
2	UF of skim milk + rinsing + cleaning	5	400
18 ageing steps → 18 x 83 ppm.d			
3	UF of skim milk + rinsing + cleaning	23	2,000
11 ageing steps → 11 x 83 ppm.d			
4	UF of skim milk + rinsing	34	2,800

*with intermediate cleaning in standard conditions allowing full recovery of the initial water flux

Appendix 2: overview of PES/PVP membrane degradation

For the sake of simplicity only an overview of the chemical impact of NaOCl on PES/PVP membrane is given here. This summary was already published in [44] with the associated references.

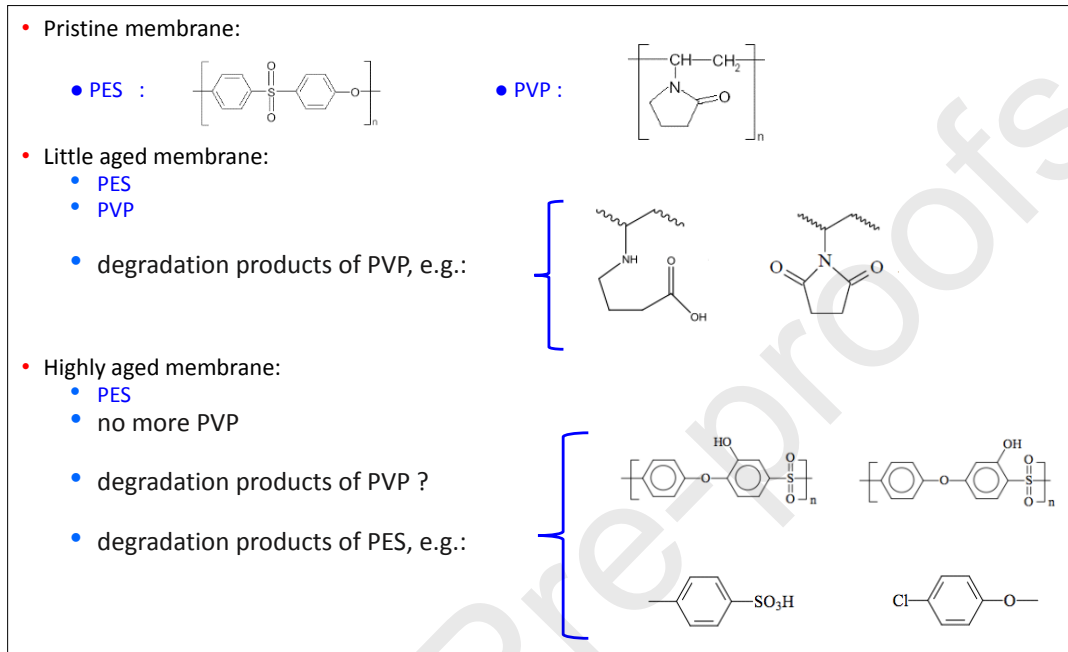


Figure A2.1: PES and PVP and their degradation products by NaOCl exposure according to available literature data.

Appendix 3: detailed data for hydraulic resistance of pristine and aged membrane

- *First case: pristine membrane (FigureA3.1)*

The initial pristine membrane hydraulic resistance $R_{m,dose} = R_{m,0}$ hereafter denoted R_m for sake of simplicity, was taken as reference, and was classically determined from the water flux measured on the cleaned and compacted pristine membrane using the well-known Darcy's law:

$$J_p = \frac{TMP}{\mu R_m} \quad (\text{A1})$$

With:

J_p : the permeate flux in water

μ : the permeate viscosity (close to that of water)

$R_m = R_{m,0}$: the hydraulic resistance of the pristine membrane

In absence of any chlorine ageing, R_m remained the membrane resistance regardless of the fouling due to skim milk.

