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Efficient and rapid multiscale approach of polymer membrane degradation and stability: application to formulation of harmless non-oxidative biocide for polyamide and PES/PVP membranes.

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Abstract:

Membrane cleaning & disinfection is a bottleneck in the filtration processes of the food industry. Disinfection by oxidative agents, such as NaOCl, have been clearly identified as the main responsible of the accelerated ageing of polymer membranes. The development of new formulated biocide detergents allowing to respect the integrity of polymer membranes is our objective. A major difficulty to overcome is to have a method making it possible to rapidly demonstrate whether the membrane will age after a long-time contact with the biocide in industrial conditions of use. However, nowadays the estimation of membrane ageing is mainly achieved by long-time consuming methods, limiting biocide & detergent developments. This paper proposes an original approach allowing a time-efficient discrimination of biocide detergent prototypes with respect to the membrane long-term ageing. The methodology is firstly based on the use of microwaves activation to accelerate the membrane degradation (if any) in the biocide solution set at a concentration selected to avoid too severe degradations never reached at industrial scale. Secondly, the combination of MW results and short time filtration gives rapidly relevant information about the suitability (or not) of a tested prototype with respect to the membrane flux behaviour. ATR-FTIR characterisation is shown to be relevant as the single analytical tool to follow the entire approach. Finally, only the promising prototype enter in long-term filtration validation tests, with a real opportunity to avoid unnecessary experiments. For the sake of the demonstration, the methodology is applied aiming at the formulation of a non-oxidative formulated biocide detergent that can be used either for RO or UF. The results evidence a non-intuitive conclusion: the new biocide validated for RO polyamide membrane (fragile toward NaOCl biocide oxidant and hydrophilic) has to be avoided for the more chemically resistant but also more hydrophobic UF PES/PVP membrane.

Keywords: Biocide; Ageing; ATR-FTIR; Micro-waves; Reverse Osmosis; Ultrafiltration;

1 Introduction

Membrane cleaning/disinfection is an absolute requirement in food industry in order to simultaneously ensure the recovery of membrane performances and the hygienic safety of both products and equipment.

In dairy applications, the cleaning/disinfection takes up to 30% of the process time and the energy consumption, both thermal and mechanical, contributes to the decrease of the overall productivity. Indeed, the cleaning/disinfection is generally made twice a day making this operation expensive because it requires cascade of several formulated detergents. Classically, either alkaline or enzymatic solutions are used, generally in combination with an acid step. The overall cleaning is followed by a final disinfection. Moreover, the solutions are not reused and huge amounts of water of high quality are needed, either for the preparation of the cleaning/disinfecting solutions or for the inter-rinsing steps. Consequently, high volumes of effluents are produced, that have to be treated before disposal in environment. The environmental impact of the cleaning/disinfection step has been estimated to be responsible of at least 1/3 of the overall environmental impact of a membrane process in dairy applications [1].

Each case is different and the fouling to remove depends on the membrane/filtered fluid couple. Indeed, the cleaning result is only partly related to the intrinsic efficiency of the detergents that is based on its formulation. The filtration conditions during the fouling (production step) have also an impact on the fouling amount and its cohesion. For instance, Diagne *et al.* [2] have studied the alkaline cleaning of a polymer membrane made of Polyethersulfone/Polyvinylpyrrolidone (PES/PVP) and fouled during ultrafiltration (UF) of skim milk. In this case, the irreversible fouling remaining after water rinsing is mainly made of proteins that are the cleaning target. Using the same cross-flow velocity and transmembrane pressure during the cleaning, the fouling removal was evidenced to be more or less the same with either NaOH or a formulated detergent of close pH when the fouling step was achieved at the limiting flux. On the contrary when the fouling was achieved at the critical flux, a scale of cleaning efficiency was reported evidencing the interest of the formulation. From these results, the authors have drawn that the intrinsic power of a given alkaline detergent can be more or less cancelled, depending on the hydrodynamics during the previous fouling step. However, regardless of the protocol and the detergent, an irreversible organic fouling always remained on the membrane after cleaning as it was shown by autopsy of cleaned membranes at the end of their industrial service life for instance [3, 4].

As said above, the cleaning is imperatively followed by a disinfection step. The role of the disinfectants/biocides is to kill the micro-organisms, not to remove them from the membrane equipment. However, the role of this step is also to polish the cleaning if the chemical or enzymatic cleaning achieved just before is not efficient enough [5, 6]. For UF polymer membranes, disinfection is generally made with oxidative agents, such as sodium hypochlorite (NaOCl) [5, 7]. However, mixtures based on H₂O₂, acetic acid and peracetic acid are generally preferred for more fragile polymer membranes, such as those made of polyamide (PA) either used in reverse osmosis (RO) or nanofiltration (NF), because NaOCl is prohibited with PA for the sake of the membrane rapid degradation.

Recent literature is quite abundant when dealing with polymer membrane degradation due to oxidative agents used during disinfection. However, the degradation intensity is very different from one polymer to another.

NaOCl induces long-term degradation of UF membrane based on PES/PVP (**Figure 1**). Disinfection by 150-200 ppm TFC (total free chlorine) solutions are currently achieved at industrial scale and membrane lifespan is generally close to 2-4 years depending on the dairy fluid filtered. Degradation mechanisms of either PES or PVP have been extensively studied [8-25] and are summarised in **Appendix 1 (Figure A1-1)**.

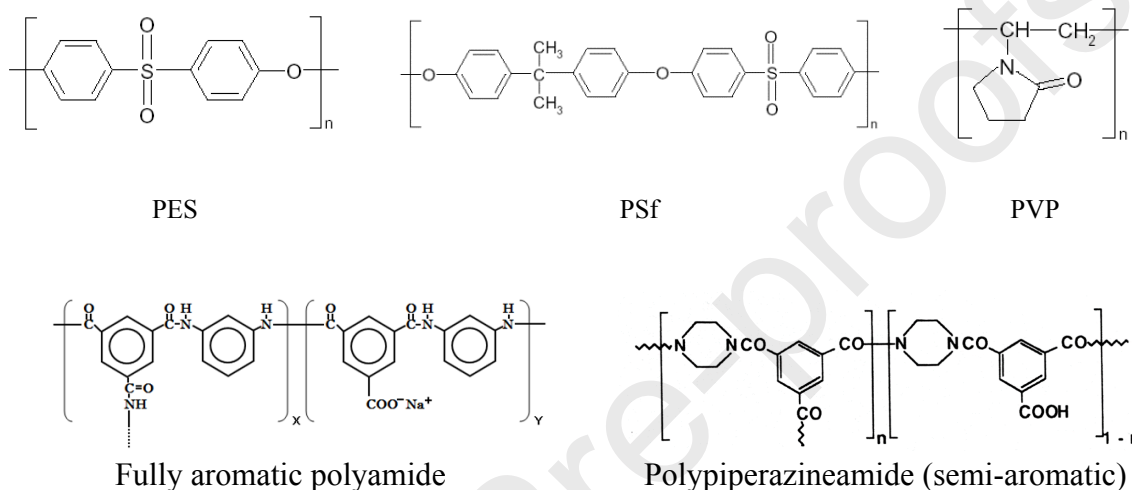


Figure 1: Polymers entering in the membrane composition.

NaOCl induces short-term degradation of polyamide RO/NF membranes. Regardless of the aromatic or semi-aromatic character of the PA (**Figure 1**), chlorine species have to be avoided or, at least, time contact and concentrations strongly limited. The degradation induces an increase (1) of the brittleness of fully aromatic PA and (2) of the ductility of semi-aromatic PA. Degradation mechanisms have been extensively studied, especially for fully aromatic PA [26-46] and are summarised in **Appendix 2 (Figure A2-1)**. The high degradation of the PA membrane can be the origin of (1) flux increase due to polymer chain scission [41-43] or physical separation of the PA layer from the PSf one on which PA is build-up [34] but also (2) to a certain extent in flux decrease due to an increase in the membrane hydrophobicity [41]. Indeed, many efforts have been made to overcome problems associated to the degradation induced by oxidative agents, for instance by modifying the membranes material to increase its resistance [47- 55].

This poor chemical resistance toward chlorine justifies why disinfection based on hydrogen peroxide systems is preferred in NF and RO as it does not provoke severe oxidation of PA. Moreover, hydrogen peroxide does not produce toxic by-products [56] and PA membranes withstand relatively high hydrogen peroxide exposures [39]. However, polymer degradation

induced by H_2O_2 can be activated by metal cations present in water (such as iron) allowing the formation of radicals such as HO^\bullet and HO_2^\bullet due to the Fenton reactions.

To date, the insufficient membrane stability during disinfection remained a current difficulty at industrial scale. To overcome the short & long-term degradation due to oxidative disinfection, one possibility is *a priori* to develop non-oxidative biocides. Among active disinfecting molecules are some carboxylic acids, such as α -halogenated acetic acids, sorbic acid, fatty acids (linear or branched) [56]. Because these last ones are generally bio-degradable, they are good candidates for an eco-friendly disinfection. However, to maximise its efficiency the active biocide molecule has to be mixed with few others ingredients (see below).

R&D teams of the cleaning industrial sector regularly formulate new detergents and biocides at laboratory scale, but besides the disinfecting intrinsic efficiency raise several questions. The first set of questions deals with the behaviour of the formulated biocide detergent in filtration conditions. More especially is there any negative impact on the flux due to a significant adsorption of at least one ingredient of the mixture? If any, is this adsorption reversible or irreversible? If the adsorption could be severe, do this ingredient be removed from the formulation? The second set of questions deals with the polymer stability. Is the formulated mixture harmless towards the membrane? If the answer can be “no” in certain conditions, then modulation can be proposed according to a second question: is the impact on membrane ageing acceptable?

These questions address the methodologies and tools already available to answer. To follow the flux behaviour during filtration of a formulated biocide is quite easy to perform. Indeed, short time filtrations are able to highlight decrease of flux together with significant irreversible adsorption. In this last case, the water flux of the pristine membrane would not be recovered after simple water rinsing. To evidence the irreversible adsorption of ingredient would be more difficult if the amount is low but cumulative over time. Last but not least, to demonstrate the membrane degradation is quite simple if the degradation is simultaneously rapid and significant. However, the main question is how to evidence long-term stability of a membrane in a short experimental time, knowing that the answer has to be representative of the degradation in condition of industrial use?

Membrane polymer integrity is often first studied by soaking small membranes coupons in the solution to evaluate. For the sake of short time experiments, the solution is often prepared at higher concentrations than the one selected for the industrial use. The main idea hidden behind such protocol is that the cumulative dose (concentration x contact time) received by the membrane would allow to reach an appropriate degradation state of the polymer. However, a same dose can be obtained by selecting a high concentration and a short contact time or *vice versa*. Indeed, several combinations of these two parameters can be made and finally no convincing demonstration has been previously made of the relevance of such approach. The representativeness of the reached chemical degradation state is clearly one of the identified limitations. For instance, to select too high concentrations can provoke reactions never encountered at industrial scale. Moreover, this approach is not able to take into account combination of both chemical and mechanical degradations that can be synergetic.

A better approach consists in putting the membrane in contact with the solution to evaluate during continuous very long filtrations. This is the way currently proposed by membrane providers such as Dow-Filmtech [57], or achieved at laboratory scale such as those reported by Simon et al. [58], Pellegrin et al. [14], or Antony et al. [28], for instance. Note that membrane providers generally used the target concentrations of use and achieve very long filtrations with few solutions for which they give recommendations and/or guarantee. Besides, academics slightly increase the target concentration and use the cumulative dose as a parameter to shorten the filtration duration, but generally they evaluate a single mixture for fundamental knowledge acquisition.

However, when developing new products, several ingredients and formulations have to be tested and such trial and error approach remains long-time consuming. The consequence is a brake to the proposal of new efficient formulations nevertheless expected by the end-users. Thus, to shorten the duration of biocide detergent validation is really challenging.

According to the best of our knowledge, no global and time-efficient methodology is known to rapidly evaluate the suitability of a formulated biocide detergent for a given membrane used in a given application.

To fulfil the methodological needs explained above, requests the use of relevant and easy-to-handle analytical tools. Moreover, they must be able to quickly evidence the membrane degradations and their impacts. Robinson *et al.* [59] reported on a wide selection of tools that have been used to study the evolution of membranes performances in water treatment. Several selected analytical techniques have given relevant data on degradation occurrence and/or degradation mechanisms. Moreover, relationships can be sometimes established between the polymer modifications and the loss in membrane performances. However, according to the best of our knowledge, in the best cases, the relationships are often just polynomial correlations evidencing phenomenological links between parameters, but without sufficient understanding in the chemical and physical fundamental aspects. Indeed, to date, none of the correlations are predictive when dealing with the membrane lifespan.

Consequently, to go ahead, and besides the checking of the disinfecting efficiency of the active molecule, made prior to the formulation, a relevant methodology to formulate a biocide detergent for membrane application and to validate its harmlessness toward the membrane must be a combination of several tools following a multi-scale and time efficient approach.

Our own feeling is that this approach must, at least, take into account the five following requirements:

- (1) the basic knowledge in formulation of biocide detergent, taking into account the positive list in active biocide ingredients provided by the European regulation n° 528/2012 [60] as well as that of other ingredients, among which are acids added for the pH control and the mineral fouling removal and surfactants aiming at decreasing the interfacial tension to favour the surface wetting by the biocide detergent. These components have also to be in a positive list, see for instance that of the French regulation [61]. The know-how

in the selection of the ingredients and about their mixing constraints is compulsory and often the proprietary of biocide detergent providers.

