# Ageing of polysulfone membranes in contact with bleach solution: Role of radical oxidation and of some dissolved metal ions

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## Abstract

In water production plants using membrane processes, contact with chemicals such as chlorine plays an important role in membrane ageing. This experimental study was aimed at gaining a better understanding of the effect of hypochlorite cleaning solutions on the properties of a polysulfone ultrafiltration membrane. Accelerated ageing of the membrane was simulated by soaking it in chlorine solutions and the mechanical properties of the membrane were monitored versus soaking time. An oxidation mechanism is validated which involves the catalytic effect of dissolved metal ions and the inhibitor effect of an antioxidant when these are present in soaking solutions.

*Keywords:* Polysulfone; Ageing; Ultrafiltration; Hypochlorite; Radical oxidation; Metal ion

## 1. Introduction

Access to clean, safe drinking water in plentiful supply is often taken for granted, but it has long been noted that human activities put a burden on water quality and quantity. Large volumes of water need to be treated in such a way that the quality of clean water meets the standards required, particularly for drinking and for medical use. The method used to disinfect the water must not leave behind any residual toxicity and it must be economically and environmentally sound.

Ultrafiltration is one of the many methods for producing safe drinking water. This membrane process, in use throughout the world, is becoming increasingly popular due to its highly efficient removal of particulates, viruses and bacteria. Increased demand for ultrafiltration has led to the need for a better understanding of the process and of the membranes used. One area of interest from a research point of view and for practical application of membrane technology is the effective cleaning of these membranes in order to optimize performance and minimize costs of the process.

For applications in water production, the most frequent procedure for cleaning membranes is quick back flushing with detergents or with chlorine at low concentration. Longer cleaning with chlorine at higher concentration, or with alkaline or acidic solutions, can also be necessary. Contact with these chemicals plays an important role in ageing the membrane and, as a result, shortens its lifetime. The consequences in a water production plant can be either the functional properties of the membrane gradually decline, till production no longer comes up to requirements in terms of volume or quality, or the membrane suddenly breaks down (especially with hollow fibers), and the plant has to be shut down for maintenance, which is expensive. For these reasons, engineers would like to foresee such changes in membrane properties (i.e. ageing), or at least understand the mechanisms behind the changes, so as to be able to take them into account in optimizing cleaning procedures. But the kinetics of this degradation and its consequences on membrane properties are still not completely understood.

The aim of this experimental study was to gain a better understanding of the effect of hypochlorite cleaning solutions on the changes observed in a hollow fiber ultrafiltration membrane made from polysulfone (PSf) and polyvinylpyrrolidone (PVP). During cleaning-in-place procedures in water production plants, hypochlorite is used during two steps as previously mentioned: first back flushing for approximately 1 min at a concentration of sodium hypochlorite NaOCl between 2 and 10 ppm not more

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frequently than every 30 min and at the pH of the water source; secondly a cleaning protocol for 1 h at a concentration of NaOCl between 20 and 400 ppm once a week (or even less frequently) and at a pH of 12. In our experimental study, an accelerated ageing of the membrane is simulated by soaking it in chlorine solutions under various conditions (pH, chlorine concentration, solution composition and so on). The approach taken in this study is based on two choices: (i) experiments have been performed in a continuous way whereas in a plant, membranes are in contact with water most of the time and with cleaning agents for short, periodic times and (ii) in the present work we started studying chemical ageing without taking into account mechanical and hydraulic ageing (due to transmembrane pressure and continuous flow).

In order to monitor the changes in membrane properties, we used a wide range of methods: distribution of the molar masses of the membrane material (analyzed by gel permeation chromatography, GPC), membrane permeability, retention of tracers, mechanical properties (tensile strength at break point, Ts and elongation at break point, El), scanning electron microscopy (SEM) and atomic composition of the membrane surface by electron spectroscopy for chemical analysis (ESCA). Only mechanical properties are reported in this paper as they have shown a high sensitivity to membrane degradation.

Polysulfone membranes were exposed to chlorine solution in combination with an antioxidant molecule or with dissolved metal ions. The results obtained have been used to validate a degradation mechanism of the membrane by radical oxidation of polysulfone chains. Finally, by means of cleaning experiments using fouled membranes, we study the effect of radicals in cleaning efficiency.

