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Simulation of membrane ageing to go ahead in fouling and cleaning understanding during skim milk ultrafiltration

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Highlights

- Systematic study of membrane ageing in NaOCl using micro-waves and ultrafiltration
- Both methodologies allow to reach similar degradation state of a PES/PVP membrane
- Fouling of aged membranes by proteins of skim milk increase with membrane ageing
- Critical and limiting conditions in skim milk UF evolve with membrane chemical ageing
- Membrane cleanliness is reduced with respect to membrane ageing

Abstract

In dairy industry, the mastering of membrane fouling and cleaning remains a bottleneck of membrane processes especially for aged and degraded membranes. This paper reports an in-depth study of the impact of membrane chemical ageing due to NaOCl disinfection on the fouling and cleaning of PES/PVP membranes.
Fouling by skim milk was performed at critical and limiting flux found to have an impact on the initial irreversible fouling, *i.e.* the one remaining after water rinsing. Furthermore, for filtrations performed with pristine membranes, the fouling removal by formulated alkaline detergents was also affected by the filtration conditions.
On the contrary, aged membranes were highly irreversibly fouled whatever the operating conditions. Furthermore, they were shown to be more difficult to clean than pristine ones.
Besides these results, this study provides the validation of an original approach based on the use of micro-waves activation to study the membrane degradation.

Keywords: PES/PVP membrane; NaOCl ageing; skim milk UF; micro-waves; cleaning; critical and limiting flux

1. Introduction

Nowadays, at industrial scale, skim milk ultrafiltration (UF) is worldwide commonly performed using polyethersulfone/polyvinylpyrrolidone (PES/PVP) spiral-wound membranes for the standardization of the protein content before the cheese making process. Despite the separation process automation, disruptions due to membrane failure still occurred at unpredictable time. Depending on the dairy factory, two strategies are commonly used to manage with membrane life duration. The first one is an emergency-based approach consisting in the replacement of the membranes when broken. The second option consists in changing the membranes at a

preselected service life, before disruption, to avoid the emergency. Besides these strong disruptions, is the stress in the production management when cleaning, always achieved in a similar way, which leads to insufficient flux recovery that is often attributed, at industrial scale, to error in the cleaning achievement. However, analyzing more in details these process disruptions one can conclude that such problems generally occur in the second part of the industrial life of the membrane. Taking into account this observation, the reason of the failures must probably have other causes than a cleaning management error. In this context, a systematic study of the impact of the membrane chemical ageing on the fouling irreversible character as well as on its cleanability has been carried out in our group for a few years.

The reader has to keep in mind that a typical industrial cleaning of PES/PVP membrane filtering skim milk consists of two consecutives cleaning steps at 50°C involving (1) a formulated alkaline detergent and (2) an acid solution (generally nitric acid). Of course, an intermediate water rinsing occurs between the two cleaning steps. Finally, a disinfection step is achieved. Most of the time, it is carried out in alkaline and oxidant conditions often using an efficient and inexpensive mixture of bleach and soda. The solution is prepared to reach a concentration of 150-200 ppm in total free chlorine (TFC) and a pH= 11.0-11.5 (Bégoin *et al.*, 2006).

The NaOCl disinfection step is known to be the main origin of the membrane chemical ageing, acting both on PVP (progressive disappearance) and PES as sums up in **Figure 1.** (Wienk *et al.* 1995; Arkhangelsky *et al.*, 2007; Yadav *et al.*, 2010; Prulho *et al.*, 2013; Pellegrin *et al.*, 2013a, 2013b; Hanafi *et al.*, 2014 and 2016; Kourde-Hanafi *et al.*, 2017). Regarding PES degradation, different mechanisms can co-exist leading either to slight modifications of the polymer backbone or to covalent bond cleavages.

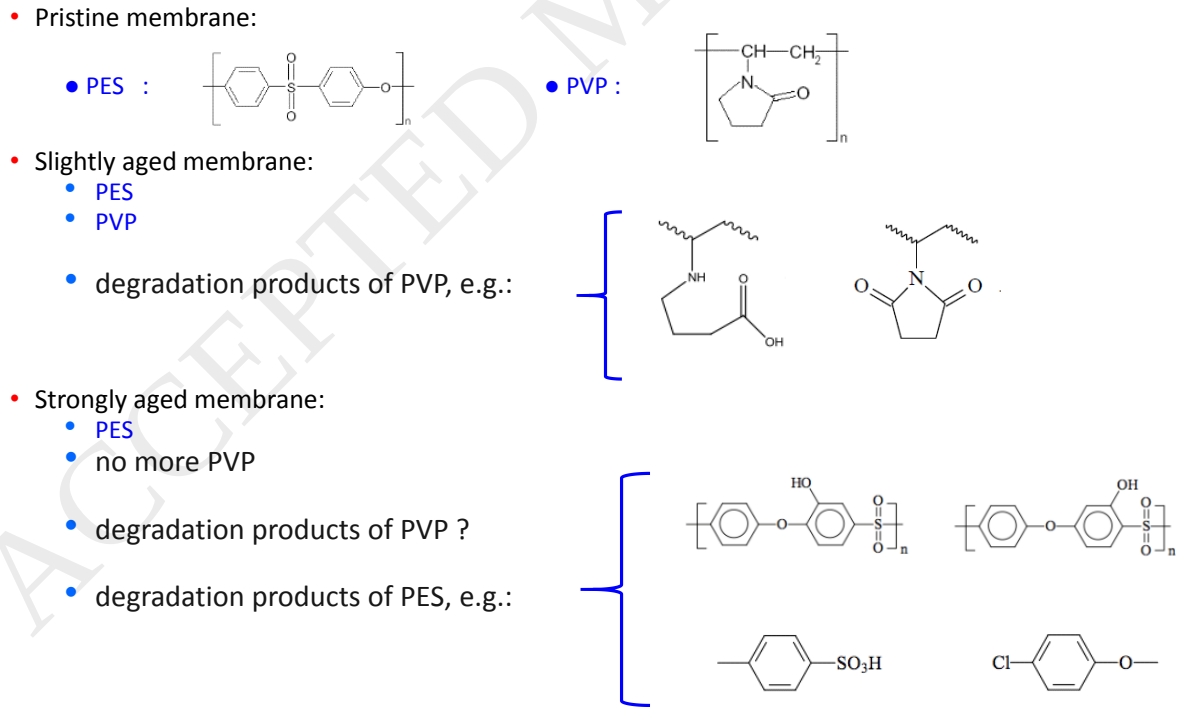


Figure 1: PES, PVP and their degradation products due to NaOCl exposure according to available literature data.

