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Chemical cleaning/disinfection and ageing of organic UF membranes: A review

C. Regula^{a,b}, E. Carretier^a, Y. Wyart^a, G. Gésan-Guiziou^{c,d}, A. Vincent^b, D. Boudot^b, P. Moulin^{a,*}

^aAix Marseille Université, CNRS, Centrale Marseille, M2P2 UMR 7340, Equipe Procédés Membranaires (EPM), Europôle de l'Arbois, Pavillon Laennec, 13545 Aix en Provence, France

^bECOLAB, 8 rue Rouget de Lisle, 92442 Issy les Moulineaux, France

^cINRA, UMR1253 Science et Technologie du Lait et de l'Œuf, 35000 Rennes, France

^dAGROCAMPUS OUEST, UMR1253 Science et Technologie du Lait et de l'Œuf, 35000 Rennes, France

Membrane separation processes have become a basic unit operation for process design and product development. These processes are used in a variety of separation and concentration steps, but in all cases, the membranes must be cleaned regularly to remove both organic and inorganic material deposited on the surface and/or into the membrane bulk. Cleaning/ disinfection is a vital step in maintaining the permeability and selectivity of the membrane in order to get the plant to its original capacity, to minimize risks of bacteriological contamination, and to make acceptable products. For this purpose, a large number of chemical cleaning/disinfection agents are commercially available. In general, these cleaning/disinfection agents have to improve the membrane flux to a certain extent. However, they can also cause irreversible damages in membrane properties and performances over the long term. Until now, there is considerably less literature dedicated to membrane ageing than to cleaning/disinfection. The knowledge in cleaning/disinfection efficiency has recently been improved. But in order to develop optimized cleaning/disinfection protocols there still remains a challenge to better understand membrane ageing. In order to compensate for the lack of correlated cleaning/disinfection and ageing data from the literature, this paper investigates cleaning/disinfection efficiencies and ageing damages of organic ultrafiltration membranes. The final aim is to provide less detrimental cleaning/disinfection procedures and to propose some guidelines which should have been taken into consideration in terms of membrane ageing studies. To carry out this study, this article will detail the background of cleaning/disinfection and ageing membrane topics in a first introductory part. In a second part, key factors and endpoints of cleaning/disinfection and ageing membranes will be discussed deeply: the membrane role and the cleaning parameters roles, such as water quality, storing conditions, cleaning/disinfection/aging agents/conditions/protocols. The third and last part will be developed the parameters, methods and ways of characterization at our disposal and commonly used to develop and implement membrane cleaning and/or ageing studies.

1. Introduction

The food industry and the drinking water industry represent a significant part of the turnover of the membrane manufacturing industry worldwide (Daufin and Aimar, 2004). Among the food processing, 45% of the main applications of membrane operations are used in the dairy industry (whey protein concentration, milk protein standardization) followed by beverages (wine, beer, fruit juices...) and egg products. In this field, the ultrafiltration (UF) is one of the most important membrane applications (Paugam et al., 2010) and its applications are manifold. The dairy industry can be given as example: advanced membrane processes allow the recovery and purification of valuable milk constituents and have become an integral part of an increasing number of dairy processes (Rosenberg, 1995; Maubois et Ollivier, 1997; Brans et al., 2004; Aimar and Daufin, 2004; Gésan-Guiziou, 2007). Ultrafiltration is largely used in the dairy sector to concentrate, fractionate and purify dairy proteins with high functional, biological and nutritional properties, and can be seen as a good alternative to chromatographic techniques. Ultrafiltration is also largely used in the water treatment sector.

Due to the high selectivity of UF membrane, UF becomes economically attractive for water purification during the last fifteen years. In these two industrial sectors, organic membranes are the most used membranes. 80–90% of the membrane area installed worldwide are organic membranes despite its limited chemical and heat resistances, and reduced lifetime (from 2 to 3 years). Their prices from 38 to 380 €m⁻² are far below those of mineral membranes (Maurel, 2008).

Regardless of the industrial fields in which organic UF membranes are applied fouling remains a persistent problem as well as membrane performance recovery, especially in the case of membranes fouled with protein solution (Gao et al., 2011; Petrus et al., 2008). Flux decline caused by the irreversible adsorption of foulants is the major obstacle to a wider implementation of UF. Flux decline leads to an increase in membrane cleaning/disinfection costs, process down time and can also result in membrane damages due to the frequency and the harshness of cleaning/disinfection conditions (Maartens et al., 2002). As a consequence reduction of fouling and cleaning/disinfection of fouled membrane have been approached in various ways since 1980: these studies include optimization of filtering conditions, production of membranes

with reduced adsorptive conditions, backflushing, cleaning and disinfection using harsh chemical agents, which result in high cleaning/disinfection costs and industrial pollution.

Looking at the work published since the eighties, one can note that there is considerably less literature dedicated to cleaning, disinfection or ageing than to fouling (Fig. 1).

As membrane replacement generally accounts for 25–40% of the total membrane plant cost (Lawrence et al., 1998) and, as cleaning/disinfection procedures represent from 15 to 20% of the operating costs (Blanpain-Avet et al., 2004), fouling, cleaning and ageing are at the heart of the industrial membrane application issues. For water applications, these percentages are not true since chemical cleaning is only operated few times a month or even a year as said by Porcelli and Judd (2010a,b): « The CIP cleaning frequency ranged from 0.2 to 50 per year with a median of 4 per year ». Cleaning and its optimization (cleaning time, cleaning parameters, cleaning costs...) has been studied more deeply since the 1990s with the aim of reducing operative costs and maintain membrane performances. Some membrane cleaning reviews have been recently published: for the dairy industry applications (D'Souza and Mawson (2005)) and for the potable water industry applications (Porcelli and Judd, 2010a; Liu et al., 2000). It was from mid-1990s that studies dedicated to membrane ageing began to be published. This is clearly visible on Fig. 1 where studies concerning the membrane ageing increased by a factor 10 from 2000 to 2010. The major part of those scientific works tried to develop a lifetime model and define minimum costs of membrane cleaning taking into account the economic lifetime of membranes (Zondervan et al., 2008; Zondervan and Roffel, 2008a,b). As far as we know, few publications have been realized until now on the combination of chemical cleaning and ageing of polymeric ultrafiltration membranes involved by cleaning. This point needs a better understanding in order to make possible a wider implementation of UF on industrial plants and a greater diversity of possible industrial applications.

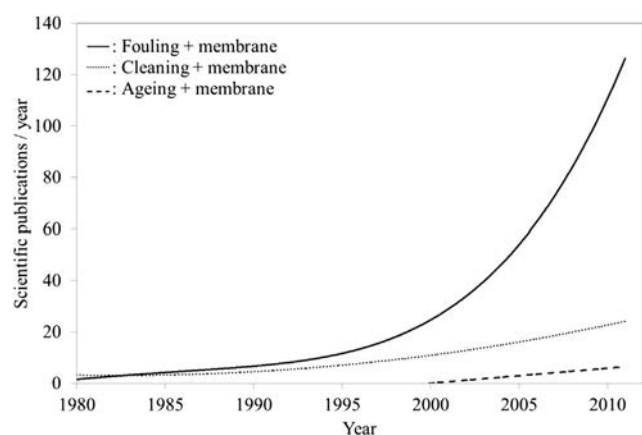


Fig. 1 – Literature dedicated to membrane fouling, membrane cleaning/disinfection and membrane ageing from 1980 until now [Number of publications in journals satisfying the research criteria “Membrane and fouling or cleaning or ageing” in the title. Data were taken from www.sciencedirect.com in May 2013].

Before we go any further, definitions of the main terms are required in order to well establish and set the framework of this study. Membrane cleaning/disinfection is the action of removing substances and matter that are not an integral part of the membrane surface or membrane bulk. These substances are generally termed as foulants (Porcelli and Judd, 2010a). Membrane chemical cleaning effectiveness depends on the cleaning/disinfection agent, the characteristics of the membrane and the cleaning/disinfection parameters. The processes by which fouled deposit is cleaned are even more poorly understood than fouling (Blanpain-Avet et al., 2004; Field et al., 2008) and many of the protocols used by the food industry have no theoretical justifications (Changani et al., 1997). Cleaning can be conducted either by using chemicals ('chemical cleaning') or mechanical forces ('physical cleaning') (Lee et al., 2001). Physical cleaning methods depend on mechanical forces to dislodge and remove foulants from the membrane surface. Physical methods include hydraulic cleaning (such as back pulse, back flush systems) (Liang et al., 2008), ultrasonic vibration (Muthukumaran et al., 2004; Jin et al., 2008; Zhang and Liu, 2003; Kobayashi et al., 1999, Chai et al., 1998, 1999, Masselin et al., 2001), air sparge and CO₂ back permeation (Ebrahim, 1994). But in some cases (protein adsorption on UF membranes for instance), physical cleanings are unavailable and a chemical cleaning/disinfection process is necessary. That is why chemical cleaning/disinfection have been widely studied. In some cases, the use of physical methods associated with chemical cleaning, such as ultrasonic vibration coupled with ethylenediamine tetraacetic acid (EDTA) (Maskooki et al., 2010), NaOH, NaOCl or HNO₃ (Lim and Bai, 2003) can offer new cleaning/disinfection prospects. Indeed, flux recovery achieved by combined physical and chemical cleaning/disinfection is better than the ones achieved by chemical cleaning/disinfection alone or sonication alone. Flux recovery is one of the tools we have at our disposal to evaluate membrane cleanliness. However, in a more general and theoretical way, membrane cleaning/disinfection effectiveness is defined according to different parameters which meet the cleaning requirements of three cleanliness scales: physical–chemical, microbiological and hydraulic cleanliness (Rabiller-Baudry et al., 2009).

- **Physical–chemical cleanliness** is based on the detection of molecules on the membrane surface. It could be characterized by methods such as Attenuated Total Reflectance-Fourier Transform Infrared spectroscopy (ATR-FTIR) or streaming potential (SP) for instance. These methods can give access to other/further information than permeability measurement but they are destructive methods and cannot be carried out for industrial applications.
- **Microbiological cleanliness** is based on the detection of microorganisms on the membrane surface. The methods used are destructive, that is why this cleanliness parameter is generally determined by analyzing the microorganisms in the effluent itself.
- **Hydraulic cleanliness** is based on the measurement of permeability after cleaning/disinfection compared to the one before cleaning/disinfection. The drawback is that permeability is a function of the components, such as surfactants of the cleaning/disinfection solution, which

can modify the surface properties and, as a consequence, the value of permeability even if the membrane cleanliness has not been achieved (Delaunay, 2007; Paugam et al., 2006; Rabiller-Baudry et al., 2006b, 2008). Nevertheless, this method is widely applied in practice because of its simplicity.

No established definition of membrane ageing can be found in the literature. In most cases, membrane ageing is reduced to polymer ageing and methods developed are based on the evaluation of polymer characterization. Membrane ageing must not be confused with membrane integrity. Membrane integrity is well-defined (Guo et al., 2010a) and has been the subject of several studies involving integrity tests with gold nanoparticles (Gitis et al., 2006a), fluorescent-dye-labeled MS2 bacteriophages (Gitis et al., 2006a,b) or magnetic nanoparticles (Guo et al., 2010b, 2011). If the level of membrane integrity can be determined, it is not possible to determine the ageing of a membrane quantitatively with no reference to the initial state and properties of the membrane. Consequently, the ageing study is a comparative study.

Restricting membrane ageing to polymer ageing only can be questioned. Indeed, the manufacturers guarantee the compatibility between detergent and polymer but in certain configurations the detergent comes also into contact with the often sensitive glue and the spacer materials (Bégoïn et al., 2006b). Then the limitations of membrane/module ageing depend on the materials used for the build-up of the whole module and not only on the chosen membrane (Krack, 1995). Therefore future works on membrane ageing would have to take into account the ageing of all the elements constituting the modules and not only the membrane constituting polymer. Based on these observations, it can be concluded that two definitions of ageing have to be taken into account in the field of membrane filtration: membrane ageing and module ageing.

Membrane ageing corresponds to the ageing of the materials which constitute the membrane. It depends on the operating conditions of both the production and cleaning/disinfection steps and results in a decrease of productivity, an increase in backwash or cleaning/disinfection step frequency, a modification of the physical-chemical properties of the membrane (elasticity/plasticity of the membrane, membrane surface zeta potential...), an alteration of the membrane selectivity and a loss of integrity.

The definition of module ageing takes up the definition of membrane ageing but the integrity of all the elements constituting the module, especially the potting zone have to be taken into account.

The purpose of this article is to assess the effects of the chemical cleaning/disinfection solutions on membrane ageing considering that membrane cleaning and ageing are correlated and cannot be dissociated, and to propose *in fine* the most significant and representative methodology of ageing study. It will thus be possible to determine which conditions must absolutely be avoided in the cleaning/disinfection procedures and so to optimize cleaning/disinfection performances.

Therefore, the bibliographical work presented in this article details the research works carried out until now about ultrafiltration membrane cleaning/disinfection and ageing.

More precisely, the article develops cleaning/disinfection/ageing studies realized on polymeric ultrafiltration membranes mainly used in dairy and drinking water industries. Thus, combining the collected information will make it possible to determine among the cleaning procedures studied until now, which ones would be apparently the less detrimental and consequently the most cost-effective. For the different cleaning/disinfection agents commonly used, the review presents:

- in a synthetic way the results from the literature in terms of cleaning/disinfection performance,
- in a detailed way the results from the literature in terms of membrane ageing.

2. Membrane cleaning/disinfection and ageing: key factors and endpoints

Because of the lack of understanding of the mechanisms of cleaning and disinfection, various cleaning protocols are proposed both in the literature and at industrial scale. It clearly appears that the cleaning/disinfection conditions are not optimized and one can consider that there are as many cleaning/disinfection protocols as industrial applications/type of membranes combinations. Despite this complexity, it is largely known that several factors may affect the cleaning performances and membrane ageing.

2.1. Impact of membrane characteristics on cleaning/disinfection and ageing

2.1.1. Membrane module geometry

If as previously demonstrated, fouling is heterogeneous within a membrane module (Bégoïn et al., 2006a,b), so will be the cleaning/disinfection. Indeed, the membrane module geometry affects its cleanability.

The comparisons between the different types of membrane configurations (Aimar and Daufin, 2004) underline that cleaning/disinfection of spiral-wound and hollow fiber modules are much more difficult than cleaning/disinfection of tubular and flat-sheet membranes (Table 1). These modules have the highest fouling trends and the lowest cleanabilities. Paradoxically, they are the most common used geometrical configurations for both the milk and water filtrations because of their low investment and energetic costs (Table 1).

If, as we have just seen, fouling and cleaning/disinfection are heterogeneous from one configuration to the other, we can assume that it also applies to ageing (Gaudichet-Maurin and Thominet, 2006). Thus, ageing of spiral-wound and hollow fiber modules has the greatest economic impact since the whole modules must be renewed when required. The economic balance of membrane processes therefore depends amongst others on the nature of the membrane modules used. The choice of spiral-wound or hollow fiber modules is no longer interesting if the cleaning/disinfection procedures are (i) neither effective: cleanliness is not reached and the initial performances of the membrane has not been recovered, (ii)

Table 1 – Comparing performances of the different membrane module geometries.

	Tubular	Flat	Spiral-wound	Hollow fibers
Investment costs (US\$.m ⁻² , 2000)	50–200	50–200	5–100	5–20
Energetic costs	High	Moderate	Low	Low
Fouling	Low	Low	Moderate	High
Cleaning	Excellent	Good	Moderate	Moderate
Membrane renewing	Tube per tube	Membrane per membrane	Whole module	Whole module
Specific surface area (m ² g ⁻¹)	–	7.5 ± 1.5	–	26.3 ± 0.8

Gaudichet-Maurin, 2005; Desclaux and Remigy, 2007; Maurel, 2008.

nor correctly controlled: ageing, membrane alterations and increase in their renewing. In the case of a constant pressure inside the hollow fibers, Cano et al. (2013) showed that during inside-out filtration for the three industrial tested module configurations and even for unrealistic conditions of filtration (for example inlet pressure of 2 bar), hollow fibers work in a homogeneous way. However, in the case of the backwash/cleaning, a greater heterogeneity (more than 10%) may appear. Within this economic and industrial context, it seems then interesting to specifically study the ageing of organic membrane presenting both spiral-wound and hollow fiber geometrical configurations.

2.1.2. Polymeric membrane material

Because of its specific chemical, heat and mechanical resistances the polymer of the membrane determines the conditions applied during the cleaning/disinfection procedures (Krack, 1995):

- **the chemical resistance** is linked to the nature of the fluid processed as well as to cleanings performed to fight against fouling and/or disinfection of plants. The aggressive cleaning/disinfection solutions and the cleaning/disinfection frequency condition the membrane lifetime.
- **the heat resistance** of materials imposes the temperature range of use.
- **the mechanical resistance** depends on the material but also on the membrane structure and geometry.

Different membrane polymers can be used depending on membrane processes (microfiltration, ultrafiltration, nanofiltration or reverse osmosis). The main membrane polymers and their specific ranges of applied pH and temperature are summarized in Table 2 (Desclaux and Remigy, 2007).

Table 2 clearly shows that membrane polymer rules the choice for the cleaning/disinfection procedures. Two examples may be given to illustrate attention to these concerns:

- Even if polyethersulfone (PES) or polysulfone (PSf) membranes are the most chemically stable (pH and temperature range, resistance to oxidation (Rabiller-Baudry et al., 2012)), degradations by chlorine exist even if they are much slower than in the case of polyamides (Gabelich et al., 2005; Ang et al., 2006; Kwon and Leckie, 2006a,b; Kang et al., 2007; Anthony et al., 2010; Etori et al., 2011; Maugin et al., 2012; Valentino et al., 2012).
- Concerning polyvinylidene fluoride (PVDF) membranes, an instability towards sodium hydroxide is widely observed (Ross et al., 2000; Momtaz et al., 2005; Zhang et al., 2006; Hashim et al., 2011; Liu et al., 2011).

Note that the things we have to consider is that if a membrane is named by the active layer polymer, the membrane material is very seldom constituted of a single polymer. Additives are often included, hydrophilic as well as blowing agents. Even if they are present in small quantities, they can have a significant role in the intrinsic and extrinsic membrane properties. They are used particularly to strengthen hollow fiber membranes mechanically. A degradation of additives could, in this case, lead to a drastic drop of the fiber tenacity up to breaking (Gaudichet-Maurin, 2005). In that context, the present review will not only focus on membrane ageing but also on what the various polymers constituting the membrane become during the membrane life.

2.2. Impact of cleaning/disinfection parameters on cleaning/disinfection and membrane ageing

2.2.1. Water quality

Before selecting cleaning/disinfection agents and cleaning/disinfection conditions, arises the question of the water to use to implement regeneration procedures. This water is used to rinse, whether it is a pre-rinse, inter-rinse or final rinse, or for the preparation of cleaning/disinfection solutions. The quality of the water used can therefore have an influence on the

Table 2 – Most commonly used polymer for ultrafiltration membranes and the advised using conditions of temperature and pH.

Material	Abbreviation	Desclaux and Remigy (2007)		Ecolab Snc	
		Maximal temperature	pH	Maximal temperature	pH
Cellulose Acetate	CA	35 °C	3–8	40 °C	4–9
Polyacrylonitrile	PAN	–	–	50 °C	2/3–10/12
Polyamide	PA	50 °C	3–11	50 °C	3–11/12
Polysulfone, polyethersulfone	PSf, PES	80 °C	2–12	75 °C	1–13
Polyvinylidene fluoride	PVDF	–	–	55 °C	2–12

performances of the cleaning/disinfection procedures and potentially have an impact on the membrane ageing. For example, Chen et al. (2003) considered water as a parameter to be taken into account in the statistical study carried out for the optimization of the membrane cleaning/disinfection.