## 2. Background

The use of membrane processes requires the use of chemicals during in-place cleaning procedures. These chemicals are selected for their oxidative, acido basic or even bacteriostatic properties. In the drinking water industry, cleaning procedures occur at a pace of once in a week to once in a month. Alkaline solutions (sodium hydroxide) are usually used due to their efficiency in the removal of natural organic matter. Moreover, in order to sanitize the system during the cleaning procedure, sodium hypochlorite is added to these solutions.

Numerous papers have been devoted to the action of hypochlorite on the properties of polymer membranes that contain PVP (to make them hydrophilic), e.g. [1–4]. In these studies, hypochlorite is used as part of a pre-treatment to improve (or stabilize) membrane permeability prior to further studies. Wienk et al. [1] were the first to report an increase in permeability, ascribed to an elimination of PVP from the membrane matrix. These authors postulate that the selective PVP elimination could be due to the opening of a ring in the PVP molecules or to chain scission of PVP by hypochlorite. Wolff and Zydney [5] who study the effect of hypochlorite on the transport characteristics of PSf/PVP hemodialyzers, underline, without investigating its origin, the fact that bleach causes significant changes in the membrane properties beyond those associated directly with the removal of PVP.

Damage to polyamide reverse osmosis membranes exposed to chlorine solution has also been demonstrated by several authors including Gabelich et al. [6]. The mechanism of degradation is chlorination of polyamides through reaction of HClO with the nitrogen of the secondary-substituted amide group, which then results in ring chlorination [6].

In a preliminary paper [7], we reported experimental work that studied the changes in properties of a PSf/PVP ultrafiltration membrane exposed to aqueous chlorine. The results obtained show that exposure to sodium hypochlorite at fairly high concentration leads to chain breaking in the PSf molecules (gel permeation chromatography results). The consequences are changes in the membrane texture (scanning electron microscopy images), which are closely related to changes in the mechanical properties of the membrane. A small number of chain scissions have a very high impact on elongation and tensile strength at break point of the membrane material (80% loss in elongation at break point for less than 2.8% of chain scissions). Membrane permeability appears to be relatively insensitive to such changes: this can be related to the fact that permeability depends mainly on skin properties. So in the following, the expression "membrane degradation" will be related to the occurrence of chain breaking in the PSf molecules and monitored via measurements of mechanical properties of the membranes because of the high sensitivity of this parameter to chain scissions in the membrane matrix.

Gaudichet and Thominette [8], who have used the same membrane and the same accelerated ageing procedures as us, have confirmed that chain scission of polysulfone molecules affects membranes exposed to hypochlorite solution. These authors have identified the most probable locations of the scission as shown in Fig. 1 by using Fourier transform IR spectrophotometry and proton NMR.

They suggested that the attack on the sulfone and the isopropylidene bridges can result from a reaction with a primary radical.

To qualify this hypothesis, hypochlorite solution chemistry must be considered. When chlorine is introduced into water, either as chlorine gas $Cl_2$ or hypochlorite $ClO^-$ (which is the case in the present study), it rapidly undergoes hydrolysis. The major reaction product is hypochlorous acid (HClO), which is a weak acid that dissociates in aqueous solution as

$$HClO + H_2O \Leftrightarrow ClO^- + H_3O^+ \qquad (1)$$
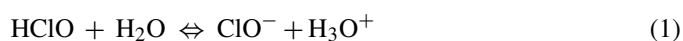
with $pK_a$ (HClO/ClO$^-$) = 7.53 at $T = 25\,^\circ$C.

The total free chlorine concentration in the solution is defined by Eq. (2), but the dissolved $Cl_2$ concentration is low enough in
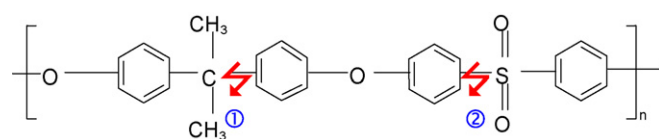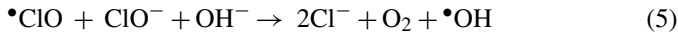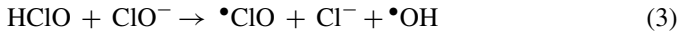


Fig. 1. Location of polysulfone chain scissions [8].