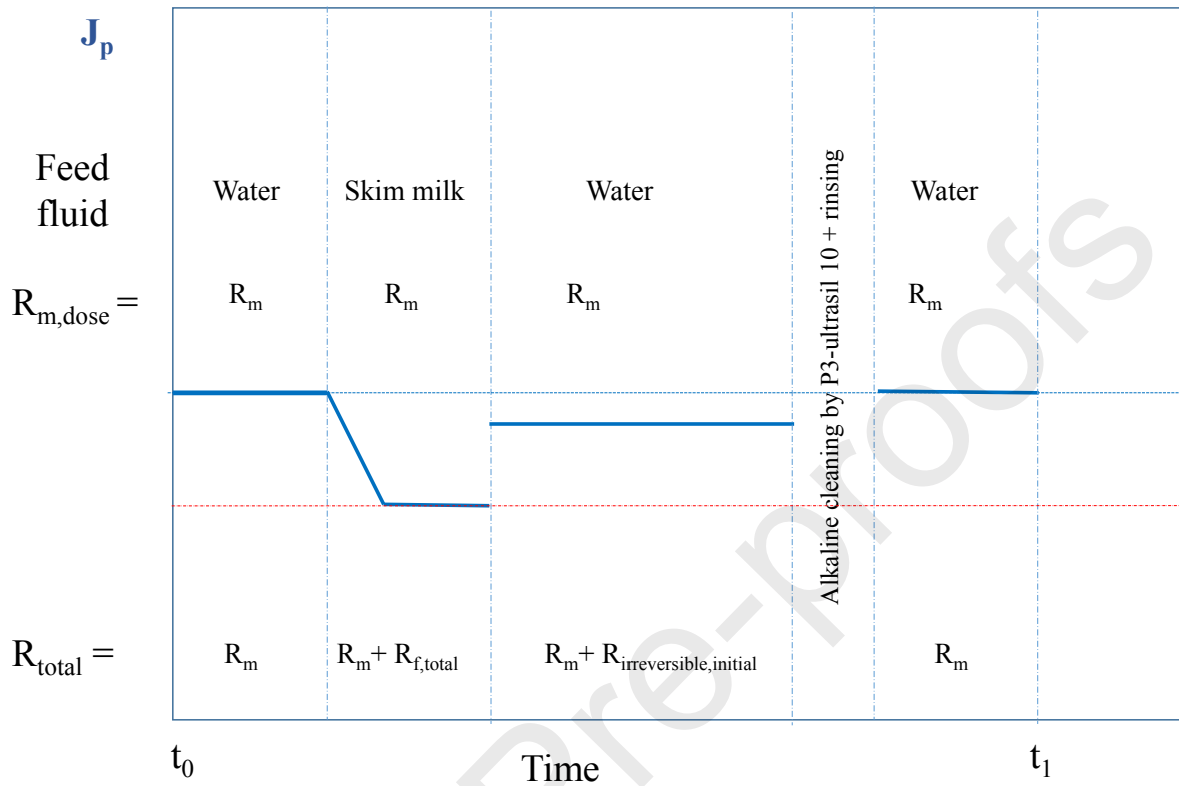


Figure A3.1: Evolution of flux (J_p , blue straight line) and of mass transfer resistances of a pristine and not aged spiral membrane element at constant TMP. $R_{m,dose} = R_{m,0} = R_m$, as initial and final chlorine dose received by the membrane was zero.

- Second case: little aged membrane just after skim milk UF + alkaline cleaning (**Figure A3.2**)

This case was for instance that of the membrane after a first chlorine dose of 83 ppm.d that have been further used for skim milk UF. Of course, the classical alkaline cleaning has been applied and the water flux was determined after rinsing. The drawn conclusion was that the hydraulic cleanliness was reached because the recovered flux was equal or greater than 90% of the water flux of the pristine membrane. However, in NaOCl during the following ageing step, the flux regularly and slowly increased with time (**Figure A3.2**). On the plot relating J_p with time in NaOCl, a single slope was evidenced. This can be interpreted as corresponding to a single phenomenon with a given kinetic, that was fully attributed to the ageing process.

