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# Ageing effect on chlorinated polyethylene membrane of an MBR caused by chemical cleaning procedures

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## ABSTRACT

The membrane lifetime has a strong influence on the competitiveness and sustainability of Membrane bioreactor (MBR) technology. Membrane replacement is highly expensive operational cost of MBR plants, besides generating residues that have been disposed at municipal landfills or incinerated. Chemical cleaning has been deemed to be one of the most significant factors that shortens membrane lifetime. Chemical cleaning is required to keep the operational flux that is likely to be shortened due to irreversible membrane fouling. This work was aimed to evaluate the influence of chemical agents on chlorinated polyethylene polymeric membrane. Two cleaning procedures were evaluated, namely, (1) cleaning with citric acid followed by sodium hypochlorite (NaOCl) and (2) oxalic acid followed by sodium hypochlorite. After each cleaning cycle, it was determined the membrane permeability. The membranes were also characterized by surface analysis using a scanning electron microscope, thermal resistance by thermogravimetric analysis, Fourier transform infrared spectrometry analysis, and hydrophilicity determination based on the contact angle measurement. The results showed a permeability decrease when the membrane was exposed to cleaning agents both, by adsorption of the evaluated acids or by oxidation of the polymeric material and/or the additives used to manufacture the membranes.

*Keywords:* Membrane lifetime; Membrane bioreactors; Chlorinated polyethylene membrane; Fouling; Chemical cleaning

## 1. Introduction

Membrane bioreactors (MBRs) represent an important technical option for wastewater reuse, being very compact and able to achieve the highest effluent quality standards for reuse. Over the last two decades, MBR technology has reached a significant market share in wastewater treatment business, and it is expected to grow at a compound annual growth rate of 13.2% [1]. However, its more extensive implementation and

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sustainability as a feasible wastewater reuse technology has been limited by its relatively high cost, particularly, regarding power consumption of procedures such as membrane aeration, permeate pumping, and membrane replacement. Substantial developments have been implemented to cut down such costs. Membrane replacement cost relates to membrane price and lifetime.

Ayala et al. [2] pointed out the main reasons for flat sheet MBR membrane replacement and therefore, the factors that influence their lifetime, namely, (1) membrane breakage due to passage of solids through the screen; (2) holes due to welding sparks; (3) membrane seal spoiling; and (4) mechanical connection failure. Cote et al. [3] also itemized main reasons for MBR hollow fiber membranes to be replaced, and pointed out: (1) hollow fiber delamination; (2) module mechanical failure; (3) change by higher performance products; (4) impairment of the junction between the membrane and the resin used to make the module; and (5) more frequent cleaning procedures. Although this work had been directed toward MBR hollow fiber configuration, other membrane configurations may be influenced by factors such as mechanical failure and more frequent chemical cleaning procedures.

The membrane lifetime has called the attention of the scientific community, since it strongly influences the competitiveness and sustainability of MBR technology. Verrecht et al. [4] estimated the cost of large-scale hollow fiber MBR, and came to the conclusion that membrane replacement is critical to determine the net actual value. According to the authors, assuming a lifetime of 10 years, the membrane cost would represent 23% of the net present value of the total cost. Other operational experiences reported that by replacing the membranes every 8-year period, the cost of an MBR system would equal the cost of CAS installations of comparable load and effluent quality [5].

Regarding MBR sustainability, even though the large amount of power required for aeration and fouling control is a primary environmental concern, the disposal of old membrane modules also comes forth as a critical issue to be dealt with. So far, worn out membrane modules have been considered as ordinary waste, and have been as a rule incinerated or disposed at municipal landfills. Thus, the understanding of membrane ageing process contributes to MBR technology sustainability. Extending membrane lifetime will reduce the consumption of raw materials and power to manufacture, while it will also reduce the quantity of membranes to be disposed.

Membrane lifetime concept remains arguable. For instance, suppliers define this concept as the time when the design flux cannot be guaranteed any longer. Other authors [6] analyze the membrane lifetime from a chemical and mechanical standpoint by accelerating the ageing process on lab scale. On the other hand, membrane lifetime may be considered as the time at which chemical cleaning cannot recover its permeability anymore [7]. Membrane module suppliers recommend that the maximum chlorine contact allowance should not be overcome during its lifetime. In the case of Zenon, a maximum exposure of 5,00,000 ppm h is recommended.

The cleaning of the membrane modules may be classified into physical and chemical [8]. Physical cleaning may be performed by backwashing or relaxation, and is performed to remove reversible fouling. However, after certain operation time, which varies depending on each system characteristics, it been noticed an irreversible fouling buildup that cannot be removed by physical processes [9]. Chemical cleaning is the primary method to recovery the membrane permeability. There are several categories of cleaning agents such as caustic, oxidants/disinfectants, acids, chelating agents, and surfactants [7]. Nevertheless, there has been no defined protocol for the membranes used in MBRs as the efficiency of such a procedure will directly depend on the properties of the effluent being treated, and its overall operational conditions.