In food applications manufacturers often use water from the supply network or borehole water previously treated and filtered (0.2 µm–1 µm) in order to limit membrane fouling. According to the geographical location of the industrial sites and the quality of the water network, reverse osmosis, ultra-filtered or even softened water may be preferred to water withdrawn from the supply network or to borehole water. According to Rabiller-Baudry et al. (2012), a 1 µm filtration treatment and an extensive demineralization by ion exchange or a reverse osmosis treatment are better than the other water sources used, to (i) reduce the mineral content (Fe³⁺, Al³⁺) of water; the minerals, residues from the treatment of classical production of drinking water, accumulate on membranes with time leading to possible membrane fouling. Silicates, for instance are compounds precipitating on and in the membranes (Bégoïn, 2004); (ii) avoid safety over-dosage of minerals in some commercial formulations and compensate for the hardness of water. Table 3 details commonly accepted water quality guide values for membrane cleaning/disinfection procedures.

The water used on-site is generally softened water and its quality is not always well controlled (Ecolab-Snc, 2013). The water hardness (expressed in hydrotimetric degrees, TH or French degrees) is generally the only parameter measured and it may vary from 5 to 12 French degrees for softened water. The fouling index is also commonly used as a criterion of water quality.

An important parameter of water quality to take into account is the ionic strength. Several authors demonstrated that cleaning/disinfection performances and rinsing steps were influenced by the ionic strength of the water used, the ionic activity of the ions and their valences (Wiley and Tran-Ha, 1997; Tran-Ha and Wiley, 1998; Matzinos and Alvarez, 2002; Tran-Ha et al., 2005). This underlined the need for vigilance with the water used for membrane cleaning/disinfection.

2.2.2. Storing conditions of membranes and modules

On industrial and particularly on dairy production sites, membranes may be stored more or less long when the production line is at a standstill or between two production phases. To prevent any bacterial growth in the modules once extracted from the production line, it is advised to store them in solutions with a biocide away from light and to avoid as much as possible temperature variations. These conditions are not always respected or even registered. However, non-optimal storing conditions of membranes (product, concentration, temperature, etc...) could be part of the observed membrane ageing and losses of filtration performances.

Relatively few studies are dedicated to the possible modifications of membranes submitted to storing phases. Lawrence et al. (1997, 1998) compared the effects of storing a PSf membrane in a metabisulphite (MBS) and a Linear Alkyl Benzene Sulfonic Acid (LABS) solution (1.0% v/v and 0.25, 0.50% w/w, to room temperature) over a 91 days period with intermediate fouling/cleaning/disinfection cycles. The results underlined an increase in water flux from 10 to 70% for the membranes stored in the LABS solution and a decrease from 5 to 80% for the membranes stored in the MBS solution. Analyses performed with FESEM (Field Emission Scanning Electron Microscopy) indicated that LABS significantly decreased the pore size of the membranes. MBS would open up membrane pores (pores of 100–150 nm have been observed using FESEM compared to the initial pores of 25 kDa). Another study showed that a prolonged exposure to light during relatively long storing periods increase the degradation of the polymer constituting the membranes (Oliveira et al., 2012). EPR (Electron Paramagnetic Resonance) analyses revealed that the exposure of the membrane to sunlight during only 1 h, generated a radical oxidation of the polymer resulting from UV rays to which they were exposed. At laboratory scale, membranes are usually stored in sodium bisulphite/cobalt chloride/sodium azide following the specifications of membrane manufacturers. Likewise, on some sites, recommended storing procedures are to put membranes in acidic or alkaline solutions at low concentrations (compare

Table 3 – Water quality commonly required for membrane cleaning/disinfection procedures.

Conductivity	Turbidity	Hardness	Fe	Silica	Al	Ca	Mn	
–	<1 NTU (NTU: Nephelometric Turbidity Unit)	<16°F (°F: French Degree)	<0.3 mg L ⁻¹	<10 mg L ⁻¹	<0.5 mg L ⁻¹	<10 mg L ⁻¹	<0.2 mg L ⁻¹	Rabiller- Baudry et al. (2009)
≤5 µS cm ⁻¹	≤1 NTU (SDI ≤ 3)	≤30–50 ppm ^b	≤0.5 ppm ^a	≤5 ppm ^a			≤0.2 ppm ^a	Krack (1995) Tragardh (1989) Osmonics Inc
–	<1 NTU (SDI < 3) (SDI: Silt Density Index)	<10°TH (TH: Hydrotimetric degree)	<0.05 ppm (<0.2 ppm if [Si] < 5 ppm)	<15 ppm ^c	<0.1 ppm	–	<0.02 ppm (<0.05 ppm if [Silica] < 5 ppm)	Ecolab, Snc

^a According to Krack (1995) if the iron and manganese content is 10 times less than described above the silicate content can be up to 40 ppm.;

Osmonics Inc advised iron and manganese concentration 10 times less (0.05 et 0.02 ppm) and silica content less than pas 5 ppm.

^b Krack (1995) advised total hardness less than 357 ppm.

^c Colloïdal silica must be totally absent.

to the commonly recommended cleaning/disinfection concentrations). But the validity of these specifications has never been rigorously verified. Storing conditions are generally set empirically in order to prevent any bacterial growth without taking into account membrane damages. Thus, storing conditions must be well thought and should be further optimized to lengthen membrane lifetime.

2.2.3. Cleaning/disinfection agents and protocols

Generally speaking, the protocols applied in the dairy industries and drinking water production plants and recommended by membrane manufacturers consist in three main steps: on alkaline and acid cleaning steps carried out after water rinse, then disinfection step. In some cases, suppliers of cleaning/disinfection products recommend a pre-wash at a detergent in a low concentration (0.2–1% according to the formulation) from 5 to 15 min in one run without retentate recycling. The pre-wash removes the foulants easily cleanable from the circuit before the forthcoming phase with retentate recycle. The alkaline and acidic cleaning phase requires concentrated solutions (0.3–2% for an alkaline, 0.3–1% for an acid) at a temperature close to the process (or higher if cleaning is difficult) but always according to conditions advised by the manufacturers. Time varies between 20 and 40 min for an alkaline and 15 and 30 min for an acid. According to the membrane applications (and consequently foulants), cleaning conditions can be modified and adapted. For instance, in the dairy industry, alkaline step must be longer than the acid one because organic matter is the main foulants and kinetics of acid reactions are faster.

As membrane cleaning/disinfection is performed mainly via chemical reactions between foulants and cleaning/disinfection agents, the operating parameters, which affect the matter transfer and chemical reactions, also affect the cleaning/disinfection efficiency. So, for each cleaning/disinfection/rinse steps, accurate operating conditions must be considered. Conditions such as duration of the step (Lee et al., 2001) and temperature (Te Poele and Van der Graaf, 2005) play a key role in the recovery of the initial flux (Al-Amoudi and Lovitt, 2007). The temperature can affect the balance of the chemical reaction, its kinetics, the solubility of foulants, the reactivity of cleaning by-products (Strugholtz et al., 2005; Nystrom and Zhu, 1997; Chen et al., 2003; Ang et al., 2006; Li et al., 2005; Liu et al., 2000). Even if the coupled effects and the interdependencies of the different cleaning/disinfection parameters remain difficult to understand (Puspitasari et al., 2010), previous works have already studied the relative influence of a number of parameters on the cleaning/disinfection of membranes for some specific agents. Although the basic principles of the membrane cleaning/disinfection have been identified, still few studies take into account ageing caused by regeneration procedures as a result of cleaning/disinfection entirely alongside the recovered performances or the hydraulic, chemical or microbiological cleanliness.

2.2.3.1. *Cleaning/disinfection agents.* « Cleaning agents » commonly refer to the chemical products which can remove efficiently the matter accumulated onto and within the membrane during the production cycle (Porcelli and Judd, 2010a). The resulting cleaning reaction is a heterogeneous

reaction, which depends as much on the cleaning agent and cleaning conditions as on the species to eliminate. The cleaning efficiency will depend on the good adequacy of foulants, cleaners and conditions. However, in most cases the choices of cleaning/disinfection conditions are not deliberated and rather the result of a trial/error process (Lee et al., 2001). The choice of cleaning/disinfection agents takes also into account other parameters such as (D'Souza and Mawson, 2005):

- compliance of the products with the regulations of Food and Drink Industries standards (FDI),
- compliance of the products with membrane materials and other components: glue, seal, spacers, etc.,
- treatability of cleaning effluents,
- required volumes of water,
- stability of the cleaning/disinfection agent,
- rinsability, foaming,
- price.

Six categories of cleaning/disinfection agents are selected classically (Table 4): alkalis, oxidants, enzymatic components, surfactants and complexing agents (Zondervan and Roffel, 2007). Formulated detergents are added to those six cleaning/disinfection agents. Because of their unknown precise composition which makes their scientific study and understanding more complex, they are less studied academically. Zondervan and Roffel (2007) and Rabiller-Baudry et al. (2009), among others, summed up the advantages, drawbacks and performances of the different cleaning/disinfection agents.

2.2.4. Most commonly used cleaning/disinfection agents and impact of cleaning performances and membrane ageing

2.2.4.1. *NaOH: cleaning performances and ageing damages.* Caustic soda is typically used to clean membranes fouled by organic and microbial foulants. The function of caustic soda is mainly solubilization (Liu et al., 2000). The role of the caustic cleaning agent is often boosted by the addition of sodium hypochlorite (200 ppm chlorine) (D'Souza and Mawson, 2005; Krack, 1995). In the same way, it may be also effective to remove inorganic colloids and silicates (Porcelli and Judd, 2010a; Kim et al., 1993).

2.2.4.1.1. *NaOH: cleaning performances.* Table 5 shows that the cleaning of UF polymeric membrane has been widely studied with sodium hydroxide solution to compare cleaning performances as well as to determine kinetic cleaning models.

- **Cleaning performances: use of caustic soda alone and comparison with other cleaning agents** Zondervan and Roffel (2007) showed that caustic soda (at a concentration $c^{\circ} = 0.05 \text{ mol L}^{-1}$) presented the best cleaning performances (in terms of difference between the transmembrane pressure at the beginning and at the end of the cleaning/the transmembrane pressure at the beginning and at an infinite time of cleaning) in the case of PSf membranes fouled by surface waters. Zhu and Nyström (1998) reached the same conclusions for PSf membranes fouled by milk proteins or lysozymes (in terms of flux recovery). In some cases, the cleaning performances using caustic soda are poor (Li et al., 2005; Kuzmenko et al., 2005; Tian et al., 2010; Evans et al.,

Table 4 – Most commonly used chemical agents or components entering in the formulation of detergents for the membrane cleaning/disinfection in dairy industries and drinking water production plants.

Basic cleaning/ disinfection agents categories	Possible interactions between cleaning/ disinfection agents and foulants	Examples	Advantages	Disadvantages
Caustic soda	Organic: Hydrolysis Inorganic: Solubilization/ Chelation Microbial: Ø	NaOH (KOH, NH ₄ OH)	Modification of the charge of ionisable solutes favoring their solubilization, particularly for organic molecules Saponification of fat matters	No protein hydrolysis at T = 50 °C during less than 1 h at pH 11.5
Acidic	Organic: Hydrolysis/ saponification Inorganic: Solubilization/ Chelation Microbial: Ø	HNO ₃ /H ₃ PO ₄ Citric	Dissolution of inorganic salts or oxide films. Solubilization of free minerals particularly divalent cations Good rinsability. Citric acid is favored because its mildness compared to nitric acid.	Contribute to nitrate/ phosphorus amount in effluents.
Oxidizing/ disinfecting	Organic: Oxidation Inorganic: Oxidation Microbial: Disinfection	NaOCl H ₂ O ₂ Peracetic acid Metabisulphite	Membrane swelling agent. Destruction of pathogenic microorganisms. Compatible with nearly all membranes. Fact acting, good rinsability. Compatible with sensitive membranes – Not oxidizing	Deteriorations of membranes. Not compatible with NF and RO membranes. Contribute to a more or less biodegradable effluents Care must still be taken to avoid corrosion. Time reaction is very long.
Enzymatic	Organic: Peptization Inorganic: Ø Microbial: peptization	Lipases, proteases	Compatible with sensitive membranes. Enzymes are specific of a fouling type. Widely biodegradable and let effluents more digestible for the microorganisms. Reduction of waste water volumes.	Cleaning has to be performed in precise conditions : 40 °C < T < 50 °C and 4 < pH < 10
Surfactants	Organic: Chelation Inorganic: Chelation Microbial: Ø	Anionic (SDS) Neutral (Tween, Triton) Cationic (CTAB)	Increase wettability promoting detergent contact with the soil; assist in solubilizing material and prevent re-deposition; modify surface charge.	Foam formation Generally forbidden in food industry
Sequestering/ complexing	Organic: Dispersion Inorganic: Dispersion Microbial: Ø	EDTA H ₃ PO ₄ Citric acid, gluconic acid, lactic acid	Prevention of re-deposition and/or removal of mineral deposits. Very efficient Middle efficient Less efficient than EDTA	Contribute to COD in effluents and not easily biodegradable Contribute to phosphorous amount in effluents Contribute to COD amount in effluents but better biodegradable than EDTA.
Others		Anti-foam Dispersion agents Corrosion inhibitors	Limitation of foam formation by surfactants Anti-refouling Corrosion limitation	Antifoaming agent can block the membranes so care in their selection is important. Contribute to a more or less biodegradable COD in effluents
Formulated detergents	Organic: Chelation Inorganic: Chelation Microbial: Ø	Ultrasil/ Aquaclean (Ecolab) 4 Aquaclean (Aquacare) Divos (Diverseylever) Triclean (Triton)	Cleaning formulations are tailored to meet the requirements for removing specific foulants and must balance the cleaning action against foulants with its effect on the membrane, its cost, and its suitability for use in a commercial manufacturing environment. The main advantage is the shorter cleaning time. Both electrostatic repulsion and surfactant hydrophobicity help to stretch and weaken the bond between membrane and foulants.	Composition not exactly known. Contribute to a more or less biodegradable effluents More expensive than no formulated chemical agents

Table 5 – Cleaning investigations performed in relation to alkaline cleaning agents of UF polymeric membranes.

Application	Alkaline agents	Membrane type	References
Skim milk (Lait de Montagne, UHT (Ultra High Temperature), Carrefour, France)	NaOH (pH = 11.5)	Ultrafiltration (UF) Polyethersulfone (PES)	Rabiller-Baudry et al. (2006a)
Skim milk (Lait de Montagne, UHT, Carrefour, France)	NaOH (pH = 11.5)	UF PES	Rabiller-Baudry et al. (2006b)
Skim milk (Lait de Montagne, UHT, Carrefour, France)	NaOH (pH = 11.5)	UF PES	Rabiller-Baudry et al. (2008)
Skim milk (Lait de Montagne, UHT, Carrefour, France)	NaOH (pH = 11.5)	UF PES	Rabiller-Baudry et al. (2010)
Skim milk (8 wt% solids)	NaOH (0.5 wt.%)	UF Polysulfone (PSf)	Makardij et al. (1999)
Skim milk (Lait de Montagne, UHT, Carrefour, France)	NaOH (pH = 11.5) Chlorinated alkaline (pH = 11.5 –200 ppm active Cl ₂)	UF PES	Paugam et al. (2006)
Skim milk (Lait de Montagne, UHT, Carrefour, France)	NaOH (pH = 11.5)	UF PES	Delaunay et al. (2006)
Milk (88% water, 3.4% protein, 3% fat, 4.9% lactose, 0.7% other)	NaOH (–)	UF PSf	Kazemimoghadam and Mohammadi (2007)
Milk (from Tehran pasteurized milk factory)	NaOH (from 0.01 to 0.5% w/w)	UF PSf	Mohammadi et al. (2002)
Bovine Serum Albumin (BSA) (0.3 g L ⁻¹)	NaOH (From 100 to 3000 ppm)	UF Cellulose (CE)	Kuzmenko et al. (2005)
BSA (0.1 wt.%)	NaOH (From 0.01 to 0.1 M)	UF PES	Kim et al. (1993)
BSA (1 g L ⁻¹ , pH = 5)	NaOH (0.055%) + EDTA (0.023%) + Mersolat W40 (0.03%)	UF PSf	Platt and Nyström (2007a)
BSA (1 g L ⁻¹ , pH = 5.0)	NaOH (0.055%–0.1%)	UF PSf	Platt and Nyström (2007b)
BSA (0.3 g L ⁻¹)	NaOH (4.0 g L ⁻¹)	UF PES UF Polyvinylidene fluoride (PVDF)	Levitsky et al. (2012)
BSA or Lysozymes (80 mg L ⁻¹)	NaOH (pH = 11.9) NH ₄ OH (pH = 10.8) Phosphate, silicate, carbonate (pH = 11.2)	UF PSf Modified PSf	Zhu and Nyström (1998)
BSA + beta-lactoglobuline (β-Ig) (1 g L ⁻¹ equimolar)	NaOH (From 0.01 to 0.4 M)	UF PSf UF PES	Chen et al. (2006)
Sweet whey (6 g L ⁻¹)			
Whey (1%, From West Cheese Factory, 6.0% < Total solids < 6.5%, 0.2% < fat < 0.3%)	NaOH (0.5%)	UF PSf	Madaeni and Sharifnia (2000)
Whey (Alkaline, 80% WPC)	NaOH (From 0.1 to 1.0 wt.%)	–	Mercadé-Prieto and Chen (2005)
Whey Protein Concentrate (WPC) (WPC 80, 3 wt.%)	NaOH (0.2 wt.%)	UF PSf	Nigam et al. (2008)
WPC (Reconstituted 3.5 wt.%)	NaOH (1.0 wt.%)	UF PES UF Polyamide (PA)	Väisänen et al. (2002)
Pulp and paper mill Pulp and paper effluent	NaOH (0.01 M)	UF CE UF PES	Maartens et al. (2002)
Glutamic acid	NaOH (0.3% w/w)	UF PSf	Li et al. (2005)
Aqueous extract of soy flour (4 wt.% solids)	NaOH (0.5 wt.%)	UF PSf	Sayed Razavi et al. (1996)

(continued on next page)

Table 5 – (continued)

Application	Alkaline agents	Membrane type	References
Spent sulphite liquor	NaOH (0.5 wt.%)	UF PES UF PSf	Weis et al. (2003)
Spent sulphite liquor	NaOH (0.5 wt.%)	UF PES UF PSf UF Regenerated Cellulose (R-CE)	Weis et al. (2005)
Sulphite pulp mill	NaOH (0.1 M)	UF PES	Wallberg et al. (2001)
Surfactin recovery	NaOH (pH = 11 and pH = 13)	UF PES UF CE	Chen et al. (2008)
Black tea liquor	NaOH (0.5 wt.%)	UF Fluoropolymer (FP) UF R-CE	Evans and Bird (2006)
Black tea liquor	NaOH (0.5 wt.%)	UF FP UF PSf UF R-CE	Evans et al. (2008)
Model tea component solutions	NaOH (0.2 wt.%)	UF PSf	Wu and Bird (2006)
Apple juice	NaOH (0.1 M)	UF PES/Polyvinylpyrrolidone (PVP)	Borneman et al. (2001)
Wastewater from banknote printing note	NaOH (1 wt.%)	UF PSf/PDC	Zhang and Liu (2003)
Wastewater from banknote printing note	NaOH (from 0.3 wt.% to 1.3 wt.%)	UF PSf/PDC	Zhang et al. (2004)
Surface water	NaOH (1.1 N and from 0.075 to 0.250 N)	UF	Liu et al. (2000)
Surface water	NaOH (pH = 12)	UF Polyacrylonitril (PAN) Microfiltration (MF) PVDF MF Polyethylen (PE)	Yamamura et al. (2007)
Surface water	NaOH	UF PES	Zondervan et al. (2007a)
Surface water	NaOH (0.5–10% w/v)	UF PSf	Arnal et al. (2008a)
Surface water	NaOH (pH = 11)	UF PSf	Arnal et al. (2008b)
Surface water	NaOH (1%)	UF Polyvinylchloride (PVC)	Tian et al. (2010)
River natural organic matter, sodium alginate	NaOH (pH = 11.0)	Reverse Osmosis (RO) CA	Wui et al. (2006)
Potable water	NaOH (0.050–0.175 mol L ⁻¹) (0.188–0.405 mol L ⁻¹)	UF PES MF Polypropylene (PP) MF PVDF	Porcelli and Judd (2010a)
Flocculated reservoir water	NaOH/H ₂ O ₂ (pH = 12)	UF PES	Strugholtz et al. (2005)
Algae-rich water	NaOH (From 0.01 to 0.03 N)	UF PSf	Liang et al. (2008)
Alga-rich water	NaOH (500 mg L ⁻¹)	UF PVC	Zhang et al. (2011)

2008), The authors explain it by the increase in hydrophobicity of the membranes (regenerated cellulose and fluoropolymer membranes) and consequently a decrease of permeability (Evans et al., 2008). This above all reveals that the cleaning performances of the protocols depend on a relation membrane material/nature of fouling and conditions/cleaning products. Kazemimoghadam and Mohammadi (2007) demonstrated that for PSf membranes fouled by milk proteins the cleaning performances of sodium hydroxide were improved when it was combined with a chelating agent or a surfactant (as well in terms of flux recovery as in terms of resistance removal). Tian et al. (2010) recommended a consecutive chemical cleaning by alkali and ethanol to restore the permeability of PVC membranes fouled by surface water.