In the present study, a UF membrane made of PES/PVP was used either in spiral (4333 module type, 6.7 m^2 filtering area) or flat configurations (127 cm^2). The general approach consisted firstly in the membrane chemical ageing by contact with NaOCl and secondly in studying the membrane behavior during the skim milk UF. This study included both the determination of the limiting and critical conditions and that of the fouling removal with respect to the membrane age.

In this study, the main difference between the two membrane configurations was related to the ageing step achievement.
Thus, on the one hand the spiral membranes were aged by filtering, at 50°C, NaOCl solutions with a 400 ppm TFC concentration at pH 8.0. On the other hand the flat membranes were also aged by contact with NaOCl (same pH and concentration as above) but under microwaves known as an accelerator of chemical reactions (Loupy, 2008). According to the best of our knowledge, our team is the first one exploring the systematic use of micro-waves to study membranes degradation. Thus, Rabiller-Baudry *et al.* (2014) and Rabiller-Baudry *et al.* (2018) have demonstrated that the micro-waves activation helps to accelerate the membranes chemical degradation when compared to time-consuming simple membrane soaking in the same disinfecting solution, as classically performed.

2. Materials and Methods

2.1. Fluids to be filtered

Water used for membrane rinsing and preparation of all solutions was demineralised and 1 µm filtered. Its conductivity was always lower than 1 $\mu S.cm^{-1}$.

For an easy providing, 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 %). The 'UHT' thermal treatment of skim milk is known to induce denaturation of about half of the whey proteins which are the milk soluble proteins (5 $g.L^{-1}$ of the 32 $g.L^{-1}$ overall concentration). During UF of skim milk submitted to a less aggressive thermal treatment than the 'UHT' one (as it is the case at industrial scale), it is evidenced that the smallest whey proteins, namely α-Lactalbumin (14 $kg.mol^{-1}$, about 1 $g.L^{-1}$), is able to go through the membrane, especially when UF is achieved with damaged membranes. Of course the rejection depends on the protein form, either native or denatured. This is a limitation of this study explaining the choice made here to avoid detailed discussion on protein retention (see below). Similarly, the main whey protein, namely β-lactoglobulin (36 $kg.mol^{-1}$ in dimer form) was shown to be involved in the irreversible fouling of the PES/PVP membrane (Rabiller-Baudry *et al.* 2008b). Knowing that about half of this protein is denatured by the 'UHT' treatment, the irreversible fouling could be slightly increased when compared to that formed at industrial scale. But, on the other hand, variation of membrane fluxes were mainly controlled by the other category of milk proteins, namely the casein micelles (27 $g.L^{-1}$ of the 32 $g.L^{-1}$ overall protein concentration), and especially by their charges, as reported by Bouzid *et al.* (2008) and Rabiller-Baudry *et al.* (2009). Even if the 'UHT' thermal treatment slightly modified these proteins, their charges remained quite similar when compared to native casein

micelles (Rabiller-Baudry *et al.*, 2005). Consequently, flux trends discussed in the present study does provide consistency for a better comprehension of the industrial application.

For membrane ageing, sodium hypochlorite (NaOCl) solutions at 400 ppm TFC were obtained by appropriate dilution of concentrated commercial bleach (MIC, bleach at 48 $g.L^{-1}$ TFC, France). The pH was adjusted to 8.0 ± 0.1 by addition of HCl of analytical grade (Acros).

A commercial formulated alkaline detergent (Ultrasil 10, powder, pH 12.0 at 4 $g.L^{-1}$) provided by Ecolab (Issy Les Moulineaux, France) was used for membrane cleaning. Its efficiency was previously demonstrated for the cleaning of the pristine membrane used in the present study and fouled by skim milk (Diagne *et al.*, 2013).

2.2. Membranes and UF conditions

2.2.1. Membranes

The UF membrane (HFK 131, MWCO= 5-10 $kg.mol^{-1}$) was provided by Koch (USA). This membrane is commonly used at industrial scale for UF of skim milk and of acid and rennet wheys. Thus, it represents about 70 % of the world market for these specific applications.

This membrane is mainly made of PES but also contains small amounts of PVP (Rabiller-Baudry *et al.*, 2015) known to be the membrane polymer that is the most sensitive to degradation induced by NaOCl. (Wienk *et al.*, 1995; Yadav *et al.*, 2010; Rabiller-Baudry *et al.*, 2015). Three different spiral membranes (6.7 m^2, 4333 K131 VYV module) of the same reference were used in the present study.

2.2.2. Filtration with spiral membranes

Two spiral membranes (further called S-CIP2 and S-CIP3) were installed on a UF pilot provided by TIA (Bollène, France) and directly used for UF experiments. They were rinsed by water and cleaned by Ultrasil 10 before their first skim milk UF. 24 L (skim milk) or 25 L (NaOCl or ultrasil 10) of solutions were processed for each filtration runs. The standard operating conditions were: Q_{feed} = 10.5 $m^3.h^{-1}$ (leading to an estimated cross-flow velocity in free channel of 0.3 $m.s^{-1}$), temperature of 50°C and a volume reduction ratio VRR= $V_{feed}^{initial}/V_{feed}^{final}$ = 1 (full recycling of both retentate and permeate). The transmembrane pressure (TMP) was equal to 2 bar in NaOCl and Ultrasil 10 or varied in the range 1.0 to 4.0 bar in skim milk. The precision on permeate flux measurements was better than 5%.

2.2.3. Filtration with flat membranes

The third spiral membrane module was cut in flat coupons of 127 cm^2 filtering area (further called "flat membranes"). Prior any other use, the preservative was removed by soaking each flat membrane in demineralised water at room temperature (the efficiency of the removal of the preservative was checked by ATR-FTIR). The membrane was then inserted in a plate and frame filtration cell (Rayflow X100, Orelis, France) between a 31 mil retentate spacer and a permeate spacer which were both collected in the spiral membrane module. Each flat membrane was then compacted by filtering water at 4 bar, at 50°C, during 4 h in cross-flow mode (Q_{feed} = 110 $L.h^{-1}$ leading to a velocity close to 0.3 $m.s^{-1}$ (estimated in free channel) until a plateau value of permeance (Lp_0) was reached.