Chemical agents primarily remove the fouling accumulated on the membrane surface. However, studies [6,10–13] have already shown the exposition of the membrane to these cleaning agents both, due to their concentration or exposure time, may come to change the membrane properties so that it will be more prone to undergo fouling. Besides altering its surface properties, the membrane may also have its mechanical resistance impaired. These processes end up shortening membrane lifetime.

Sodium hypochlorite remains a popular choice as a membrane cleaning agent because its availability, affordable price, and capacity to remove biofouling. Although widely used as membrane cleaning agent, NaOCl has been long suspected to degrade the membrane [13–18]. The oxidizing properties of NaOCl, and its elevated working pH, have the potential to damage membranes over their functional period. Rouaix et al. [16] and Gaudichetmaurin and Thominette [17] observed that NaOCl treatment caused some damages to polysulfone membranes, as evidenced by the enlargement of the membrane pores, and lower membrane elasticity. According to Kwon and Leckie, [15] NaOCl treatment causes membrane chlorination and increases membrane surface hydrophilicity of polyethersulfone (PES) membranes. Arkhangelsky et al. [13] also reported that breaking polymeric functional groups by chemical cleaning may cause them a gradual deformation of the membrane skin layer, and impair its mechanical strength of the ultrafiltration (UF) membranes.

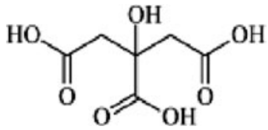
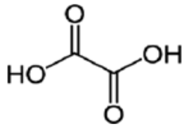
Puspitasari et al. [10] suggested that the impact of the chemical agents on the temporal changes of the membrane properties occurred by two-stage degradation mechanism: when NaOCl was used to age polyvinylidene fluoride (PVDF) microporous membrane, decrease in water permeability was first clearly observed, followed by a significant increase is membrane relative hydrophilicity. The permeability decrement was imputed to the removal of surface-modifying substances, while the subsequent permeability increase occurred probably due to membrane pore structure enlargement.

Recent studies have reported the potential impact of chemical agents used for membrane chemical cleaning, not only on the membrane polymeric material, but also on the additive used to manufacture it. The commercially available virgin membrane usually contains preservatives such as sodium bisulfite and glycerol, which are added to the process by the manufacturers to lengthen the product lifetime by preventing biological growth over the membrane [19]. Moreover, additives are widely used in the casting solution for pore forming and/or surface modification of the membrane [20,21]. These additives are also used to increase the relative hydrophilicity of the membrane (otherwise strongly hydrophobic). Those additives are potentially less mechanical and chemical resistant and can be easily affected by the cleaning process. For instance, the chemical cleaning of PES membrane was reported to remove the membrane additives, which resulted in smaller contact angle and higher pore size, because of polymeric chain session [13].

There are few works reported in the literature that describe the influence of using acids to clean the membrane over its lifetime. Usually, organic acid cleaning is done by removing inorganic incrusted matters. Mineral acids such as hydrochloric or sulfuric acids may be used, and as well basic substances such as sodium hydroxide [8]. Citric acid is extensively used to clean membranes, and it is a tricarboxylic organic acid, while oxalic acid is a dicarboxylic organic acid. Table 1 shows the structural formula of these molecules.

Due to the high cost associated with membrane replacements in MBR [2] process, it turned out to be necessary to determine the influence of cleaning agents on the membrane material wearing process that determines membrane lifetime. Although many studies have striven to understand the influence of chemical cleaning on MBR membrane lifetime, only few studies have investigated such an influence on chlorinated polyethylene membranes. Most of the studies have been focused on the effects of hypochlorite, while only few studies have investigated the effect of acid cleaning on membrane ageing process. Furthermore, most of these studies have been mainly based on accelerated membrane ageing strategies, which cannot always be considered as a realistic situation to represent chemical cleaning procedures applied to MBR standard operations. Only a few studies have examined cyclical cleaning effects on membrane integrity and performance [22].

Table 1
Structure formulas of citric acid, oxalic acid, and chlorinated polyethylene

| Matter | Structural formula |
|---|---|
| Citric acid |  |
| Oxalic acid |  |
| Chlorinated polyethylene | $-(CH_2-CHCl-CH_2-CH_2)_n$ |

Therefore, this work is aimed to investigate the effect of using acid and oxidant cleaning agents on the lifetime of chlorinated polyethylene flat membranes used in MBR.

## 2. Materials and methods

### 2.1. Membranes

To carry out the trials, flat chlorinated polyethylene polymer membranes were used with pore size of 0.4 μm, area of 0.0108 $m^2$, free of fouling. The flat plates were cut into a rectangular shape measuring 15.2 cm length and 7.1 cm height, so that they could be placed on an acrylic permeation module for hydraulic permeability determination. The membranes were divided into four pairs. Each pair was submitted to cleaning, and one of the membranes was submitted to permeability measurement, while the other was used to supply a sample that was collected after each washing procedure for other analyses.