- **Cleaning mechanisms and kinetics:** cleaning mechanisms and kinetics involved when the cleaning agent is a sodium hydroxide solution were proposed and verified by Blanpain-Avet et al. (2004). The authors confirmed that the removal of the major part of the fouling resistance takes place within the first few minutes of cleaning (between 0.3 and 12 min). The qualitative cleaning model of UF/MF membranes fouled by protein suspensions proposed is based on the existence of several deposit species which have different removal characteristics (species loosely bound and easily solubilized by hydroxide sodium solution and species more tightly bound and more difficult to remove by cleaning and rinsing process).
- **Effect of concentration on cleaning performances:** Bartlett et al. (1995), Kim and Fane (1995) and Väisänen

et al. (2002) studied more precisely the concentration effect on simple alkaline solution cleaning performances. They demonstrated the existence of a 0.2% mass concentration optimum for different membrane materials. Higher or lower concentrations do not improve significantly the cleaning performances in terms of flux recovery.

- **Effect of temperature on the cleaning performances:** The main conclusion of these studies is that cleaning with caustic soda has an optimal efficiency at 50 °C (Bartlett et al., 1995; Kim and Fane, 1995; Bird and Bartlett, 2002; Rabiller-Baudry et al., 2002; Väisänen et al., 2002; Zhang et al., 2004; Evans and Bird, 2006; Kazemimoghadam and Mohammadi, 2007).
- **Effect of cleaning time on cleaning performances:** The results obtained on PSf membranes showed that above a certain cleaning time the performances of flux recovery did not improve significantly (Madaeni and Mansourpanah, 2004). This optimum depends on the concentration and the study parameters (membrane material and nature of fouling).

2.2.4.1.2. *NaOH: Membrane ageing and damages.* Zhu and Nyström (1998) showed an increase in the flux of the pre-cleaned and modified PSf membranes, with oxalic acid as well as with NH_4OH . Even if the differences are very small anyhow and hardly outside the statistical range of the average flux values, the zeta potential values of the PSf membrane pre-cleaned with NaOH changed a lot compared to NH_4OH . FTIR analyses showed some modifications of the spectra concerning the aromatic compounds. On the contrary, the zeta potential of modified PSf membranes did not change with alkaline cleaning. Bégoïn et al. (2006a,b) did not find modifications of the SEM-EDX and ATR-FTIR analyses of the samples of PES membranes aged in alkaline conditions (NaOH pH 11.5) at 50 °C for 4 months, contrary to P3-Ultrasil 10 (0.4wt.%, unmodified pH 12.0) in the same conditions.

Several publications studied the effect of NaOH on PVDF (degradations, discoloration, cracks, polymer modifications...) (Vigo and Uliana, 1984; Nguyen, 1985; Hashim et al., 2011, etc...). For further information, the reader can refer to Liu et al. (2011). No particular effect was observed on the performance of PVDF membranes, which have been exposed to water, wool scouring waste water, acids, calcium chloride and sodium bisulfite at different concentrations. However, the performances of PVDF membranes were affected by concentrated sodium hydroxide and sodium hypochlorite, in accordance with (Momtaz et al., 2005) who underlined the progressive hydrolysis of the esters linkages and the dissolution of the upper surface of PVDF membranes in basic conditions (Lithium hydroxide 1 N). The chemical reactions between PVDF and NaOH can be explained as a phenomenon of dehydrofluorination resulting from the elimination of hydrogen fluoride (HF) units from the polymer, in agreement with (Ross et al., 2000). The study is completed by Zhang et al. (2006) who studied precisely the production of radicals during the degradation mechanism. The authors found that radicals are produced

by the attack of the main chain of PVDF by OH. It was shown that the concentration of free radicals increased with the time of exposure and the concentration of alkaline. FTIR and FT-Raman analysis indicates the deprotonation of $-\text{CH}_2$ when alkaline attacks the PVDF chain structure and the formation of C=C double bonds, due to dehydrofluorination process. This formation increases with the time of exposure up to 3 h and alkaline concentration up to 10 g L^{-1} . Above these conditions, membranes become black and brittle in agreement with Hashim et al. (2011). On the contrary, Abdullah et al. (2012) found that PVDF membranes aged in NaOH (pH 12, 40 °C for 4.5 months) do not become brittle after ageing.

Hashim et al. (2011) studied the flux reduction and the mechanical properties of PVDF membranes after NaOH treatment. The flux reduction as a consequence of ageing was observed to be relatively lower in diluted NaOH solution for 12 months compared to the ones stored in tap water (Vigo and Uliana, 1984). While the elongation resulted from 1 wt.% and 4 wt.% NaOH treatments were observed to be moderate, NaOH treatment at higher concentration (10 wt.%) showed a drastic reduction in the elongation of the hollow fibers. The authors also studied the impact of temperature on the deterioration of the mechanical properties. They also compared two different PVDF membranes and their abilities to maintain their elongation properties after being treated with NaOH.

2.2.4.2. *Acids: cleaning performances and ageing damages.* Acids are used primarily to remove scales and metal dioxides from fouling layers (Liu et al., 2000).

2.2.4.2.1. *Acids: cleaning performances.* Whilst strong mineral acids can solubilize deposits, organic acids, such as citric and oxalic acids, are more effective for formation and transportation of organic-metallic foulants from the membrane to the bulk solution (Porcelli and Judd, 2010a).

Table 6 details studies about cleaning of organic ultrafiltration membranes performed with organic or mineral acids. The obtained results in terms of cleaning performances are very diverse. Besides, it is necessary to take into account the essentially proteic nature of the fouling of the studied cases in order not to conclude to misinterpretations too quickly as far as cleaning performances of acid cleaning agents are concerned.

According to these studies, the most implemented acid cleanings are carried out with hydrochloric or nitric acids. The latter is particularly used in the cleaning of membranes fouled by milk and whey. Nitric acid or phosphoric acids are mainly used in the cleaning of membrane plants. However, citric acid is increasingly favored because of its mildness compared to nitric acid; it also rinses easily and does not corrode surfaces (D'Souza and Mawson, 2005). Hydrochloric and sulfuric acids are predominantly used in the cleaning of potable water membranes, because of their low costs (Porcelli and Judd, 2010a). Paugam et al. (2006) highlighted that the classical combination of acid and alkaline cleanings is not necessarily the most efficient for all the membranes, but it should be adapted to the filtered liquid and to the membrane.

Table 6 – Cleaning researches performed in relation to acidic cleaning agents of UF polymeric membranes.

Application	Chemical agent	Time/ TransMembrane pressure (TMP)	Temperature (°C)	Remarks and benefits	Membrane type	References
Skim milk (Lait de Montagne, UHT, Carrefour, France)	HCl (pH = 1.6) HNO ₃ (pH = 1.6)	1 h TMP = 2 bar	50 °C	HNO ₃ revealed inefficient even if it lead to an increasing flux (due to nitrate adsorption)	Ultrafiltration (UF) Polyethersulfone (PES)	Paugam et al. (2006)
Milk (88% water, 3.4% protein, 3% fat, 4.9% lactose, 0.7% other)	HCl HNO ₃	30 min No pressure	30 ± 1 °C	HCl: Flux Recovery (FR) = 9% HNO ₃ : FR = 2%	UF Polysulfone (PSf)	Kazemimoghadam and Mohammadi (2007)
Milk (From Tehran pasteurized milk factory)	HCl (From 0.01 to 0.1 M) HNO ₃	30 min No pressure	30 ± 1 °C	HCl (0.01 M): FR = 40% HNO ₃ : not acceptable results	UF PSf	Mohammadi et al. (2002)
Bovine Serum Albumin (BSA)	HCl (From 0.01 to 1 M) HCl (From 0.01 to 0.1 M)	1 h Stirring	–	pH 5 fouling : Resistance Removal (RR) = 85% pH 7 fouling : RR = 54% Best RR achieved for 0.1 M Best RR achieved for batch with permeation	UF PSf	Kim et al. (1993)
BSA (80 mg L ⁻¹) Lysozymes	Citric acid (0.5 wt %, pH = 2.7) Oxalic acid (0.5 wt %, pH = 1.6)	1 h Stirring	80 °C	Oxalic ≈ Citric: FR = 89% < NaOH (95%) but > NH ₄ OH (82%) PSf (0.1 M): FR = 40% < NaOH < SLS < Terg-A-Zyme (TAZ) PES (0.05 M): FR = 38% < NaOH < SDS < Protease	UF PSf Modified PSf	Zhu and Nyström (1998)
BSA + β-Ig (1 g L ⁻¹ equamolar)	HCl (From 0.01 to 0.3 M)	–	–	HCl: FR = 18%	UF PSf	Chen et al. (2006)
Sweet whey (6 g L ⁻¹)	HCl (From 0.01 to 1 M)	–	–	HNO ₃ : FR = 25%	UF PES	
Whey (1%, From West Cheese Factory, 6.0% < Total solids < 6.5%, 0.2% < fat < 0.3%)	HCl, HNO ₃ , H ₃ PO ₄ , H ₂ SO ₄ , Sulphamic acid, Citric acid (0.05%)	–	25 °C	H ₃ PO ₄ : FR = 44% Sulphamic acid: FR = 45% Citric acid: FR = 62%	UF PSf	Madaeni and Sharifnia (2000)
WPC (Reconstituted 3.5 wt %)	HNO ₃ (0.3 wt.%)	30 min TMP = 0.5 bar	–	Decrease of flux in all conditions tested	UF PES UF Polyamide (PA) UF Cellulose (C)	Väisänen et al. (2002)
Pulp and paper mill	HCl (0.03% w/w, pH = 1.4)	–	–	FR = 46% < NaOH < H ₂ O ₂ < SDS < P3-Ultrasil 11	UF PSf	Li et al. (2005)
Glutamic acid	HCl (0.5 wt.%, pH = 1.5)	30 min TMP = 15 kPa	50 °C	Ineffective in removing membrane fouling	UF PSf	Sayed Razavi et al. (1996)

Lignosulphates	HNO ₃ (0.1 vol. %, pH = 2)	30 min TMP = 1 bar	50 °C	<5 fouling and cleaning cycles : HNO ₃ > P3-Ultrasil 11 >5 fouling and cleaning cycles : HNO ₃ < P3-Ultrasil 11 Sever reduction of flux with HCl due to the formation of a denser gel layer	UF PES	Weis and Bird (2001)
Wastewater from banknote printing note	HCl (0.1 N)	30 min TMP = 0.1 MPa	40 °C	Citric acid without ultrasound: FR = 66.3% Citric acid with ultrasound: FR = 81%	UF PSf/PDC	Zhang and Liu (2003)
Waste water	Citric acid (2 g L ⁻¹) Ultrasound	7 h	–	None components affected membrane permeability	UF Polyvinylidene fluoride (PVDF)	Jin et al. (2008)
Bottle washing solutions	Uronic acid (0.02 vol. %) Phosphonic acid (0.01 vol. %) Fatty acid (0.009 vol. %) Used as additives with to a 2% caustic soda solution	– TMP = 2–10 bar	60 °C		UF PES Nanofiltration (NF) PES	Rögener et al. (2002)
Swine manure	HNO ₃ (0.1 N, pH = 2)	– TMP = 20–40 kPa	25 °C, 37 °C or 50 °C	Complete removal of inorganic precipitates but no flux recovery	UF PES	Zhang et al. (2007)
Surface water	HCl (pH = 2) Oxalic acid (0.5%)	24 h Soaking	20 °C	PAN & PVDF: HCl < Oxalic acid < NaOH < NaOCl PE: similar results	UF Poly Acrylonitrile (PAN) Microfiltration (MF) PVDF MF Polyethylene (PE) UF	Yamamura et al. 2007 Zondervan and Roffel (2007)
Surface water	HCl (0.05 mol L ⁻¹) H ₂ SO ₄ (0.05 mol L ⁻¹) Citric acid (0.05 mol L ⁻¹) Other acid (0.05 mol L ⁻¹) Citric acid (0.5–10% w/v)	– Backflush	–	Citric acid < P3-Ultrasil 70 < HCl < H ₂ SO ₄ < H ₂ O ₂ < P3-Ultrasil 115 < NaOCl < NaOH		
Surface water (from irrigation pond)		24 h Soaking	40 °C	No effects in removing membrane superficial fouling	UF PSf	Arnal et al. (2008a)
Surface water (from irrigation pond)	Citric acid (1–3%)	20 min every 7 days	–	Decrease of flux and microbiological contamination RR = 10.9%	UF PSf	Arnal et al. (2008b)
Surface water	Citric acid (2%)	30 min	–		UF Polyvinylchloride (PVC)	Tian et al. (2010)
Potable water	Citric acid (0.003–0.009 mol L ⁻¹)	– 30–90 min	5–35 °C	Impact of operating and cleaning factors on operating cost variation	UF PES MF Polypropylene (PP) MF PVDF	Porcelli and Judd (2010b)
Flocculated reservoir water	HCl (pH = 2) Citric acid (2 g L ⁻¹)	2 h (with 30 s backwashing every 30 min)	20 °C or 40 °C	HCl was not suitable for organic removal HCl + NaOH was low temperature-sensitive NaOH + HCl was high temperature sensitive FR = 40–60%	UF PES	Strugholtz et al. (2005)
Algae-rich water	Citric acid (From 1% to 3%)	10, 20 or 30 min TMP = 120 kPa	–		UF PSf	Liang et al. (2008)
Algae-rich water	HCl (500 mg L ⁻¹)	1 h Soaking	–	500 mg L ⁻¹ HCl > 500 mg L ⁻¹ NaOH + 150 mg/L EDTA 500 mg L ⁻¹ HCl < 100 mg L ⁻¹ NaOCl	UF PVC	Zhang et al. (2011)

2.2.4.2.2. *Acids: ageing of PSf & PES membranes.* Bégoïn (2004) made PES membranes (HFK 131, Koch, USA) age in nitric acid (pH = 1.6) under industrial conditions at 50 °C, for a cumulated time corresponding to 15 years of use in a plant. Regardless of the analysed carried out (EDX, ATR-FTIR) the treated membrane remains slightly identical to the reference membrane and the membrane does not present any sign of alteration of the active skin. Ageing tests in extreme conditions have also been performed at a 1 M concentration at 50 °C for 4 months. No modification of the ATR-FTIR spectrum of the membrane aged in these conditions has been observed. SEM images performed on PSf membranes fouled by milk and cleaned with a nitric acid solution at 0.5% have pointed out alterations of the membrane surface (Makardij et al., 1999). Zhu and Nyström (1998) showed that the flux of PSf membranes would be liable to increase after a pre-cleaning with oxalic acid. No study about ageing of organic ultrafiltration membranes with hydrochloric and sulfuric acids has been carried out so far.

2.2.4.3. *Disinfectants and oxidizing agents.* Membrane cleaning generally ends with a disinfection step either with chlorinated alkalines, which generate active chlorine (sodium hypochlorite) or with oxidizing solutions, which generate active oxygen (i.e. peracetic acid). A good disinfectant must have a wide spectrum: kill several types of microorganisms, be efficient at low concentrations and above all be non-toxic for the user (Bégoïn, 2004). The main drawbacks of these products are that they can (i) damage the chemical structure of the membranes and the devices (seal, glue, module). The use guidelines recommended by the manufacturers of membranes and detergents have to be taken into account (Table 7). They can (ii) corrode the system, (iii) represent considerable pollutant loads with a decrease of efficiency due to a tolerance of microorganisms. It is necessary to alternate the use of different bactericides, particularly on the plants with daily procedures. The choice for such products must be carefully undertaken: « efficiency – toxicity – cost » is still relevant.

On dairy production plants, bleach is an oxidizing disinfectant used extensively (Bégoïn, 2004). Nevertheless, other oxidizing agents, such as hydrogen peroxide or peracetic acid can be used.

Table 7 – Organic material tolerance to oxidants (Ecolab Snc (2013) Internal Documents).

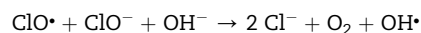
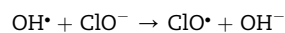
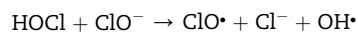
Material		Tolerance		
		Chlorine	Peracetic acid (PAA)	Hydrogen peroxyde (H ₂ O ₂)
Cellulose	CA	50 ppm max	75 ppm max	930 ppm max
Acetate				
Polyacrylonitrile	PAN	200 ppm max	Unknown	Unknown
Polyamide	PA	No oxidants		
Polysulfone	PSf	200 ppm max	75 ppm max	930 ppm
Polyvinylidene fluoride	PVDF	350 ppm max	Unknown	Unknown

On drinking water treatment plants, disinfection of ultrafiltration membranes is achieved by cleaning with chlorine (Gaudichet-Maurin, 2005) using:

- a backflushing every 3 min at 2–10 ppm during 1 min and a weekly chemical cleaning/disinfection at 20–400 ppm during 1 h (Gaudichet-Maurin, 2005; Rouaix et al., 2006)
- a backflushing every 6 h at 5 ppm during 20 min and a monthly chemical cleaning/disinfection at 400 ppm during 2 h (Pellegrin et al., 2012).

It is then interesting to observe to which extent these redundant cleaning/disinfections may affect the membrane behavior.