After such pre-treatment, several virgin flat membranes were used in skim milk UF performed at various TMPs in standard conditions, namely: 50°C, 0.3 $m.s^{-1}$ and VRR=1.
The rest of flat membranes were voluntary aged in NaOCl by immersion under micro-waves (see below) after the preservative removal as described previously. The membranes were subsequently re-compacted at 4 bar in water and finally used for skim milk UF at various TMPs in standard conditions.
Regardless of the membrane state, either virgin or NaOCl aged, UF of skim milk was achieved both at constant TMP during 200 min or with gradual TMP increase from 0.5 to 4.0 bar. For these last cases the TMP was increased only when a plateau value of flux was reached. After skim milk UF, each membrane was carefully rinsed by water. The membrane was then either (1) demounted or (2) cleaned at 2 bar and 50°C by Ultrasil 10, rinsed with water and then demounted for autopsy.

2.2.4. Determination of the limiting and the critical fluxes

For a given membrane, filtering a given fluid at a constant cross-flow velocity, two particular values of the permeate flux can be defined: the limiting flux ($J_{limiting}$) and the critical flux ($J_{critical}$). These two values can be determined by plotting the permeate flux (J) *vs* TMP.

The limiting flux is defined as the maximum flux that can be reached when increasing the TMP (Michaels, 1968; Porter, 1972). In the following, the limiting TMP is thus defined as the lower pressure for which this flux is reached. Nowadays, at industrial scale, UF of skim milk is usually performed at limiting flux despite the fact that this flux is known to be responsible of the occurrence of strongly irreversible fouling.

The 'critical flux' concept, has been extensively discussed by Field *et al.* (1995) before being modified by Field and Pierce (2011). This concept provides a theoretical approach of the control of membrane fouling during filtration of a given fluid by a given membrane. Using this approach, the experimental filtration conditions can be chosen aiming at minimising the occurrence of the initial irreversible part of the fouling (which might be defined as the part of the fouling remaining on the membrane after a first water rinsing at the end of the filtration step). These conditions are defined with respect to a critical point the coordinates of which are ($TMP_{critical}$,$J_{critical}$) in the J *vs* TMP plot for given hydrodynamic conditions.
This critical point delimits two fouling behaviours of the membrane (Wu *et al.* 1999; Youravong *et al.*, 2003). Below the critical point, the fouling is fully reversible whereas above this point the fouling turns to irreversible. The critical flux concept has been previously shown to be relevant for skim milk filtration either for microfiltration (MF), UF, nanofiltration (NF) and reverse osmosis (RO) and extended to UF, NF and RO of pH modified skim milks (pH range from 3.7 to 11.5) (Gésan-Guiziou *et al.*, 1999; Bouzid *et al.*, 2008; Rabiller-Baudry *et al.*, 2009).
Different form of critical flux have been defined: strong, weak, threshold (Wu *et al.* 1999; Field and Pierce, 2011). Diagne *et al.* (2013) have demonstrated that, for skim milk UF, it is a threshold form (meaning that even below and at critical flux, a minimum amount of proteins remains on the membrane after a first water rinsing). According to our knowledge, no systematic study has been achieved to correlate the use of critical conditions during the production step (fouling) and the membrane ability to be cleaned with respect to its age.

From a practical point of view, the procedure described by Bouzid *et al.* (2008) for spiral membranes and adapted by Diagne *et al.* (2013) for flat membranes has been used to determine

the two following couples: ($TMP_{critical}$,$J_{critical}$) and ($TMP_{limiting}$,$J_{limiting}$). In the experimental conditions of the present study, the critical point corresponds to the last point of the linear part of the J *vs* TMP plot during skim milk UF.

2.3. Physico-chemical characterisation by ATR-FTIR

Membrane degradation by NaOCl, as well as protein amount on membrane, was followed by ATR-FTIR. Before analysis, membranes were carefully dried in a dessiccator under dynamic vacuum during few days to remove water.

Spectra were acquired with a FTIR Jasco 4100 spectrometer (Jasco) equipped with an ATR accessory (Miracle, ZnSe crystal, mono-reflexion, incidence angle of 45°, 20 scans, resolution 2 cm^{-1}). Membrane samples were maintained on the crystal with a press system (maximum pressure using a flat tip). The spectrometer was equipped with the spectra manager software. **Figure 2** shows typical spectra of a virgin membrane (after preservative removal). All bands can be assigned to PES except the band located at 1658 cm^{-1} that is the single one assigned to PVP (C=O). The good superimposition of several spectra underlines that the PVP to PES ratio is constant.

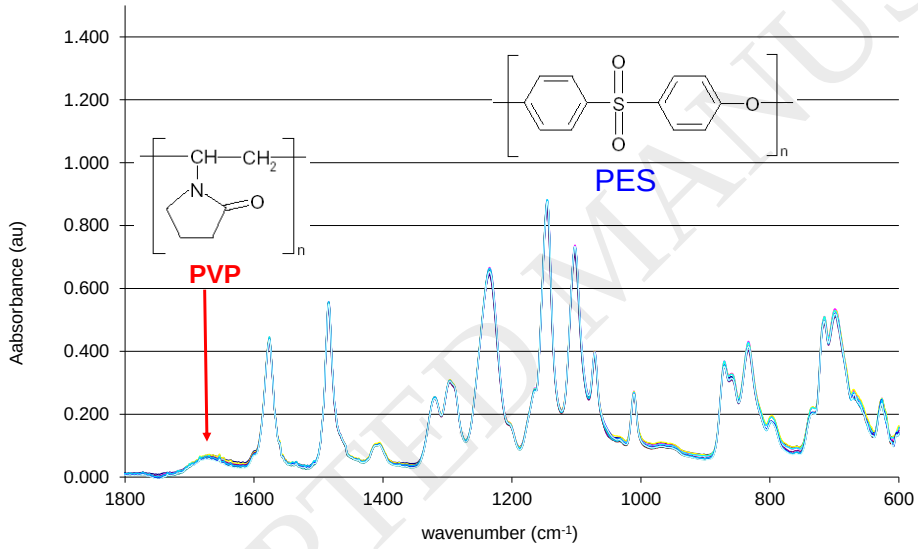


Figure 2: ATR-FTIR spectra of the virgin membranes (after preservative removal)

2.3.1. Quantification of the proteins directly on membrane

Nowadays, even if the global fouling of PES/PVP membrane during skim milk UF is not fully understood, it is largely admitted that it is a complex multi-layer fouling.

For pristine membranes, moving from the bulk to the membrane wall, one can encounter a reversible deposit among which is the classical polarisation layer and a gel mainly made of caseins that is intrinsically cohesive but easily removed by water rinsing (Delaunay *et al.*, 2008; Rabiller-Baudry *et al.*, 2008a). This complex 'reversible' layer is build-up on a cohesive multi-layer fouling, itself strongly adherent to the membrane. In other words, this last one is not removed by water rinsing and corresponds to the initial irreversible fouling. This is the main target of the alkaline chemical cleaning. Delaunay *et al.* (2008) and Rabiller-Baudry *et al.*

(2008a) have proposed a description of this initial irreversible layer involving β-lactoglobulin (the main soluble protein of milk) at the membrane surface and small amount of α-lactalbumin inside the membrane pores.