### 2.2. Chemical cleaning

A sequence of exposures to a chemical used to take place due to an acid cleaning followed by a hypochlorite cleaning. Such a cleaning sequence was determined based on preliminary data collection done during a study carried out earlier [23]. Two membranes were submitted to cleaning with citric acid solution followed by sodium hypochlorite solution (Membrane I and III) and other two membranes were cleaned with oxalic acid solution followed by sodium hypochlorite solution (Membranes II and IV). Initially, the membrane pairs were soaked in a 2.5 pH citric or oxalic acid solution for two hours. After the first acid cleaning, the membrane was soaked in a 5,000 ppm of sodium hypochlorite solution for two more hours.

## *2.3. Evaluation of chemical cleaning effect on membrane lifetime*

To isolate the effects of the chemical agents only, the study used brand new membranes free of fouling. Acid and hypochlorite cleaning procedures were repeated to the point of substantially damaged membrane permeability. Thirty-eight cleaning cycles were performed to each pair of membranes, which totalized 152 h of exposure to chemical agents. The integrity of the membranes was checked after each cleaning cycle and was evaluated by checking the membrane hydraulic permeability, and the surface and membrane structure were analyzed by means of scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Fourier transform infrared spectrometry (FTIR), and contact angle.

### *2.3.1. Membrane permeability*

Membrane permeability was checked before and after each cycle of exposure to the cleaning agent. The permeability tests were carried out after microfiltration membrane compaction. Compaction is described as an irreversible mechanical deformation of the membrane porous layer when it is submitted to a certain pressure gradient.

The initial membrane compaction ensures that variations occurred during the membrane permeability determination procedure will depend only on the changes undergone by the polymer when exposure to cleaning agents. That is, it is not about its mechanical deformation.

The values found for the permeate flux were reported in $\mathrm{L\,h^{-1}\,m^{-2}}$, and they were then graphically represented by the transmembrane pressure applied, that is, (0.59; 0.49; 0.39; and 0.29 bar) applying a feeding flow of $3.2\,\mathrm{L\,h^{-1}}$ at the room temperature (average of 22˚C). The score obtained was linearized and the straight line angular coefficient represents the membrane permeability.

### *2.3.2. Analysis by SEM*

The use of SEM allows for a characterization of a microfiltration membrane conformation. To apply this characterization method, the sample must be preserved by coating, to avoid changing the characteristics of the samples due to the high-voltage electron beam [24], in order to maintain its structural conformation.

After the 1st, 7th, 15th, 20th, and 30th exposure time of the samples to cleaning agents, they were characterized using a JEOL JSM-6360LV model of a scanning electron microscope under a high-vacuum range. Samples were coated by a slim gold layer of nearly 30 ηM by using a MEDO20 model of a BALTEC Metalizer.

### *2.3.3. Thermogravimetric analysis*

Polymer membranes were submitted to TGA analyses after the 1st, 7th, 10th, 15th, 20th, 25th, 30th, and 35th exposition time to cleaning agents. The thermograms were obtained using TGA 7 model of a Perkin-Elmer thermogravimetric analyzer.

About 5 mg of the sample was inserted into a platinum cell, and was submitted to a temperature of 10˚C $\mathrm{min^{-1}}$, in a nitrogen atmosphere at temperature range between 25 and 1,000˚C. That trial was intended to monitor the sample mass loss due to temperature variation in order to evaluate the changes regarding the membrane thermal degradation after being exposed to cleaning agents.

### *2.3.4. Infrared spectrometry (FTIR) analysis*

FTIR analysis was performed to evaluate the changes in the membrane surface composition as it provides qualitative information on the actual functional groups [13]. The trials were carried out using a Shimadzu IR-prestigio-21 model Infrared device in ATR module. The samples after the 1st, 7th, 10th, 15th, 20th, 25th, 30th, and 35th of being exposed to cleaning agents were analyzed by direct exposure of the sample compressed by radiation in the ATR module in the range from 400 to $4{,}000\,\mathrm{cm^{-1}}$, and resolution of 4.0. Readings were done based on percent transmittance.

## *2.4. Contact angle analysis*

The contact angle (θ) is used to determine the hydrophilicity or hydrophobicity degree of certain material. The membrane hydrophilicity or hydrophobicity degrees were obtained from the contact angle determination by applying sessile drop method using goniometer SCA20 version 2, Dataphysics, at a temperature of 23˚C. The deionized water was the solvent used. The drop volume was controlled using a syringe. The needle was positioned close to the surface and the liquid was squeezed out the syringe in order to place a drop onto the membrane surface. The membrane contact angle values found represent the mean values of the three experiments on different parts of the membrane surface.