2.2.4.3.1. *NaOCl.* The sodium hypochlorite solution has been widely studied for its cleaning and disinfection properties (Gaudichet-Maurin, 2005). Holst (1954) published a review about the chemistry of oxidation and bleaching agents. In this article he presented the action of halogenated compounds and particularly chlorine compounds (Cl₂, ClO⁻, ClO₂) that he described in terms of oxidation-reduction potentials and solubility. From a study of the cellulose degradation, he proposed a radical mechanism explaining the constitution of reactive species in chlorine and which could justify the oxidant character of the solution. The proposed mechanism is the following one:



This mechanism shows two reaction intermediates, ClO[•] and OH[•] radicals, liable to damage the polymer. Classically the total chlorine concentration involves the 3 following species: chlorine (Cl₂), hypochlorous acid (HClO) and hypochlorite ion (ClO⁻), major species respectively for acid, neutral and alkaline pH. Reactive species will therefore be dependent of the solution pH (Fig. 2). It can depend on the concentration, or can be corrected by addition of acid or soda.

It has to be mentioned that disinfections of industrial spiral-wound UF of skimmed milk are performed at pH = 11.5. At pH = 9, the NaOCl action is more disinfecting and less deterging than at pH = 11.5 (Bégoïn, 2004). As far as drinking water production is concerned, backflushings operated in plants for unfouling and disinfection of ultrafiltration modules are achieved at pH = 8 (Gaudichet-Maurin, 2005).

Table 8 details the studies realized on UF polymeric membrane cleaning/disinfection with oxidants and disinfectants.

Due to the fact that disinfectant NaOCl is considered as the most detrimental used cleaning/disinfection agent, the major part of the ageing studies has been focused on this product. Several explanations are proposed to explain the membrane degradation observed when NaOCl is used. The structure of the membrane can be damaged (Gitis et al., 2006a) and

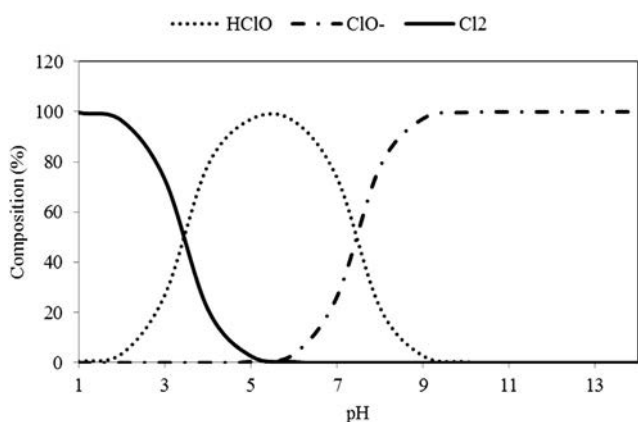


Fig. 2 – Chlorinated species predominance diagram: Cl₂, HClO and ClO⁻ as a function of pH.

partially destroyed due to the contact with NaOCl at high concentrations. NaOCl can also cause damages in membrane depth, so that a direct relation between the membrane pore size and the duration of the bleach treatment was evidenced (Wolff and Zydney, 2004; Yadav and Morison, 2010) for PSf and PES membranes. The membrane can also become more hydrophilic due to the contact with NaOCl (Mohammadi et al., 2002) resulting in a flux increase (Wienk, 1995; Nystrom and Zhu, 1997). Kwon and Leckie (2006a) confirmed this fact emphasizing that NaOCl modified the physical–chemical properties of the membranes by changing the zeta potential and the contact angle of the membrane.

Degradations caused by NaOCl are dependent on the polymeric material constituents. In the following part, Polysulfone (PSf), Polyethersulfone (PES) and Polyvinylidene fluoride (PVDF), which are the most commonly used materials of polymeric ultrafiltration membranes, will be largely detailed. At the same time, the current knowledge about ageing due to sodium hypochlorite on additives (i.e. polyvinylpyrrolidone (PVP) will also be detailed). Indeed, if they are also in small quantities, these additives can have a great impact on membrane properties.

Note that researches have also been achieved on the ageing comparison of fibers and films. The results show that both samples underwent chemical degradations at practically the same rate but in contrast, the embrittlement rate was about 4 times faster in fibers than in films, which revealed the great interest of mechanical studies on failure criteria of porous samples (Thominette et al., 2006). Gaudichet-Maurin and Thominette (2006) highlighted that hypochlorite ageing on PSf films and fibers caused the same chemical degradation.

• Degradations of polysulfone (PSf) membranes

In terms of permeability modifications, the study of hemodialyzers composed of PSf/PVP soaked in a bleach solution revealed a continual increase in permeability with increasing bleach exposure (Wolff and Zydney, 2004). This study is consistent with the results obtained by Qin and Wong (2002) who observed a fivefold increase in permeability after an 8 h exposure of their membranes to a 0.4% NaOCl solution,

and with Mohammadi et al. (2002) who observed a flux recovery higher than 100%.

In terms of polymer modifications, the membranes are more modified at high pH according to Rouaix et al. (2006). This is visible especially with the loss of mechanical properties, particularly for elongation. This decrease of performance is attributed to the PSf degradation and not to the PVP removal since it is not involved as a major component in the material strength. These results suggested that the cleaning/disinfection steps combining with the bleaching agent and alkaline chemicals should definitely avoid the pH range between 8 and 10 and better be run at pH around 7 or 12. Moreover, the addition of tertbutanol, an anti-radical component, reduces the degradation by radical oxidation of the membrane whereas the addition of metallic ions (Cu²⁺ and Fe²⁺) have a catalytic effect on the degradation of the membrane (Causserand et al., 2006, 2008). These results suggested that cleaning/disinfection procedures should give more importance to the ionic water profile used.

In terms of ageing mechanisms, Causserand et al. (2006) showed that exposure to NaOCl (100 ppm at 25 °C, pH 5-7-8-10) led to chain breaking in the PSf molecules involving changes in the mechanical properties. Gaudichet-Maurin and Thominette (2006) emphasized the appearance of two new peaks on ATR-FTIR analyses (28 days at 4000 ppm pH 8) which allowed the proposal of different mechanisms of degradation of the various components of the membrane. Until now, several mechanisms of degradations have been established. Instead of degradation mechanisms involving the formation of phenylsulfonate (Arkhangelsky et al., 2007a,b; Gaudichet-Maurin and Thominette, 2006; Thominette et al., 2006; Yadav et al., 2009) proposed a chain scission into two parts with one end terminated by a sulfonic acid group and the other part terminated by a phenyl chloride group.

• Degradations of polyethersulfone (PES) membrane

In terms of macroscopic modifications, Yadav and Morison (2010) highlighted three effects resulting from an exposure of PES membrane to chlorine:

- a decrease of the whey flux,
- an increase in the flux to water,
- a significant leakage of milk proteins, α -Lactalbumin (α -La) and β -lactoglobulin (β -Ig), in the permeate.

Two mechanisms at least are involved: an increase in the pore size, which explains the increase in the flux to water and the degradation of retention towards milk proteins and a modification of the surface properties, which would lead to an increased fouling due to proteins, reducing the whey flux. Another explanation is brought by Paugam et al. (2010), for this flux reduction: a chlorine disinfection after an incomplete cleaning/disinfection of PES membrane would be particularly negative on the flux during the skimmed milk filtration. Bégoïn (2004) made PES membranes (HFK 131, Koch, USA) age in chlorine industrial conditions at 200 ppm (pH = 9), at 50 °C, for a cumulated contact time corresponding to 15 years of use in a plant. The membrane treated in a solution at 200 ppm of active chlorine (pH = 9) shows signs of embrittlement of the

Table 8 – Cleaning/disinfection researches performed in relation to oxidizing/disinfecting agents of UF polymeric membranes.

Application	Membrane type	Oxidizing/disinfecting agent	References
Skim milk (Lait de Montagne, UHT, Carrefour, France)	Ultrafiltration (UF) Polyethersulfone (PES)	NaOCl (200 ppm) P3-Oxonia (1 or 10% w/w) P3-Oxonia Active (1 or 10% w/w) PVP-iodine (200 ppm)	Paugam et al. (2010)
Milk (88% water, 3.4% protein, 3% fat, 4.9% lactose, 0.7% other)	UF Polysulfone (PSf)	NaOCl (–)	Kazemimoghadam and Mohammadi (2007)
Milk (From Tehran pasteurized milk factory)	UF PSf	NaOCl (From 0.01 to 0.2% w/w)	Mohammadi et al. (2002)
Bovine Serum Albumin (BSA) (0.3 g L ⁻¹)	UF Cellulose (CE) UF PES	NaOCl (From 100 to 5000 ppm) H ₂ O ₂ (From 100 to 3000 ppm)	Kuzmenko et al. (2005)
BSA (0.3 g L ⁻¹)	UF PES UF Polyvinylidene fluoride (PVDF)	NaOCl (0.5 g L ⁻¹)	Levitsky et al. (2011)
BSA (0.3 g L ⁻¹)	UF PES	NaOCl	Levitsky et al. (2012)
BSA or Lysozymes (80 mg L ⁻¹)	UF PVDF UF PSf	(from 5 to 120 g.h.L ⁻¹) NaOCl	Zhu and Nyström (1998)
Whey (5% whey medium by mixing WPC with sterilized lactose and artificial whey permeate)	UF modified PSf UF PES	(0.5 wt.%) NaOCl (200 ppm) O ₃ (0.5 ppm)	Tang et al. (2010)
Aqueous extract of soy flour (4 wt.% solids)	UF PSf	NaOCl (150 ppm)	Sayed Razavi et al. (1996)
Pulp and paper effluent	UF PES	H ₂ O ₂ (2%)	Maartens et al. (2002)
Tannery effluent (100–120 kg of COD per ton of raw hide)	UF PVDF	NaOCl (750–1000 mg L ⁻¹)	Mendoza-Roca et al. (2010)
Glutamic acid	UF PSf	H ₂ O ₂ (from 0.3% to 1% w/w)	Li et al. (2005)
Oily waste water	UF PSf	NaOCl (400 ppm)	Lindau and Jönsson (1994)
Surface water	UF	NaOCl (0–5000 ppm)	Liu et al. (2000)
Surface water	UF Polyacrylonitrile (PAN) Microfiltration (MF) PVDF MF Polyethylene (PE)	NaOCl (700 ppm)	Yamamura et al. (2007)
Surface water	UF	NaOCl H ₂ O ₂	Zondervan and Roffel (2007)
Surface water	UF PES	NaOCl	Zondervan et al. (2007b)
Surface water	UF PSf	NaOCl (1.1–10% w/v) H ₂ O ₂ (1.1–10% w/v) Cupric sulfate (0.5–10% w/v)	Arnal et al. (2008a)
Surface water	UF PSf	NaOCl (100 ppm)	Arnal et al. (2008b)
Potable water (from the drinking water distribution network – a 150 µm sand filter and a 25 µm MF)	UF PSf	NaOCl (100 ppm)	Arnal et al. (2010)
Potable water	UF PES MF PP MF PVDF	NaOCl (From 0.001 to 0.002 mol L ⁻¹)	Porcelli and Judd (2010b)
Flocculated reservoir water	UF PES	NaOCl (50 ppm) H ₂ O ₂ (250 ppm)	Strugholtz et al. (2005)
Algae-rich water	UF PSf	NaOCl (From 50 to 150 mg L ⁻¹)	Liang et al. (2008)
Algae-rich water	UF Polyvinylchloride (PVC)	NaOCl (100 mg L ⁻¹)	Zhang et al. (2011)

active skin. The problem seems to maintain the adhesion of the active skin and the anisotropic layer of the substrate. A disintegration of the membrane surface has also been outlined by Levitsky et al. (2012). An interesting fact is that this disintegration has not been observed for a coupling of NaOCl with a surfactant (Tween 20). Besides, the fouling degree is much higher in the first case (NaOCl alone) than in the second case (NaOCl + Tween 20). This can be explained by the results of Paugam et al. (2010) detailed above. If cleaning/disinfection is misperformed, a chlorine disinfection could modify the residual proteins, which could then become nuclei favoring fouling.

As we have noticed up to now, most of the studies show a prevailing effect of chlorine on ageing of macroscopic properties of PES membranes. Zondervan et al. (2007b) works are the opposite of the general observations. The authors underlined that for the studied parameters the fouling degree and the number of backflushings were the most detrimental parameters to the membrane. The addition of chlorine (1000 ppm at pH = 11.5) does not seem to have a significant impact on permeability, neither on mechanical properties.

In terms of microscopic modifications, the influence of pH was studied by Yadav et al. (2009). Cracks and important modifications of the surface are observed at pH = 9 (for all the tested ageing conditions) unlike at pH = 12 where no morphology modification has been observed. However, ATR-FTIR analyses carried out on the same samples indicate that modifications of the polymer occurred including the samples where no crack was detected. The absorbance fall can be viewed at both pH, but it is more marked at pH = 9. These spectroscopic analyses also showed that ageing mechanisms were identical whatever the pH. This point will be detailed in the following paragraph about degradation mechanisms. Yadav et al. (2009) works confirmed the works of Bégoïn et al. (2006a,b): at pH = 9.5, intensities of absorption bands evolve and new bands appear (at 1205 cm⁻¹ particularly), whereas at pH = 12.5, no other peak appears even if the intensity of absorption bands evolves. Finally, another modification of the membrane polymer was underlined by Bégoïn et al. (2006a,b). With SEM-EDX analyses, the authors detected chlorine on membranes. A mechanism proposed by Yadav et al. (2009) made it possible to explain the results.

The microscopic degradations observed when NaOCl is coupled with a surfactant (Tween 20) are different from the ones observed when NaOCl is used alone. No significant degradation has been observed (Levitsky et al., 2012).

In terms of ageing mechanisms, different proposals were made as the studies progressed. A first degradation mechanism of PES was proposed by Gaudichet-Maurin and Thominet (2006). This mechanism shows the formation of sodium sulfonate (Fig. 3), a highly unstable compound. Indeed, the sodium salts are liable to hydrolyse within water. Sulfonates groups become sulfonic acid end-groups. Arkhangelsky et al. (2007a,b) also concluded to the formation of a phenylsulfonate group. The different authors agree to say that the observed polymer modifications would be supplemented with mechanical modifications (elongation, Young's modulus) and morphological modifications (distribution of pore size) of the material. However, this mechanism does not explain the presence of chlorine detected on the

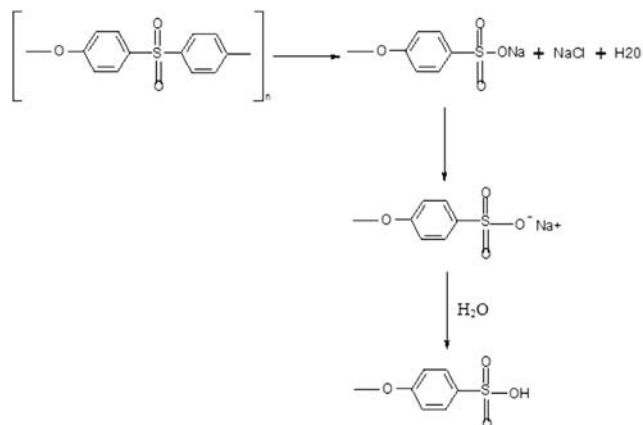


Fig. 3 – PES degradation mechanism. Gaudichet-Maurin and Thominet, 2006; Arkhangelsky et al., 2007a.

same type of membrane by SEM-EDX analyses performed by Bégoïn et al. (2006a,b): as a matter of fact a new band appears (1205 cm⁻¹) at pH = 9.5. It was allocated to a new group Cl-SO₂-R. This band could be allocated to SO₂ in an environment Cl-SO₂-R (Silverstein et al., 1991). The result is a change of environment of the other absorber groups and the decrease of the corresponding absorptions, particularly the ones of the aromatic ring and the SO₂ group in an environment Ph-SO₂-Ph. It indicates that the chemical ageing mechanism of PES membranes is a membrane oxidation leading to partial disruption of ((Ph-SO₂-Ph-O)_n) bonds.

This bond is particularly sensitive to photodegradation and would lead to a new degradation mechanism of PES (Fig. 4): a mechanism of chain breaking down leading to a group ended by a sulfonic acid (1034 cm⁻¹) and another one ended by a chlorinated phenylic group (1205 cm⁻¹). This mechanism could initiate and propagate the mechanism of formation of “holes” observed on the active surface of PES membranes by Yadav et al. (2009). The latter confirmed a mechanism of chain breaking down at the level of the sulphone bond and the formation of sulphonic acid with the appearance of a new band on ATR-FTIR analyses at 1034 cm⁻¹. Ageing tests in extreme conditions were also implemented at a 7600 ppm (pH = 11.6) active chlorine concentration, which corresponds to a concentration 40 times higher than the normal conditions of use at 50 °C, during 2 months. The membrane skin is strongly damaged. ATR-FTIR spectra show an intensity decrease of the absorption bands with a complete disappearance of the PVP peak.

As far as the other membrane materials are concerned, Gitis et al. (2006a) showed a greater impact of the chlorinated solutions on ageing on cellulose acetate or cellulose ester

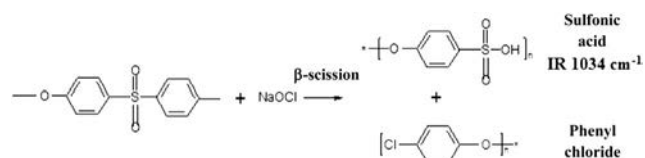


Fig. 4 – PES degradation mechanism. Bégoïn, 2004, 2006b; Yadav et al., 2009.

membranes than on PES membranes. Jung et al. (2004) and Qin et al. (2004) studied the effect of sodium hypochlorite on PAN/PVP membranes, Xu et al. (1999) on PEI/PVP membranes and Qin et al. (2003) on CA/PVP membranes.

• Degradations of polyvinylidene fluoride (PVDF) membranes

PVDF generally presents a distinctive chemical stability against most of chemicals, including a wide range of harsh chemicals such as halogens and oxidants, inorganic acids, as well as aliphatic, aromatic and chlorinated solvents (Liu et al., 2011).

Puspitasari et al. (2010) studied the ageing of PVDF membranes in 1% NaOCl from 1 to 18 weeks. The authors observed the disappearance of the carbonyl group coupled with modification of membrane surface properties and pore size distribution. The carbonyl group belongs to the surface alteration substances used by the manufacturer to make the membrane more hydrophilic. NaOCl was responsible for the consecutive increase in the membrane hydrophilicity as shown by contact angle results. The increase in membrane hydrophilicity was found to occur faster when ageing was carried out at high temperature. Any change of pore sizes due to the ageing process in the tested conditions was observed. Those results are in agreement with Wang et al. (2010): no modification of the chemical structure of MF after cleaning/disinfection with NaOCl has been observed. Membranes have become hydrophilic. The pure water flux decreased faster with the extension of the operating time and the mechanical properties also presented modifications after cleaning/disinfection. Levitsky et al. (2012) also found a decrease of the contact angle of the membrane after soaking in NaOCl. Those modifications would be due to the elimination of the residues of preservatives. Abdullah et al. (2012) found that PVDF aged for 4.5 months in NaOCl (pH 11.2, $C \times t = 13.10^6$ ppm h at 40 °C) was not mechanically deteriorated, the molecular mass distribution and the degree of crystallinity were not modified. On the contrary, in the same conditions, PVDF/Additive membranes had a degree of crystallinity which increased of 23% coupled with a loss of hydrophilicity properties of the membrane. The ageing of the same membranes in NaOH (pH 12.0 in the same conditions) revealed a modification of the molecular mass but not of the crystallinity degree.

• Degradations of Polyamide membranes

The present review is dedicated to ultrafiltration membrane cleaning/disinfection and ageing so, for more details about the effects of sodium hypochlorite, about changes in chemical and morphological properties of cross-linked polyamide reverse osmosis membranes, the reader can refer to (Gabelich et al., 2005; Kwon and Leckie, 2006a,b; Ang et al., 2006; Kang et al., 2007; Anthony et al., 2010; Etori et al., 2011; Oliveira et al., 2012).