At the end of 5 h of ageing the chlorine dose received by the membrane was “dose 1 = 83 ppm.d” and the membrane resistance was $R_{m,dose\ 1} = R_{m, 83\ ppm}$. A water rinsing was performed after this ageing step, and $R_{m,dose\ 1}$ was easily calculated from the following water flux measurement thanks to the Darcy law changing R_m for $R_{m,dose\ 1}$ in **equation A1**.

The question now is “how to calculate $R_{m,dose}$ between $R_{m,0}$ and $R_{m,dose 1}$? There is no special difficulty to apply **equation A1** changing the water flux for the flux in NaOCl because the only resistance to mass transfer was due to the membrane. This allowed the determination of the variation of $R_{m,dose}$ with contact time with NaOCl and at least with respect to the received chlorine dose.

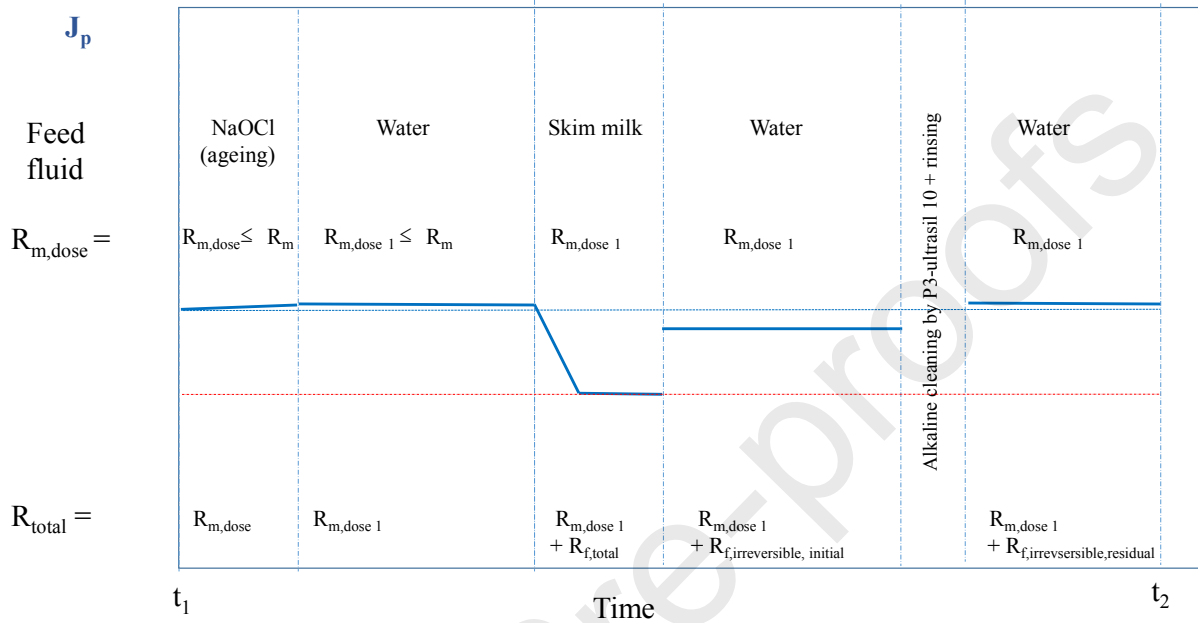


Figure A3.2: Evolution of flux (J_p , blue straight line) and of mass transfer resistances taking into account the first ageing step of the spiral membrane element at constant TMP. $R_{m,dose} = R_{m,0}$ at t_1 (similar to $t1$ of **Figure A3.1**) when ageing started but evolved toward $R_{m,dose 1} = R_{m, 83 \text{ ppm}}$ at the end of ageing and then remained constant with time up to t_2 . The dashed lines are given to highlight small variations compared to the initial water flux corresponding to R_m value (dashed blue line) and the lower flux reached in skim milk corresponding to $R_m + R_{f,total}$ (dashed red line).