The protein quantification, directly on the PES/PVP membrane, was achieved by a method previously established in our team (Rabiller-Baudry *et al.*, 2008a; Delaunay *et al.*, 2008). A minor adaptation was required in the present study because the initial calibration has been established with another ATR-FTIR spectrometer (Paragon 1000 also known as Spectrum 1000, Perkin Elmer). **Equation 1** gives the initial calibration straight line. The quantification is possible from 1 to 350 µg of proteins per square centimetre of membrane (geometric area) with a precision of 1 $\mu g.cm^{-2}$. 19 samples of fouled pristine membranes were used to establish this equation, allowing to reach $r^2 = 0.997$.

$$[P] = (H_{1539}^{\text{protein amide II}} / H_{1240}^{\text{PES}} - H_{2060\text{-}2240}^{\text{baseline}}) / 0.0034 \qquad (1)$$

With:
[P]: the protein concentration on membrane in $\mu g.cm^{-2}$
H_i^X: the band height corresponding to the absorbance intensity at a given wavenumber (w_i) and corresponding to the X material that can be assigned to PES or to a functional group of proteins such as the protein amide II group.
$H_{2060\text{-}2240}^{\text{baseline}}$: the average height (absorbance) of the baseline measured in the 2060-2240 cm^{-1} range of wavenumbers. This value was equal to 0.0165 because of the occurrence of non-specific absorbance in this spectrum region.

This calibration can be adapted to the spectrometer used in the present study according to Rabiller-Baudry *et al.*, (2015) with a simple adjustment of the wavenumber positions.
For this purpose, the PES band located at 1240 cm^{-1} with Spectrum 1000 and now located at 1237 cm^{-1} with Jasco 4100 was used as an internal standard position for wavenumber determination, thus **equation 1** turns to **equation 2** for the Jasco 4100 spectrometer.

$$[P] = (H_{1536}^{\text{protein amide II}} / H_{1237}^{\text{PES}} - H_{2057\text{-}2237}^{\text{baseline}}) / 0.0034 \qquad (2)$$

With:
H_{1237}^{PES} the height of the band at 1237 cm^{-1} attributed to PES on the registered raw spectrum
$H_{1536}^{\text{protein amide II}}$ the height of the band at 1536 cm^{-1} attributed to protein amide II band
$H_{2057\text{-}2237}^{\text{baseline}}$: the average height of the baseline measured in the 2057-2237 cm^{-1} range of wavenumbers. Value equal to 0.0165.

Figure 3 shows typical spectra of pristine membranes, either fouled or un-fouled in the wavenumber range of interest. It is noticeable that the amide II band (CN + NH) at 1536 cm^{-1} of proteins was easily evidenced whereas the amide I band (C=O) of proteins was superimposed with the C=O band of the PVP contained in the membrane.

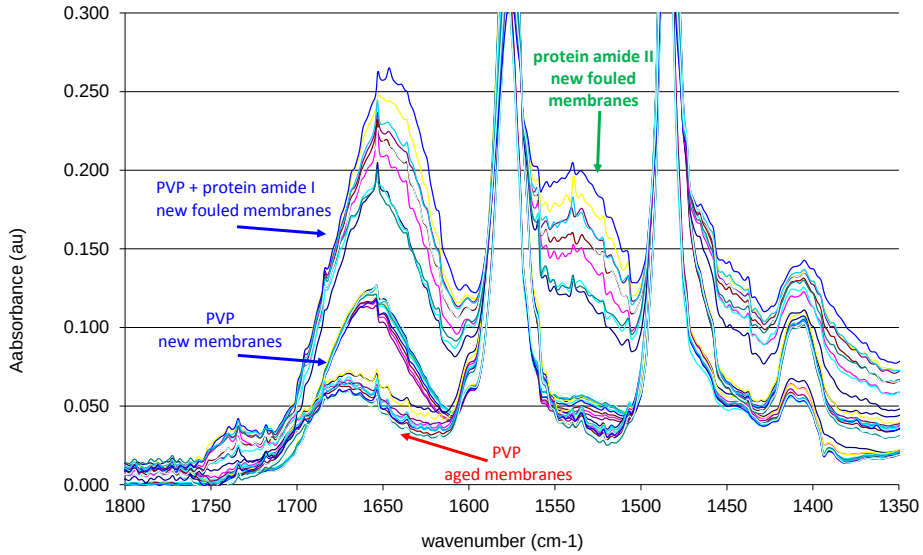


Figure 3: ATR-FTIR spectra highlighting the evolution of the PVP amount according to NaOCl ageing with respect to the band located at 1661 cm^{-1} with or without protein fouling.

2.3.2. Membrane degradation followed by ATR-FTIR

According to the provider, the membrane used in this study was guaranteed up to a cumulative received NaOCl dose equal to 5,000 ppm.d TFC. However, no information is given about the way to reach this dose. In the present study, the membrane 'age' was estimated with respect to two main markers: the PES backbone modification and the PVP disappearance.

The PES evolution was easily evidenced by the increase of a band located at 1027 cm^{-1} (**Figure 4**). This band was common to C-OH due to hydroxylation in ortho position of phenyl group of PES and to sulfonate groups due to PES backbone cleavage (**Figure 1**). It is out of the scope of this study to distinguish the two different forms of degradation that can be simultaneously present as revealed by streaming potential measurements (Hanafi *et al*., 2014 and 2016). In the following, the degradation level will be expressed as the $H^{PES\text{-}backbone}{}_{1027}/H^{PES}{}_{1237}$ ratio because no modification of the height of the PES band located at 1237 cm^{-1} was observed with membrane ageing.