• Degradations of cellulose acetate (CA) membranes

In terms of integrity properties, Gitis et al. (2006a) found that CA membranes, as Cellulose ester (CE) membranes and contrary to PES membranes, were chemically unstable under free chlorine attack (70 ppm at pH 11.0) and exhibited some

degree of penetration of MS2-bacteriophages into the permeate after 72 h of soaking.

In terms of polymer modifications, Qin et al. (2003) studied the effect on NaOCl on CA/PVP UF membranes. SEM images revealed that PVP additive in the dope would favor the suppression of macrovoids and that the thickness of inner skin increased with increasing air gap. PVP contents in the blend membrane could be significantly removed by hypochlorite treatment and the pore size of the treated membrane was increased. Arkhangelsky et al. (2008) found the same results: chlorine cleaning/disinfection of CA membranes affected their pore size distribution. Indeed, there is an enlargement of membrane pore size. There are also a gradual degradation of membrane surface, a deterioration of mechanical characteristics such as mechanical strength at break and Young's modulus (decrease from 240 to 80 MPa), with formation of carboxyl, aldehydes and ketones end groups.

• Degradations of polyetherimide (PEI) membranes

Commercially, sodium hypochlorite is widely used as a bleaching chemical for textile fibers and as a post-treatment agent for membranes. The effects of hypochlorite on the performance of cellulose fibers, PEI/PVP and PES/PVP membranes have been studied extensively. In the investigations of PEI/PVP membranes, post-treatment with sodium hypochlorite has increased the permeability of membranes (Roesink et al., 1991; Wienk et al., 1993). Xu et al. (1999) studied PEI hollow fibers with two different additives: polybenzimidazole (PBI) and PEG used for oil-surfactant-water separation. Contrary to previous studies, the authors did not find a significant change in water fluxes after post-treatment with sodium hypochlorite. There was a hypothesis that NaOCl tended to decrease PVP molecular weight and facilitate the removal of residual PVP out of membrane pores and thus improved the overall flux (Roesink et al., 1991; Wienk et al., 1993). Concerning the elongation at break, it was significantly decreased after post-treatment with sodium hypochlorite for PEI/PBI/PEG membranes.

• Degradations of cellulose ester (CE) membranes

In terms of integrity properties, CE membranes pre-cleaned with NaOH (72 h at 300 ppm) or NaOCl (72 h at 40 ppm) showed higher fluxes than the ones of the virgin membrane (Gitis et al., 2006a). This increase is attributed by the author to a deterioration of the membrane integrity. The deteriorations confirmed by ATR-FTIR analyses, which revealed a larger number of water molecules, retained in the pores. The spectra interpretation leads to conclude on a possible pathway of cellulose oxidation including the formation of various end groups such as carboxyl COOH, aldehyde -COH, and ketone -C=O. The deterioration was also visualized by SEM with visible different disintegration steps of CE in function of the applied conditions. Then, gold probes and MS2-bacteriophages were used to evaluate the membrane integrity all along the study. The results of ageing in chlorine conditions showed the influence of the pH with a critical value around pH 8.5, where the membrane has a low chemical stability. Moreover, higher concentrations of free chlorine caused

a faster destruction of the membrane skin layer and an earlier appearance of gold nanoparticles in the permeate. MS2-bacteriophages into the permeate was first detected for the CE membranes among the tested membranes (CE, CA and PES) after 48 h of NaOCl soaking (70 mg L^{-1}).

- **Degradations of polyvinylchloride (PVC) membranes**

Lu et al. (2011) tested NaOCl on PVC membranes for different periods of time and for both virgin and polluted membranes. Enlargement of pore size was observed after exposure to NaOCl less than 1%, and twist and wrinkles appeared when NaOCl was above 1%, which caused TMP and BSA rejection first declined and then increased. 1% NaOCl should be avoided in cleaning/disinfection.

For their part, Zhang et al. (2011) showed that the FTIR spectra of the membrane after NaOCl (100 mg L^{-1}) cleaning/disinfection was nearly identical with that of the original one. Those results are in agreement with SEM images and AFM results which show that almost all the membrane foulants were eliminated and that the pores are visible as well as on the original membrane. So, it appeared that NaOCl would be an efficient chemical agent for PVC membranes fouled by algal-rich water.

- **Degradations of polyvinylpyrrolidone (PVP)**

Membranes are generally polymerized from blends including several polymers to improve their performances or modify their properties. For instance, it has been underlined that PVP consumption, most frequently used additive, can influence membrane transport properties and generate an increase in permeability, or induce a drop of tracer retention and a decrease of membrane hydrophilicity resulting in and increase in fouling.

As a first step, we will focus on the PVP compound to try to understand how it can be affected during a chemical ageing. From a chemical point of view, PVP is a polymer soluble in water. It is a polymeric lactam with an internal amid bond. If we consider the structure of the monomer unit, PVP has an amphiphilic character since it has a particularly polar amid group which gives it hydrophilic properties. It also has a hydrophobic character because of the non-polar methylene groups in its carbonaceous backbone and the aromatic ring. Polyvinylpyrrolidone (PVPP) is a synthetic organic

polymer very similar to PVP but whose polymerization is obtained with potassium hydroxid, whose effect breaks the pyrrolidone cycle. The obtained polymer is used as a stabilizer for active substances sensitive to humidity (i.e. enzymes).

If we revert to the studies focusing on PVP used in ultra-filtration membranes applied to the drinking water treatment, Wienk (1995) were the first to study the effect of a treatment with sodium hypochlorite on a PES/PVP membrane. The immersion of the membrane, for pH included between 3.9 and 11.5, leads to a disappearance of PVP. Two mechanisms proposed by Roesink et al. (1991) deal with the mechanism of PVP elimination induced by the action of sodium hypochlorite according to pH :

- in alkaline medium, an opening mechanism of the PVP cycle under the action of hypochlorite ion (Fig. 5). This reaction is considered as a PVP oxidation in alkaline medium. The results show that 1% of PVP cycles were opened during the immersion, whatever the pH. The decrease of the molecular weight is mainly observed for the highest pH (11.5). The drop is due to a breaking mechanism of chains resulting from a macroradical rearrangement induced by hydroxyl radicals.
- in acid medium, a scission mechanism of PVP chains under the action of hydroxyl radicals (Fig. 6). This reaction prevails for pH between 2 and 7.5, interval for which hypochlorite is under its HClO protonated form. The formation of hydroxyl radicals is explained by Holst (1954). The mechanism presented in Fig. 5 leads to the formation of chains of PVP smaller and easily evacuated during cleaning/disinfection.

More recently, a photo-oxidation and thermo-oxidation study of PVP was achieved by Hassouna et al. (2009) leading to the whole possible products resulting from radical reactions or PVP β -scission with sodium hypochlorite (Fig. 7). The results of PVP photo-oxidation in solid state and aqueous solution show that the mechanisms can occur according to two ways. Oxidation involving secondary carbon leads to oxidation products of the pyrrolidone nucleus with some cyclic imides with no chain scission. Oxidation on tertiary carbon leads to non-cyclic imids and unsaturated products with macromolecular chain scission (Fig. 7). Thermo-degradation results show that the solid PVP samples exposed during 400 h at a $60 \text{ }^\circ\text{C}$ temperature do not show any degradation.

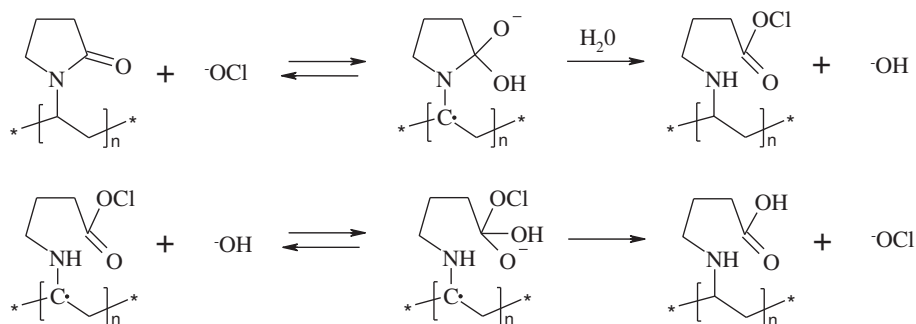


Fig. 5 – PVP degradation mechanism in alkaline conditions. Roesink et al., 1991.

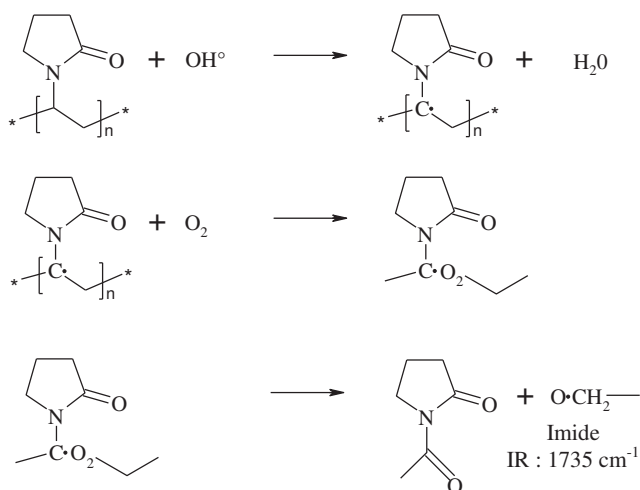


Fig. 6 – PVP degradation mechanism in acidic conditions. Roesink et al., 1991.

Prulho et al. (2012) demonstrated that ageing of PES/PVP membranes in a chlorinated medium was initiated by PVP. Indeed, contrary to PVP in the same conditions, PES alone would not decline. As it does not have any unstable hydrogen, it could therefore not be oxidized.

2.2.4.3.2. *Hydrogen peroxide, peracetic acid and other oxidizing agent: cleaning/disinfection performances and ageing*

damages. Table 9 details the studies realized on UF polymeric membrane cleaning/disinfection with free chlorine oxidants.

It is easy to note that there are far less studies of membrane cleaning/disinfection about non-chlorinated oxidants than about sodium hypochlorite. Moreover, no study has been carried out up to now about the effects of hydrogen peroxid or peracetic acid on organic ultrafiltration membrane ageing.

2.2.4.4. *Surfactants and chelatants: cleaning performances and ageing damages.* Taken separately, surfactants and chelatants do not constitute cleaning/disinfection agents in themselves. Most of the time, they are part of commercial and detergent solutions. Studies have been achieved aiming at assessing the efficiency of these compounds on the cleaning on PSf and PES membranes. Again, no ageing study has been carried out about these compounds.

Surfactants, because of their low surface tension, increase significantly the wettability of the fouled membrane, which favors the contact between the chemical agents and the deposit and reduces the adhesion forces between the fouling layer and the membrane. They remove in particular lipids by emulsifying the fat. Their efficiency is optimal when they are used at their critical micelle concentration (Rabiller-Baudry et al., 2006a). The main constraint lies in their compatibility with the membrane materials, the spacers and substrates.

In their works about the optimization of membrane cleaning processes, Chen et al. (2006) incorporated surfactants and enzymes to their cleaning solutions in order to respectively better remove fatty acids and proteins from the

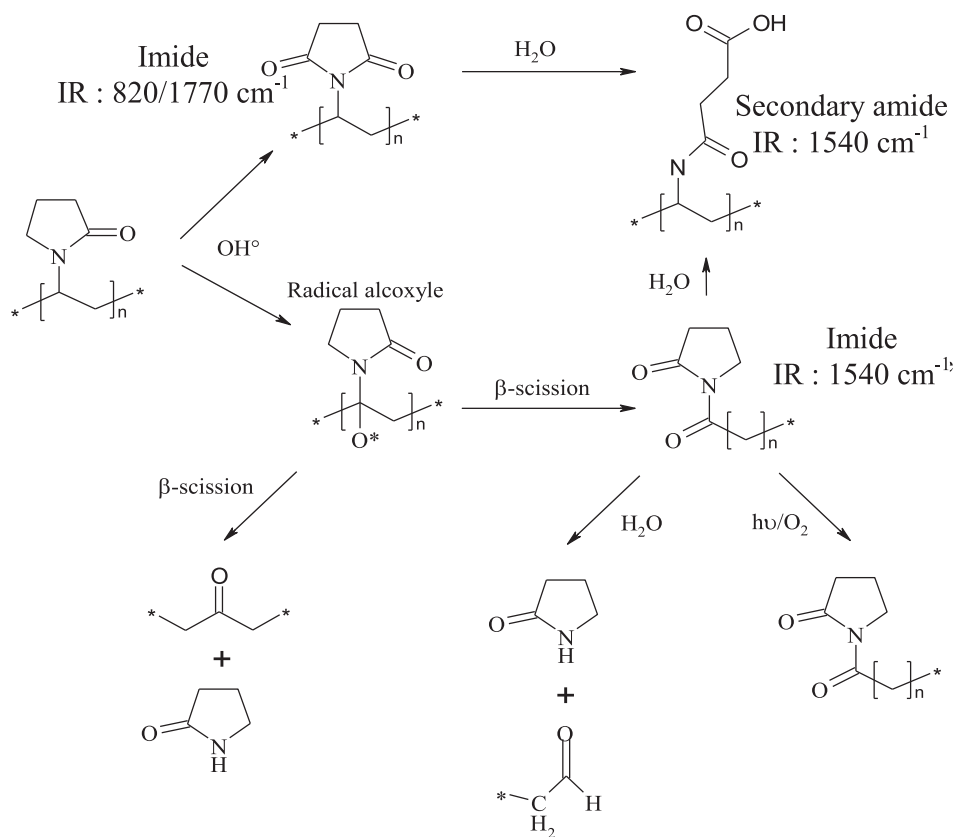


Fig. 7 – PVP degradation mechanism. Hassouna et al., 2009.

Table 9 – Cleaning/disinfection researches performed in relation to free chlorine oxidizing/disinfecting agents of UF polymeric membranes.

Application	Membrane type	Oxidizing/Disinfecting agent	References
Skim milk (Lait de Montagne, UHT, Carrefour, France)	Ultrafiltration (UF) Polyethersulfone (PES)	NaOCl (200 ppm) P3-Oxonia (1 or 10% w/w) P3-Oxonia Active (1 or 10% w/w) PVP-iodine (200 ppm)	Paugam et al., 2010
Bovine Serum Albumin (BSA) (0.3 g L ⁻¹)	UF Cellulose (CE)	H ₂ O ₂	Kuzmenko et al., 2005
Whey (5% whey medium by mixing WPC with sterilized lactose and artificial whey permeate)	UF PES	(From 100 to 3000 ppm)	
Pulp and paper effluent	UF PES	NaOCl (200 ppm) O ₃ (0.5 ppm)	Tang et al., 2010
Glutamic acid	UF Polysulfone (PSf)	H ₂ O ₂	Li et al., 2005
Surface water	UF PSf	(From 0.3% to 1% w/w)	
Flocculated reservoir water	UF PES	NaOCl (2.2–10% w/v) H ₂ O ₂ (2.2–10% w/v) Cupric sulphate (0.5–10% w/v)	Arnal et al., 2008a
		NaOCl (50 ppm) H ₂ O ₂ (250 ppm)	Strugholtz et al., 2005

membrane surface and to hydrolyse the proteins responsible for fouling, namely BSA in their study. They concluded that the use of surfactants at 1% mass was the most probing solution. However, the surfactant seemed to act on the structural properties of the membrane without having an efficient cleaning (Paugam et al., 2006). Three main surfactants were studied in the literature:

- **Triton X100, non-ionic surfactant:** Maartens et al. (1996), Pontié et al. (1997), Maartens et al. (1998), Pontié et al. (1998), Madaeni and Sharifnia (2000), Maartens et al. (2002), Allie et al. (2003).
- **Sodium dodecyl sulfate (SDS), anionic surfactant:** Kim et al. (1993), Maartens et al. (1996, 2002), Mohammadi et al. (2002), Muthukumaran et al. (2004), Li et al. (2005), Rabiller-Baudry et al. (2006a, 2006b), Wui et al. (2006), Kazemimoghadam and Mohammadi (2007), Rabiller-Baudry et al. (2008, 2010), Mendoza-Roca et al. (2010).
- **Cetyl trimethylammonium bromide (CTAB), cationic surfactant:** Kim et al. (1993), Li et al. (2005).

Like surfactants, complexing and chelating agents mostly compose commercial solutions and detergents. Chelation is a physical–chemical process during which is constituted a complex called chelate by reaction between a complexing agent called chelator and a metal, then complexed, thus chelated. The role of these compounds is to react with multivalent ions (metal, calcium, magnesium, etc...) by moving the precipitation balances and thus prevent their deposit/re-deposit. The most used complexing agents are orthophosphates, polyphosphates, EDTA, gluconic acid and gluconates. EDTA is undoubtedly the most studied complexing agent as shown in Table 10.

Table 10 gathers studies which were achieved in order to determine which agent among the different ones in a given formulation was responsible for the recovery of the membrane cleanliness and which concentrations produced an optimal cleaning.

2.2.4.5. *Enzymatic agents: cleaning performances and ageing damages.* During the last years, the use of enzymatic solutions has particularly expanded in the procedures of membrane cleaning. Their advantage is their efficiency to remove the fouling matter because of their high hydrolysing power at moderate temperature and pH, which has some interest for membranes whose pH is restricting (D'Souza and Mawson, 2005). Enzymatic solutions can therefore replace classical chemical solutions, more aggressive and often more expensive in energy. They have several advantages among which:

- their biodegradability: reduction of volumes of effluents, volumes of water necessary to rinse, no required neutralization of effluents,
- their reuse for several subsequent cleaning steps,
- the possibility to reduce the quantity of disinfectant/disinfection steps necessary to ensure the level of hygien of a plant,
- use of low concentrations,
- use of pH and temperatures very slightly aggressive for the membrane. In some applications, enzymatic cleaning has tripled the membrane lifetime (Rabiller-Baudry et al., 2012)

The advantages in terms of energy, productivity, safety, respect of environment and extension of membrane lifetime allow a positive outcome in favor of enzymatic products

Table 10 – Cleaning researches performed in relation to chelating agents of UF polymeric membranes.