- Third case: more aged membrane just after skim milk UF + alkaline cleaning (**Figure A3.3**)

For sake of clarity, we considered at start, that the membrane resistance was $R_{m,dose 1} = R_{m,83 \text{ ppm}}$. When filtration of NaOCl start just after the UF of skim milk + alkaline cleaning + water rinsing, it was observed that the flux increase with time can be described in 2 consecutive parts evidencing 2 slopes. That was interpreted as corresponding to two different phenomena with different kinetics (**Figure A3.3**). Firstly, the flux increase was rapid (during maximum 100 min) then the flux increase was slow (contact time with NaOCl greater than 100 min). It was assumed that in the second part the flux behavior can be attributed only to the ageing process. On the contrary, in the first part, the increase of flux was the result of the superimposition of ageing and polishing of the previous alkaline cleaning that was (in this case) not sufficiently efficient. At the end of the ageing the membrane resistance was $R_{m,dose 2} = R_{m, 250 \text{ ppm}}$. A water rinsing was performed after this ageing step, and $R_{m,dose 2}$ can easily be calculated from the following water flux measurement thanks to the Darcy law changing R_m for $R_{m,dose 2}$ in **equation A1**.

The determination of $R_{m,dose}$ between $R_{m,dose 1}$ and $R_{m,dose 2}$ followed the same procedure as in the previous case between R_m and $R_{m,dose 1}$. This allowed to determine the variation of $R_{m,dose}$ with contact time with NaOCl and to establish a trend that can be easily fitted by a polynomial curve.

The difficulty concerned the first part of the plot where the total resistance to transfer is due to the irreversible fouling remaining after alkaline cleaning but progressively decreasing by contact with NaOCl and the membrane that progressively aged. One can reasonably consider that $R_{m,dose}$ follows the same trend as that observed in the second part, and that consequently, the polynomial fitting curve described above can be extrapolated.

The same procedure was used to determine $R_{m,dose}$ for all similar situations, namely for the ageing steps immediately following a skim milk UF + alkaline cleaning, for cumulative chlorine dose received by the membrane equal or greater than 250 ppm TFC.

- *Fourth case: aged membrane after another ageing step not consecutive to skim milk UF*

Regardless of the chlorine dose previously received by the membrane, when filtration of NaOCl started just after another one having increase the cumulative dose by 83 ppm.d, the flux increased regularly with time. That can be interpreted as corresponding to only one kinetic that was attributed to the membrane degradation. The determination of $R_{m,dose}$ was then achieved following the same approach as that used in the second part of the flux vs time plot of the third case previously explained.