## 3. Results

### 3.1. Evaluation of chemical cleaning effect on the membrane lifetime

#### 3.1.1. Membrane permeability

The polymer membranes were submitted to a sequence of 38 cleanings with oxalic or citric acids followed by hypochlorite totalizing 152 h of exposure to chemical agents. The membrane behavior when exposed to cleaning agents was monitored after determining the permeability of a brand new membrane and after each washing stage using distilled water. The results found in these first trials are shown in Fig. 1.

After monitoring the hydraulic permeability over a sequence of 38 washing procedures, it was noticed that permeability of the membranes exposed to cleaning agents has not undergone significant changes during the first cleaning time. Nevertheless, after the 14th cleaning time, it was notice a considerable permeability decrease. It was expected that membrane permeability would increase due to polymer lixiviation when it is exposed to the cleaning agent. Such a behavior may be related to the membrane polymer structure change, which substantiates the studies reported in the literature [11]. Similar behavior has been observed when PVDF membranes were exposed to sodium hypochlorite in which the authors noticed a membrane pore size change as the number of chemical cleaning procedures was increased due to membrane surface change [6].

It may be noticed that membrane I lost 79% of its permeability after being exposed to 59,500 ppm h of citric acid, and 380,000 ppm h of sodium hypochlorite, while the membrane II had its permeability decreased by 59% after being exposed to 15,352 ppm h of oxalic acid, and 380,000 ppm h of sodium hypochlorite. The greater permeability decrease of the membrane 1 in relation membrane 2 may be associated with citric acid structure. The citric acid has three carboxyl groups against two carboxyl groups present in oxalic acid. These carboxyl groups may react with the membrane polymer reducing its permeability due the pore size reduction. The presence of carboxyl groups in the polymer structure can contribute to reducing the effective pore space in function of this group volume.

Therefore, it can be concluded that using oxalic acid to clean membranes has less impact on membrane lifetime than citric acid regarding membrane permeability. Such results suggest that the permeability found in this study may have been influenced by the acid cleaning or by the interactions between the acid cleaning agents and sodium hypochlorite.

#### 3.1.2. Membrane surface analysis

Figs. 2 and 3 show microscopic surface images after the 1st, 7th, 15th, 20th, and 30th washing proce-