- (2) a rapid identification of the possible adsorption of some ingredients of the formulated biocide detergent on the membrane, especially if the adsorption is severe and irreversible. For the sake of time efficiency, this cannot be a systematic determination of the adsorption isotherm of each ingredients and a way of quick selection have to be proposed.
- (3) an experimental approach to accelerate the membrane ageing, if any, in the formulated biocide detergent. The aged states reached by the polymer membrane have to be representative of the evolution of the membrane over its lifespan at industrial scale.
- (4) the selection of relevant analytical tools, moreover accessible in routine and able to study ingredient adsorption on membrane and polymer membrane degradation.
- (5) Appropriate filtration experiments to validate the flux behaviour in the formulated biocide detergent and the acceptability of its value as well as its rinsing ability by water evidenced from water flux recovery.

This study reports on an original approach aiming at the development of a new efficient & rapid methodology able to validate the suitability and harmlessness of a biocide detergent toward polymer membranes. Our proposal (see below, **Table 1**) takes into account the requirements 2 to 5 exposed above. Note that requirement 1 is focused on the primary formulation and is out of the scope of this study (for confidentiality purpose). However, ingredient(s) that have to be avoided were detected thanks to the described methodology inducing modifications of the initial formulation.

Our main objective was the development of a non-oxidative formulated biocide detergent for membranes commonly used in dairy industry. The selected membranes were a reverse osmosis PA membrane and an ultrafiltration one made of PES/PVP.

As no data was available dealing with the long-term stability of the two membranes toward ingredients entering in the composition of the initial biocide detergent, a reference was required to establish a convincing accelerated ageing protocol. Indeed, literature dealing with degradation of PA and PES/PVP membranes induced by chlorine and oxygen has been used to establish a protocol involving micro-waves (MW) activation furthermore validated thanks to comparisons made with membranes that have been autopsied at the end of their service life at industrial scale.

2 Methodology description

Our methodology is mainly based on the choice of 3 sets of data: (1) the membrane material analyses, (2) the protocol of ageing acceleration and (3) the classical filtration experiments to check flux and rejection behaviours. The two first ones are detailed in this section, after the

description of the overall methodology, whereas filtrations being conducted in quite classical way are mainly detailed in the experimental section.

2.1 Overall methodology

The general approach, in three steps, is detailed in **Table 1**.

Dealing with the membrane integrity, the methodology is first based on the comparison of the physico-chemical characterizations (mainly ATR-FTIR, see next section) of a pristine membrane and small coupons or flat membranes after a certain contact time with the evaluated biocide detergent. Indeed, the contact between the membrane material and the solution is achieved according to two different ways.

In **step 1**, membrane coupons were immersed in a solution putted inside a micro-wave oven aiming at the acceleration of ageing mechanisms thanks to MW activation (see below). This allowed to evidence (i) potential long-term degradation of the polymer membranes and (ii) adsorption of formulated biocide ingredients. If any, the species might be adsorbed in a reversible or irreversible way that can be easily evidenced by comparing ATR-FTIR spectra before and after water rinsing. If the water rinsing failed at desorbing the ingredient, then an appropriate subsequent cleaning has to be found. In this last case, identification of the problematic ingredient is required to imagine an efficient way of removal.

Table 1: Overall methodology for membrane integrity validation toward a formulated biocide detergent

| | Physico-chemical approach step 1 | Short filtration step 2 | Overall validation step 3 |
|--------------------------------|---|---|---|
| objective | quick information dealing with possible long-term membrane chemical ageing and residual adsorption of ingredients | flux behavior during filtration of biocide, water rinsing ability, and residual adsorption of ingredients | (1) flux and rejection performances (2) integrity of the spiral membrane |
| general way | immersion under pulsed micro-waves RO: 170 W UF: 510 W | filtration | filtration |
| Membrane area | small coupons: 10-20 cm ² RO: 10 cm ² UF: 18 cm ² | small flat membrane RO: 140 cm ² UF: 127-140 cm ² | spiral membrane: 2-7 m ² RO: 2.5 m ² UF: 6.8 m ² |
| Biocide concentration at start | 4-8 times the target concentration of use | 2 times the target concentration of use | 2 times the target concentration of use |
| Biocide volume | (6 - 15 mL.cm ⁻²) RO: 60 mL UF: 250 mL | (31 - 72 mL.cm ⁻²) RO: 10 L UF: 4 - 10 L | (3.5 - 4.0 L.m ⁻²) RO: 10 L UF: 25 L |
| Duration | RO: 7 h | 3 h | 50 h |

| | UF: 3 h Slot time application | in continuous mode | in discontinuous mode* |
|---------------------|----------------------------------|------------------------------------|------------------------------------|
| temperature | natural increase ** | 50°C (target of industrial use) | 50°C (target of industrial use) |
| Routine analysis | ATR-FTIR | flux and ATR-FTIR | flux and rejection*** |

–* possibility of water inter-rinsing - ** must be as close as possible to 50°C and lower than 70°C thanks to the time mastering of discontinuous MW application - *** membrane autopsy is possible for ATR-FTIR final evaluation.

The second step dealt with the flux behaviour during the filtration of the formulated biocide detergent by a pristine membrane. For instance, if the flux was too low the biocide prototype was rejected because the overall productivity of the process was negatively affected. The flux decrease highlighted the existence of polarization concentration and/or fouling due to the formulated biocide. Such phenomena have mainly to be related to the adsorption of certain ingredients on the membrane surface and/or into the pores. As already explained for step 1, the water flux recovery after a final water rinsing was able to make the distinction between the reversible and irreversible adsorption of ingredient(s) if significant amount remained in/on the membrane. The potential need of a complementary cleaning was then evidenced as in step 1 and a subsequent step was imagined and its efficiency tested.

The third and last step aimed at the overall validation with a spiral membrane and was much more time-consuming. The procedure required two different filtrations that were alternatively performed. The first one was a long-time filtration of the biocide detergent. The second one was that of a reference solution in order to check the rejection and flux performances of the membrane from time to time, with respect to the overall contact time with the biocide.

The reference solution has to be selected with respect to the membrane application fields. For RO membranes, it can be NaCl at few g.L⁻¹ for instance. However, to avoid misleading interpretation due to thermally induced changes in the polymer structure that are not related to the chemical ageing, the NaCl filtration has to be performed at the same temperature as that used for the biocide filtration (here 50°C).

For low UF membrane the choice has to be modulated depending on the target. For milk industry, UF of a single protein could be selected, such as lysozyme at 1 g.L⁻¹ that is not too expensive and has a size close to the smallest protein of milk (α -lactalbumin, 14 kg.mol⁻¹, expensive). However, UF has to be achieved at a sufficient high ionic strength (typically about 100 mmol.L⁻¹) to avoid electrostatic exclusion that can screened variation of size rejection [13, 62] and consequently the impact of membrane pore enlargement. More complex mixtures, such as skim milk, leading to severe fouling during the process, can also be used aiming at finding a compromise between an acceptable degradation and the industrial target.

The main benefit of this methodology is the saved time. Several solutions can be tested simultaneously under MW and unsuitable ones, provoking strong membrane degradation, would be quickly eliminated. Formulations leading to low permeate flux would be abandoned. Moreover, for the sake of efficiency, step 1 and step 2 can be achieved in parallel or

independently. Indeed, only formulated biocide detergent passing the two first steps (meaning un-probable long-term strong chemical ageing and acceptable flux behaviour) goes to the time-consuming third step.

2.2 Choice of the analytical tool for routine use

From literature review, ATR-FTIR appears to be the relevant technique: (i) it is used in numerous papers dealing with membrane degradation and (ii) adsorption of ingredients on membrane could be detected (if sufficient amount). Moreover, ATR-FTIR fulfils two of our others important criteria: (i) availability in routine in many laboratory either academic or industrial ones and (ii) easy-to handle. ATR-FTIR was selected as the unique analytical tool used in routine in this methodology (see also below the justification with respect to MW activation and industrial membrane autopsy).

ATR-FTIR registered spectra of new membranes and membranes with “long contact time” with biocide detergents must be studied seeking for: (1) disappearance of bands (degradation) and (2) appearance of new bands (degradation and/or adsorption).

The literature provides an extensive knowledge of the PA and PES/PVP membrane degradation using this technique that allows to make comparison and give fundamental explanations about mechanisms, especially in the case of oxidative biocides based on chlorine species. For the sake of clarity, the main results are repealed in the following paragraphs, as they provide the only available references, even if the biocide detergents formulated in this study were not oxidative ones.

2.2.1 Impact of chlorine disinfection on PES/PVP membrane ageing

NaOCl induced long-term degradation of UF membrane based on Polyethersulfone/Polyvinylpyrrolidone (PES/PVP) have been extensively studied [8-25].

The minor polymer, PVP, was evidenced to be the Achille heel of the membrane because it is rapidly attacked. Nevertheless, the PES backbone can also suffer from little modifications such as hydroxylation of phenyl rings but also from more problematic polymer chain scission (**Figure A1-1a & b** in **Appendix 1**). ATR-FTIR allows to evidence these two PES modifications, but not to discriminate them as both lead to a new band located at 1030 cm⁻¹.

To quantitatively check the evolution of PES and PVP, the PES band located at 1237 cm⁻¹ can be used as an internal reference as proposed by Rabiller-Baudry *et al.* [12] because there is no overlapping with PVP bands. This allows to calculate the ratio of the absorbance of the PVP band located at 1660 cm⁻¹ to that of PES at 1237 cm⁻¹ ($H_{1660}^{PVP} / H_{1237}^{PES}$). Moreover, the PES degradation can be evidenced from the ratio of the absorbance of the new band located at 1030 cm⁻¹ to the internal reference ($H_{1030}^{PES \text{ degradation}} / H_{1237}^{PES}$) (**Figure A1-2** in **Appendix 1**).

Polysulfone (PSf, **Figure 1**) often used as intermediate layer of RO and NF membranes suffers more or less from the same degradations as PES. Moreover, specific attack on the isopropylidene unit can occur, eventually associated to chain scission (**Figure A1-1 c** in **Appendix 1**). ATR-FTIR allows to evidence the PSf attack as it results in the formation of an

alkene unit that can be evidenced by ATR-FTIR by the appearance of a new band located at 1644 cm^{-1} .

2.2.2 Impact of chlorine disinfection on Polyamide membrane ageing

Polyamide membranes for RO and NF can be either fully aromatic or poly-piperazine-amide (**Figure 1**). The PA active layers of these membranes are prepared by interfacial polymerisation on a PSf intermediate layer.

PAs are much less stable than PES and PSf toward chlorine and degradation of polyamide RO membrane by NaOCl is well-known. Degradation mechanisms were reported, mainly for fully aromatic PA [26-46, 63] (**Figure A2-1 in Appendix 2**).

The high sensitivity is due to the nitrogen of the amide group of aromatic PA [26, 32, 36, 37, 44, 63-65]. One of the well-known routes involves a reversible N-chlorination, and 2 main mechanisms are proposed (**Figure A2-1 a & b in Appendix 2**):

- chlorine species attack on the electron pair (N or O atom) of the amide group followed by rearrangement into a N-chloroamide group
- direct chlorination on the phenyl group : the ring is attacked by the chlorine species followed by a substitution in para-position.

As the obtained N-chlorinated forms are not stables, the irreversible Orton s' rearrangement can occur at acid pH, inducing the formation of a chlorinated polymer on the phenyl group (**Figure A2-1 c in Appendix 2**).

However, none of these modifications are accompanied by the main chain scission besides the Cl incorporation in the polymer structure.

On ATR-FTIR RO membrane spectra, the superimposition of PA and PSf bands is observed. Regardless of the intensity of the PA degradation and the PA character (fully aromatic or semi-aromatic) the attention must be focused on the amide bands located at 1660 , 1609 and 1541 cm^{-1} (**Table A3-1 and Figure A3-1 in Appendix 3**).

For instance, Ettori *et al* [26] reported on the increase in non-associated C=O (1680 cm^{-1}) and a decrease of hydrogen bonded C=O (1660 cm^{-1}).

More important degradation could occur leading to hydrolysis of the amide group and allowing to recover an amine/ammonium group and a carboxylic acid/carboxylate one.

To quantitatively check the evolution of PA and PSf, the PSf band located at 1237 cm^{-1} can be used as an internal reference and ratio of the absorbance of the target band to this reference can be calculated as explained above for UF membranes (**Figure 3 a**).

2.3 Accelerated ageing by membrane immersion under microwaves (MW)

To date, microwaves are well-known to be able to activate chemical reactions and are widely used to accelerate organic syntheses [66, 67]. The acceleration is partly due the accurate energy delivery close to the reactants and the mastering of the temperature distribution inside the synthesis reactor. Other specific actions of the MW can be superimposed, but a full description is out of the scope of the present paper (see [66, 67] for instance for an overview).

For instance, we have previously shown that the ATR-FTIR spectrum of a PES/PVP membrane immersed 45 min in deionised water under MW at 680 W remained unchanged when compared to that of the pristine membrane [68, 13]. When the membrane was immersed in 400 ppm TFC NaOCl without any MW, degradation took several weeks either at pH= 8.0 (favourable degradation) or pH= 11.5 (pH of use at industrial scale, less favourable degradation) to be evidenced on the ATR-FTIR spectra. On the contrary, the spectrum was significantly modified when the membrane was immersed during 45 min in NaOCl under MW, evidencing the interest provided by the micro-wave activation to induce polymer membrane degradation due to active molecules dissolved in water [68, 13]. In the following this protocol, that is both a chemical & MW ageing protocol, was referred as MW accelerated ageing. Our main objective was to rapidly obtain, membranes with controlled aged states. These deliberately aged membranes would then be used in systematic studies of the impact of the membrane degradation on the filtration performances (flux, rejection, fouling, cleaning) [13, 16].

The main bottleneck of the MW accelerated ageing was the representativeness of the obtained aged states when compared to those reached at industrial scale over a membrane lifespan. For the sake of the validation, comparisons were achieved between the deliberately MW aged membranes and a set of membranes used as references (see below).