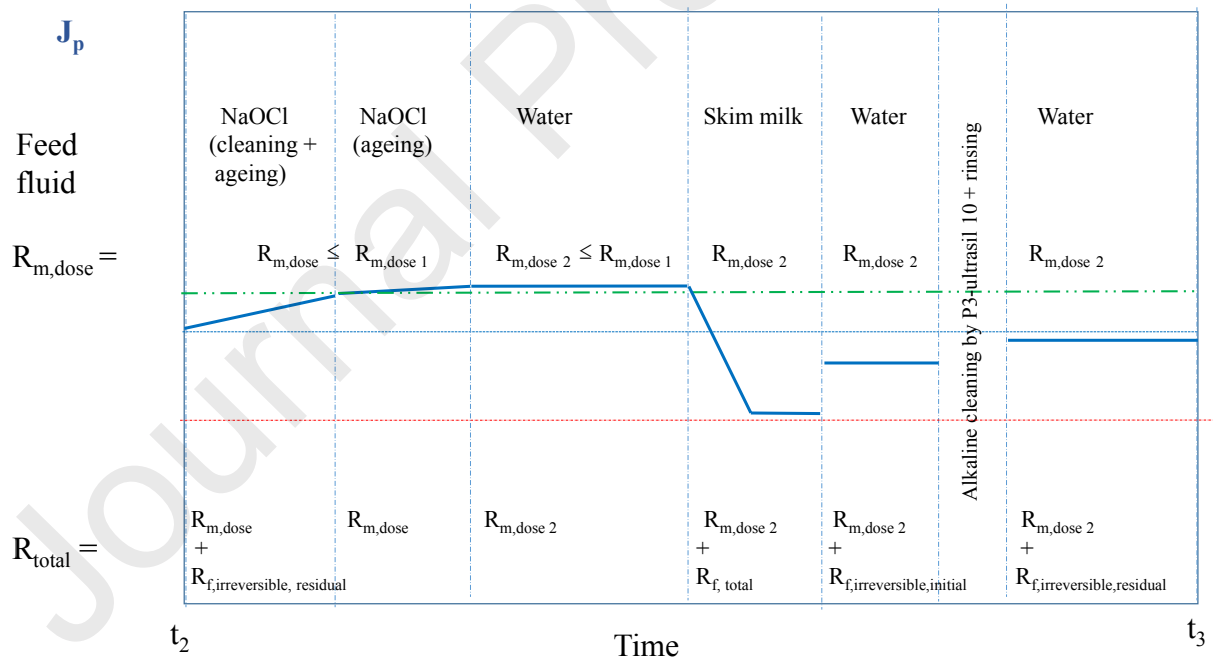


Figure A3.3: Evolution of flux (J_p , blue straight line) and mass transfer resistances taking into account the second ageing step of the spiral membrane element at constant TMP. $R_{m,dose} = R_{m,dose 1} = R_m$, 83 ppm at t_2 (similar to t_2 of **Figure A3.2**) when ageing started superimposed to polishing of cleaning but evolved toward $R_{m,dose 2} = R_m$, 250 ppm at the end of ageing and then remained constant with time up to t_3 . The dashed lines are given to highlight small variations compared to the initial water flux corresponding to R_m value (dashed blue line) and the lower flux reached in skim milk corresponding to $R_{m,dose 2} + R_{f,total}$ (dashed red line) or to the flux recovered at the end of the cycle corresponding to $R_{m,dose 2}$ (dashed green line).

Appendix 4: supplementary figures for hydraulic resistance of the S-CIP-2 membrane vs chlorine dose