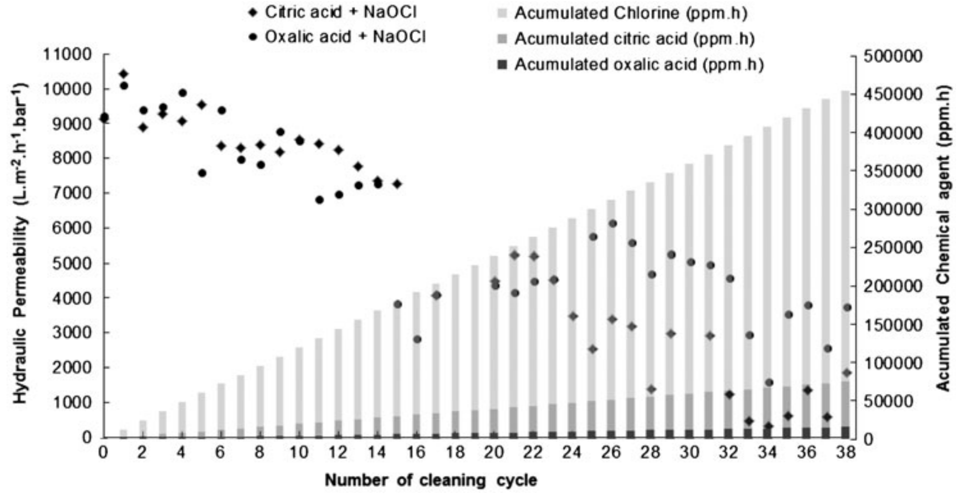
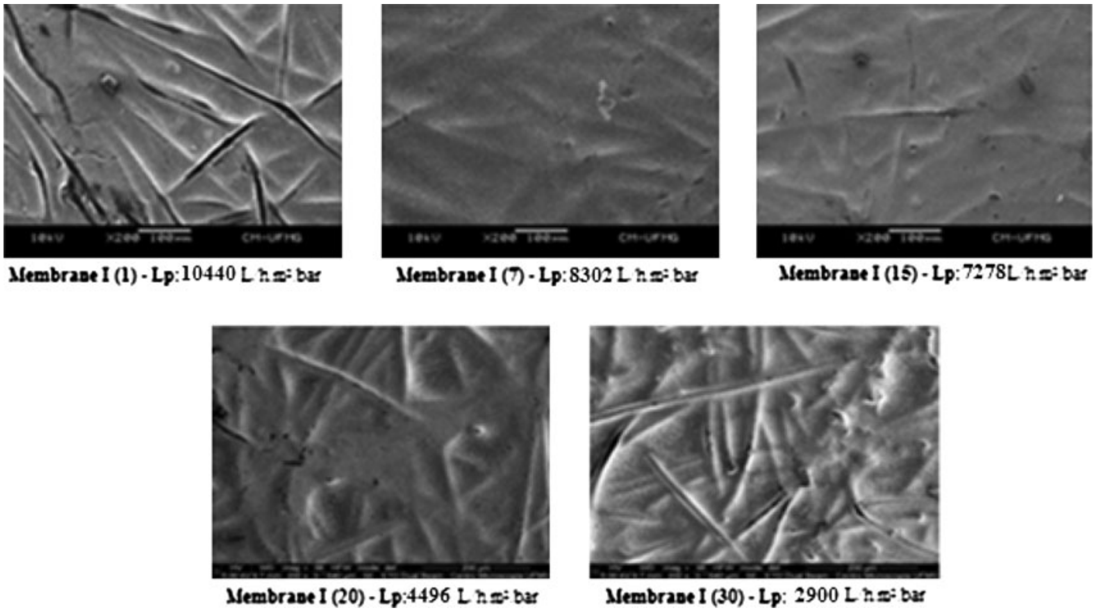
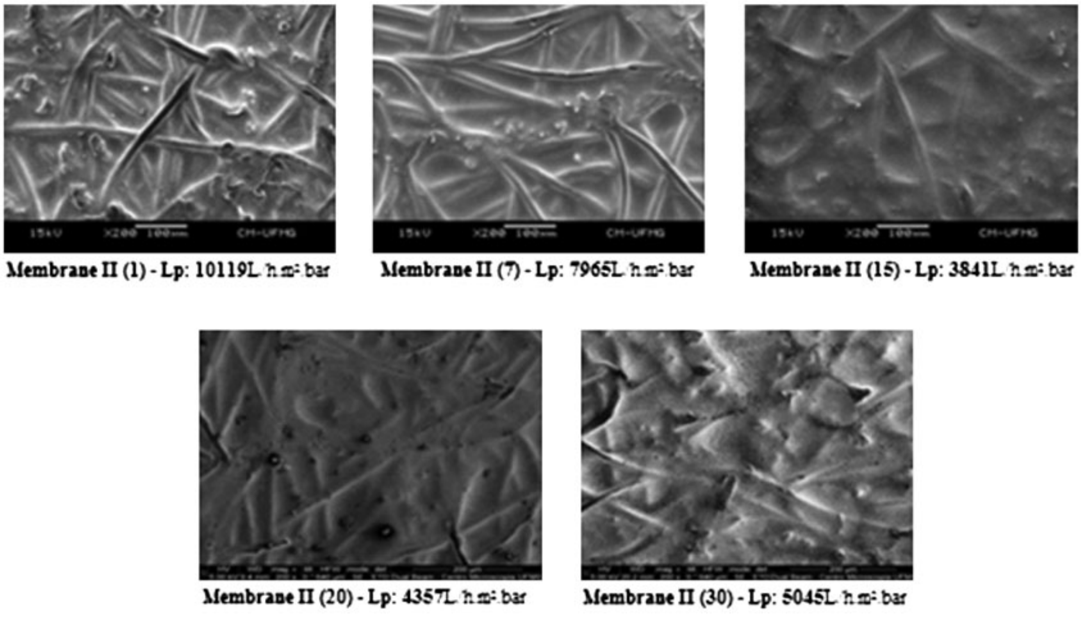


Fig. 1. Hydraulic permeability measures of membranes (I and II) plotted by number of cleaning procedures and time of exposure to chemical agents.



**Membrane I (1) - Lp:** 10440 L/h m$^2$ bar
**Membrane I (7) - Lp:** 8302 L/h m$^2$ bar
**Membrane I (15) - Lp:** 7278L/h m$^2$ bar
**Membrane I (20) - Lp:**4496 L/h m$^2$ bar
**Membrane I (30) - Lp:** 2900 L/h m$^2$ bar

Fig. 2. Photomicrography of a brand new membrane after being cleaned with citric acid and sodium hypochlorite. 200× magnification.



**Membrane II (1) - Lp: 10119L/h m$^2$ bar**
**Membrane II (7) - Lp: 7965L/h m$^2$ bar**
**Membrane II (15) - Lp: 3841L/h m$^2$ bar**
**Membrane II (20) - Lp: 4357L/h m$^2$ bar**
**Membrane II (30) - Lp: 5045L/h m$^2$ bar**

Fig. 3. Photomicrography of a brand new membrane after being cleaned with oxalic acid and sodium hypochlorite. 200× magnification.

dures of membranes I and II with a 200× magnification followed by permeability values.