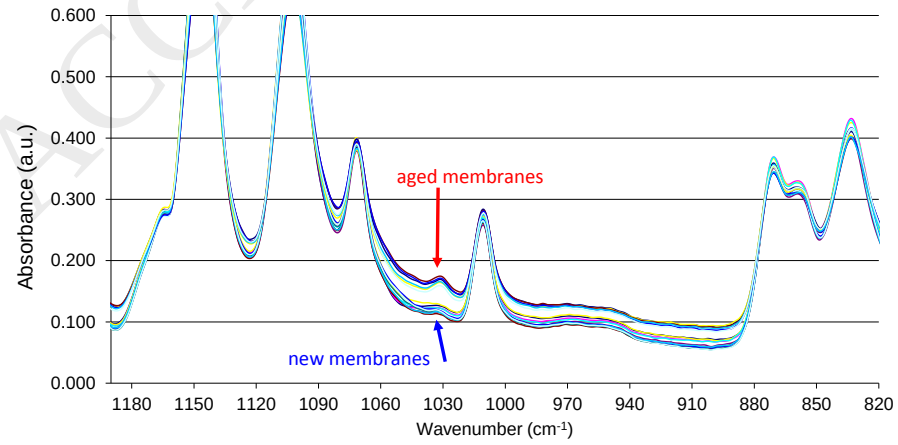


Figure 4: ATR-FTIR spectra highlighting evolution of the PES backbone according to NaOCl ageing with respect to the band located at 1027 cm^{-1}.

The progressive disappearance of PVP was easy to highlight for un-fouled virgin and aged membranes, simply by following the decrease of the 1658 cm^{-1} band on spectra (**Figure 3**). However, as explained above, because of the superimposition of the PVP band and the amide I band of proteins, a direct visualization of spectra was not sufficient in the case of highly fouled or insufficiently cleaned membranes (**Figure 3**). In order to tackle this issue, a method was previously developed to treat raw spectra in order to be able to get rid of the protein fouling presence and to monitor the PVP band height. Roughly, the amide I band height was calculated from the unambiguous measurement of the amide II band. Then, the amide I height was subtracted to the registered band height. This procedure allowed evidencing the PVP contribution to this raw registered band. Accordingly, following this protocol reported by Rabiller-Baudry *et al.* (2015) and including the wavenumber adjustment as explained above, the following equation was used in the present study:

$$H_{1658}^{\text{raw spectrum}} / H_{1237}^{\text{PES}} = (H_{1658}^{\text{PVP}} / H_{1237}^{\text{PES}}) + (H_{1658}^{\text{protein amide I}} / H_{1237}^{\text{PES}}) \quad (3)$$

With
H_{1237}^{PES}: the height of the band at 1237 cm^{-1} attributed to the PES on the raw spectrum
$H_{1658}^{\text{raw spectrum}}$: the height of the band at 1658 cm^{-1} on the raw spectrum
H_{1658}^{PVP} : the contribution of PVP (amide I, C=O vibration) to the height of the band located at 1658 cm^{-1} deduced from the calculation
$H_{1658}^{\text{protein amide I}}$: the contribution of protein amide I to the height of the band located at 1658 cm^{-1} that can be estimated from **equation 4**.

$$H_{1658}^{\text{protein amide I}} = 0.87 \times H_{1536}^{\text{protein amide II}} \quad (4)$$

With
$H_{1658}^{\text{protein amide II}}$: the height of the protein amide II band on the raw spectrum.
The 0.87 coefficient was determined for a range of PVP amount in the PES/PVP membrane and a wide range of protein amounts on the membrane according to the procedure reported in (Rabiller-Baudry *et al.*, 2015) and compatible with the present study.

2.4. Protocols for membrane ageing

2.4.1. Accelerated ageing of flat membrane by immersion under microwaves

The ageing protocol used in this study is an original one. Each entire flat membrane was immersed in 1 L NaOCl solution and placed in a domestic (multi-mode) micro-wave oven (Samsung, 23 L, delivering pulsed microwaves at 2450 MHz, **Figure 5**). The power was set at 600 W that was an optimised value for this oven (knowing that if the magnetron is generally the same in all micro-wave ovens, the statistical dispersion of waves is different because of the cavity size, the wave guide and the dispersion system geometry, even with a rotating plate, etc.). These operating conditions allowed the membrane degradation to occur. The membrane state was estimated by ATR-FTIR and compared to the maximum degradation level determined by the means of the characterisation of an industrial aged membrane at the end of its service life previously autopsied as reported in Bégoin *et al.* (2006). Moreover to avoid a significant

evaporation of the solution and a too high increase of temperature, the power was applied in a discontinuous mode for a cumulative time of 36 min. It was reached by applying the power 12 times during 3 min with 20-25 min without any applied power between each microwave application. The height of the PVP band (1661 cm^{-1}), as well as that of the PES degradation (1027 cm^{-1}), was controlled for each sample by ATR-FTIR according to the protocol described above. The comparison of these two band heights with those of the industrial aged membrane allowed to estimate that aged membranes prepared at laboratory scale could be close to half-life membranes.

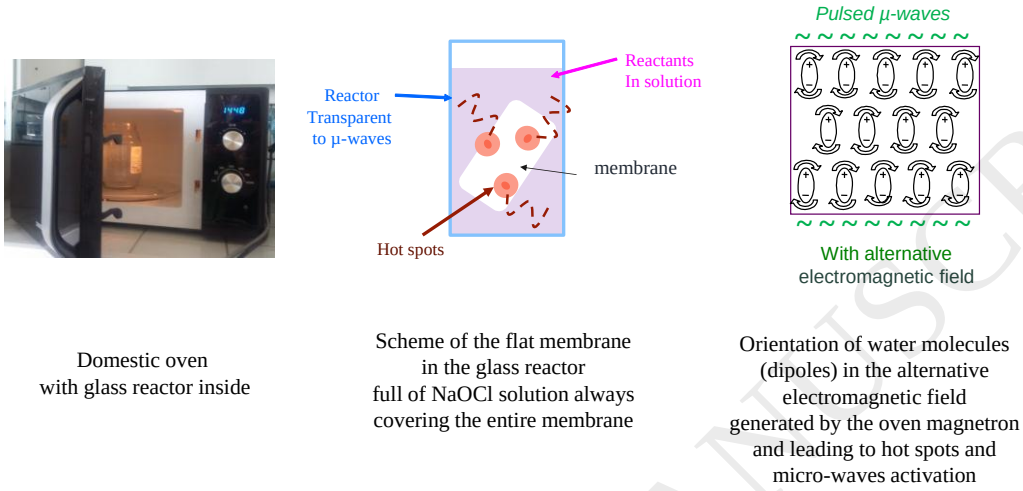


Figure 5: Pictures of the glass reactor inside the micro-wave oven and principle of pulsed micro-wave application on the entire flat membrane

2.4.2. Ageing of the spiral membrane in UF conditions

In order to accelerate the spiral membrane ageing, UF of the NaOCl solution was achieved at 2.0 bar and 50°C. The treatment duration varied and was classically summarised in the form of a cumulative dose (ppm in TFC) expressed according to **equation 5**.