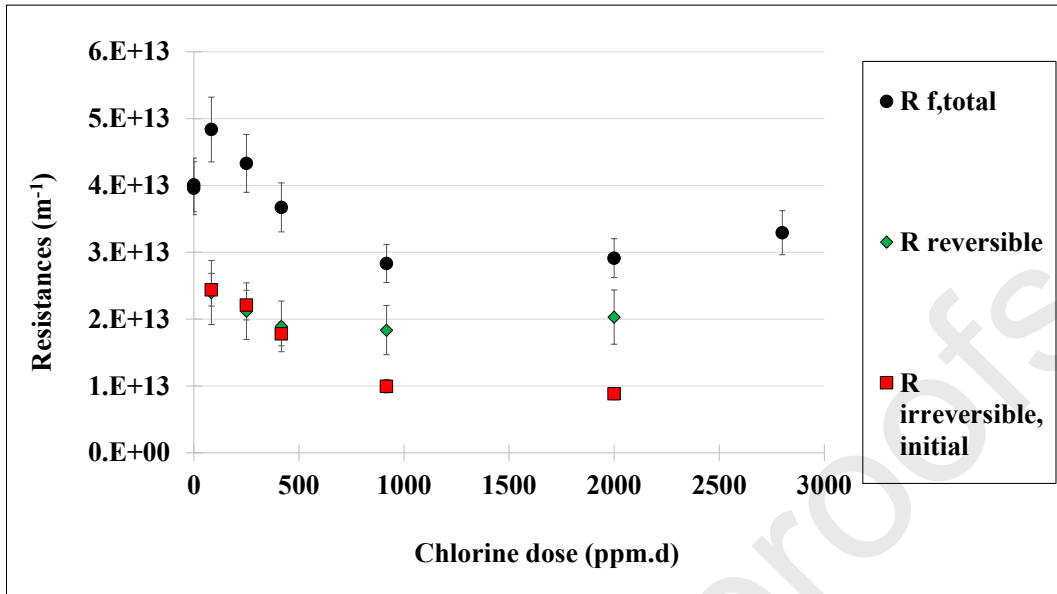


Figure A4.1: Variation of $R_{f,total}$, $R_{reversible}$ and $R_{irreversible, initial}$ (as defined in equation 4-6) at 4.7 bar with membrane chlorine dose exposition (all points correspond to S-CIP-2 membrane except 2,800 ppm.d corresponding to S-CIP-3 membrane)

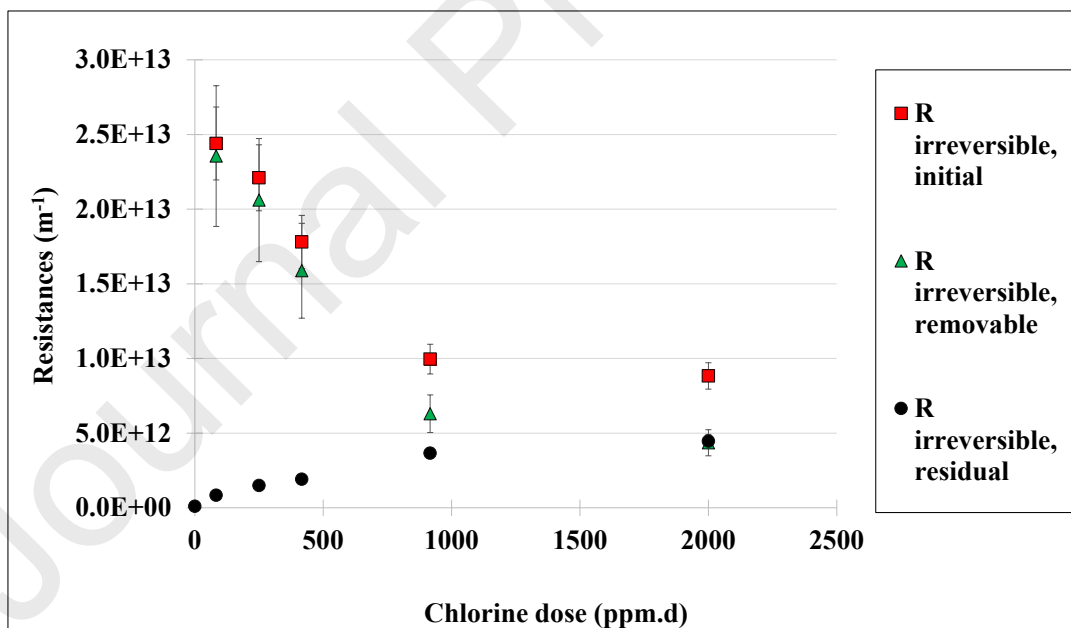


Figure A4.2: Evolution of resistances with chlorine dose received by the membrane, due to: (a) irreversible fouling removable by alkaline cleaning ($R_{irreversible, removable}$) - (b) residual fouling after this cleaning ($R_{irreversible, residual}$) deduced from equation 4-6