From microscopic analyses of the membrane being submitted to cleaning procedures with citric acid (membrane I) and oxalic acid (membrane II), both combined with sodium hypochlorite (NaOCl), it was found that membrane surface structure becomes more homogeneous as the cleaning cycles are carried out. Such a fact has been evidenced by minimizing the fiber exposure between the 1st and the 20th cleaning procedure. The fiber is used as a supporting material for the membrane. From the 20th cleaning procedure, the supporting fiber once again become more evident in this matrix specially, regarding the membrane that was submitted to citric acid cleaning. Such a change reinforces the hypothesis previously considered that the exposure to chemical cleaning agents accounts for the membrane surface structure change, which has an effect on the permeability decrease. Such membrane permeability decrease has been related to the change in the pore sizes in which such a reduction will lead to increase the transport resistance of liquids through the membrane. Such a membrane pore size reduction has been related only to cleaning agents as the membrane has not been in contact with materials that account for fouling buildup.

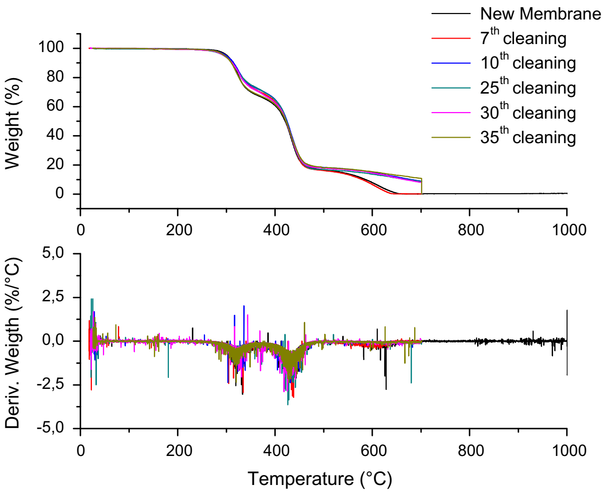


Fig. 5. TGA of membrane cleaned with oxalic acid and NaOCl solution (membrane II).

### 3.1.3. Thermogravimetric analysis

To better complement the results regarding polymeric change on membrane surface, complementary analyses were carried out by TGA. In Figs. 4 and 5, the graphics obtained by TGA of the respective membranes I and II are shown.

The decomposition profile of the membranes submitted to citric acid and sodium hypochlorite (membrane I), and oxalic acid and sodium hypochlorite (membrane II) show two stages of thermal degradation for all samples. The initial temperature for the first degradation stage was approximately 250 and 400˚C for the second degradation stage, for membrane I and II undergo the two cleaning procedures. This result indicates that even after the two cleaning procedures did not exhibit significant changes as the thermal resistance of the membrane as the mass loss.

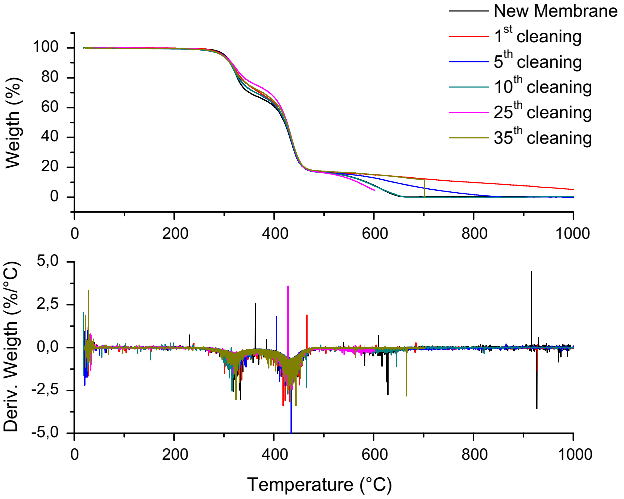


Fig. 4. TGA of membrane cleaned with citric acid and NaOCl solution (membrane I).

The membranes when submitted to the two different cleaning procedures showed some changes in the thermograms especially at temperatures above 500˚C. The residual mass at such a temperature represent the inorganic matter, probably cleaning agent residues, which suggests adsorption of citric and oxalic acids, or chemical reaction between hypochlorite and the membrane. The same behavior was observed by Kar et al. [25].

### 3.1.4. Analysis of Fourier transform infrared spectrometry (FTIR)

FTIR analyses were carried out to identify possible changes in the functional groups that compose the membrane surface. Figs. 6 and 7 show the spectrum found for the membranes that have been submitted to citric acid cleaning procedures together with sodium hypochlorite (membrane I) and oxalic acid with sodium hypochlorite (membrane II), respectively.

Table 2 shows the main chemical groups identified in the spectrum (Figs. 6 and 7). Some of these spectra characterize specific CPE material, while others characterize cleaning agents or additives. The chlorinated polyethylene membrane shows stronger C–H stretches, bends, and weaker C–Cl stretches. The C–Cl stretches appear at 660 and 609 $\mathrm{cm}^{-1}$. The methylene wag appears as a broad band at 1,263 $\mathrm{cm}^{-1}$. The methylene stretches at 2,929 and 2,856 $\mathrm{cm}^{-1}$ are present, and the methylene bend at 1,460 $\mathrm{cm}^{-1}$ is also present [26].