NaOCl dose (ppm.d) = 400 ppm x number of days (5)

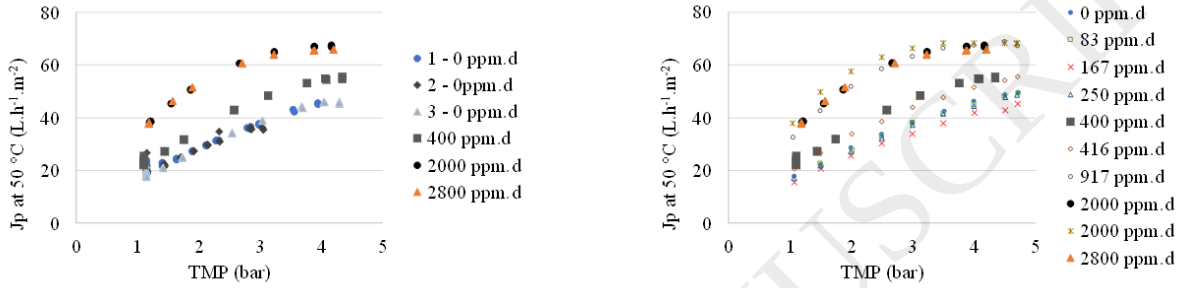
From a practical point of view, 3 UF of skim milk were consecutively performed for each pristine membrane. After alkaline cleaning by Ultrasil 10, each membrane was then aged in NaOCl up to a given cumulative dose. Then, another UF of skim milk was performed. After an alkaline cleaning by Ultrasil 10 expecting at the recovery of the membrane flux, the membrane was aged in NaOCl up to a greater cumulative dose, then another UF of skim milk was performed and so on. After the final skim milk UF achieved on a membrane aged until a given NaOCl dose (2,000 ppm.d dose for S-CIP2 or 2,800 ppm.d dose for S-CIP3), the membrane was carefully rinsed by water (but not cleaned) and demounted. The two membranes were finally entirely analysed by ATR-FTIR (336 spectra each).

3. Results and discussion

3.1. Spiral membrane behaviour in skim milk with respect to membrane age

Figure 6 shows the evolution of the permeate flux (J_p) of the two spiral membranes in skim milk with respect to the cumulative dose received by the membrane.

The reproducibility was excellent as shown by the fairly good superimposition of the 3 consecutives assays on the pristine membranes, referred as 1- 0 ppm.d, 2-0 ppm.d and 3-0 ppm.d on **Figure 6a** for the S-CIP3 membrane that also matches very well with the 0 ppm.d experiment with the S-CIP2 membrane depicted on **Figure 6b**.



(a) (b)

Figure 6: UF of skim milk at 50°C with the two spiral membranes with respect to their chemical ageing expressed by the NaOCl cumulative dose (ppm in TFC) received by the membrane. (a) zoom on S-CIP3 results- (b) flux with the two spiral membrane S-CIP2 and S-CIP 3.

Figure 6 depicts that the limiting flux increased with the membrane exposure to NaOCl. Simultaneously, $TMP_{limiting}$ slightly decreased. The critical flux increased also with the NaOCl exposure and simultaneously $TMP_{critical}$ slightly decreased. Whatever the cumulative dose received by the membrane, TMP= 4 bar was slightly higher than $TMP_{limiting}$ and TMP= 1 bar was slightly lower than $TMP_{critical}$.
For the two pristine membranes, the alkaline cleaning by Ultrasil 10 allowed the membrane water flux recovery. However, for NaOCl aged membranes, even for cumulative dose as low as 83 ppm.d, the alkaline cleaning only by Ultrasil 10 was not sufficient. Nevertheless, after an additional NaOCl treatment the water flux was recovered. Furthermore, up to a 2,800 ppm.d dose, the membrane cleaning remained possible.
The increase of the NaOCl dose received by the membrane induced a decrease in the water flux recovery after the Ultrasil 10 cleaning. Thus, an increasing part of the initial irreversible fouling was only removable by the NaOCl additional treatment. This highlighted the change in the fouling layers adhesion on the 'aged' membrane and perhaps in its own internal cohesion as well, this last assumptions being less probable.
These results obtained at lab. scale were in good agreement with the behaviour commonly reported at industrial scale about increasing difficulties in membrane cleaning with the membrane service life.

The S-CIP3 spiral membrane, potentially the most aged one, was finally autopsied.

Table 1 shows (1) the homogeneous distribution of PVP on the membrane and (2) its significant decrease when compared to the PVP in the pristine membrane. Thus, the PVP relative intensity ($H^{PVP}_{1658}/H^{PES}_{1237}$) was divided by a factor of about 2. This value was higher than that measured on a membrane aged at industrial scale at the end of its service life for which the PVP band was no more visible, at first sight, on the spectra.
PES degradation ($H^{PES\text{-}backbone}_{1027}/H^{PES}_{1237}$) had also started (**Table 1**) but remained far from the membrane aged at industrial scale.
The combination of these two results, together with the received NaOCl dose, let us to think that S-CIP3 membrane was close to its half-time life when compared to the industrial membrane.

3.2. Validation of the membrane ageing protocol using micro-waves thanks to ATR-FTIR characterisation

To go ahead in the fouling characterisation, and to increase the in-depth comprehension of the spiral membranes cleanability, a second set of experiences was achieved with flat membranes voluntary aged to reach, as close as possible, the S-CIP3 membranes age.

It required to first validate that the chosen ageing protocol involving micro-waves was pertinent on the chemical ageing point of view, before proposing a systematic in-depth study of fouling and cleaning.

31 flat membranes were aged by immersion under micro-waves as described in the experimental part. It is out of the scope of this paper to detail how this protocol was progressively established over the last ten years, but the characterisation of the obtained membranes was required for the following.

Table 1 shows the ATR-FTIR results obtained when estimating the PVP amount of 16 virgin membranes (10 spectra per membrane) used in this study, belonging to the same spiral membrane module as those used for the ageing experiments. The PVP band ($H^{PVP}_{1658}/H^{PES}_{1237}$) appeared similar to that determined in 2015 from flat membranes sampled in a different spiral membrane of the same reference.

After NaOCl ageing under microwaves, the PVP band significantly decreased for the 31 aged membranes (10 spectra per membrane). The PVP disappearance was roughly the same as those determined for the S-CIP3 membrane aged on the UF pilot, but remained less than the quasi-full disappearance observed on the industrial aged membrane.