Indeed, a spiral membrane entirely autopsied at the end of its service life at industrial scale was used as a reference of the ultimate degradation (hereafter denoted “membrane U”, 4 years lifespan for 8000 h skim milk ultrafiltration - see [3] for the full autopsy of this membrane). Except the severe water flux increase, the only chemical degradations evidenced on the ATR-FTIR spectra of “membrane U” was the full disappearance of PVP and the appearance of a new band located at 1030 cm^{-1} due to the PES backbone attack (H_{1660}^{PVP} and $H_{1030}^{\text{PES degradation}}$, see above) [13].

With respect to the combination of the NaOCl concentration & pH, the MW duration and the MW applied power (see below), a scale of degradation states, can thus be obtained, with more or less disappeared PVP and PES backbone attack. All obtained results were ranging from the pristine membrane to the “membrane U”. The degradation overall state was quantitatively measured thanks to ATR-FTIR through the evolution of the two following absorbance ratios: $H_{1660}^{\text{PVP}} / H_{1237}^{\text{PES}}$ and $H_{1030}^{\text{PES degradation}} / H_{1237}^{\text{PES}}$ (see section 2.2.1) [13]. Indeed, results were in good accordance with the literature data dealing with mechanisms of membrane ageing obtained either by static immersion or dynamic filtration (see introduction).

For the sake of honesty, it must be underlined that the in-depth degradation of a membrane, in conditions of industrial use, is due both to the NaOCl chemical ageing and the mechanical ageing and/or their combination, including their synergetic effects, if any [14]. To date, our results suggest the need of a combination of a short time filtration in NaOCl followed by MW

accelerated ageing to rapidly reach such in-depth highly aged states. However, the differences between the membranes after either MW accelerated ageing or short UF + MW were mainly evidenced when dealing with the membrane flux increase and slightly with ATR-FTIR data [13]. Consequently the use of MW accelerated ageing appeared as a simple and rapid way to evidence chemical long-term degradation, if any.

Besides the membrane area to solution volume ratio, several parameters have to be controlled for direct comparison when ageing membrane under MW: material, form and size of the reactors in which are the solutions and membrane coupons, global volume of solution in the MW oven (number of reactors simultaneously in the oven), MW type depending of the mode of MW delivering (either continuous or pulsed), overall volume of the MW oven, applied power (few hundred of Watt), duration of MW application, etc.

The MW application mode is an important parameter that have to be mastered in order to be able to draw conclusions from the chemical & MW ageing protocol. Indeed, the MW activation can be achieved in several ways, but the use of pulsed-MW delivered by a domestic oven (multi-mode oven) was preferred. This choice was driven by the sake of oven availability. Moreover, it allowed to treat membranes of sufficient filtering area (100-150 cm²) to further achieved cross-flow filtration with plate and frame modules [16].

One main question concerned the selection of the MW power. According to our knowledge, our initial study (started in 2010 but reported for the first time in 2014 [68]) was the first one dealing with the polymer membrane ageing using MW activation. No reference data were available at start. To maintain the membrane immersed all the time in the solution, the evaporation has to be limited. The evaporation is partly correlated to the temperature increase. However for long time MW delivery, without coverage of the reactor, 60 W must be the maximum applied power to keep the temperature equal or lower than 50°C (temperature use for NaOCl disinfection in dairy) [13]. Such low power is not provided by domestic ovens (minimum is often close to 150-170 W). Thus, to cover the reactor using MW resistant film was required. Moreover, combinations of MW power and MW application duration have to be found to limit the temperature increase. The proposed compromise was a time-slot MW delivery mode with few minutes with and few tens of minutes without MW application.

On a theoretical point of view, the MW penetration depth inside a material immersed in a given solution depends on the oven frequency (and its associated wavelength), on the solvent and on the material itself (dielectric constants) [66, 67]. This suggests that the MW applied power required to rapidly reach an expected ageing state can be either solution or polymer dependent. The less reactive is the membrane/solution system the higher must be the applied power to provoke the membrane degradation (if any) in a short time.

On a practical point of view, with respect to the lack of reference, the MW power and its application mode were selected by a trial and error approach aiming at avoiding (1) that the membrane burned and (2) the apparition of cracks (that were neither evidenced on the “Membrane U” nor on several NF and RO membranes from dairy that were autopsied in our

laboratory over the last 15 years). With respect to these criteria and to the domestic oven performances, the selected power were in the range 170-680 W [13].

In this paper we have used a set of MW conditions adapted from those described in [13], aiming at the study of the long-term stability of a PES/PVP ultrafiltration membrane in bleach.

The adaptations were established by comparison to the “membrane U”, but only aiming at evidencing on the ATR-FTIR spectra all the degradation markers due to oxidative agents. For the sake of the validation of these changes, the efficiency of the ageing acceleration was first checked in NaOCl by putting the membrane in 800 ppm TFC NaOCl (4-5 times the target concentration of use) at pH= 8.0 and pH= 11.5 under pulsed micro-waves at 510 W during 7 h in a discontinuous way (time slot MW application) (**Table 2, step 1**). Note that after the same treatment in deionised water, no degradation was observed in ATR-FTIR on the UF membrane whereas some degradation markers were already depicted after 1 h in NaOCl. In absence of any other reference, the 7 h MW treatment at 510 W in prototype biocide detergents was supposed to provoke reactions that could require higher activation, for instance because they could be less efficient (if any) than those with NaOCl.

However, the conditions had to be found for the PA membranes. First, the PA degradation is easier in chlorine solutions compared to the PES/PVP membrane as it can be drawn from the literature review. Trial and error approach have shown that 170 W can be sufficient to evidence degradation in 800 ppm TFC NaOCl at pH= 8.9, moreover strongly limiting the solution evaporation (**Figure 3**). It can be underlined that 7 h at 170 W were sufficient to provoke some PSf backbone attack (**Figure 3d**).

For the sake of a complementary validation, the same conditions have been applied with another oxidative agent known to be much less aggressive than bleach toward PA membranes. A 800 ppm DEPTIL PA5 solution (mixture of hydrogen peroxide, peracetic and acetic acid, see Experimental part) at pH= 2.8 was tested (**Figure 3b**) highlighting, as expected, the better stability of the membrane in the oxidative oxygen-based conditions.

Knowing from literature that the PVP degradation of the PES/PVP membrane is more rapid than that of the PES backbone, conditions established for the RO membrane were also tested with the UF membrane aiming at evidencing the relative stability of PVP when compared to the PA layer.

Accordingly, in the following, 7 h at 170 W (allowing to both evidence the PA degradation with chlorine and its relative stability toward oxygen species) were applied to evaluate the possible degradation of the RO membrane by the non-oxidative biocide detergents. The concentration at start was increased up to 4-8 times the concentration of use as it has been previously made with NaOCl and Deptail PA5; however this concentration choice remained more or less arbitrary (**Table 2, step 1**).

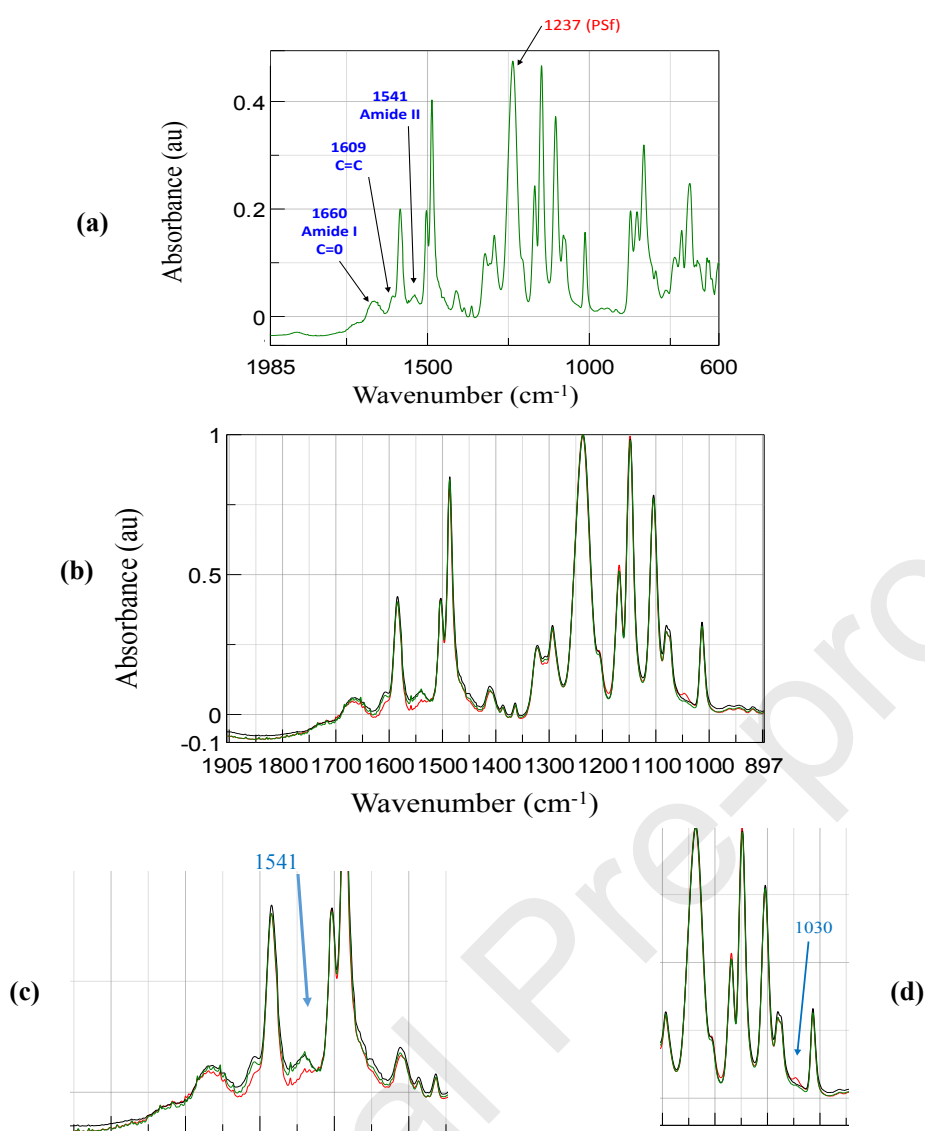


Figure 3 : ATR-FTIR spectra of PA membrane used in this study (TFC-HR), MW = 170 Watt.
 (a) New membrane,
 (b) Aged membranes compared to new membrane: black: pristine membrane similar to membrane after 7h under MW in water, red: after 7 h under MW in NaOCl, green: after 7h in DEPTIL PA5 under MW.
 (c) zoom of (b) in PA region highlighting membrane degradation by NaOCl evidenced from decrease of the 1541 cm⁻¹ band
 (d) zoom of (b) in PSf backbone region highlighting membrane degradation by NaOCl evidenced from appearance of the 1030 cm⁻¹ band

3 Experimental

3.1 Water, solutes and solutions

Water used for membrane rinsing and preparation of all solutions was deionised and 1 µm filtered. Its conductivity was always lower than 1 µS.cm⁻¹.

Simple alkaline solution was prepared at pH 11.0 from NaOH pellets (analytical grade, Acros).

800 ppm TFC sodium hypochlorite solutions were obtained by appropriate dilution of concentrated commercial bleach (MIC, bleach at 48 g.L⁻¹ in total free chlorine (TFC). The pH was adjusted by NaOH addition. The concentration of use at industrial scale is 150-200 ppm TFC with UF membrane of dairy industry.

800 ppm DEPTIL PA5 solutions containing hydrogen peroxide, acetic acid and peracetic acid in equilibrium was prepared from commercial DEPTIL PA5 (liquid disinfectant) provided by Kersia (France).

Several commercial formulated alkaline detergents were used. They were provided either by Ecolab (P3-Ultrasil 10, powder, natural pH= 11.0 at 0.4 g.L⁻¹, France) or by Kersia (DEPTAL UF 117 L, liquid, natural pH =11.0 at 0.8 g.L⁻¹, France).

NaCl solution set at 2 g.L⁻¹ was used at its natural neutral pH for the evaluation of the RO spiral membrane (purity: > 99.9%, Aqua Pro). The concentration of NaCl, either in the retentate or in the permeate, was measured by conductivity with an accuracy better than 1%. Consequently, the NaCl rejection was calculated with an accuracy better than 2%.

3.2 Formulated biocide detergent prototypes

As a general rule, simple solutions only containing the active biocide molecule can be used for disinfection (for instance an inorganic disinfectant such as NaOCl). However, formulated biocide detergents in which an organic molecule acting as an active biocide is mixed with other ingredients can be prepared. In this case disinfection and detergency are combined for the sake of an increasing efficiency. This last choice was the one selected in this study. Except the active molecule (a carboxylic acid) and an ingredient adjusting the pH (an alkyl sulfonic acid), the formulated prototypes contained a complex mixture of at least four ingredients among which were surfactants. These last ones can be either non-ionic, anionic or zwitterion surfactants. For the sake of the confidentiality, only one of these last ingredients is given with more details: an ethoxylated compound with a fatty carbon chain, hereafter noted surfactant 1 (**Table 2**).

Several non-oxidative biocide detergent prototypes with proprietary compositions were formulated and provided by Kersia (France). They are hereafter called Biocides A, B & D (**Table 2**). All prototypes were based on the same non-oxidative biocide: octanoic acid, also known as caprylic acid (simple Biocide C, **Table 2**). Note that to measure the biocide activity of these prototypes was out of the scope of this study only focusing on the impacts on membrane integrity.

The carboxylic acid biocide being active in acidic media, the appropriate pH of the 3 formulated prototypes (A, B, D) was obtained by dissolving methanesulfonic acid (strong acid) in the overall liquid matrix. Note that methanesulfonic acid was only partly retained by the RO membrane and thus crossed the membrane toward the permeate.

Biocide A was similar to Biocide B except the presence of surfactant 1. When comparing Biocides B & D, concentration of ingredient 2 was increased in Biocide D, and ingredient 3 was substituted by ingredient 4. No more information can be given because of the proprietary rights.