Chemical agent	Application	Time/TransMembrane Pressure (TMP)	Temperature	Membrane type	References
Ethylene diamine tetra-acetic acid (EDTA) (-)	Milk (88% water, 3.4% protein, 3% fat, 4.9% lactose, 0.7% other)	30 min	30 ± 1 °C	Ultrafiltration (UF) Polysulfone (PSf)	Kazemimoghadam and Mohammadi (2007)
EDTA (0.2%, pH = 10.8–11.0)	Surface water	Zero pressure and 600–800 L h ⁻¹ , 10 min at 800–1000 L h ⁻¹ , 15 min at 1800–2000 L h ⁻¹ 15–60 min	25 °C	Naofiltration (NF) Polyamide (PA)	Liikanen et al. (2002)
EDTA (From 0.5 mM to 2 mM)	River natural organic matter, sodium alginate		20 °C	Reverse Osmosis (RO)	Wui et al. (2006)
EDTA (1 mM and 3 mM, pH = 11)	Skim milk (1% solid content concentration)	30 min	20 ± 2 °C	Cellulose Acetate (CA) UF Polyethersulfone (PES)	Maskooki et al. (2010)
Ultrasound	Skim milk (1% solid content concentration)	30 min	20 ± 2 °C	Microfiltration (MF) Polyvinylidene fluoride (PVDF) UF PSf	Maskooki et al. (2010)
EDTA (0.023%) Anionic, amphoteric Surfactants	Bovine Serum Albumin (BSA) (1 g L ⁻¹ , pH = 5)				Platt and Nyström (2007b)
Mersolat W40 (From 0.03 to 0.2%)					
EDTA (From 0.1 to 0.8 wt %)	Wastewater from banknote printing note	20–30 min/1.5 m.s ⁻¹	50–60 °C	UF PSf/PDC	Zhang et al. (2004)
EDTA (0.5% combined with 1% Na ₃ PO ₄ adjusted to pH 10 with NaOH or using 0.1 HNO ₃ (pH 2)	Swine manure	1.0–1.5 m.s ⁻¹ /20–40 kPa	25, 37, 50 °C	UF PES	Zhang et al. (2007)
EDTA (20 mM)	Surface water	24 h/Soaking	20 °C	UF Polyacrylonitrile (PAN) MF PVDF MF Polyethylene (PE) UF Polyvinylchloride (PVC)	Yamamura et al. (2007)
EDTA (150 mg L ⁻¹)	Algae-rich water	1 h/Soaking	–		Zhang et al. (2011)
EDTA (From 0.5 to 1% w/w)	Milk (From Tehran pasteurized milk factory)	30 min with no pressure	30 ± 1 °C	UF PSf	Mohammadi et al. (2002)

(Rabiller-Baudry et al., 2009). Nevertheless, some constraints and drawbacks can be pointed out:

- each enzyme has a pH and temperature optimum for its peak activity. Beyond some pH and temperature values, they can denature.
- The action of enzymes is limited to organic matter and with a great specificity. An additional acid phase must be considered to remove mineral matter.
- The necessity to fully control the deactivation step: extreme pH, heat shock or oxidizing step (Rabiller-Baudry et al., 2012),
- the activity of enzymes is relative and some deteriorious effects of proteolytic enzymes on some membrane materials were listed (Coolbear et al., 1992; D'Souza and Mawson, 2005). Even if polyacrylonitrile and polysulfone membranes withstand well to enzymatic cleanings, Rabiller-Baudry et al. (2009) give an example of destruction of a new module within five days after the application of an enzymatic procedure with an unoptimized choice of enzymes (polyamide membrane). In the same way, cellulose membrane cannot be submitted to enzymatic cleaning procedures.

The high cost of enzymes is no longer an admissible argument to use enzymatic products less in the cleaning of membrane processes. Indeed, prices have decreased substantially and as membrane lifetime has been increasing, the economical balance has been reached (Rabiller-Baudry et al., 2009).

Enzymes used in cleaning procedures almost exclusively belong to a same class: hydrolases. These enzymes catalyze hydrolysis reactions, namely the degradation of organic matter in aqueous medium. Hydrolases degrade the bonds between the different blocks of the organic macromolecules: peptide bonds in proteins, alpha or beta bonds of polysaccharides, ester bonds in triglycerides of fat (Rabiller-Baudry et al., 2012). What makes the action of an enzyme different from the one of a classical detergent based on the action of surfactants lies in the irreversible transformation of the matter. Surfactants act on the surface tension at the water/soiling interface and lift it off the surface to maintain it in solution. Enzymes degrade soiling in an irreversible way and solubilize the products resulting from the degradation. The enzyme hydrolytic power is much greater than the one of soda or of a strong acid. This hydrolytic power is constant whereas the hydrolytic power of a reagent is poorer with the reactions. Besides, the temperature necessary to the optimum enzyme hydrolytic power (50 °C) is much lower than the temperature of reagents (80 °C). Several studies were carried out in order to have a better comprehension of the mechanisms involved and to gain more insight into the choice of parameters of an enzymatic cleaning (Table 11).

As far as we know, no study has been realized on the ageing effects involved by enzymes on polymeric ultrafiltration membranes. However, it would be interesting to study more deeply the degradation mechanisms of PA and CE membranes in contact with enzymes. Even if PSf membranes are compatible with enzymes, the stability of PVP

often used to make PSf membranes more hydrophilic (Causserand et al., 2008), which are composed of amide bonds possibly attacked by enzymes (Rabiller-Baudry et al., 2009) can be questioned.

The formulated commercial detergents are often made up with pre-defined blends of chemical compounds belonging to the different classes summarized in Table 4: surfactants, dispersants, corrosion inhibitors, antifoaming agents (to compensate for the anionic effects of surfactants generally very foaming), enzymes and chelating agents.

2.2.4.6. Formulated detergents: cleaning performances and ageing damages. Table 12 details the studies about cleaning of organic ultrafiltration membranes, which were undertaken with formulated agents. It indicates that:

- enzymatic detergents are less studied than formulated alkaline and acid detergents,
- the physical–chemical composition and characteristics of the formulated detergent, namely presence or not of surfactant, interfacial energy, pH are not known precisely,
- the main techniques used to characterize cleaning are the flux measurement, microscopic and spectroscopic techniques.

According to Table 12:

- one single ageing study only was achieved with an alkaline formulated detergent. It was carried out by Bégoïn et al. (2006a,b). A 4 month ageing in a P3-Ultrasil® 10 solution at 50 °C seems to affect the chemical structure of the polymer since a new band has appeared at 1035 cm⁻¹ on the spectrum ATR-FTIR.
- no study has been published so far about membrane ageing due to acid formulated solutions during regeneration phases.

3. Membrane cleaning/disinfection and ageing: studied parameters, methods of characterization and implemented approach

3.1. Parameters

3.1.1. Cleaning/disinfection parameters

Parameters used to characterize cleanliness depend on the aspect of the concerned cleaning/disinfection: hydraulic, physical–chemical or microbiological cleanliness. For a long time, the first definition of cleanliness has mainly been studied. For this purpose, the developed parameters are quantitative parameters, **parameters related to flux** and **parameters related to resistance**.

The main advantage of the parameters related to flux is that they work with the system fluxes. However, the main drawback is that they are strongly dependent of the trans-membrane pressure. Several parameters are used and detailed by Astudillo et al. (2010). The most commonly used is the **flux recovery (FR)**. It is used to compare the membrane water flux after cleaning/disinfection with the original membrane water flux.

Table 11 – Cleaning Researches performed in relation to enzymatic agents of UF polymeric membranes.

Application	Types of enzymes	Time	Temperature (°C)	Membrane	Reference
Bovine Serum Albumin (BSA) (0.1 wt.%) RWPC (0.1 wt.%) BSA + beta-lactoglobuline (β-Ig) (1 g L ⁻¹ equimolar) Sweet whey powder solution (6 g L ⁻¹) BSA (1 g L ⁻¹) BSA + β-Ig (1 g L ⁻¹ equimolar) Whey	Terg-A-Zyme (TAZ) (0.75 wt.%) α-Chymotrypsin (From 0.02 to 0.1 wt.%) TAZ (From 0.25 to 1 wt.%) Protease A (From 0.0005 to 0.1 wt.%) Protease Type M “Amano” (Aspergillus Orizae) (From 0.02 to 0.1 wt.%) Bacillus EA 1 (0.1 M) Thermus T351 (0.1 M) Thermus Tok3 (0.1 M) Thermus Rv4.1A (0.1 M) Proteases & lipases: Reflux E2001 (0.2% v/v) Proteases: Reflux E1000 (0.2% v/v) Lipase, protease, cellulose, amylase: Quatrozyme (0.3% v/v) Protease type XXIII (3 mg mL ⁻¹) Protease type II (3 mg mL ⁻¹) Lipase Type II (3 mg mL ⁻¹) Trypsin protease (3 mg mL ⁻¹) Esterase A (3 mg mL ⁻¹) Lipase (1 mg mL ⁻¹) + Triton X100 (0.1%) followed by Trypsin Protease (1 mg mL ⁻¹) Cellulase CPT (0.5%) Cellulase CPT (0.5%) + Triton X100 (0.1%) Horse radish peroxidase (0.5%) Zumizyme AP (0.5%) Protease type XXIII (Aspergillus Orizae) (3 mg mL ⁻¹) Lipase type II (3 mg mL ⁻¹) Lipase type II (3 mg mL ⁻¹) + Triton X100 (0.1%) Lipase type II (1 mg mL ⁻¹) + Triton X100 (0.1%) followed by Protease (1 mg mL ⁻¹)	120 min (min) 60 min 15–60–120 min 30 min 45 min 45 min 30 min 60 min 60 min 60 min 60 min 60/60 min 2 h 60 min 60 min 60 min 60/60 min	45 °C pH = 7.5–8.5 (40 °C) – pH = 9 (25 °C) pH = 7 (70 °C) pH = 8 (70 °C) pH = 8 (70 °C) pH = 8 (70 °C) pH = 8.5–9.5 (48 °C) pH = 9.0–10.0 (48 °C) pH = 7.0–8.0 (48 °C) pH = 7.5 (37 °C) pH = 7.5 (37 °C) pH = 7.5 (35.5C) pH = 7.5 (37 °C) pH = 4.8 (28 °C) pH = 4.8 (28 °C) pH = 7 (28 °C) pH = 4.8 (28 °C) pH = 7.5 (37 °C) pH = 7.5 (37 °C)	Ultrafiltration (UF) Polysulfone (PSf) UF PSf UF Polyethersulfone (PES) UF PES UF UF PES UF PSf UF PES UF PSf	Muñoz-Aguado et al. (1996) Chen et al. (2006) Petrus et al. (2008) Coolbear et al. (1992) Tang et al. (2010) Maartens et al. (1998) Maartens et al. (2002) Maartens et al. (1996)
Wool-scouring effluent					
Pulp and paper effluent					
Abattoir effluent					

Abattoir effluent	Lipases:	UF PSf	Allie et al. (2003)
	<i>Candida cylindracea</i> (1 mg mL ⁻¹)		
	<i>Pseudomonas mendocina</i> (10 mg mL ⁻¹)		
	<i>Aspergillus oryzae</i> (10 mg mL ⁻¹)		
	Proteases:		
	Protease A (0.0005 mg mL ⁻¹)		
	<i>Bacillus licheniformis</i> (0.005 mg mL ⁻¹)		
	<i>Aspergillus oryzae</i> (0.005 mg mL ⁻¹)		
	Sulphidogenic proteases		
Abattoir effluent			
	TAZ (0.75 wt.%)		
Aqueous extract of soy flour	NaOCl (150 ppm)/TAZ (0.75 wt. %)/NaOCl (150 ppm)	UF PSf	Melamane et al. (2002) Sayed Razavi et al. (1996)
Tannery effluents (100–120 kg of COD per ton of raw hide) Wastewater	Defat 50 (1 g L ⁻¹) Riberzim MPX (1 g L ⁻¹) EDTA (5 g L ⁻¹) Protease (-) + Divos 110	UF PSf UF Polyvinylidene fluoride (PVDF)	Mendoza-Roca et al. (2010)
Surfacting recovery	TAZ (1 wt.%)	UF	Te Poele and Van der Graaf (2005)
		UF PES UF Cellulose (CE)	Chen et al. (2008)

The main advantage of parameters related to membrane resistance is that they give information related to membrane resistance. The information is independent of transmembrane pressure. For membrane cleaning/disinfection quantification, different concepts are used and detailed by Astudillo et al. (2010). The most commonly used is the **resistance recovery (RC)**. It compares the membrane residual resistances with the hydraulic membrane resistance.

For the two generally used parameters (FR and RC), it is possible to find different acceptable limit values to define a good cleaning/disinfection according to the studied membrane:

- Gan et al. (1999): RC < 15%
- Argüello et al. (2003, 2005): RC < 6.7%
- Blanpain-Avet et al. (2004): RC < 5%
- Daufin et al. (1991): RC < 4.8%
- Field et al. (2008): FR > 95%
- Gésan et al. (1996) and Rabiller-Baudry et al. (2002) FR > 0.90.
- GE Healthcare supplier: 65% < FR < 95%
- Zondervan and Roffel (2007) defined criteria to quantify the overall cleaning effectiveness.

However, from the above summary, clear challenges and hindrance have to be overcome:

- The cleaning studies principally describe the cleaning/disinfection efficiencies for specific fouling in a few membrane/water systems via prescribed cleaning/disinfection processes (Lin et al., 2010). Using similar terminologies, researchers are dealing with different cleaning/disinfection phenomena, but the comparison for the used cleaning agent/procedures derived from different studies is difficult. A systematical analysis about the reaction of a cleaning/disinfection agent with foulants and membrane is required to provide a common platform for cleaning/disinfection and ageing studies.
- So, conventional assessment of cleaning/disinfection by flux measurement has been used in the last decades in order to optimize and evaluate the cleaning/disinfection procedures (Porcelli and Judd, 2010a). However, two industrial examples underlined the controversial representativeness of the cleanliness parameters based on flux measurement (Rabiller-Baudry et al., 2009), in agreement with Weis et al. (2005) and D'Souza and Mawson (2005) who underlined that permeate flux is therefore a poor indicator of surface condition contrary to FTIR and Zeta potential techniques. Indeed, the pure water flux changes with time because the load on the membrane surface is affected. Rabiller-Baudry et al. (2008) showed that surfactants tend to adsorb on polyethersulfone (PES) leading to either hydraulic resistance variation or only to surface energy variation. Evans and Bird (2006) established that the cleaning step with NaOH modifies the hydrophobicity to a value ranged from fouled surface to cleaned surface and consequently the permeability values vary. As a consequence, complementary methods of cleaning/

Table 12 – Cleaning researches performed with formulated detergents of UF membranes.

Application	Detergents	Membrane type		References
Skim milk (Lait de Montagne, UHT, Carrefour, France)	P3-Ultrasil 10 (–) Ultraclean II (–)	Ultrafiltration (UF) Polyethersulfone (PES)	The weaker the interfacial energy is, the more efficient the formulated detergent is in terms of cleaning.	Rabiller-Baudry et al. (2006a)
Skim milk (Lait de Montagne, UHT, Carrefour, France)	P3-Ultrasil 10 (0.1 or 0.4 wt.%) Ultraclean II (0.3 vol.%)	UF PES	An efficient formulated detergent must have an interfacial energy $\approx 25 \text{ mJ m}^{-2}$ and a non-polar character.	Rabiller-Baudry et al. (2006b)
Skim milk (Lait de Montagne, UHT, Carrefour, France)	P3-Ultrasil 10 (0.1 or 0.4 wt.%) Ultraclean II (0.3 vol.%)	UF PES	P3-Ultrasil® 10 and Ultraclean® II have the greatest cleaning efficiencies. An efficient formulated detergent at pH 11.5 and 50 °C must have an interfacial energy $<30 \text{ mJ m}^{-2}$ and have strongly non-polar surfactants.	Rabiller-Baudry et al. (2008)
Skim milk (Lait de Montagne, UHT, Carrefour, France)	P3-Ultrasil 10 (0.4% w/w) P3-Oxonia (1% or 10% w/w) P3-Oxonia Active (1% or 10% w/w)	UF PES	P3-Ultrasil® 10 makes it possible to have back a hydraulic cleanliness of 92%. However, flux cannot be recovered, should the procedure of chlorine cleaning not be followed.	Paugam et al. (2010)
Skim milk (Lait de Montagne, UHT, Carrefour, France)	P3-Ultrasil 10 (0.1 wt.%) Ultraclean II (0.3 vol.%)	UF PES	Surfactants in the formulation of Ultraclean tend to adsorb and increase the membrane resistance. However, it seems more efficient than P3-Ultrasil® 10 to remove residual proteins.	Delaunay et al. (2006)
Bovine Serum Albumin (BSA) (80 ppm)	P3-Ultrasil 10 (From 0.1 to 1 wt.%)	UF Polysulfone (PSf) UF	Polyvinylidene fluoride (PVDF)	The cleaning temperature must not exceed 60 °C. At high temperature, P3-Ultrasil® 10 removes possible residuals resulting from polymerization process making the membrane more hydrophilic.
Nyström and Zhu (1997)				
BSA (1 g L ⁻¹ , pH = 5)	F80 FILTER HE (1%) F83 FILTER E (1%) F86 FILTER VE (1%) F89 FILTER HH (1%) F91 FILTER VH (0.5%)	UF PSf	A static cleaning at 50 °C during 30 min with a detergent with a surface tension of 37 –38 mN m ⁻¹ and a pH of 10.98 removes all the residual proteins.	Platt and Nyström (2007b)
Whey Protein Concentrate (WPC) (Reconstituted 3.5 wt.%)	P3-Ultrasil 11 (0.5 wt.%) Libranone 960 (0.1 wt.%)	UF PES UF Polyamide (PA) UF Cellulose (CE)	Libranone 960 is the most efficient detergent (flux, Scanning Electron Microscopy, Atomic Force Microscopy and Fourier Transformed Infra-Red).	Väisänen et al. (2002)
Pulp and paper mill WPC (WPC80 reconstituted with DIW)	P3-Ultrasil 75 (0.14% w/w) P3-Ultrasil 91 (0.45% w/w)	UF PSf/ Polypropylene (PP) UF PVDF UF PES	The cleaning characterization obtained by the use of the streaming potential measurement confirms the results obtained by the control of flux.	Lawrence et al. (2006)
WPC (Lacprodan 80) + Dextran T40	P3-Ultrasil 10 (0.5–1%) P3-Ultrasil 02 (0.2%) P3-Ultrasil 75 (0.3%) P3-Ultrasil 67 (0.5%) P3-Ultrasil 69 (0.8%)	UF PSf Microfiltration (MF) PSf		Lipnizki et al. (2005)
Glutamic acid	P3-Ultrasil 11 (pH = 12.0)	UF PSf	P3-Ultrasil® 11 has the most important cleaning efficiency (99.5%).	Li et al. (2005)
Spent sulphite liquor	P3-Ultrasil 11 (0.5 wt.%)	UF PES UF PSf	For 6 fouling/cleaning cycles, NaOH and P3-Ultrasil® 11 have the same cleaning performances. Beyond 6 cycles, P3-Ultrasil® 11 has cleaning performances higher than NaOH	Weis et al. (2003)

Table 12 – (continued)

Application	Detergents	Membrane type		References
Spent sulphite liquor	P3-Ultrasil 11 (From 0.05 to 0.5 wt.%)	UF PES UF PSf UF Regenerated Cellulose (R-CE)	Despite high fluxes after cleaning protocols, the characterization of the membrane surface (Fourier Transformed Infra-Red and Zeta potential) shows that cleaning does not help recovering the initial characteristics of the membrane.	Weis et al. (2005)
Lignosulfates	P3-Ultrasil 11 (0.1 wt.%)	UF PES	For 5 fouling/cleaning cycles, HNO ₃ has cleaning performances higher than P3-Ultrasil 11 [®] . Beyond 5 cycles, P3-Ultrasil [®] 11 has the best cleaning performances.	Weis and Bird (2001)
Sulphite pulp mill	P3-Ultrasil 96 (0.6 vol.%) P3-Ultrasil 75 (0.5 vol.%) Berocell 537 (0.25 vol.%)	UF PES- PolyAcrylate (PlyA)	The results provided by the different cleaning procedures with acid as well as alkaline detergents are not satisfactory and must be improved.	Wallberg et al. (2001)
Goat milk Beetroot juice Cow milk	P3-Ultrasil 10 (0.25% w/v) P3-Ultrasil 11 (1% w/v)	Ceramic Nanofiltration (NF) Polyethylene (PE)	To assess the efficiency of the cleaning on the permeability recovery, it is advisable not to use one pressure value only. A new cleaning parameter is defined by the author.	Astudillo et al. (2010)
Wastewater	Triclean 212F (High pH cleaner)	UF PES Reverse Osmosis (RO) Polyamide (PA)	According to design of experiments, the most important recovery of flux was at 50 °C for a 0.85% concentration.	Chen et al. (2003)
Wastewater	Divos 110 (pH = 9.3) Divos 2 (pH = 1.5) Divos 25 (pH = 2.0)	UF	The results display a full recovery of flux after the procedure of enzymatic cleaning.	Te Poele and Van der Graaf (2005)
Oily waste water	P3-Ultrasil 70, P3-Ultrasil 75, P3-Ultrasil 11, P3-Ultrasil 91 (1%)	UF PSf	Recoveries of flux after the use of P3-Ultrasil [®] 70 are better than P3-Ultrasil [®] 75, which are better than P3-Ultrasil [®] 11 and P3-Ultrasil [®] 91. The most important recovery of flux is obtained with NaOCl.	Lindau and Jönsson (1994)
Surface water	4 Aquaclean Fer 12, P3-Ultrasil 70, Kleen MTC 411, P3-Aquaclean Sal, P3-Ultrasil 115 (0.05 mol L ⁻¹)	UF	The best cleaning efficiency is obtained with P3-Ultrasil [®] 115. Cleaning efficiency with 4Aquaclean Fer [®] 12, P3-Aquaclean Sal [®] , P3-Ultrasil [®] 70 and Kleen MTC [®] 411 is lower and lower.	Zondervan and Roffel (2007)
Surface water	Auxiclean B.13 (0.5–2% w/v)	UF PSf	After soaking at 40 °C for 24 h, the best results were obtained with H ₂ O ₂ , Auxiclean B.13 and NaOCl.	Arnal et al. (2008a)

disinfection characterization have to be used in order not to skew the achieved results.