Peak at 1,729 $\mathrm{cm}^{-1}$ represents the carbonyl group (C=O), which could have come from polyvinylpyrrolidone (PVP), which indicates that PVP was used as an

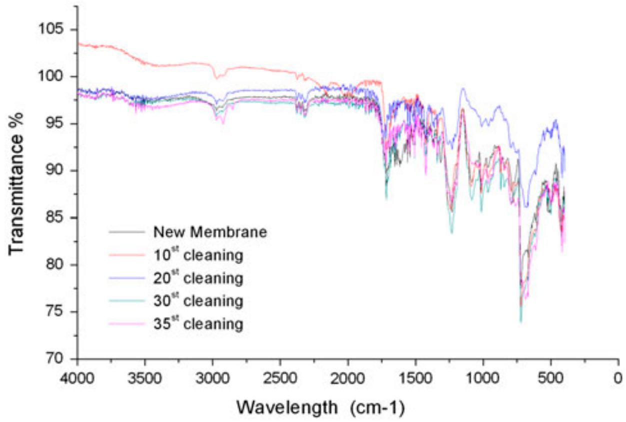


Fig. 6. Spectrum determined by FTIR analysis of membrane I cleaned with citric acid and NaOCl solution.

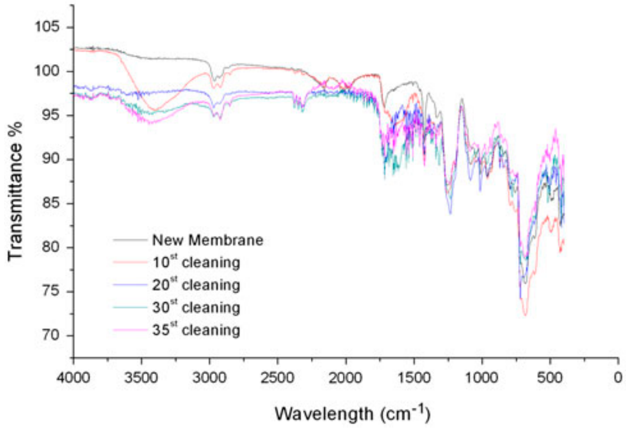


Fig. 7. Spectrum determined by FTIR analysis of membrane II cleaned with oxalic acid and NaOCl solution.

Table 2
Identification of the main peaks of FTIR spectrum obtained

| Peak value ($cm^{-1}$) | Type vibration |
|---|---|
| 609 | C–Cl |
| 660 | |
| 1,080 | C–C stretching |
| 1,263 | $CH_2$ wagging |
| 1,460 | $CH_2$ bending |
| 1,729 | C=O PVP |
| 1,766 | C=O stretching |
| 2,856 | $CH_2$ stretching |
| 2,929 | |
| 3,430 | O–H stretching |
| 2,870 | C–H stretching |

additive in this membrane. PVP has been studied as an additive in various membrane manufactures [27,28], and has been found to increase membrane hydrophilicity [28]. It may be observed that PVP reduction in the membrane that has been cleaned up with citric acid and hypochlorite. The PVP reduction has probably favored a greater permeability decrease observed in this membrane.

Some changes may be observed after membrane cleaning procedure. The infrared adsorption bands at 1729 $cm^{-1}$ indicate that the presence of PVP decreased as the number of chemical cleaning was increased. PVP content decrease may have contributed to the permeability reduction observed. Hajibabania [6] found that PVP content decreases, and permeability decreases accordingly in PVDF membranes when they are cleaned with NaOCl solution. These findings confirm the mass loss rate curves.

The infrared adsorption bands at 3,430 $cm^{-1}$ and at 1,766 $cm^{-1}$ appeared after both chemical cleaning, and disappeared after the 10th cleaning procedure, and appeared again after the 30th and 35th cleaning procedure with oxalic acid. These two bands are imputed to stretching vibrations of O–H and C=O groups, respectively, which could be associated to the adsorption of citric or oxalic acid. Citric and oxalic acid adsorption on membrane surface was also substantiated by the increase in the infrared absorption bands at 2,870–2,950 $cm^{-1}$ and 1,080 $cm^{-1}$, which were assigned to aliphatic C–H and C–C stretching vibrations, respectively. These findings confirm the SEM results as it was noticed, reduction changes on the exposure of the fibers used as supporting material that may be related to citric and oxalic acid adsorption. In the case of the membrane submitted to citric acid cleaning procedure, the exposure of the fibers once more increases after the 20th cleaning procedure, which is consistent with the FTIR analysis results that showed no citric acid adsorption after the cleaning procedures. On the other hand, in the case of the membrane submitted to oxalic acid cleaning procedure, the exposure of the fibers takes place again after the 20th cleaning procedure, and decreases again after the 30th cleaning procedure, which is consistent with the results of the FTIR analysis.