Table 2 : Overview of the composition of the simple and formulated biocide detergent prototypes

| Composition | specific function | Liquid Biocide | | | |
|---|-------------------------|----------------|------|------|------|
| | | A | B | C | D |
| Acid matrix : Methanesulfonic acid | SO ₃ H group | + | + | 0 | + |
| Non-oxidative biocide octanoic acid | CO ₂ H group | + | + | + | + |
| Surfactant 1 (ethoxylated compound) | C-O bound | + | 0 | 0 | 0 |
| Ingredient 2* | ? | + | + | 0 | ++ |
| Ingredient 3* | ? | + | + | 0 | 0 |
| Ingredient 4* | ? | 0 | 0 | 0 | + |
| Target concentration of use (wt%) | | 0.75 | 0.75 | 0.75 | 0.50 |
| Filtration tested concentration = 2 x target concentration (wt%) | | 1.5 | 1.5 | 1.5 | 1.0 |
| pH (± 0.05) | | 1.45 | 1.87 | 1.61 | 1.88 |

*: proprietary composition of Kersia

3.3 Membranes and filtration cell

Several membranes were used either for RO or UF, either for flat or spiral configuration.

3.3.1 RO membranes

The reverse osmosis membrane was a polyamide membrane hereafter noted TFC-HR provided by Koch (USA) and commonly used in dairy industry. Two different spiral wound membrane elements were used (2540 module, filtering area = 2.5 m²).

The first module (called S-TFC-HR-cut-CIP 1) was first cut in small coupons that were further used for immersion tests under micro-waves (10 cm², step 1 in **Table 2**). Second the module also provided small flat membranes, the filtering area of which was 140 cm², further used during the step 2 of the methodology.

The second spiral membrane (called S-TFC-HR-CIP 1) was used in RO experiments during which either a NaCl solution or a formulated biocide (step 3 in **Table 2**) were filtered. Before the first use, compaction at 35 bar in water followed by an alkaline cleaning by P3-ultrasil 10 and DEPAL UF 117L was achieved on the membrane. It was thus checked that the water flux measured after cleaning was the same, regardless of the formulated alkaline detergent, and can be used as a relevant reference.

3.3.2 UF membrane

The ultrafiltration membrane was a PES/PVP membrane hereafter noted HFK-131. This membrane provided by Koch (USA) is widely used in worldwide dairy industry for skim milk filtration aiming at protein standardisation before the cheese making process. Its molecular weight cut-off is $MWCO = 5-10 \text{ kg.mol}^{-1}$ according to the provider. One spiral membrane (4333 module, filtering area = 6.7 m^2) was used, hereafter noted S-HFK 131-cut -CIP 3, in which small pieces were cut. Either small coupons of 18 cm^2 or flat membranes (filtering area = 140 cm^2) were sampled and further used in the steps 1 and 2 of the methodology, respectively.

3.3.3 Filtration cell for flat membranes

Before use, regardless of the membrane, either RO or UF, the preservative was removed by soaking the membrane in deionised water. The efficiency of the removal was systematically checked by ATR-FTIR during the final autopsy of each flat membrane, being possible as part of the membrane was not immersed in the liquid channel during filtration. Retentate (31 mil) and permeate spacers were sampled in the S-HFK 131-cut -CIP 3 spiral membrane.

Flat membranes were then inserted in a plate and frame SEPA cell (GE Osmonics, USA) equipped with two stainless steel shims. Indeed, the membrane was in sandwich between one retentate spacer inserted in the liquid feed channel and one permeate spacer on the permeate side, as in a spiral membrane. In such conditions the free channel thickness was measured to be 1.25 mm (the thinner one we were able to obtain) whereas it was 31 mil (= 0.79 mm) in the spiral membrane.

Prior to further other use:

- each RO flat membrane was once again rinsed by water in filtration conditions then compacted at 35 bar by filtering deionised water at 50°C during at least one hour. This duration was sufficient to reach a plateau value of flux. It was evidenced that the membrane hydraulic resistance (R_m , calculated according to the Darcy equation) varied in a reversible way when increasing the temperature from the room temperature to 50°C . However, the kinetic of recovery was slow. Consequently, all filtrations, including those of NaCl, were achieved at 50°C in order to keep R_m constant.
- each UF flat membrane was once again rinsed by water in filtration conditions then compacted at 2.5 bar by filtering deionised water at 50°C during at least 4 h that allowed to reach a plateau value of flux. The membrane hydraulic resistance did not varied

significantly between the room temperature and 50°C, nevertheless, all filtrations were achieved at 50 °C.

3.4 Pilot for cross-flow filtration

RO and UF were achieved on the same pilot designed for NF/RO by TIA (Bollène, France). It was alternatively equipped with the RO spiral membrane or the SEPA cell in which the flat RO or UF membranes were inserted (see above).

3.4.1 Standard conditions

The filtration was achieved by processing 10 L of solution at different transmembrane pressures (TMP) either by increasing the TMP from 10 to 35 bar for RO or at a constant TMP of 2.5 bar for UF. The volume reduction ratio was VRR= 1 as both the retentate and the permeate were fully recycled in the feed tank. In standard conditions, the temperature was 50 °C.

The feed flow rate was:

- $Q_{\text{feed}} = 565 \pm 6 \text{ L.h}^{-1}$ corresponding to a cross-flow velocity close to 1.3 m.s^{-1} with the flat membrane (as estimated in free channel).
- $Q_{\text{feed}} = 950 \pm 10 \text{ L.h}^{-1}$ with the spiral RO membrane corresponding to a cross-flow velocity in a free channel close to 0.3 m.s^{-1} as estimated according to the calculation proposed by Rabiller-Baudry *et al.* [69].

3.4.2 Biocide filtration with flat membrane

Different filtrations were performed with the flat membranes.

3.4.2.1 Biocide single filtration (step 2)

Filtration of biocide prototypes were achieved at 50 °C during 1 h in standard conditions, either at 20 bar (RO) or 2.5 bar (UF). After filtration, each flat membrane was carefully rinsed by deionised water then demounted and dried before ATR-FTIR analysis.

The membrane flux (J_p , $\text{L.h}^{-1}.\text{m}^{-2}$) and permeance (L_p , $\text{L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$) were followed during the whole filtration of the biocide and compared either to the reference values measured in water after compaction or to the recovered flux measured after the final water rinsing (by 3x10 L of water). Accuracy on fluxes and permeance were better than 10%.

3.4.2.2 Biocide and alkaline detergent in cascade (step 2)

Some experiments were achieved using a biocide prototype and an alkaline detergent in cascade.

Filtration of the biocide solution was first achieved at 50 °C during 1 h in standard conditions, either at 20 bar (RO) or 2.5 bar (UF). After a careful rinsing with 3x10 L of water, an alkaline cleaning step was achieved at 50°C during 1 h either at 20 bar (RO) or 2.5 bar (UF) using either P3-ultrasil 10 or DEPTAL UF 117L at pH=11.0. The alkaline cleaning was then followed by a final water rinsing until a neutral pH was recovered either in the retentate or in the permeate

sides. This “biocide + alkaline detergent” cascade, hereafter called a cycle, was repeated 3 times. After the final water rinsing, the membrane was demounted and dried before ATR-FTIR analysis.

3.5 RO with spiral membrane (step 3)

The different steps and conditions are detailed in **Table 3**.

Table 3: Sequences of RO at 50°C for the final validation of Biocide D with the spiral membrane.

| Steps | Concentration | pH | TMP (bar) | Duration |
|-----------------------------------|----------------------|---------|-----------|----------------------------|
| Alkaline CIP * | | 11.0 | 20 | 1 h |
| Water rinsing 3x10 L + water flux | | | | |
| NaCl | 2 g.L ⁻¹ | neutral | 15-35 | ~ 2 h |
| Water rinsing 3x10 L + water flux | | | | |
| Biocide D | 10 g.L ⁻¹ | 1.87 | 20 | 25 h ** |
| Water rinsing 3x10 L + water flux | | | | |
| Alkaline CIP * | | 11.0 | 20 | 1 h |
| Water rinsing 3x10 L + water flux | | | | |
| NaCl | 2 g.L ⁻¹ | neutral | 15-35 | ~ 2 h |
| Water rinsing 3x10 L + water flux | | | | |
| Biocide D | 10 g.L ⁻¹ | 1.87 | 20 | 25 h (cumulate = 50h)** |
| Water rinsing 3x10 L + water flux | | | | |
| Alkaline CIP * | | 11.0 | 20 | 1 h |
| Water rinsing 3x10 L + water flux | | | | |
| NaCl | 2 g.L ⁻¹ | neutral | 15-35 | ~ 2 h |
| Water rinsing 3x10 L + water flux | | | | |

* *Cleaning in Place (CIP) with P3-Ultrasil 10 or DEPTAL UF 117L (no matter of the alkaline detergent because the same results were obtained)* - ***The biocide has been filtered during a cumulative time of 25 h (or 50 h) achieved by daily continuous filtration of about 10 h. For technical needs the spiral membrane was rinsed by water every day and stocked in water over night. Then filtration of the biocide was repeated the next day.*

3.6 Ageing experimental conditions under pulsed micro-waves (step 1)

Accelerated membrane ageing (if any) have been carried out by immersion of small membrane coupons under microwaves in the tested solutions. At start, the concentration of the tested biocide was selected to be 4 times that of the target use at industrial scale (**Table 2**).

Each RO membrane coupon of 10 cm² was immersed in a 100 mL borosilicate glass reactor filled, at start, with 60 mL solution (**Figure 4**). Indeed, one reactor contained deionized water whereas four others were filled with the biocide solution to be evaluated. The five filled reactors containing a membrane coupon were then simultaneously introduced in the MW oven. The conditions were slightly adapted for UF membrane as each one of the five 18 cm² membrane coupons was immersed in a 300 mL borosilicate glass reactor filled with 250 mL solution at start.

The membrane accelerated ageing was achieved in a multi-mode oven (domestic MW oven, 31 L, 2.45 GHz, Moulinex) delivering pulsed MW (**Figure 4**). In such domestic oven, the power is applied in a pulsed way and consequently the accurate mastering of the temperature is not possible, as already said.

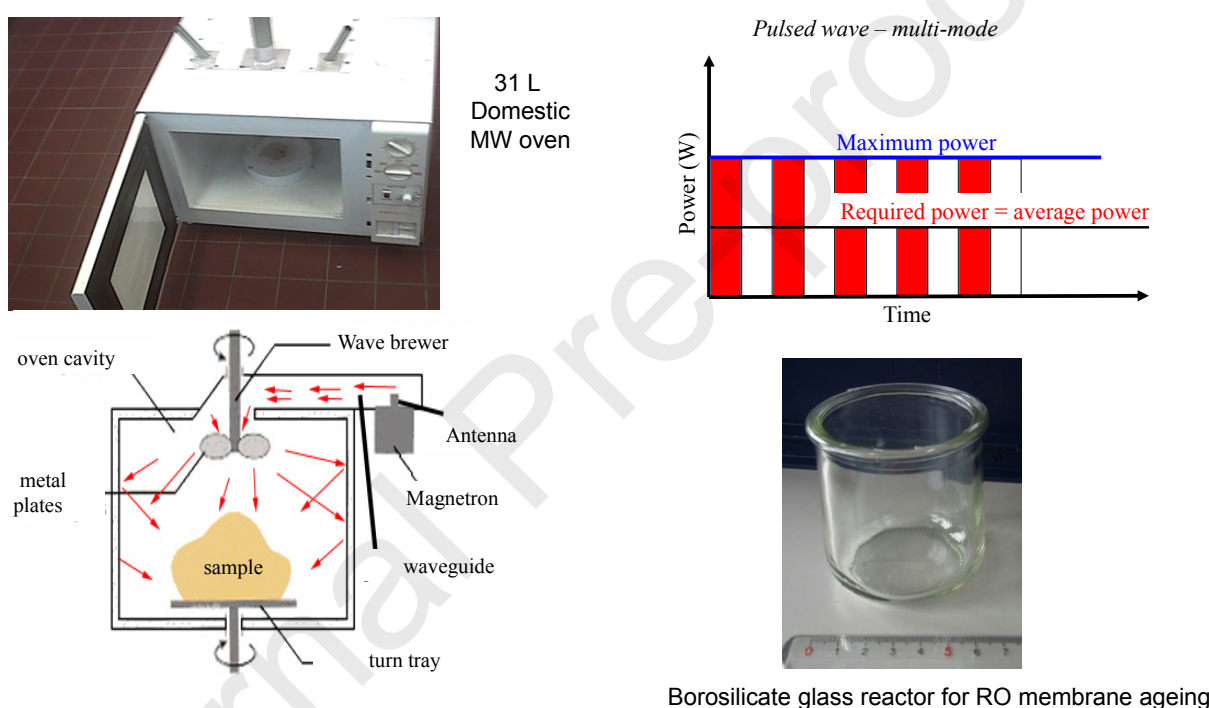


Figure 4 : Domestic multi-mode micro-wave oven used for membrane ageing allowing the supply of pulsed MW at 170 W (RO membrane) and 510 W (UF membrane). The MW application was achieved in a discontinuous mode with time slots MW delivering.

With the RO membrane, the pulsed MW (170 W) were applied with a time-slots delivering mode during a maximum duration of 7 h. One by one, each coupon in the tested biocide solution (but not the corresponding reactor) was sampled at selected MW time : 0.5 h , 2 h, 4.5 h, 7 h. The coupon immersed in water was collected after 7 h under MW for the sake of comparison.

To limit the solution evaporation, each reactor was covered with a film that was resistant to MW. Moreover, MW were stopped every 0.5 h and the coupons were let to whistand in the solution that cooled down naturally at room temperature. Two days were needed to achieve the overall protocole with the RO membrane (4.5 h MW during day 1 and 2.5 h MW during day 2). Finally, each coupon was carrefully drained before analysis (but not systematically rinsed, see results).