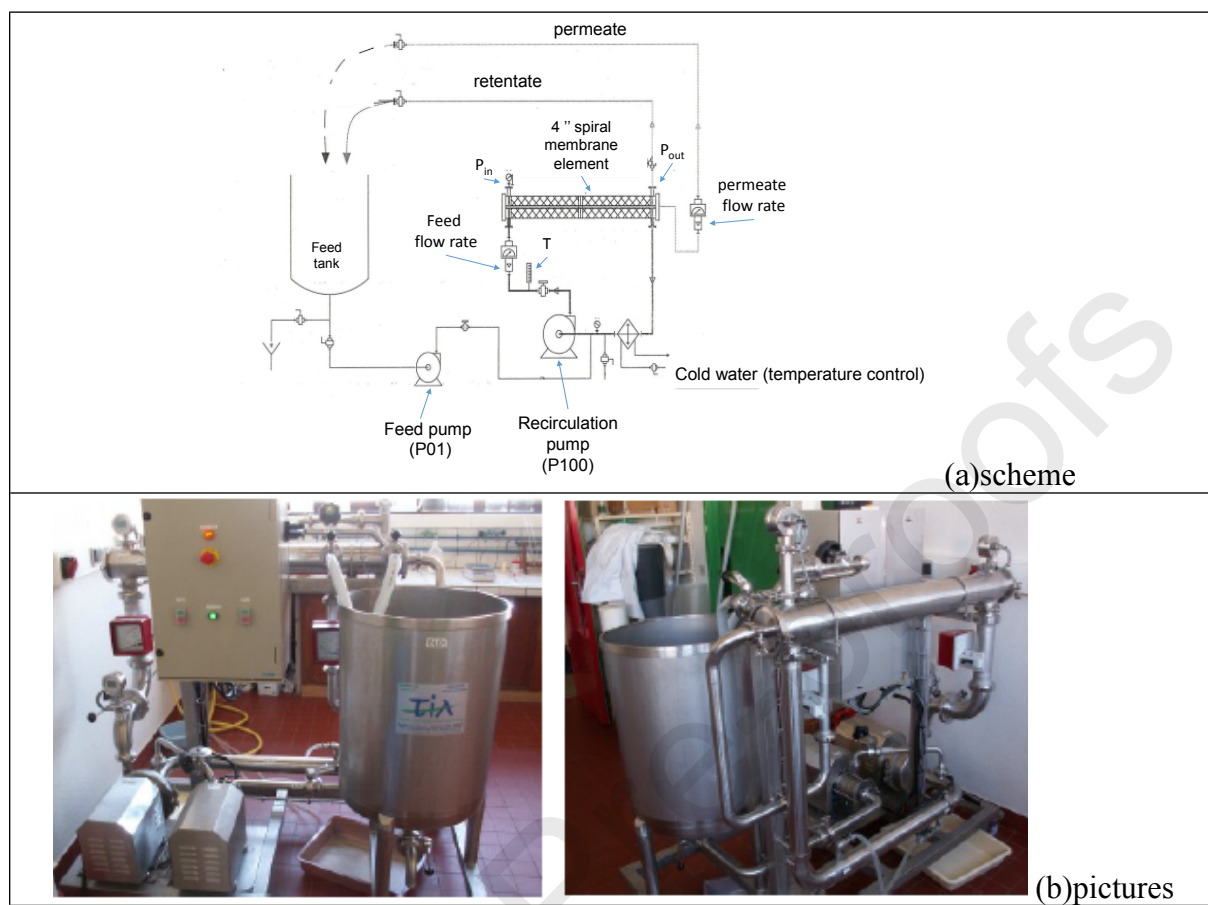
Appendix 5: Scheme of the pilot equipped with one spiral membrane element (4 inches)

Figure A5.1: Scheme and pictures of the pilot equipped with a 4" spiral wound membrane element

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CONFLICTS OF INTEREST:

Nothing to declare

HIGHLIGHTS

- *Critical/threshold and limiting fluxes are modified by NaOCl membrane ageing*
- *ATR-FTIR shows both the membrane ageing and the related fouling increase*
- *Membrane hydraulic resistance has decreased of 40% at mid-term life*
- *Correlation exists between residual fouling after cleaning and membrane resistance*
- *Due to ageing, water flux recovery is misleading when dealing with cleanliness*

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