Citric and oxalic acid adsorption may reduce membrane pore sizes, which may also cause permeability decrease. Therefore, membrane permeability reduction may be imputed to PVP concentration reduction and to the adsorption of citric and oxalic acids on the membrane surface. The smallest permeability reduction noticed on the membrane submitted to oxalic acid cleaning may be imputed only to the oxalic acid adsorption on the membrane surface as no significant PVP reduction was noticed.

### 3.1.5. Analysis of the contact angle

The analysis of the contact angle was carried out to evaluate possible polarity changes on membrane surfaces. It is not possible to measure the angle on a brand new membrane due to the prompt absorption of the water drop, which wets the membrane, and changes its appearance around the drop adsorption spot as may be seen in Fig. 8.

The analysis of membranes I and II after the 35th cleaning showed contact angle values of 104.0° and 110.4°, respectively. Such results confirm that after being submitted to chemical cleaning procedure, the membrane becomes more hydrophobic, and then it has its fouling potential increased. The result observed confirm the findings of the study carried out by Phuntsho et al. [29] who proved that, after some years of use, the membrane shows higher hydrophobicity compared with a brand new membrane. Some works showed an opposite effect with the membrane hydrophobicity decrement after some cleaning cycles [6,11]. Nonetheless, the contact angle results depend on the membrane conformation characteristics such as roughness and pore size [6]. For these works, a PVDF membrane was used with structure different from the one used in this work. Furthermore, the hydrophobicity increase corroborates with the hydraulic permeability results found for the membrane after being subjected to cleaning procedures. It is believed that hydrophobicity takes place due to the removal of the additives that are added to the membrane to increase its relative hydrophobicity [6].

### 3.2. Membrane lifetime subjected to accumulated chemical agent contact

Taking into account the relation between membrane lifetime and chemical cleaning, and assuming that is possible to work by reducing the permeability by 50% of the permeability value of a brand new membrane without changing the plant productive capacity significantly, the results have shown that it is possible to perform 20 and 32 cleaning procedures using citric acid and sodium hypochlorite, oxalic acid and sodium hypochlorite, respectively. Considering the performance one recovery cleaning procedures every six months, it is expected a lifetime from 10 to 16 years for membranes submitted to citric acid combined with sodium hypochlorite, and also oxalic acid combined with sodium hypochlorite, respectively.

Fenu et al. [30] estimated the average lifetime of PVDF hollow fibers membranes used in MBR of 11.6 years based on the concept of permeability decline. During these 11.6 years, a decline of 62% was observed in membrane permeability, higher than that is considered in this study (50%).

It is worth pointing out that such a forecast takes into account the membrane degradation caused by chemical cleaning, however, it has not taken into account operational conditions, effluent and sludge properties that also influence membrane lifetime. Nonetheless, such results have already shown the importance of selecting the chemical agent. Citric acid has been the most used cleaning chemical agent to remove inorganic matter from MBR membranes. However, its replacement by oxalic acid will result in longer membrane lifetime, and even more effective fouling removal work as reported by Carvalho et al. [23].

Fenu et al. [30] analyzed the lifetime of four MBRs, and estimated its lifetime endpoint after 50,000 ppm h, and estimated membrane lifetime between 15 and 16 years depending on the frequency and cleaning conditions over 5 operational years. Ayala et al. [2] estimated MBR lifetime in real scale, and suggested that the membrane welding strength may drop down after 900 $m^3$ per cartridge of permeate, or after 1.3 kg NaOCl dosed (per cartridge), to below the threshold minimum welding strength for a virgin membrane cartridge set by the manufacturers, which correspond to a lifetime of 7 years.

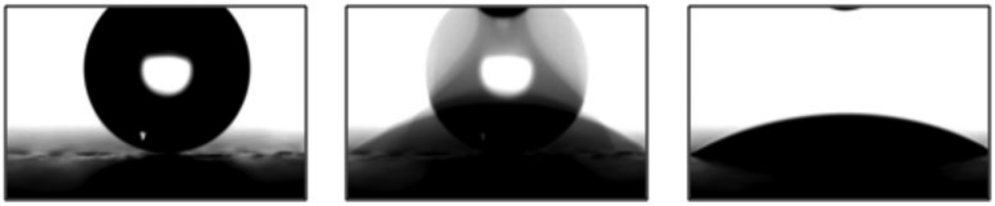


Fig. 8. Analysis of the contact angle of a brand new membrane.

## 4. Conclusion

Based on the results found in this study, it may be stated that exposure to chemical agents lead to a reduction of membrane permeability either due to the adsorption of the acids being analyzed, or due to the oxidation of polymeric material and/or additives used to manufacture membranes. Membrane chemical cleaning with citric acid resulted in more substantial permeability loss compared with loss caused by oxalic acid, which shows the importance of a careful selection of the chemical agent to be used. Citric acid has been the most used cleaning chemical agent to remove inorganic matter from MBRs. Nevertheless, its replacement by oxalic acid results in longer membrane lifetime, and even a more effective fouling removal. The results show the importance of understanding membrane ageing process for a more substantial MBR technology sustainability and competitiveness.

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