With the UF membrane coupons, with respect to the higher power applied (510 W), MW were only applied during a cumulative time of 3 h. Finally, each coupon was carrefully drained then rinsed with water in order to remove the reversible adsorbed ingredients before analysis.

It has been checked by ATR-FTIR that the MW treatment applied in deionised water have no impact neither on the virgin RO membrane nor on the pristine UF membrane. Consequently all the modifications evidenced on the ATR-FTIR spectra can be attributed to interactions between the formulated biocide ingredients and the membrane (adsorption or degradation).

3.7 ATR-FTIR analysis of membranes

Prior spectra registration membranes were carefully dried in a desiccator under dynamic vacuum during several days in order to remove traces of water. This allowed to avoid any misleading interpretation when dealing with the C=O band of PA and PVP: water has an OH band close to 1660 cm^{-1} (see **Figure A4-1** in **Appendix 4**) that can be superimposed to these C=O bands.

Spectra were acquired with a FTIR 4100 spectrometer (Jasco, **Figure A5-1** in **Appendix 5**) equipped with an ATR accessory (Miracle, ZnSe Crystal, mono-reflexion, incidence angle of 45°, scan in the 600-3700 cm^{-1} region, average of 180 scans per spectrum, resolution 2 cm^{-1}). The background was registered in the air. Membrane samples were maintained on the ATR crystal thanks to a press system (maximum pressure must be applied using a flat tip). The data were acquired and treated with the Spectra Manager software.

As explained in section 2.2, a membrane spectrum results in the superimposition of the active and intermediate layers of the membrane as well as that of the fouling layer due to adsorption of the biocide ingredient(s) if any. The quantitative interpretations of the spectra were made by measuring the absorbance at a given wavenumber w , hereafter noted H_w , toward an internal reference. This reference was selected as the band belonging both to PES and PSf and located at 1237 cm^{-1} (H_{1237}^{PES} , H_{1237}^{PSf}). The baseline selected for the absorbance measurement was chosen in a quite flat region of the spectra (1800-1900 cm^{-1} range) for both RO and UF membranes.

4 Results and discussion

The methodology described in **Table 1** was entirely achieved with the RO membrane. Only the promising biocide validated for the RO membrane was then used with the UF membrane. This order to evaluate the formulated prototypes was chosen assuming *a priori* that a suitable biocide

for fragile PA membrane would probably be correct for UF membrane (this assumption will be discussed below).

4.1 How to evidence the possible adsorption of formulated biocide ingredients on membrane

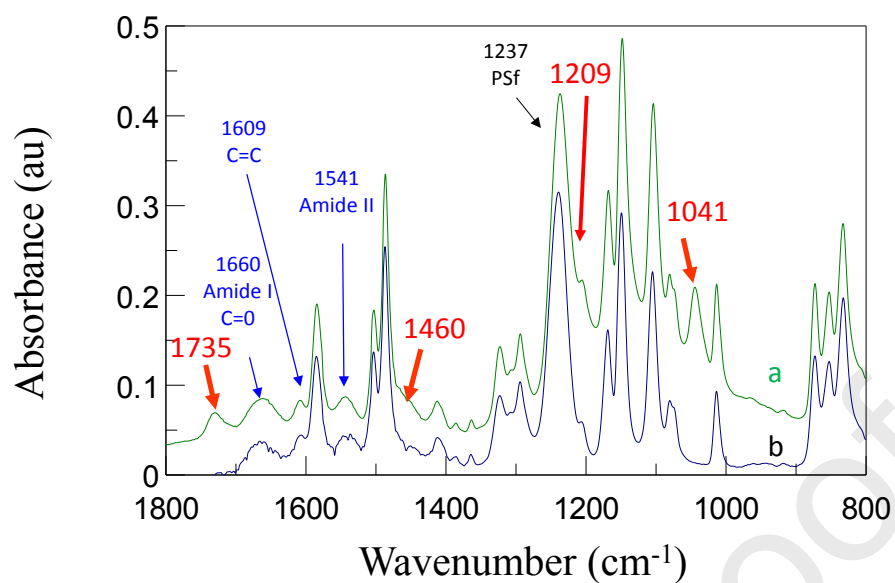
The main question at start was that of ATR-FTIR reference spectra for “each” ingredient of the formulated biocide detergents. Indeed, to overcome the problem related to the proprietary rights we had to register a reference spectrum for each entire formulated biocide detergents instead of those of each individual ingredient. In this case all ingredients were mixed in the appropriate proportions and more difficult to individually identify.

The simplest way would be to register the ATR-FTIR spectra of each biocide solutions. After the removal of bands due to water, the bands belonging to the other ingredients would be found (see **Appendix 4** for example dealing with this procedure). However, it was not possible to register the spectrum of each solution with the ZnSe ATR crystal: this last one would be attacked because of the too acidic pH.

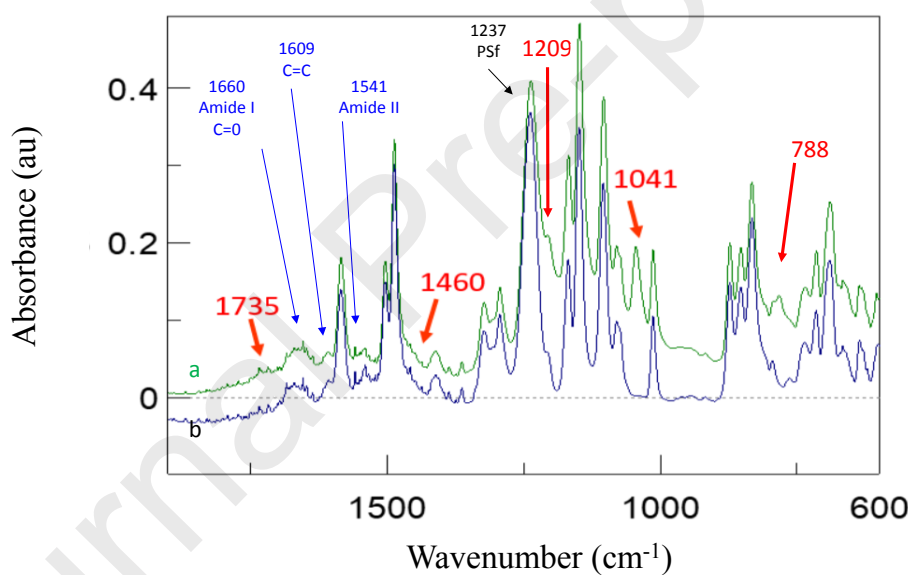
To overcome this second difficulty, immersion of RO membrane coupons was achieved at room temperature in the concentrated (“pure”) liquid biocides: A (1047 h), B & C & D (3 h), without any further rinsing. Consequently, all ingredients of a given biocide would be deposited on the membrane. After drying, only water would be removed and the registered spectra would be the superimposition of the membrane spectrum and those of all ingredients that can be evidenced by ATR-FTIR. Note that this sample preparation was not able to make the distinction between ingredients that tend to naturally adsorbed on the membrane and others. Here the membrane was only used as a support, and any other solid material could have been selected to characterise the deposit. With the membrane as support, the objective was also to underline the appearance of new bands that can be easily assigned to the formulated biocide ingredients when comparing the immersed membrane spectra to that of the pristine membrane. Moreover, the identified functional groups of the ingredients given in **Table 2** were used to help at the assignment. Some coupons have been rinsed to remove ingredients that were “adsorbed” in a reversible way. The comparison of the membrane spectra obtained before and after rinsing, has helped at the assignment. All spectra are given in **Appendix 6** and the bands have now to be selectively attributed to the several ingredients of the formulated biocides.

Firstly, the membrane bands were attributed. On the ATR-FTIR spectrum of the pristine RO membrane (**Figure 5b**), numerous bands correspond to the polysulfone (PSf) backbone of the intermediate layer and only few ones have to be attributed to the PA active layer (**Table 4**). The three main PA bands are those located at 1541 cm^{-1} (amide II, CN+NH), 1609 cm^{-1} (C=C) and 1660 cm^{-1} (amide I, C=O). A very small band at 1735 cm^{-1} corresponds to very few un-reacted carboxylic acid group (CO_2H). By comparison with spectra of RO and NF membrane reported in literature (see **Appendix 3**, [71]) this membrane could be a semi-aromatic one.

The absorbance ratios of a set of PA bands to the internal PSf reference band (1237 cm^{-1}) were calculated for the pristine membrane and served as references of the not-aged and not fouled membrane (**Figure 6**).



(a): immersed 3h in Biocide B, (b): pristine



(a): immersed 3h in Biocide D, (b): pristine

Figure 5: Example of ATR-FTIR spectra of RO membranes

Table 4 : Assignment of bands of the RO and UF membranes + adsorbed ingredients

| Wavenumber (cm ⁻¹) | RO membrane | UF membrane | Wavenumber (cm ⁻¹) | bound | ingredient |
|--------------------------------|-------------|-------------|--------------------------------|----------------------------------|---|
| 1735 (very small) | PA | | 1735 (strong) | C=O in CO ₂ H | Octanoic acid |
| 1660 | PA | PVP | | | |
| 1609 | PA | | | | |
| 1541 | PA | | | | |
| 1460 (small shoulder) | | PVP | 1460 (medium shoulder) | | Octanoic acid |
| 1237 | PSf | PES | | | |
| | | | 1209 | | Ingredient 2 |
| | | | 1041 | SO in SO ₃ H C-O ? | Sulfonic acid of acid matrix + Surfactant 1 ? |
| | | | 788 | | Ingredient 2 |

The ingredients' bands have now to be found. In absence of any chemical degradation of the membrane, the presence of an ingredient deposited on the membrane can be easily evidenced by an increasing ratio at a given wavenumber w . This case was that of Biocides B&C&D after 3 h contact time with the RO membrane: the 1541 and 1660 cm⁻¹ PA bands remained similar to that of the pristine RO membrane (**Figure 6**). When compared to the RO membrane spectrum, several additional bands appeared on spectra of membranes immersed in Biocide B & D (see also **Appendix 6**). Consequently, they were attributed to the different ingredients belonging to these two prototypes:

- 1735 cm⁻¹ and 1460 cm⁻¹ (shoulder) was attributed to octanoic acid without any ambiguity. This attribution was confirmed by the spectrum of the RO membrane soaked in Biocide C only containing this acid.
- 1041 cm⁻¹ was assigned to the sulfonic acid group of the methanesulfonic acid of the acid matrix acid. Once again the attribution was made without any ambiguity as the sulfonic group has been extensively studied in literature. Note that in anionic form (SO₃⁻, $w = 1030$ cm⁻¹ whereas at acidic pH where the SO₃H group is predominant $w = 1040$ cm⁻¹).
- 1209 cm⁻¹ and 788 cm⁻¹ were assigned to ingredient 2 (**Table 2**) as it is the only “other ingredient” present in Biocides B&D but at different concentration. Note that these two

bands disappeared after careful water rinsing and finally no matter if there are not attributed with more accuracy.

No new band was evidenced for only Biocide B or Biocide D. It was thus drawn that ingredients belonging to only one of these prototypes were not detected (ingredient 3, ingredient 4, **Table 2**). However, it cannot be totally excluded that they can have functional groups similar to those of ingredient 2, octanoic acid and methanesulfonic acid, leading to band superimposition.

To evidence new band due to ingredients was more difficult in the case of a simultaneously degraded and fouled membrane. This was the case of the RO membrane immersed in Biocide A. After 1047 h contact time: the 1541 and 1660 cm^{-1} PA bands have significantly decreased (**Figure 6**). However the relative ratio of the 1735 cm^{-1} and 1460 cm^{-1} bands, both due to the CO_2H group of the octanoic acid, remained roughly similar to those observed after 3 h in Biocides B&D. This result (i) confirmed the presence of the octanoic acid in Biocide A and (ii) that none of these bands had any superimposed ingredient.

On the contrary, it has to be mentioned that C-O-C bound of an ethoxylated compound such as Surfactant 1 of Biocide A might have a more or less large band in the 1000-1100 cm^{-1} region (see **Appendix 4**). However, with respect to the low concentration of surfactant 1 a very small and large C-O-C band was expected, moreover close to that of the sulfonic acid group. The acid being at much higher concentration than that of the surfactant 1, it was logically drawn that this last one cannot be evidenced in the presence of methasulfonic acid.

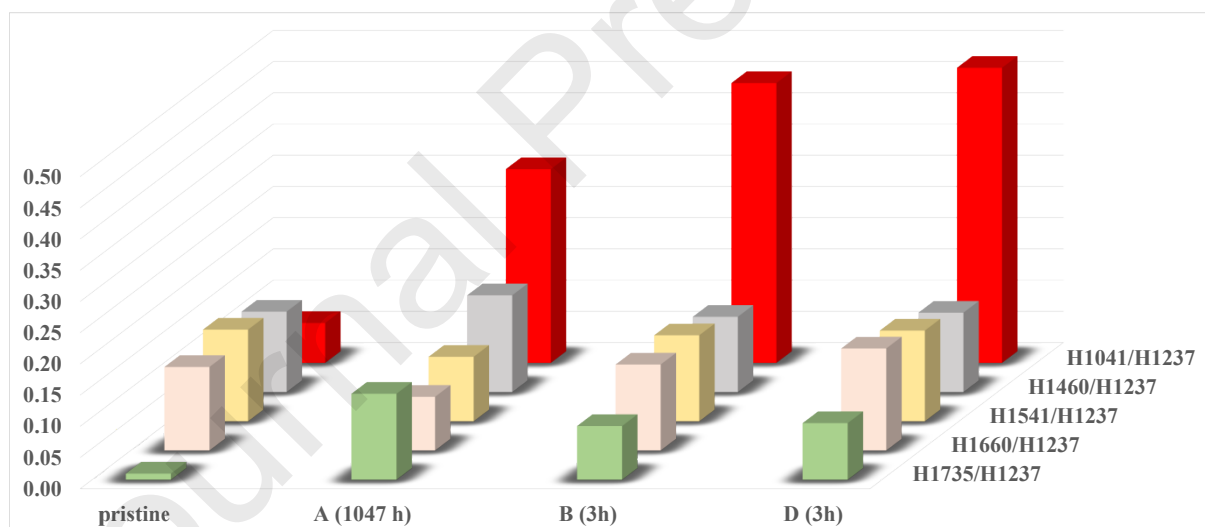


Figure 6: ATR-FTIR of RO membrane: evolution of H_w / H_{1237}^{PSf} ratio for selected bands located at wavenumber w before and after soaking at room temperature in concentrated biocides A (1047 h), B & D (3h).