3.1.2. Ageing parameters

Contrary to cleaning/disinfection quantitative parameters, no quantitative values have been defined to determine the level of damage of the membrane. Even if ageing can arise on macroscopic scale by several characteristic symptoms (increase of permeability, modification of retention and mechanical properties...) no quantitative criterion has been defined yet to delimit the boundaries of the ageing field. Concerning the microscopic scale, the ageing characterization remains mainly qualitative even if some quantitative studies have been recently published (Wyart et al., 2011). For instance, the surface roughness analysis is used as an ageing parameter. This measurement has been applied on polyvinylchloride membrane (PVC) before and after chemical cleaning by Zhang et al. (2011).

As for cleaning/disinfection determination, it should emphasize the controversial representativeness of the ageing

parameters based on flux measurements since it has been proved that the modification of flux could not be representative of cleanliness (Rabiller-Baudry et al., 2009). The parameters based on flux should then be used carefully and it should be advised to use microscopic and macroscopic methods simultaneously in order to get complementary data.

3.2. Microscopic and macroscopic cleanliness and ageing methods of characterization

As a natural consequence, new methods of characterization have been developed for cleaning/disinfection characterization as well as for ageing characterization in order to achieve a better and deeper understanding of membrane performances all along its use. Microscopic and macroscopic, qualitative or quantitative information is available using:

- Structural characteristics,
- Surface characteristics,
- Material characteristics.

Initially, these methods were used to help membrane manufacturers to create new types of membranes, and improve their filtration properties. Then these methods have been quickly applied to the study of fouled membranes in order to understand the mechanisms involved in the build-up of the fouling. One thing leading to another, the same methods have been applied to membrane cleaning/disinfection characterization (Table 13), in order to establish more appropriate cleaning/disinfection protocols. Ageing has become the new bone of contention of studies dedicated to membrane characteristics and researches. As membrane ageing is a direct result of a wrong cleaning/disinfection procedure or an unoptimized cleaning/disinfection procedure, it is therefore natural to evaluate cleaning/disinfection and ageing characterization simultaneously and to have cleaning/disinfection as well as ageing methods of characterization.

At first, mainly microscopic, spectroscopic and surface characterization methods (SEM, ATR-FTIR, etc...) were applied to characterize new membranes (Table 13). Indeed, as well as for cleaning/disinfection and ageing characterization, permeability recovery alone is itself insufficient to characterize changes in membrane fouling in response to cleaning/disinfection as well as changes in membrane active layer in response to ageing (Porcelli and Judd, 2010a). At present, there are several modern surface analysis techniques that can assist precisely and rapidly in optimizing the cleaning/disinfection processes (Al-Amoudi et al., 2007). However, these methods are destructive, not practical for the industrial routine use but useful for more fundamental researches, autopsies (Darton and Fazel, 2001) or post-understanding of the problems encountered on the industrial plants. Al-Amoudi et al. (2007) reviewed some methods of assessing the cleaning/disinfection efficiency of nanofiltration membranes (NF), which are the most commonly used according to the authors. New techniques to assess the cleaning/disinfection efficiency and the ageing proportion are being developed or could be developed in the future: High Resolution Scanning Electron

Microscopy (HRSEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Confocal Laser Scanning Microscopy (CLSM), Scanning Probe Microscopy (SPM), Field Emission Scanning Electron Microscopy (FESEM), Thermal analysis using Differential Scanning Calorimetry (DSC), MALDI-MS and mechanical tests. Thus, modern instrumentation will help to have systematic more predictable view of cleaning/disinfection processes.

There currently exists a variety of analytical tools to characterize the morphology of polymeric membranes (Cuperus and Smolders, 1991). Causserand (2006), Fontyn et al. (1988) and Al-Amoudi et al. (2007) detailed the operating principles of some of these techniques of characterization. Some of the more popular and used methods have been detailed in the following part (Scanning electron microscopy, Fourier-transformed Infrared spectroscopy).

3.2.1. High resolution scanning electronic microscopy (HRSEM)

Scanning electron microscopy is based on electrons–matter interactions. The sample is impinged by an electron beam emitted from an electron gun in a high vacuum. Electrons interact with matter. Scanning electron microscopy analyzes electrons reflected by the sample: secondary electrons and back-scattered electrons (Causserand, 2006). Secondary electrons are emitted by atoms occupying the sample surface and produce a surface image. The image contrast is determined by the image morphology of the sample. Back-scattered electrons are primary electrons reflected by atoms in the solid. However, the quality of images obtained by scattered electrons is inferior to the quality by secondary electrons. SEM imaging is mainly performed from secondary electrons. Applied to the study of membranes, it has proved to be a performing method to:

- locate and identify foulants: Kim et al. (1993), Bartlett et al. (1995), Väisänen et al. (2002), James et al. (2003),

Table 13 – Main methods of fouling and cleaning/disinfection characterization (Causserand (2006)).

Methods	Atomic Force Microscopy	High Resolution Scanning Electron Microscopy	Scanning Electron Microscopy –Energy Dispersive X-Ray	Other microscopic methods	Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy	Streaming potential Zeta potential	Contact angle	Permeability	Retention	Ultrasonic methods	Colorimetric methods
New membrane											
Membrane topography	X	X		X							
Pore size distribution	X	X	X								
Chemical composition			X								
Surface roughness	X			X							
Surface charge						X			X		
Hydrophilic/hydrophobic balance							X				
Fouled / cleaned membrane											
Fouling detection	X	X		X	X		X			X	X
Fouling characterization			X		X						
Surface modifications by surfactants						X		X			
Membrane adhesion	X							X			

- **compare chemical cleaning/disinfection efficiencies:** Zhang and Liu (2003), Sayed Razavi et al. (1996), Wallberg et al. (2001), Zhang et al. (2011), Lindau and Jönsson (1994), Li et al. (2005),
- **assess cleaning/disinfection efficiency and to validate new cleaning/disinfection protocols:** Rabiller-Baudry et al. (2002), Zhang et al. (2004, 2007),
- **understand cleaning/disinfection mechanisms:** Li et al. (2005),
- **characterize membrane ageing and morphological modifications:** Bégoïn et al. (2006a,b); Rouaix et al. (2006); Momtaz et al. (2005); Lawrence et al. (1998); Lu et al. (2011); Qin et al. (2003). After 16 days of an oxidative ageing in NaOCl, Rouaix et al. (2006) underlined the correlation between a change in the apparent membrane morphology and the weakening of the mechanical properties and the chain length reduction. Similarly, Momtaz et al. (2005) used HRSEM to visualize the modifications of PVDF surface topography in contact with chloroform, acetonitrile, dimethyl sulfoxide, dioxane and ethyl acetate. Lawrence et al. (1998) used FEHRSEM to analyze the membrane surface and the pore size of the membranes after cleaning/disinfection and storage, and also the deposited layer thickness after each stage of cleaning/disinfection. Lu et al. (2011) observed an enlargement of the pore size of PVC hollow fibers exposed to less than 1% NaOCl. This method of characterization allowed the observation of twist and wrinkles on membranes when NaOCl was above 1%.

In spite of the wide range of cleaning/disinfection characterization by HRSEM, three major drawbacks can be underlined: HRSEM can be limited in terms of threshold of detection. For instance, there was insufficient relief to acquire detailed images by HRSEM (James et al., 2003) and AFM may prove more adapted. The second drawback lies in the instability of some polymeric material under the electronic beam. A field-emission HRSEM (FESEM) can be used to minimize sample damages. This method provides narrower probing beams than the HRSEM ones, at low as well as high electron energy resulting in both improved spatial resolution and minimized sample charging and damage (Kim et al., 1993). Then, the third drawback remains in the sample preparation. Indeed, in order to preserve the high vacuum necessary inside HRSEM during measurement and to avoid any contamination of the microscope, the samples are always dried. However, drying could lead to uncontrolled shrinkage of the membrane material and undesired changes in the membrane morphology (Borneman et al., 2001). To have a better and more realistic view of the membrane morphology Borneman et al. (2001) used cryo-SEM to examine PES and PES/PVP membranes used in the filtration of apple juice and cleaned with NaOH. Wyart et al. (2011) used HRSEM to correlate morphological parameters, mean pore size and recovery rate, with the permeability decrease.

3.2.2. Atomic force microscopy (AFM)

A wide range of use offered by AFM could be considered in terms of membrane characterization (Dietz et al., 1992; Fritzsche et al., 1992, 1993; Khayet and Matsuura, 2003; Kim et al., 1999; Wyart et al., 2008) as well as in terms of

assessment of membrane cleaning/disinfection and membrane ageing.

This technique was primarily used to probe surface topography and interactions on the atomic–molecular scale (Bowen and Doneva, 2000). It has been used extensively to characterize the structure and morphology/topography of various types of clean microfiltration and ultrafiltration membranes. James et al. (2003) used AFM coupled with SEM and X-ray photoelectron microscopy to visualize the fouling layer. Al-Amoudi and Lovitt (2007) showed an accumulation of the particles in the valleys of rough membranes causing more severe flux decline than smooth membranes. Huisman et al. (2000) used AFM pictures to illustrate the influence of the fouling solution pH on the pore sizes on three different PSf membranes fouled with bovine serum albumin (BSA). Tian et al. (2010) used AFM analyses of surface and section of polyvinylchloride (PVC) membranes fouled by river water and cleaned with NaOH and ethanol to underline the ability of these two chemicals to eliminate the surface fouling as well as the in-pore fouling. Väisänen et al. (2002) used AFM to compare roughness of ultrafiltration membranes (UF) made of different materials. However, it should be noted that AFM images are distorted by convolution between pore shape and cantilever tip shape and, therefore, the quantitative determination of pore size from an AFM image is not always straightforward (Singh et al., 1998). Moreover, one of the main drawbacks of the AFM is the relatively small area which can be scanned at any given time. Such a limited scan-size makes it difficult to determine how representative the measured image of the surface is at large (Koyuncu et al., 2006). According to the authors, optical interferometry is a rather new technique, which may be used to characterize membrane surfaces as far as surface morphology and structure are concerned. This method was recently applied on nanofiltration membrane by Espinasse et al. (2012) in order to compare the cleaning/disinfection efficiency of different cleaning/disinfection agents (NaOH, HCl, NaOCl P3-Ultrasil 110).

In terms of ageing, AFM compares the roughness of polyvinylidene fluoride (PVDF) and Polyethersulfone (PES) membrane changes after NaOCl cleaning/disinfection and after post-cleaning fouling. The increase is more deeply emphasized for PVDF than for PES. The authors explain this increase by a gradual elimination of the preservation residues (Levitsky et al., 2011). AFM was performed on bovine serum albumin (BSA) fouled PES membranes and then cleaned in chlorine conditions by Arkhangelsky et al. (2007a). Comparing these results with those obtained with streaming potential measurements, XPS, ATR-FTIR and virus filtration, the authors concluded to an enlargement of the pores of chlorine treated membranes. Kwon and Leckie (2006a) showed no modification of the roughness of polyamide (PA) reverse osmosis (RO) membranes aged in 2000 ppm h at pH 4 or pH 9 using AFM. Möckel et al. (1999) used AFM to underline the correlation between the degree of carboxylation and the surface roughness. In the meantime, they showed that the rougher the membrane was, the better the cleaning/disinfection index was.

3.2.3. Attenuated Total Reflectance Fourier-Transformed InfraRed Spectroscopy (ATR-FTIR)

The main spectroscopic technique used to characterize new, fouled, cleaned and aged membranes is Fourier Transformed

Infrared Spectroscopy (FTIR). It is a powerful analytical tool for the characterization and identification of organic molecules. It is the most used technique to characterize new membranes (Causserand, 2006). In Attenuated Total Reflection mode (ATR), this spectroscopy identifies functional groups present on a thickness of about 1 μm . The penetration depth depends on the wavelength, the angle of incidence of the beam compared with the normal within the crystal and the crystal material. During the analyses, the sample is maintained in contact with a crystal provided for a total internal reflection. An infrared beam enters the crystal where the sample to study is laid. The internal reflection of the beam at the crystal creates an evanescent wave, which at each reflection continues beyond the surface in the crystal surface and penetrates the sample. Spectra are thus obtained. They represent the variations in absorbance according to the wavelength. Absorption peaks of the spectra are typical of the functions at the membrane surface. In order to take into account the differences of penetration of the incident beam in the membrane material, intensities of each characteristic peak of the membrane are adjusted to the height of a characteristic peak of the studied polymer (at $1,243\text{ cm}^{-1}$, characteristic peak of the polymer (bond SO_2) for membranes HFK 131). It is then possible to compare ratios H_x/H_{1243} from a spectrum with the other (Bégoïn et al., 2006a).

This technique was used to characterize:

- **PSf and PES membranes:** Oldani and Schock (1989), Zhu and Nystrom (1998), Belfer et al. (2000), Maruyama et al. (2001), Rabiller-Baudry et al. (2002),
- **PVDF membranes:** Hashim et al. (2011), Puspitasari et al. (2010), Abdullah et al. (2012)
- **cleaning/disinfection and presence or not of residual foulants:** Oldani and Schock (1989), Zhu and Nyström (1998), Belfer et al. (2000), Rabiller-Baudry et al. (2002),
- **ageing and identification of affected bonds:** Bégoïn et al. (2006b), Causserand et al. (2006), Arkhangelsky et al. (2007a,b), Yadav et al. (2009), Gaudichet-Maurin (2005), Thominet et al. (2006), Gaudichet-Maurin and Thominet (2006), Delaunay (2007); etc.

SEM, AFM, ATR-FTIR, surface (zeta, streaming potential and contact angle) were with permeability measurements the most commonly used techniques for cleaning/disinfection and ageing characterization. These methods provide the most important cleaning/disinfection and ageing data. The required conditions of measurement and sampling are now well known. However, to gain access to more or/and other information, new methods of cleaning/disinfection and ageing characterization can also be used: microscopic methods (X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Fourier Transformed – Raman spectroscopy (FT-Raman)) as well as spectroscopic methods (Confocal laser scanning methods (CLSM), Scanning Probe Microscopy (SPM), epifluorescent microscopy).

3.2.4. New spectroscopic methods for cleaning/disinfection and ageing characterization

XPS is a very specific technique for surface analysis. It was used to determine the presence of organic compounds on the

surface of the membrane (Labbe et al., 1990; Lindau and Jönsson, 1994) after the cleaning/disinfection of PSf UF membrane fouled with oily waste water. XPS experiments were realized on BSA fouled PES membranes by Arkhangelsky et al. (2007a) in order to determine the surface variations of composition of the membrane involved by fouling and cleaning/disinfection. An examination of the concentrations of the elemental C, S and O on the membrane surfaces highlighted the modifications due to the hypochlorite exposure. According to the author, the elevated concentrations of sulfur and carbon in the upper part of the PES membrane may indicate a partial scission of the sulfonyl Ph–S bond. A degradation mechanism is proposed. Ross et al. (2000) and Momtaz et al. (2005) used XPS to underline the progressive hydrolysing of the ester bonds and the dissolution of the upper surface of PVDF membranes in basic conditions (Lithium hydroxide 1 N). Kwon and Leckie (2006a) proved the possible bounding of chlorine to the surface of cross-linked PA membranes degraded in NaOCl at different concentration and pH. XPS can also give information about additives used in membrane polymerization. XPS demonstrated a significant loss of PVP, with the bulk of the PVP removal occurring within the first hour of bleach exposure of PSf/PVP dialyzer (Wolff and Zydney, 2004). Exposure to bleach caused nearly a threefold reduction in the concentration of PVP. Moreover, the method determined if chlorination of the polymer involved by bleach occurred or not. Rouaix et al. (2006) used XPS with permeability, retention and mechanical properties of the membrane to underline the influence of PVP only on macroscopic properties and not in the material strength. Concerning the PVDF membranes, this technique was applied to identify the modifications of the membranes after a hypochlorite ageing by Puspitasari et al. (2010). Coupling XPS and ATR-FTIR results, the author identified the disappearance of the carbonyl group within the first week of the ageing.

XRD analysis has been performed to examine the crystal structures and structural changes of PVDF after the formation of hollow fiber membrane and the effect of NaOH treatment on the membranes (Hashim et al., 2011).

FT – Raman spectroscopy was used by Ross et al. (2000) and Zhang et al. (2006) to provide information about conjugated structure and chain skeleton of PVDF membranes treated with KOH alcohol solution. Coupled with Time-of flight, secondary ion mass spectrometry (ToF-SIMS), XPS, FT-IR and ESR, this method allows the identification of the main steps of the ageing degradation mechanism of PVDF membranes in alkaline conditions.

3.2.5. New microscopic methods for cleaning/disinfection and ageing characterization

Spettmann et al. (2008) studied the membrane deposits. The chosen model of foulants was bacterial stained with the fluorescent dye rhodamine 6G. They visualized them by confocal laser scanning microscopy. Uncleaned, weakly cleaned and completely clean membranes could be distinguished by means of **Confocal Laser Scanning Microscopy (CLSM)**. CLSM in combination with image analysis is suitable to visualize the three-dimensional distribution of fluorescently labeled foulants in multi-layered deposits and to

evaluate the efficiency of cleaning/disinfection measurements for deposit removal.

Scanning Probe Microscopy (SPM) was used by Arkhangelsky et al. (2007b) to compare images of native membrane and NaOCl treated membrane. The micrographs of the pristine membrane showed a smooth surface unlike the fiber surface of the hypochlorite-exposed PES membrane where pits and exfoliated regions could be observed.

Epifluorescent microscopy was used by Kuzmenko et al. (2005) to visualize the protein patches on membrane surfaces after different cleaning/disinfection procedures. The obtained micrograph suggests that residuals of BSA after chlorine treatment can serve as centers for further protein accumulation. It was proved that the cleaning/disinfection agent was found to be important in term of future fouling. Effective oxidation with free chlorine resulted in complete restoration of the initial flux but caused a faster fouling for the next filtration step. It is argued that the probable cause of this phenomenon is the alteration of the membrane surface which could explain the decrease of flux observed by Levitsky et al. (2011, 2012). However, disintegration of UF membranes with introduction of free chlorine was observed only when the oxidant was applied as a primary cleaning/disinfection agent.