Table 1: ATR-FTIR analysis of virgin and aged flat membranes and comparison to S-CIP3 spiral membrane and industrial aged one.

membrane	$H^{PVP}_{1658}/H^{PES}_{1237}$	$H^{PES\text{-}backbone}_{1027}/H^{PES}_{1237}$	reference

Virgin flat 6 membranes but 54 spectra	0.14 ± 0.01	0.04	Rabiller-Baudry *et al.*, (2015)
S-CIP3 (2,800 ppm.d) 1 membrane but 336 spectra	0.08 ± 0.02	0.13 ± 0.06	Rabiller-Baudry *et al.*, (2015)
Aged membrane at industrial level (end of service life)	0.06	0.29	Bégoin *et al.* (2006) Rabiller-Baudry *et al.*, (2015)
Flat membranes			
Virgin 16 membranes but 160 spectra	0.15 ± 0.03	0.18± 0.08	This study
NaOCl aged under microwaves 31 membranes but 310 spectra	0.09 ± 0.03	0.32 ± 0.08	This study

The $H^{PES\text{-}backbone}{}_{1027}/H^{PES}{}_{1237}$ ratio might evidence the PES backbone degradation (**Figure 4**). The PES was clearly attacked by the ageing protocol under micro-waves (**Table 1**). The 1027 cm^{-1} band was about twice that of the pristine membranes sampled in the same spiral membrane. Firstly, it must be said that, after a similar treatment under micro-waves but in pure water, no variation of the PVP band was shown allowing to draw the conclusion that the degradation was due to the combination of NaOCl and micro-waves actions. Secondly, it must be underlined that this band was much higher on the virgin membranes of the present study than on the pristine membranes of the study achieved in our lab. in 2015. The origin of such differences remains unexplained, but could be related to either a change in the membrane fabrication procedure (no information available from the provider) or to conservation conditions in the lab. (knowing that light can also activate the radical degradation of PES according to Prulho *et al.*, 2013). Nevertheless, the increase in the $H^{PES\text{-}backbone}{}_{1027}/H^{PES}{}_{1237}$ ratio appeared roughly of the same order for both S-CIP3 and the flat aged membranes.

Moreover, during skim milk UF, the rejection of overall proteins was full (as measured from ATR-FTIR with a precision close to 10%) with the virgin flat membranes, whatever the TMP in the range 0.5-4.0 bar. However, the rejection decreased down to 81 % after the microwave ageing treatment, highlighting the significant membrane degradation thanks to this protocol. Finally, it is concluded that flat membranes aged under microwaves in presence of NaOCl fulfilled the requirements of our study and seemed representatives of the chemical ageing of the S-CIP3 membrane aged in UF conditions.

3.3. Flat membrane behaviour in skim milk according to NaOCl ageing under micro-waves

The flat aged membranes described above were used in skim milk UF using hydrodynamic conditions as close as possible to those used with the spiral membrane.
Figure 7 depicts the behaviour of the permeate flux when varying the TMP. Both $J_{critical}$ and $J_{limiting}$ increased with ageing, in good agreement with results obtained with the spiral membrane (**Figure 6**). Similarly, in both configurations, $TMP_{critical}$ and $TMP_{limiting}$ decreased with ageing.

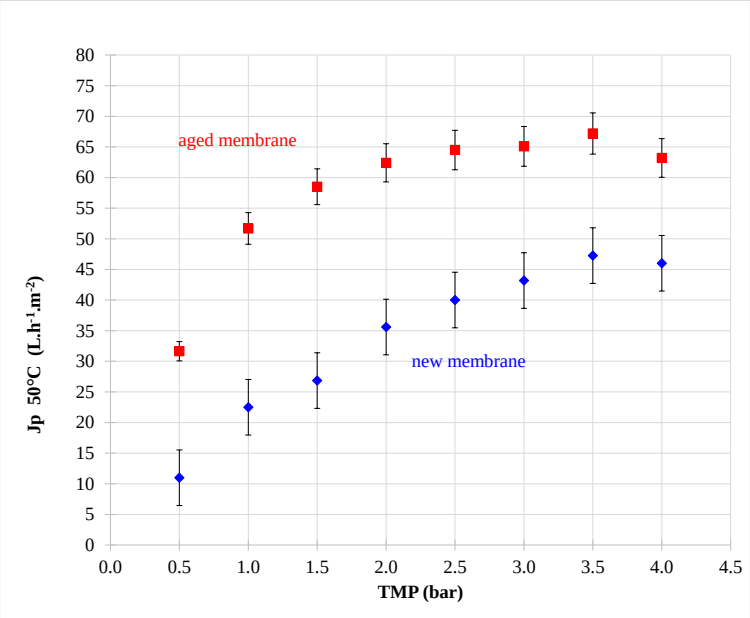


Figure 7: Flux in skim milk at 50°C for new and flat membranes aged under micro-wave versus TMP

Permeance of membranes during skim milk UF performed at constant TMP were shown in **Figure 8**, either at TMP= 1 bar (equal or lower than $TMP_{critical}$,) and at TMP= 4 bar (slightly higher than $TMP_{limiting}$). **Figure 9** shows the permeance in skim milk for the flat aged membranes at various TMPs.
Results were once again in good agreement with those observed with the spiral S-CIP3 membrane, confirming that the membranes aged under microwaves were a good model when dealing with membrane fouling.

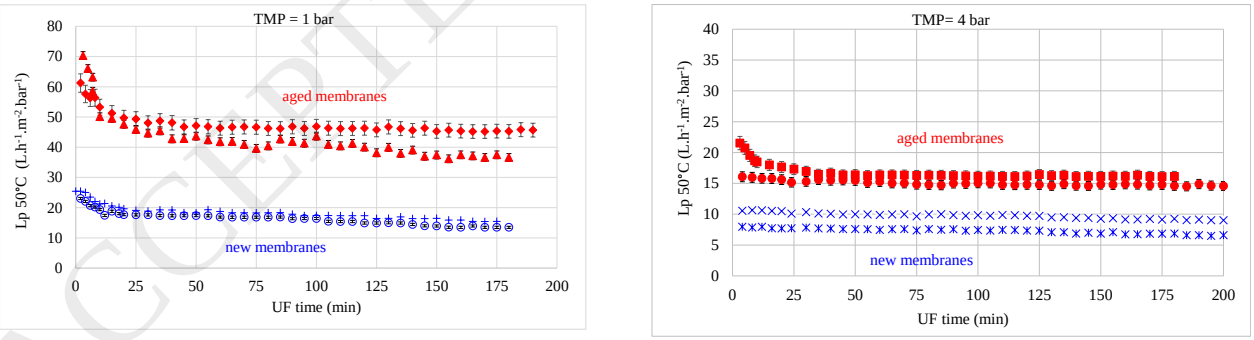


Figure 8: Permeance in skim milk at 50°C at constant TMP, either 1 bar (below or equal the critical conditions) or 4 bar (slightly greater than the limiting conditions) for flat membranes both new and aged under micro-waves