A similar approach was applied to the UF membrane. Could the octanoic acid adsorption be depicted at 1735 cm^{-1} (CO_2H)? Yes in absence of the PES/PVP membrane oxidative degradation. Remember that the PVP oxidative degradation can lead to a new band at the same $w = 1735\text{ cm}^{-1}$. Moreover, the shoulder at 1460 cm^{-1} related to the carboxylic acid group of octanoic acid could be superimposed to the shoulder due to un-degraded PVP. Could the methanesulfonic acid adsorption be evidenced at 1040 cm^{-1} ? Once again, yes in absence of the PES/PVP membrane oxidative degradation. Remember that PES oxidative attack was previously shown to lead to either hydroxylation of phenyl ring (leading to a phenol group) or evolution of the sulfone group (SO_2) in a sulfonic one. Both transformation lead to a single band at 1030 cm^{-1} at neutral and alkaline pH. However, at acid pH the OH group of phenol was expected to remain located at the same $w = 1030\text{ cm}^{-1}$ whereas the sulfonate after protonation was expected to move at $w = 1040\text{ cm}^{-1}$. In conclusion, as the prototype biocides are non-oxidative ones, the selected bands at 1735 cm^{-1} and 1040 cm^{-1} can be used unambiguously to evidence presence of octanoic acid and methanesulfonic acid on the UF membrane (not shown, **Table 4**).

It can be underlined here, that the same comments can be written for the PES and the PSf oxidative degradations that cannot be suspected here. Consequently, all assignment discussed for the RO membrane only dealing with the PA aged state remained good when also taking into account the PSf intermediate layer, the spectrum of which being superimposed to that of PA and ingredients.

As a conclusion, **Table 4** summarizes all the bands of interest for the pristine membranes (RO and UF) and the biocides' ingredients in absence of membrane degradation. In the following the absorbance of the selected bands shown on **Figure 6** have to be followed. Moreover, if any additional bands are evidenced during the ageing tests they have to be considered as an evidence of membrane degradation.

4.2 Membrane accelerated ageing under microwaves (step 1)

The first step of the methodology was applied to RO and UF membrane and the main results are shown in this section.

4.2.1 RO membrane (up to 7h at 170 W)

Only Biocides B & D were tested here. Biocide A was not studied because step 2 was achieved in parallel to step 1 and led to its rejection (see below) with respect to the flux behaviour.

Figure 7 a shows that the evaporation of Biocide B solution at 6 wt% at start was linear with the MW application duration. After 7 h, half of the solution was removed. The same evaporation was obtained with deionised water and Biocide D at 4 wt% at start. Indeed, these results highlighted the constant evaporation rate of water and allowed the direct comparison of the impact of all the biocides as all the trials were achieved in a similar way.

Figure 7 b depicts the ATR-FTIR band variation vs MW application duration in Biocide B. The membranes were not rinsed before the spectra registration. Consequently ingredients adsorbed on the membrane either in a reversible way or an irreversible one were evidenced on the spectra. 3 sets of data have to be distinguished (see spectra in **Figure A7-1** of **Appendix 7**):

- those increasing with MW time, that were attributed to progressive adsorption of ingredients with time and concentration (ingredient concentrations were more or less two times the initial ones after 7 h): 1735, 1460 and 1041 cm^{-1}
- one remaining constant: 1541 cm^{-1} (amide II of PA)
- one decreasing after 0.5 h but then remaining constant: 1660 cm^{-1} (amide I of PA)

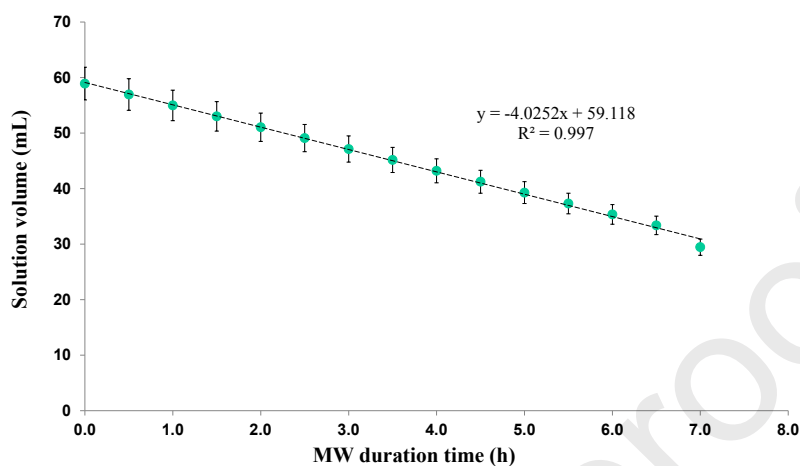
The amide II band slight evolution suggested that the PA could be slightly modified at short-term. However, after that PA band remained constant over time. This phenomenon has already been observed by Etti *et al.* [26] when studying degradation induced by NaOCl. These authors have attributed this variation to a decrease in hydrogen bonding. Indeed, the stability of the amide II band after this first change suggested also that the PA layer was roughly long-term stable.

After 7 h under MW in Biocide D, the RO membrane evidenced a higher adsorption of the methanesulfonic acid (1040 cm^{-1}) but a lower one of the octanoic acid (1735 cm^{-1}) when compared to Biocide B. Moreover, the amide bands (I & II) remained quite similar to those of the pristine membrane (**Figure 7**) - (see spectra in **Figure A8-1** in **Appendix 8**).

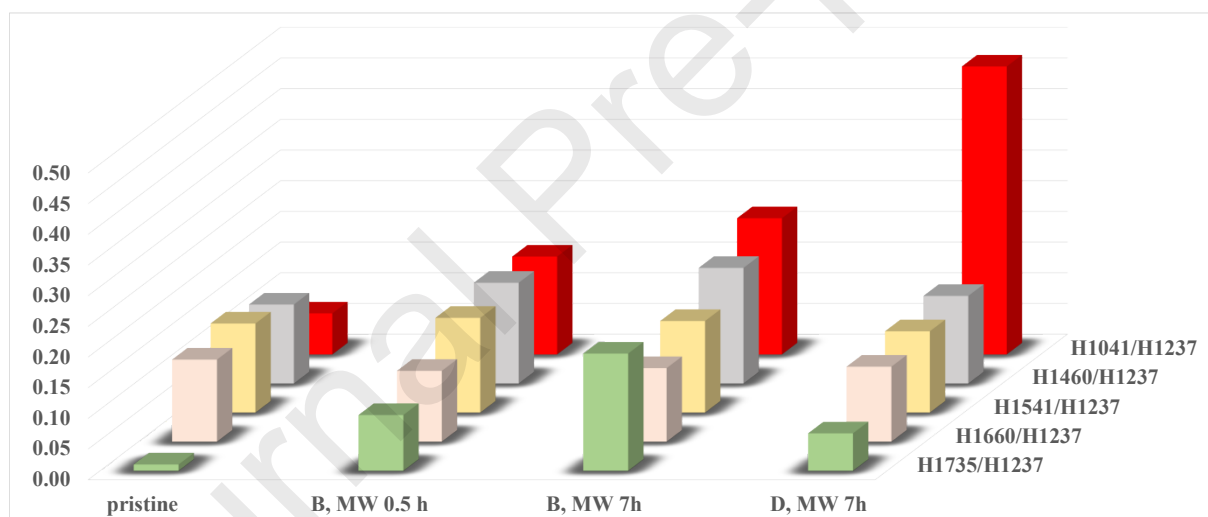
The MW ageing protocol suggested thus that Biocide B & D would not degrade the RO membrane. For the sake of a long term validation, a supplementary immersion of the RO membrane in Biocide B set at 1.5 wt% (twice the target concentration of use) was achieved during 1882 h at room temperature and the intensity of the two amide bands were similar to those measured after 7 h under MW (not shown).

As a complementary validation, we have tried to provoke the membrane degradation by using extreme conditions that would never be used in industrial applications. Thus, experiments have been made using more or less long contact time between the RO membrane and the concentrated (“pure”) Biocides used at room temperature but without any dilution (remember that the target concentrations were lower than 1 wt%, **Table 2**). With concentrated Biocides B & D, a 3 h contact time was not able to induce RO membrane chemical degradation (**Figure 6**). After 1047 h in Biocide A, the PA layer was evidenced to be slightly degraded as the two amide bands (either I at 1660 cm^{-1} and II at 1541 cm^{-1}) have decreased (**Figure 6**).

At the end of step 1, the MW results suggested that Biocide D could be a better formulation than Biocide B with respect to the membrane degradation.



(a)



(b)

Figure 7 : MW treatment at 170 W (5 reactors simultaneously in the oven) in the case of Biocide B at 6 wt% in water at start - (a) Remaining volume in on single reactor during the overall treatment - (b) ATR-FTIR band evolution, note that membranes were not rinsed with water before spectra registration .

4.2.2 UF membrane (3h at 510 W)

Only the most promising Biocide D have been tested with the UF membrane, aiming at the proposal of a single formulation useful either for RO or UF applications, as already said in introduction.

Figure 8 depicts the ATR-FTIR spectra in the regions where changes were observed. Note that the membranes were carefully rinsed with water before the registration. Consequently the ingredients adsorbed in a reversible way were removed and cannot be evidenced on these spectra contrary to those irreversibly adsorbed.

The only changes evidenced after a careful inspection of the spectra were the decrease of the PVP band (1660 cm^{-1}) and the absorbance increase close to 1030 cm^{-1} , but without appearance of a well-defined new band (see below).

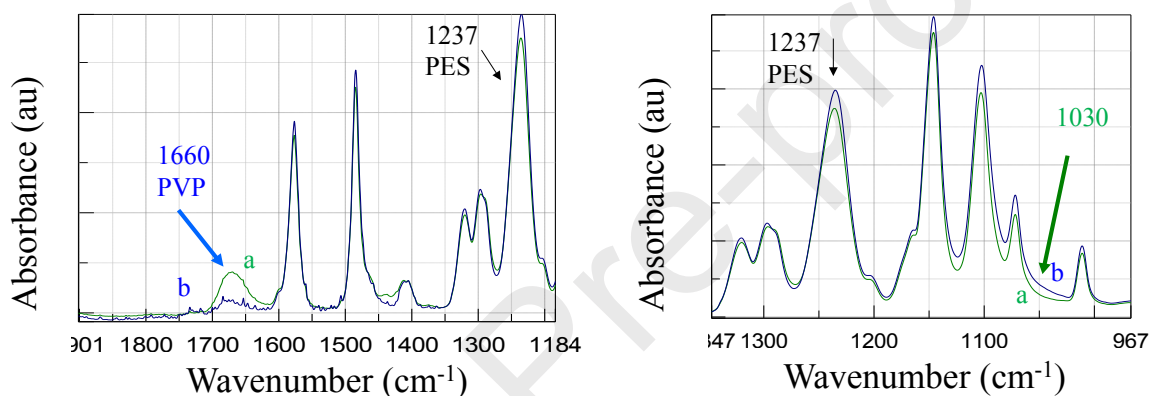


Figure 8: ATR-FTIR spectra of the UF membrane: a (green) before MW and b (blue) after MW (510 W) during 3 h in Biocide D at 4 wt% at start. The membranes were carefully rinsed before the spectra registration and species adsorbed in a reversible way were thus removed.

As the PVP partial disappearance was proved, the first arising question was that of the acceptability of this attack. The same MW treatments were thus repeated with NaOCl either at pH= 8.1 (conditions for strong degradation of PVP according to the literature) and pH= 11.2 (close to the pH of use when disinfection is achieved at industrial scale and provoking less degradation).

Figure 9 shows that PVP removal due to Biocide D (4 wt% = 8 times its concentration of use at start) was close to that obtained with 800 ppm TFC NaOCl at start (4-5 times the concentration of use), regardless of the pH.

These results suggest that Biocide D could be use with the UF membrane with at least the same life time as with NaOCl. This last one being commonly used at industrial scale, the degradation level due to Biocide D could be considered as acceptable.