Until now, the methods of the detailed characterization have been used to characterize fouling/cleaning/disinfection and then have been applied to ageing. However, membrane ageing researches are more and more examined and, in the same time, new scientific aims have appeared (ageing mechanisms, polymer modifications, etc). As a consequence, methods of characterization have undergone some changing. Methods of characterization normally applied to the polymer-bound materials evolved towards ageing characterization of membranes. Thus, the *measurement of the mechanical properties* has become a significant and efficient way to study ageing of polymeric membranes. Other methods are being developed such as **Electron Paramagnetic Resonance (EPR)**, **Electron Spin Resonance (ESR)**, **Thermal analysis using (DSC)**, but their use is sporadic and not well developed yet.

3.2.6. Newly applied ageing methods of characterization

3.2.6.1. Mechanical properties. The measurement of the mechanical properties is a destructive method and it is not used as a cleaning/disinfection characterization method, but mainly as an ageing characterization method. Practically, all the mechanical parameters are not interesting. Rouaix et al. (2006) and Causserand et al. (2008) highlighted the fact that elongation at break point is more sensitive to membrane degradation than tensile strength.

Generally, this method of characterization is applied on hollow fibers but some results are presented on polymeric films (Thominette et al., 2006). Childress et al. (2005) compared the mechanical properties of different UF and MF membranes. The incidence of fiber failure can be divided into four categories (Childress et al., 2005):

- **Deteriorations by chemical attack (oxidation):** failure due to oxidation can be easily attributed to the incompatibility of chemicals in the feed water with the membrane material. Causserand et al. (2006) used this method to evaluate the impact of the pH soaking of bleach solutions on the

radical degradation of PSf hollow fibers. Tensile tests coupled with the study of the PES molecular mass were used by Thominet et al. (2006) to compare the oxidative ageing of PES film and PES fibers. On the contrary, Zondervan et al. (2007b) found no modification of the mechanical properties of PSf membrane after intense exposure to NaOCl. Mechanical properties of clean modules back pulsed with water and sodium hypochlorite were similar, in agreement with Huisman and Williams (2004). Hashim et al. (2011) found a reduction of the mechanical strength of PVDF membranes with an increase in concentration and/or temperature of NaOH solutions. PVDF membranes totally lost their mechanical integrity in very short time under harsh treatment conditions.

- **Deteriorations due to the presence of foreign bodies:** failure due to scoring and cleaving can be readily identified by examining a failed module for the presence of foreign bodies.
- **Deteriorations during operation resulting from faulty installation:** Huisman and Williams (2004) showed that PSf UF hollow fibers were mainly damaged by mechanical forces: high local shear forces or vibrations and not by chemical agents.
- **Deteriorations due to faulty membrane/module structure:** It was found that additional stresses at the juncture of the potting material and the hollow fiber membranes exist and can lead to the formation of fractures.

In fact, the degradation of the mechanical properties would rather be a combination of these four factors than a unique effect. Indeed, Zondervan et al. (2007b) found that the following combinations (among all the tested combinations) were the most deteriorated for permeability: fouling status + number of back pulses, fouling status + NaOCl concentration + magnitude of the back pulse and fouling status + magnitude of the back pulse + number of back pulses. Similarly, Gijsbertsen-Abrahamse et al. (2006) gathered the impacts of all the process parameters on the different variables of the mechanical properties of the studied hollow fibers (elasticity modulus, tensile strength and relative deformation at the point of breakage).

3.2.6.2. Electron Paramagnetic Resonance (EPR), Electron Spin Resonance (ESR), Thermal analysis using DSC. Oliveira et al. (2012) introduced EPR as a powerful technique to follow membrane ageing. Indeed, this technique allows the detection of free radicals formed in polymeric membrane materials which could give important information about molecular and structural changes when membranes are exposed to NaOCl for instance. Zhang et al. (2006) investigated the structure of alkaline treated PVDF membranes with ESR, FTIR and FT-Raman. The results allowed the accurate identification of the mechanism involved based on the radicals produced in the process of deprotonation and defluorination of PVDF.

Based on *the thermal analysis using DSC* results, it can be concluded that the PVDF hollow fiber membranes had been attacked by the NaOH solution under all tested conditions, which led to a decrease of the melting temperature, melting

enthalpy and crystallinity. Furthermore, the decrease was accelerated at a high temperature or in a concentrated NaOH solution. The degree of crystallinity of the PVDF hollow fiber membranes was reduced over the course of the NaOH treatment (Hashim et al., 2011).

3.3. Methods

So far, the bibliographic review was led independently from the approach implemented. Only the used products, the current knowledge about them and the characterization methods used were studied. The state of the art of the methodological approaches that it is possible to develop for a cleaning/disinfection and a membrane ageing study will be the aim of this part.

3.3.1. Implemented methods of cleaning/disinfection study

As far as cleaning/disinfection studies are concerned, everyone strives to reproduce at the laboratory scale the conditions experienced at the industrial scale more or less successfully. Concentrations, cleaning/disinfection times and temperatures used are generally those used on the site. Optimization studies aim at making the parameters varying in order to determine the optimal value for the considered case. But, the studied values still have a meaning towards the studied membrane applications.

3.3.2. Implemented methods of ageing study

3.3.2.1. Accelerated ageing: concentration per time of contact parameter: $c \times t$ parameter. As far as ageing studies are concerned (mainly carried out with chlorine medium), the choice of parameters may seem anarchic and approaches not adapted. Protocols can be either accelerated procedures (Arkhangelsky et al., 2007a,b; Yadav et al., 2009, 2010; Levitsky et al., 2012) or occasional experiences (Wienk, 1995; Bégoïn, 2004; Delaunay, 2007). For accelerated tests, the product of concentration by the contact time (parameter « $c \times t$ ») is the recurring concept: 1,600 ppm day (Rouaix, 2006; Gaudichet-Maurin, 2005); 10,000 ppm d, 25,000 ppm d (Arkhangelsky et al., 2007); 10,000 ppm day, 20,000 ppm day (Yadav and Morison, 2010), 13.10⁶ ppm h namely 541,667 ppm d (Abdullah et al., 2012); 236,000 ppm h namely 9,833 ppm d (Prulho et al., 2012). The use of this concept suggests that ageing generated by a high concentration during a short time equals to the one attributed to a low concentration during a long time. This consideration has already been applied in several fields such as the ageing studies of paper (Batterham and Rai, 2008; Weyermann and Spengler, 2008); stability of pharmaceuticals (Waterman and Adami, 2005); polymer ageing: isostatic polypropylene (Rosa et al., 2005); polyvinylchloride (Jakubowicz et al., 1999), high density polyethylene (Edidin et al., 2000; Whelton and Dietrich, 2009), polychloroprene gums (Le Gac et al., 2012), etc... All these studies compared the accelerated ageing in laboratory with the observed natural ageing. But the adequation of the results from both approaches is not always well observed. Batterham and Rai (2008) underline that each type of paper has its own criteria in terms of transposition from natural ageing to accelerated ageing. They also point out the fact that it is impossible to make reliable predictions on the basis of

accelerated tests. For Mohammadian et al. (2010), tests of accelerated degradation are most of the time carried out not to assess a material lifetime but to study the evolution of its physical properties in the course of time. It seems that by reducing the experiment time via parameter « $c \times t$ », one distorts the obtained results. They no longer represent the considered phenomenon. Indeed, Whelton and Dietrich (2009), in their critical analysis of the accelerated high density polyethylene ageing used in drinking water treatment plants, highlight that in spite of standardized tests on accelerated ageing (ASTM D6284), some factors, such as alkalinity, pH control, instability and disproportionation of chlorine species, are not taken into account. Authors advise to update these standardized tests.

Generally speaking, the reliability of accelerated test may be legitimately questioned and a different innovative and representative approach must be used to study membrane ageing in order to predict membrane lifetime in given conditions (Regula et al., 2013d).

3.3.2.2. Designs of experiments (DoE). Considering the number of parameters on which depend cleaning/disinfection and membrane ageing (hydrodynamic conditions, nature of detergent, concentration, temperature, cleaning/disinfection sequences...) Design of Experiments arises naturally (Regula et al., 2013c).

Designs of Experiments have been used over one century. They were first of all used in agronomy with Fisher's works (1925), one of the founders of modern statistics, during his genetic research. Then Designs of Experiments were used in other process areas, such as chemistry to improve formulation. They are an essential part of a hypothetical-deductive approach, which considering an objective and constraints allows for an experimental and optimal strategy. Indeed by multi-parameter studies, experiment strategies generally lead to a lot of useless trials and a volume of results difficult to process. The purpose of this methodology is to optimize a campaign of industrial or scientific experiments while ensuring that there are the necessary relevant data to take the decision (Chagnon, 2005). Design of Experiments is used to set relationships between factors and responses (values depending on one or several factors of the system) by using mathematical models, in order to minimize the number of experiments for a reduced cost of study in the case of an industrial application. Until shortly, the method was restricted to systems, which could be modeled by polynoms of first or second degrees. It can now be applied to non-linear phenomena (Xiao and Vien, 2004; Banga et al., 2000).

If the methodology of Designs of Experiments is used to study membrane ageing, it must be adapted to the study of objectives. The method consists in selecting strategically the trials to perform within the experimental domain to model the studied surface. Upon completion of the design, the statistical analysis of the model verifies whether the obtained regression surface produces a good approximation of the actual system. Before applying this methodology, it is necessary to choose a design of experiments that will allow the definition of the conditions of experiments to carry out in the considered experimental field. There are different models:

- **First order designs** (« factorial designs »): both studies performed on membrane ageing via DOE use these models: Chen et al. (2003): 6×2 factorials (6 factors, 2 levels); Zondervan et al. (2007b): 4×2 (4 factors, 2 levels). These designs cannot however be used when data have curvature effects. Some parameters such as pH and temperature have however non-linear effects on the cleaning/disinfection efficiency and on ageing (Chen et al., 2003). Such designs cannot illustrate the complexity of the effects of membrane ageing.
- **Quadratic designs** can be used when the observed effects cannot be described by a linear equation: Box-Behnken (Ferreira et al., 2007), central composite, and Doehlert (Bezerra et al., 2006) designs. When there are additional constraints (irregularities of the experimental domain, minimization of the number of experiments, necessity of non-linear regressions), more complex designs of experiments are required, such as D-optimal matrices. Their use is justified when there are some constraints which cannot be solved with classical regular designs. This type of DOE depends on a selection criterion and a given number of experimentations (Triefenbach, 2008). The selection criterion chosen for this study is the variance function. It is an uncertainty measurement of the predicted response (Sergent et al., 1995). The ideal situation would be to have the smallest variance function as possible, which would lead to a minimum deviation between the predicted and the experimental values (Aguiar et al., 1995).

Furthermore, statistical analysis tools validate or not the performed designs. Among them, one can quote ANOVA, Analysis Of Variance, which is used to compare the effects of the different studied factors with the experiment measurement errors. It is thus possible via statistical tests (Fischer-Snedecor, Student...) to determine the significance of designs and different factors or factor combinations (Zondervan and Roffel, 2007; Régula et al., 2013a,b).

4. Conclusion: towards the development of an optimized membrane ageing study

Many of the protocols used in the industry have often no theoretical justifications. The cleaning/disinfection of membranes and related equipment are conducted in an empirical

way and the operating choice of the conditions is based on industrial experiment (Rabiller-Baudry et al., 2009). That is why membrane cleaning/disinfection was considered for a long time as one of the technical bottlenecks of the membrane processes and felt as a difficulty and even a brake in the development of membrane processes. Indeed, the most difficult remains in the listing of all the cleaning/disinfection parameters, the hydrodynamic ones as well as the physical and chemical ones. Up to now, the cleaning/disinfection studies realized have been focused on the cleaning/disinfection efficiency and on the evaluation of commonly used cleaning/disinfection agents: acid, alkaline and oxidants (Fig. 8a). Ageing induced by cleaning/disinfection procedures has been considered only recently. This explains why very few information is available on this subject. Moreover, the limited information supplied from literature is mainly based on oxidant ageing and especially sodium hypochlorite (Regula et al., 2012, 2013a) (Fig. 8b).

The situation evolves slowly and, to make the situation even more difficult, membrane processing industries have to face new challenges: better use of energy and water resources, increasing restrictions on the usage of chlorine, phosphates and EDTA due to poor biodegradability and aquatic pollution. Membrane processes have to face the needs of evolving towards even more productive processes, but also more environment-friendly regulations. For example new detergents (phosphate-free or EDTA-free formulations) are being offered to increase biodegradability of cleaning/disinfection compounds. The wider use of enzymes meets these expectations but their cleaning/disinfection efficiency and the ageing damages they involve are not clearly identified. Further experiments are needed to better understand the mechanisms involved and to well define the criteria for identifying which enzymes for which foulant and which membrane under which conditions. On the other hand, CIP methods with more modest temperatures and low chemical usage are being evaluated using life cycle assessment to provide better alternatives in terms of environmental impacts. However, the costs and cleaning/disinfection times remain crucial factors to determine the viability of these alternatives, particularly in the food industry. Long term ageing of membranes and membrane modules need further investigations to reduce disposal costs and environmental impacts of the membrane processes.

Considering these information, this review was divided in 2 parts: (i) the key factors of the membrane cleaning/

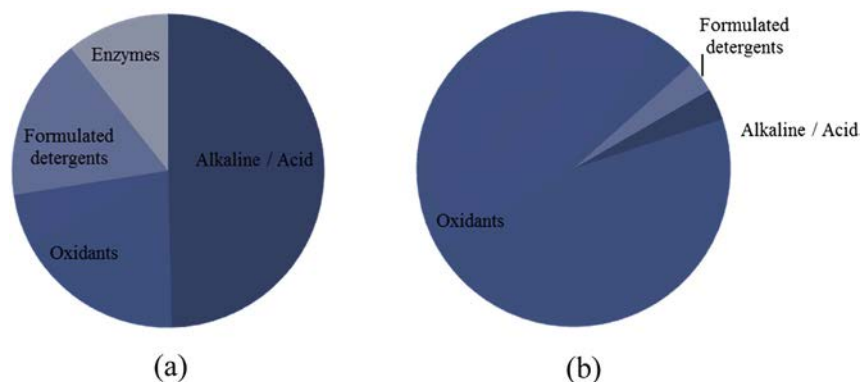


Fig. 8 – Cleaning/disinfection agents studied in cleaning/disinfection studies (a) and in ageing studies (b).

disinfection and ageing to put in light the membrane characteristics and the operating parameters (water quality, protocols, etc.) to better understand the impact of chemical agents on cleaning performances and membrane ageing; (ii) the studied parameters associated with the characterization methods. Whatever the considered membrane application, based on this critical analysis of the state of the art of ultra-filtration membrane cleaning/disinfection and ageing, some advice can be given in order to undertake an optimized study on ageing. It is necessary to take into account:

- intrinsic factors of the membrane: module geometry, membrane material,
- factors about cleaning/disinfection procedures: water, cleaning/disinfection agents and applied conditions.
 - o To pay particular attention to the water used for the cleaning/disinfection solutions as well as for rinsing. Tap water cannot be used. Indeed, the physico-chemical characteristics of water must be known and controlled beforehand.
 - o To choose carefully the membrane ageing and storing: away from light, at a controlled temperature,
 - o To pay particular attention to the choice of biocide (sodium bisulfite, formulated biocide, infinitely dilute solutions).
- The methodology selected for the study of membrane ageing must be thought thoroughly (Regula et al., 2013c). In order to show the complexity of the ageing phenomena, designs of experiments resorting to quadratic designs could be used in the case of quantitative ageing values.
- The selection of cleaning/disinfection and ageing products must be specific to each considered triplet fluid/membrane/operating conditions. Ageing conditions must represent the encountered industrial conditions.
- The characterization techniques of ageing must be planned. A non-destructive control of the transfer properties of the membrane, permeability and retention, may be interesting. It is besides a reference to the membrane characteristics in industrial conditions. The ageing characterization will also have to develop the use of microscopic, spectroscopic and mechanical methods in order to capture all the possible information and to avoid any misinterpretation. So, the whole membrane properties must be assessed and a global vision of ageing will be considered. Techniques, which can be selected because easy to implement, are scanning electron microscopy (SEM) and Attenuated Total Reflectance Fourier Transformed Infrared spectroscopy (ATR-FTIR).

To conclude, this review is focused on the cleaning/disinfection recoveries and the ageing deteriorations of the membrane performances involved. Until now, several works have revealed that membrane chemical cleaning/disinfection methods are widely implemented in order to regenerate the membrane performances. There are several chemical cleaning/disinfection agents directly used to remove fouling material and an understanding of the roles in chemicals has been developed. The success of chemical cleaning/disinfection depends on many factors such as the nature of the foulant type, cleaning/disinfection agents, temperature, pH, concentration

of the cleaning/disinfection chemicals, contact time with the chemical solution, the cleaning/disinfection sequences and the operating conditions such as cross-flow velocity and pressure. These factors affect the outcome of the cleaning/disinfection procedure and therefore need a thorough investigation in order to establish the optimum cleaning/disinfection system and the smallest membrane degradations. However, even if at the current stage, the basic principles governing the key requirements for the most effective and the least harmful membrane cleaning/disinfection have been identified and are generally well-known, researches are still in progress. Indeed, as membrane detergent and materials evolve, as new processing applications develop, and as environmental and cost pressures drive further changes in the industry, there is a continuous need for investigation to elucidate the cleaning/disinfection mechanisms and incorporate them into qualitative and quantitative cleaning/disinfection models. It is also essential for such studies to be conducted under conditions that mimic the industrial process and have sufficiently long run lengths (Regula et al., 2013d) and repeated periods to ensure the best match between the outcomes coming from the research activities and the needs of industrial practitioners.

Appendix A: Nomenclature

α -CT	Alpha-chymotrypsin
α -la	Alpha-lactalbumin
ATR-FTIR	Attenuated Total Reflectance Fourier Transform Infra-Red
β -lg	Beta-lactoglobulin
BSA	Bovine serum albumin
$^{\circ}$ C	Celsius degree
C	Cellulose
CA	Cellulose Acetate
CE	Cleaning efficiency
CEs	Cellulose ester
CTAB	Cetyl trimethylammonium bromide
DIW	Deionized water
EDTA	Ethylenediaminetetraacetic acid
EPR	Electron Paramagnetic Resonance
ESCA	Electron Spectroscopy for Chemical Analysis
ESR	Electron Spin Resonance
FESEM	Field Emission Scanning Electron Microscopy
FP	Fluor polymer
FR	Flux recovery
HF	Hydrogen fluoride
MF	Microfiltration
min	Minute
NF	Nanofiltration
NOM	Natural organic matter
NS	Not specified
PA	Polyamide
PAN	Polyacrylonitrile
PBI	Polybenzimidazole
PE	Polyethylene
PEG	Polyethylene glycol
PEI	Polyetherimide
PES	Polyethersulfone

pH	Hydrogen potential
PlyA	PolyAcrylate
PSf	Polysulfone
PSf/PDC	Dichlorophenyl sulfone-phenolphthalein condensation polymer
PVC	Polyvinylchloride
PVDF	Polyvinylidifluoride
PVP	Poly(vinyl pyrrolidone)
RC	Resistance recovery
R-CE	Regenerated cellulose
RO	Reverse osmosis
RR	Resistance removal
RWPC	Reconstitute whey protein concentrate
SDS	Sodium dodecyl sulfate
SLS	Sodium lowry sulfate
SEM	Scanning Electron Microscopy
TAZ	Terg-A-Zyme
ToF-SIMS	Time-of-flight secondary ion mass spectrometry
UF	Ultrafiltration
WPC	Whey protein concentrate
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

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