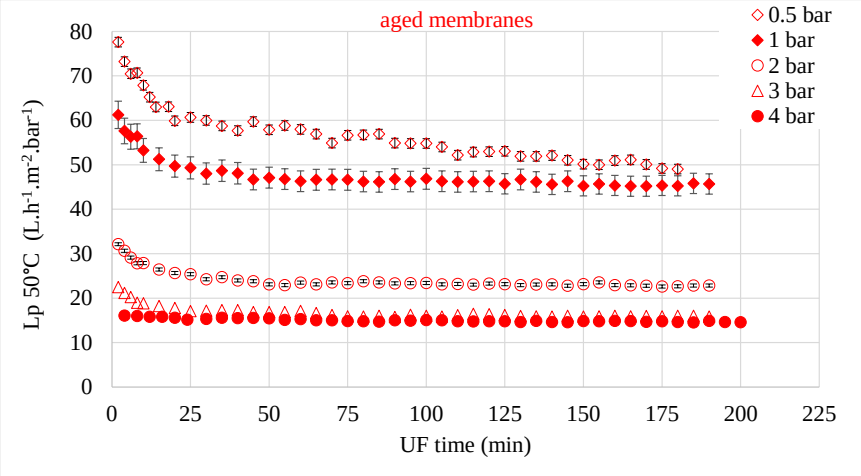


Figure 9: Permeance in skim milk at 50°C at several constant TMP for flat membranes aged under micro-waves.

3.4. Cleanability of flat membranes NaOCl aged under micro-waves

The fouled aged membranes were rinsed by water. As general trends, the water flux recovery was slightly lower when the TMP during fouling was higher. The water flux recovery of the aged membranes depended on the TMP applied during the fouling, but systematically remained below that of the pristine membrane fouled at the corresponding TMP (not shown).

The protein amount remaining after rinsing (initial irreversible fouling) was then determined by ATR-FTIR with respect to the TMP applied during the fouling step (**Figure 10**). It was always greater than 80 µg.cm^{-2} for the aged membranes and increased slightly with the TMP increase. These values were much higher than those measured for the pristine membranes always lower than 30 µg.cm^{-2}, regardless of the TMP during fouling. These results revealed unambiguously an increase in the initial irreversible fouling with the membrane ageing.

Several fouled and subsequently rinsed aged membranes were finally cleaned at 50°C by Ultrasil 10 during 1 h and then rinsed by water once again. Of course, the water flux recovery increased after the cleaning step but the hydraulic cleanliness was not obtained, in good agreement with experiences achieved with the S-CIP2 and S-CIP3 spiral membranes at their higher ageing state.

The residual protein amount on cleaned membranes was, once again, determined by ATR-FTIR (**Figure 10**). It was always greater than 30 µg.cm^{-2} with the flat aged membranes, whereas it was always lower than 20 µg.cm^{-2} with the pristine membranes. These results revealed unambiguously an increase in the cleaning difficulty for aged membranes. The impact of the TMP during the fouling step on the membrane cleanability seemed to be not significant, contrary to what happened with the pristine membranes.

It can be underlined that results obtained with the pristine membranes of the present study were in good accordance with those obtained by Diagne *et al.* (2013). They have used a PES/PVP membrane of similar reference with similar amount of PVP but less degradation of the PES

backbone (the membrane used by Diagne *et al.* were sampled in the same spiral membrane as that used by Rabiller-Baudry *et al.* (2015) and already discussed in **Table 1**).
This last comment suggests a major role of the PVP departure compared to that of PES backbone slight evolution in the cleanability decrease for membranes up to half-time life.

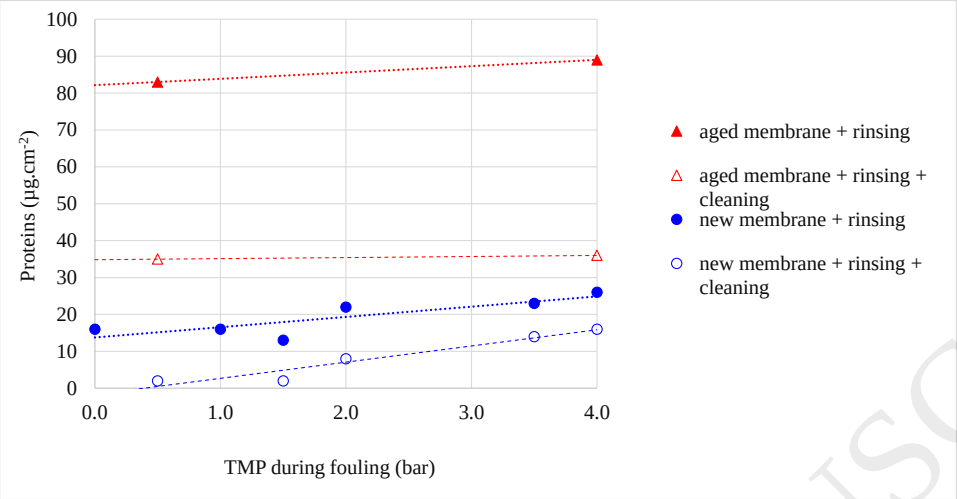


Figure 10: Protein amount determined from ATR-FTIR for new and aged flat membranes versus TMP during fouling by skim milk. The cleaning was always achieved at 2 bar, 50°C.

4. Conclusions

According to the best of our knowledge, this study presents, for the first time, a systematic fundamental study of the impact of the chemical ageing due to NaOCl, an oxidant commonly used for disinfection in dairy, on the membrane cleanability in close relationship with the fouling conditions.
Chemical ageing provoked a decrease in the critical pressure together with an increase in the critical flux according to the determination mode used, inspired from that used with similar pristine membranes. Similar trends were observed for the limiting conditions.
Whereas the filtration at critical or limiting flux was shown to have a major impact on the irreversible fouling amount and its cleanliness by an efficient formulated alkaline detergent with pristine PES/PVP membranes, no more differences were evidenced with NaOCl aged membranes being simultaneously highly irreversibly fouled and more difficult to clean.
The results suggest that disinfection by a non-oxidant biocide harmless toward the membrane material could be a good idea for a better mastering of the overall skim milk UF process. Finally, this paper opens a new question on the interest/applicability of the critical flux concept to chemically aged PES/PVP membranes proned to easily fouled.

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