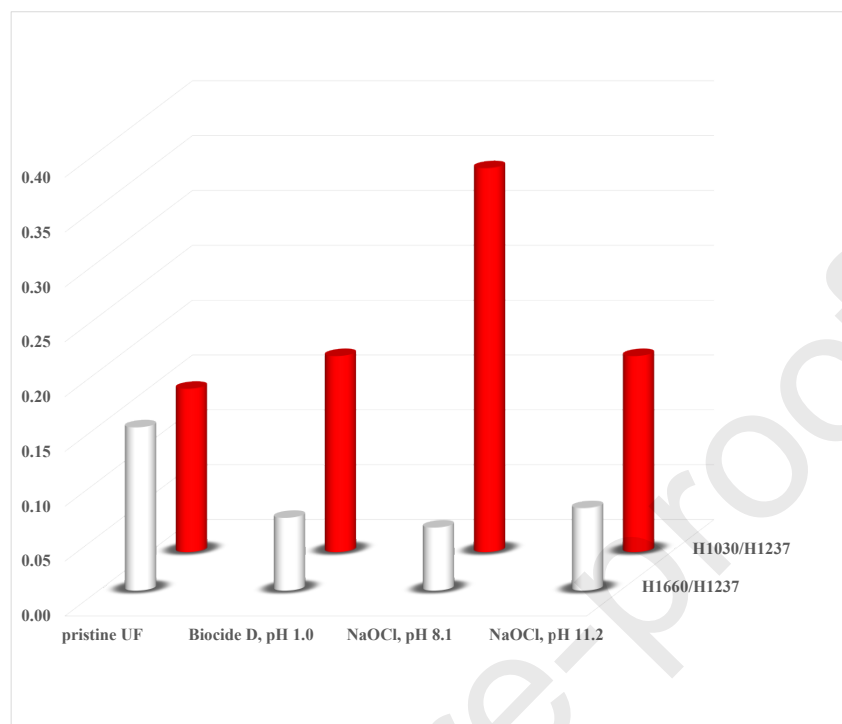


Figure 9: ATR-FTIR ratio of the UF membrane before and after 3 h under MW (510 W) in different solutions at initial concentration equal to x times that of use ($x=8$ for 4 wt% Biocide D, $x=4-5$ for 800 ppm NaOCl). The membranes were carefully rinsed before the spectra registration and species adsorbed in a reversible way were thus removed

The second arising question was related to the absorbance increase in the region close to 1030 cm^{-1} (**Figure 8**, **Figure 9**). Could it be due to methane sulfonic acid adsorption and/or to PES degradation?

When methanesulfonic acid was adsorbed on the RO membrane, a band with a well-defined shape located at 1040 cm^{-1} (SO_3H group in acid form) was evidenced as depicted **Figure 5**. Consequently, in absence of a similar well-defined band on the spectrum of the UF membrane, it can be drawn that this acid was not adsorbed on the membrane (or at concentration below the detection limit). Note that the band evidenced on the not-rinsed RO membrane, regardless of the biocide prototype, has totally disappeared after a careful water rinsing meaning that the methanesulfonic acid was reversibly adsorbed (see spectra in **Appendix 6**, **Appendix 7**, **Appendix 8**). Thus, it can be drawn that if any adsorption of this acid occurred on the UF membrane, it was removed by the water rinsing achieved before the spectrum registration (**Figure 8**).

What about the PES backbone? In the case of an oxidative attack by neutral or alkaline NaOCl solutions, the two resulting products (PES hydroxylation and/or sulfone (SO_2) group evolving into SO_3^- group) were reported to give a well-defined shape band at 1030 cm^{-1} (see **Figure A1-2** in **Appendix 1**). Such band can move toward 1040 cm^{-1} in very acid conditions (protonation of the sulfonate group) but its shape must remain well-defined. **Figure 10** depicts that the origin of the absorbance increase cannot be the same for Biocide D and NaOCl. Consequently it can be drawn that neither hydroxylation nor sulfonation occurred on the UF membrane in Biocide D. This is in good agreement with the non-oxidative character of this biocide.

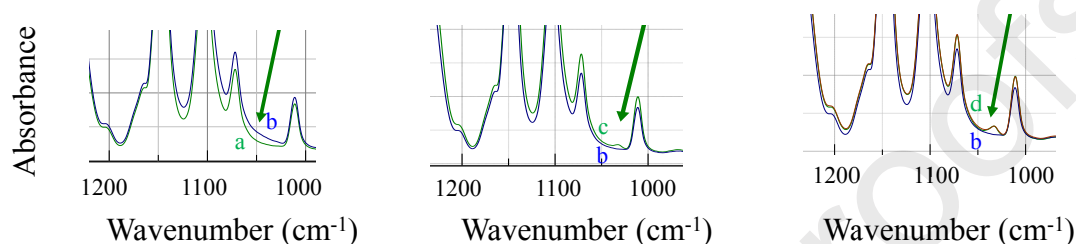


Figure 10: ATR-FTIR spectra of UF membrane before and after 3 h under MW (510 W) in different solutions at initial concentration equal to x times that of use ($x=8$ for 4 wt% Biocide D, $x=4-5$ for 800 ppm NaOCl). The membranes were carefully rinsed before the spectra registration and species adsorbed in a reversible way were removed – (a): pristine membrane – (b): membrane in Biocide D – (c) membrane in NaOCl pH= 11.2 – (d) membrane in NaOCl pH= 8.2.

What was then the origin of the absorbance increase in this region? One important point to underline is the very large and not-well defined shape of the absorbance in this region. What kind of chemical bounds are known to give such very large band in the IR region? This is the typical case of organic compounds having several C-O and C-O-C ether bounds [70]. For the sake of clarity, the reader can see in **Appendix 4** a set of ATR-FTIR spectra of compounds having such bounds and the associated very large bands in the $1000-1100\text{ cm}^{-1}$ region. For the sake of illustration, one of the selected compounds was a non-ionic surfactant (Tween 20) that was not used in the formulation of the different biocide prototypes. Indeed, if such ingredients were adsorbed on the UF membrane, then superimpositions of several very large bands occurred. Consequently, the overall absorbance would be increased in the $1000-1100\text{ cm}^{-1}$ region without evidence of a well-defined band. However, the absorbance at 1030 cm^{-1} would be increased too.

Finally, it was drawn that with Biocide D the origin of the absorbance increase in the $1000-1100\text{ cm}^{-1}$ region was more likely due to adsorption of ingredient(s) than to PES degradation.

4.3 CIP in filtering conditions with flat membrane (step 2)

Even if Biocide D appeared as the most promising formulation for the RO membrane, for the sake of the demonstration, Biocides A, B & D were used during the next step 2.

4.3.1 RO membrane in formulated biocide detergents at twice the target concentration of use

RO was achieved in standard conditions with the flat membranes. The initial permeance to water (L_{p0}) was determined for 14 membranes and varied from 3.5 to 5.1 L.h⁻¹.m⁻².bar⁻¹. These variations highlighted the heterogeneity of the membrane material.

The permeance in each biocide ($L_{p_{biocide}}$, at 1.5 wt% or 1.0 wt%, depending on the target concentration of use) was followed versus time. It required more than 30 min to reach a plateau value in Biocide A whereas the plateau was reached in about 5 min with the two other biocides (**Figures A9-1 to A9-3 in Appendix 9**). **Table 5** shows the significant drop of the permeance at the plateau values.

After a careful rinsing with water, the membrane permeance in water ($L_{p_{after\ rinsing}}$) increased differently for the 3 formulated biocide solutions. The hydraulic cleanliness of the membrane (at least 90% of water flux recovery) was reached for Biocide B & D. However, the flux recovery was far from being sufficient with Biocide A. It was drawn that this last biocide detergent has to be excluded because of both the high flux decrease during RO and the insufficient rinsing ability.

As the only difference between Biocides A & B was the surfactant 1 (**Table 2**), the origin of difference in flux behaviour was attributed to this ingredient.

Table 5 : Permeance drop at plateau value during RO at 50°C of the 3 formulated biocide detergents with flat virgin membranes at 1.5 wt% (Biocide A & B) or 1 wt% (Biocide D)

| Biocide | $L_{p_{biocide}}/L_{p0}$ (%) | $L_{p_{after\ rinsing}}/L_{p0}$ (%) | Number of tested flat membranes |
|-----------|---------------------------------|--|---------------------------------|
| Biocide A | 13 ± 1 | 52 ± 3 | 2 |
| Biocide B | 51 ± 5 | 88 ± 8 | 7 |
| Biocide D | 57 ± 4 | 91 ± 7 | 5 |

After rinsing, regardless of the biocide, one band at 1735 cm⁻¹ (octanoic acid) was systematically evidenced on all registered spectra (**Figures A10-1 to A10-4 in Appendix 10**).

Figure 12 depicts the evolution of the relative intensity of the band at 1735 cm⁻¹. This highlights the lower adsorption of octanoic acid of Biocide D when compared to Biocide B; this lower adsorption can be related with the higher flux recovery.

ATR-FTIR failed at evidencing any explanation dealing with the Biocide A flux recovery in close relationship with the octanoic acid adsorption. Indeed, this last one appeared in between that of Biocides B & D. This result was not in contradiction with the major impact of surfactant 1 on the flux that was suggested above for Biocide A.

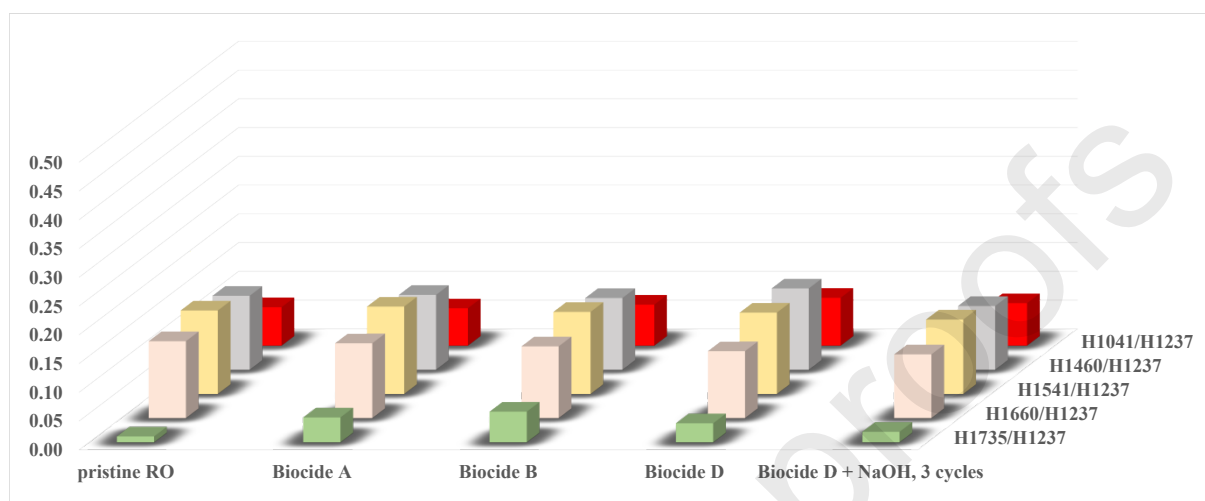


Figure 12: ATR-FTIR of RO membrane: evolution of H_w/H_{1237}^{PSf} ratio for selected bands located at wavenumber w before and after 70 min RO of biocides with 1.5 wt% (A & B) or 1 wt% (D) and water rinsing – and after 3 cycles of 60 min in Biocide D + 60 min NaOH pH=11.0 and water inter- and final rinsing with water.

As some octanoic acid remained on the RO membrane after water rinsing, the arising question was: could accumulation occurred over time? Aiming at increasing the octanoic acid removal, a complementary alkaline cleaning step was achieved.

The reason of this choice was related to the octanoic acid form with respect to the pH. The biocide treatment being in acid conditions, the octanoic acid was in its molecular form ($\text{R-CO}_2\text{H}$), corresponding also to its more hydrophobic one. By increasing the pH, the octanoic acid turned to its more hydrophilic salt form (R-CO_2^- , Na^+). The salt was expected to have less affinity toward the organic polymer membrane and to be more soluble in water.

3 cycles of alternative cleaning with Biocide D (1h) and NaOH pH=11.0 (1h) were thus achieved (**Figure 13**).

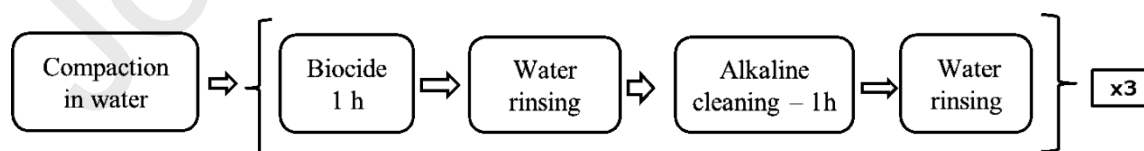


Figure 13: Cycles of Biocide D and NaOH at pH= 11.0

The water flux of the virgin membrane was fully recovered, evidencing the efficiency of the cascade. The ATR-FTIR of the rinsed membrane shows that the octanoic acid adsorption was less than the adsorption after only one step with Biocide D (**Figure 12**).

As a conclusion for the second step, Biocide D was the best solution to privilege. When considering the MW study achieved with Biocide B&D this choice was also in good accordance with that issued from the step 1.

Moreover, the cascade of Biocide D + alkaline cleaning was proved to improve the octanoic acid removal, preventing from long-term accumulation. Consequently, Biocide D was the only one tested in step 3.

4.3.2 UF membrane

Filtration was only achieved with Biocide D, because of the promising performances obtained with the RO membrane.

Table 6 depicts the huge drop of the UF membrane permeance, moreover reached in about 5 min. The flux recovery after water rinsing was 50% and even after NaOH complementary cleaning the flux recovery remained insufficient.

Complementary filtrations were achieved with less concentrated Biocide D, 0.5 wt% being the target concentration of use. The permeance drop remained very high, but the rinsing was easier and the alkaline step allowed to recover the initial permeance (**Table 6**).

Table 6: Permeance drop at plateau value during UF at 50°C of Biocide D with flat virgin membranes and after alkaline cleaning with NaOH

| concentration wt% | $L_{p_{biocide}}/L_{p_0}$ (%) | $L_{p_{after\ rinsing}}/L_{p_0}$ (%) | NaOH pH | $L_{p_{post\ NaOH,\ after\ rinsing}}/L_{p_0}$ (%) |
|--|-------------------------------|---|---------|---|
| Biocide D | | | | |
| 1.0 | 5 ± 2 | 50 ± 7 | 9.0 | 80 ± 4 |
| | | | 11.5 | 88 ± 5 |
| 0.7 | 13 ± 1 | 88 ± 5 | 11.5 | 99 ± 5 |
| 0.5 | 10 ± 1 | 92 ± 5 | 11.5 | 99 ± 5 |
| “Biocide D Matrix” without octanoic acid | | | | |
| 1.0 | 85 ± 4 | 78 ± 4 | 11.5 | 79 ± 4 |

Finally, a special prototype was prepared, hereafter called “Biocide D matrix”, the composition of which being that of Biocide D in which only octanoic acid was removed. Permeance during filtration of the matrix at 1 wt% (all ingredients at the same concentration as in 1 wt% Biocide D) was quite good (85% of the initial permeance). It was concluded that the octanoic acid was the main responsible of the permeance drop in Biocide D.

However, the alkaline following step had no impact on the flux recovery, reaching the same value as in Biocide D at the same concentration. This result suggested the irreversible adsorption of one of the matrix ingredients.

Aiming at its identification ATR-FTIR spectra were registered (**Figure 14**) and the band evolution calculated (**Figure 15**). After the overall cascade of Biocide D + NaOH, only the octanoic acid was evidenced from these spectra and ATR-FTIR failed at evidencing any other residual adsorbed ingredient, suggesting thus that the additional adsorbed ingredient was below its detection limit.

The alkaline cleaning allowed to decrease the octanoic acid on the membrane, however part of it remained irreversibly adsorbed. This result highlighted the more hydrophobic character of the UF membrane when compared to the RO one. The octanoic acid (and the probably adsorbed but not identified ingredient of the acid matrix) could perhaps be better removed by using a formulated alkaline detergent instead of NaOH, with respect to the possible efficiency of surfactant in such mixture, however this was not tested.

Finally, and quite surprisingly, Biocide D that exhibited nice performances with the RO membrane appeared not suitable for the UF one.

This conclusion was mainly drawn with respect to the flux and not to the membrane stability that was good enough. Permeances during the biocide UF were very low and even if rinsability was correct at the target concentration of use (0.5 wt%) or even slightly above (0.7 wt%) it failed down when increasing the concentration. Finally, to date, the use at industrial scale appeared too risky. So, reformulation has to be made (out of the scope of this study) and step 3 was not achieved.

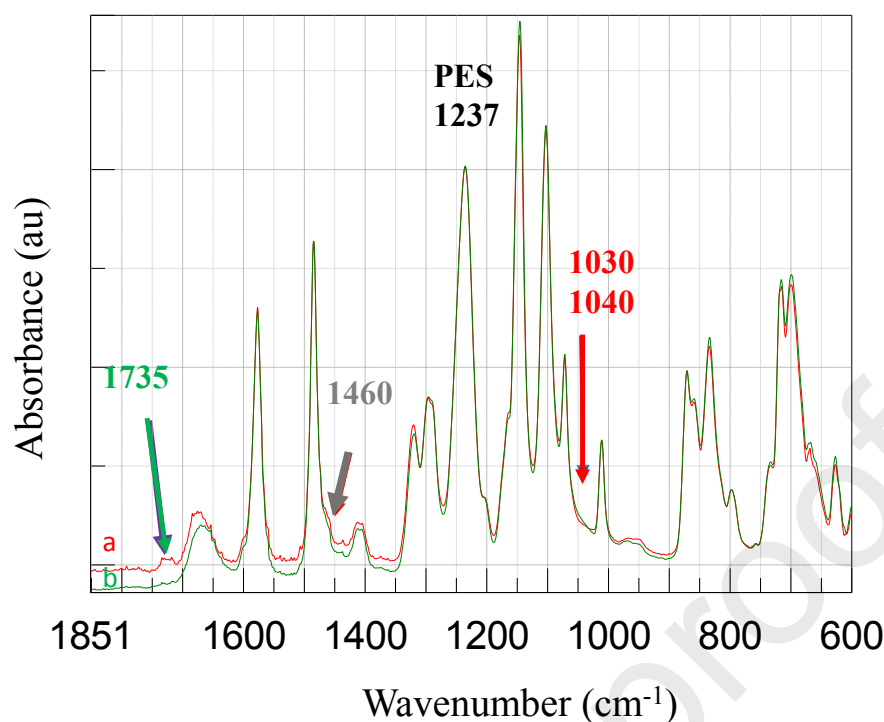


Figure 14: ATR-FTIR spectra of UF flat membrane (b, green) before and (a, red) after cleaning 60 min in Biocide D + 60 min NaOH pH 11.5 + water inter-rinsing - Note that a final rinsing with water was achieved in both cases.

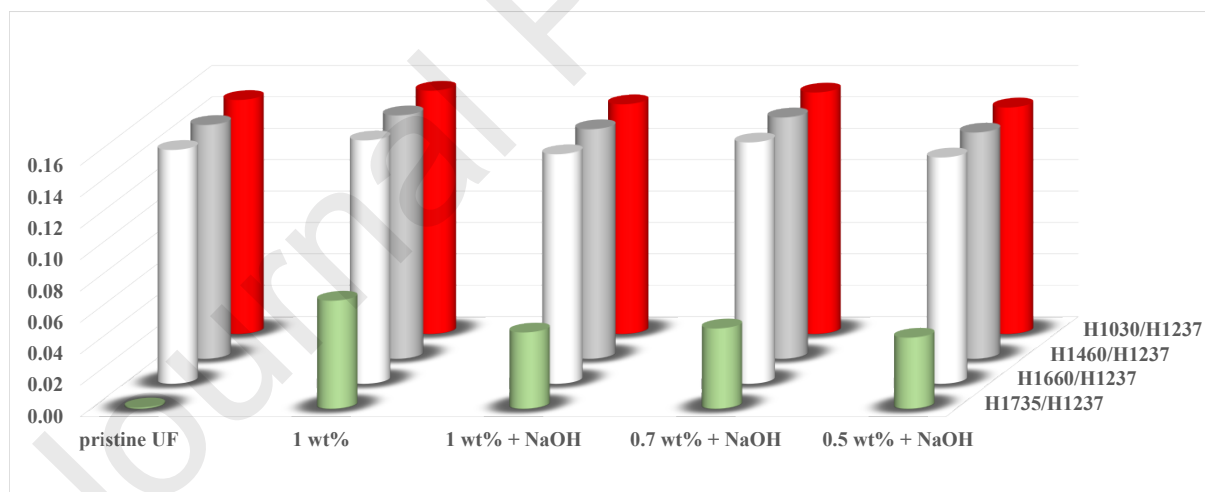


Figure 15: ATR-FTIR of UF membrane: evolution of H_w / H_{123}^{PES} ratio for selected bands located at wavenumber w before and after 60 min filtration of Biocide D at various concentration (wt%) followed by 60 min of alkaline cleaning with NaOH at pH= 11.5 and inter rinsing with water. Note that a final rinsing with water was achieved in all cases.

4.4 Long-time tests with spiral wound RO membrane (step 3)

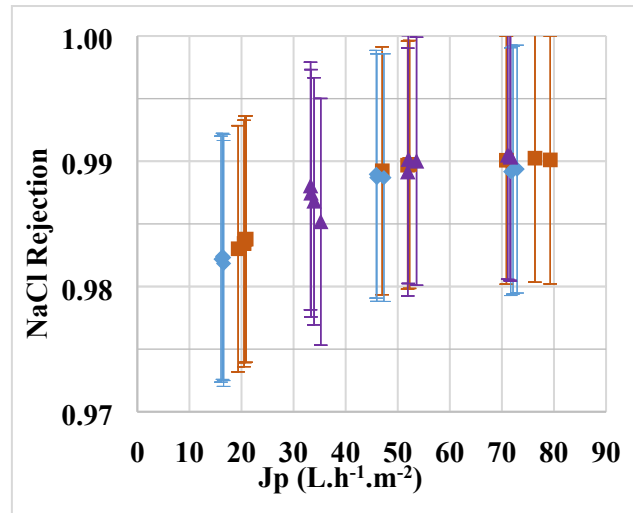
Continuous operations are the most relevant experiments for the final validation. The RO spiral membrane has been tested in filtration conditions at 50°C for 50 h in Biocide D at 1 wt% (twice the target concentration of use). Alkaline cleaning has been achieved at start and after 12, 25, 37 and 50 h to *a priori* prevent a possible accumulation of octanoic acid and of other unidentified ingredient(s), if any, on the membrane.

It was shown from these long-term experiments that a formulated alkaline solution can be preferred to single NaOH of similar pH. In such conditions, no significant evolution of the permeance in Biocide D as well as after water rinsing was evidenced during the overall validation step.

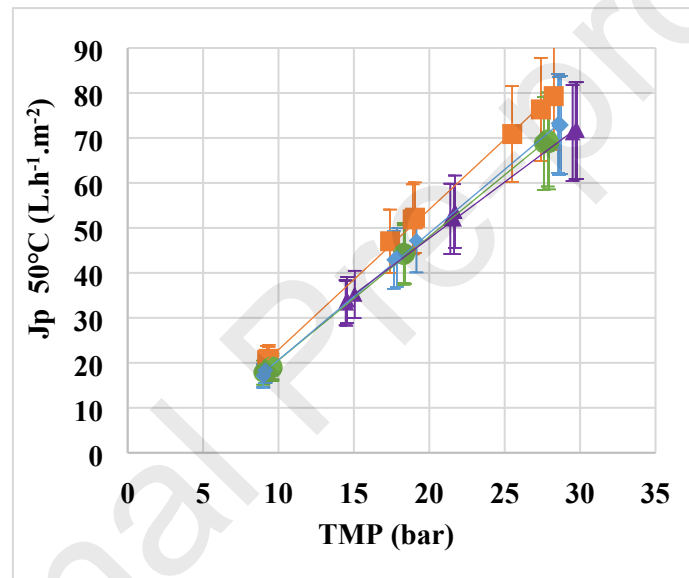
RO of NaCl set at 2 g.L⁻¹ was achieved at start to have a reference and after 25 h and 50 h in Biocide D (**Figure 16**).

In NaCl, flux variation remained lower than 15% when comparing the pristine membrane and that having filtered Biocide D during 50 h. Moreover, rejection of NaCl was constant all over the procedure.

This final test confirmed the conclusions drawn from steps 1& 2, validating the global approach of **Table 1**. More particularly, Biocide D was evidenced to be suitable for polyamide RO membrane and is now commercialized as DEPTACID WCM®.



(a)



(b)

Figure 16. Filtration of 2 g.L⁻¹ NaCl at 50°C by the spiral RO membrane after long time filtration in Biocide D (1 wt%). (a) NaCl rejection - (b) Permeate flux (Jp), caption and straight lines equations: 0h Biocide ■ $y = 3.1183x - 8.2667$, $R^2 = 0.998$ – 1h Biocide ● $y = 2.7447x - 6.8359$, $R^2 = 0.9992$ – 25 h Biocide : ◆ $y = 2.8235x - 7.609$, $R^2 = 0.9994$ – 50h Biocide: ▲ $y = 2.5x - 2.3039$, $R^2 = 0.9981$ –.

5 Conclusion

The original methodology has been applied to validate or invalidate several formulated biocide detergents for RO polyamide (and by extension NF polyamide) and UF PES/PVP membranes.

An increase of the biocides' concentration compared to the target of use was combined to MW activation to try to accelerate polymer membrane degradation that could be due to some ingredients of the biocide prototypes. These treatments were achieved aiming at evidencing long-term possible degradation by using a short-time experiment. For instance, with the best candidate (Biocide D), no degradation was highlighted for the RO membrane after 7 h at 170 W whereas some PVP attack was evidenced after 3 h at 510 W for the UF PES/PVP membrane. By the mean of this approach, for a given membrane, long-term ageing can be compared in several solutions and particularly those already used at industrial scale in order to evidence if improvements can be expected by using new formulations. ATR-FTIR proved once again to be an efficient tool available in routine to achieve the main part of the study.

Besides information on degradation/integrity of the membranes, the methodology highlighted the occurrence of both reversible and irreversible fouling (partly due to adsorption) involving certain ingredients of the formulated biocide prototypes. Water flux recovery sometimes suggested residual adsorption of ingredients that were not always identified by ATR-FTIR. Such results mean (1) that the amount was sometimes very low and probably lower than the detection limit and (2) that the combination of material analysis and flux was required to go ahead. However, thanks to ATR-FTIR some residual adsorbed ingredients were also identified allowing to find the way for their removal (as the alkaline cleaning to remove octanoic acid from RO membrane for instance).

One surprising result was that a non-oxidative formulated biocide can be validated for a RO membrane but not for a UF one, contrary to our initial *a priori* that were only based on the relative stability of the polymers. Indeed, a biocide can appear as not suitable for filtration purpose (low flux, rinsing difficulty) even if the membrane stability is good.

Acknowledgments

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See Supplementary/ Appendix in the complementary associated file

Nomenclature

| | |
|----------|---|
| ATR-FTIR | Infrarouge à transformée de Fourier – Réflectance totale atténuée |
| H_w | ATR-FTIR absorbance at $w \text{ cm}^{-1}$ |
| J_p | Permeate flux ($\text{L.h}^{-1}.\text{m}^{-2}$) at 50°C |
| L_p | Permeance ($\text{L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$) at 50°C |
| PA | Polyamide |
| PES | Polyethersulfone |
| PSf | Polysulfone |
| PVP | Polyvinylpyrrolidone |
| R_m | Pristine membrane hydraulic resistance |
| TFC | Total free chlorine (ppm) |
| TMP | Transmembrane pressure (bar) |
| VRR | Volume reduction ratio (VRR= 1 in batch mode) |

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Conflicts of interest:

Nothing to declare

Highlights :

- New methodology to study long term chemical degradation of a polymer membrane
- Combination of micro-wave activation, filtration and ATR-FTIR is relevant
- Application to long term impact of a non oxidative biocide on polymer membranes
- octanoic acid use is suitable for RO membranes combined with alkaline cleaning
- biocide suitable for RO is not suitable for UF mainly because of fouling