our experimental conditions (pH > 5) to be neglected

$$[TFC] = [Cl_2] + [HClO] + [ClO^-] \quad (2)$$

However, hypochlorite can also form radicals. Two mechanisms have been found in the literature. The first was proposed by Wienk et al. [1], according to the following equations:

$$HClO + ClO^- \rightarrow {}^\bullet ClO + Cl^- + {}^\bullet OH \quad (3)$$

$${}^\bullet OH + ClO^- \rightarrow {}^\bullet ClO + OH^- \quad (4)$$

$${}^\bullet ClO + ClO^- + OH^- \rightarrow 2Cl^- + O_2 + {}^\bullet OH \quad (5)$$

The overall reaction can be written as

$$HClO + 3ClO^- \rightarrow 3Cl^- + {}^\bullet ClO + O_2 + {}^\bullet OH \quad (6)$$

This equation shows that both forms of hypochlorite (HClO and ClO$^-$) need to be present for hydroxyl radicals to be formed. Depending on solution pH, the limiting form is either ClO$^-$ or HClO.

The second mechanism proposed by Fukatsu and Kokot [9] is

$$HClO \rightarrow {}^\bullet OH + Cl^\bullet \quad (7)$$

$$Cl^\bullet + HClO \rightarrow {}^\bullet OH + Cl_2 \quad (8)$$
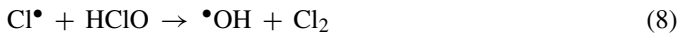
These equations can be written in the overall form

$$2HClO \rightarrow 2 {}^\bullet OH + Cl_2 \quad (9)$$

In this case, HClO is the limiting species. The presence of ClO$^-$ does not seem necessary for hydroxyl radicals to be formed.

Numerous studies on advanced oxidation processes have shown that transition metal ions act as effective catalysts in these processes by reducing the oxidant present in solution and by producing hydroxyl radicals. The Fenton reaction, known for over 100 years, involves ferrous ions reacting with hydrogen peroxide as shown in the following equation:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \quad (10)$$
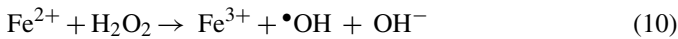
Other transition metals and oxidants can be used to create the ${}^\bullet OH$ and these reactions are called "Fenton-like" reactions [10]. In recent work, ferrous iron $Fe^{2+}$ has been shown to catalyze both the reduction of monochloramine $NH_2Cl$ [11] and the reduction of hypochlorous acid HClO [12] according to the following "Fenton-like" reaction:

$$Fe^{2+} + HClO \rightarrow Fe^{3+} + {}^\bullet OH + Cl^- \quad (11)$$
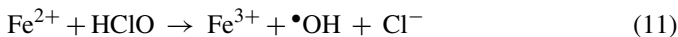
Studies on the kinetics of hypochlorous reactions [12] have demonstrated that $Fe^{2+}$ reacts with HClO much faster than with $H_2O_2$: $k_{Fe^{2+}/HClO} \sim 10^4 \, L \, mol^{-1} \, s^{-1}$ to be compared to $k_{Fe^{2+}/H_2O_2} \sim 70 \, L \, mol^{-1} \, s^{-1}$ in acidic solution.

Gabelich et al. [6] showed that reverse osmosis polyamide membranes exposed to HClO and $NH_2Cl$ in the presence of ferrous iron undergo an accelerated deterioration due to ring chlorination. The mechanism was found to be autocatalytic. A similar conclusion was drawn by Murphy [13] concerning the reaction between aqueous chlorine and cellulose acetate membranes.

If it is assumed that polysulfone membrane degradation occurs by radical oxidation, then depending on the reaction involved in forming ${}^\bullet OH$ in the chlorine solution, either the HClO concentration in one case (Eq. (9)) or the ratio between the HClO and ClO$^-$ concentrations in the other case (Eq. (6)) should play a major role in the kinetics of degradation. Moreover, all conditions that favor the formation of ${}^\bullet OH$ should enhance membrane degradation (irradiation [14]; presence of metal ions in solution [6]) and all the conditions that limit the formation of ${}^\bullet OH$ should inhibit the membrane degradation (presence of antioxidant in solution).

## 3. Materials and methods

As explained in Section 1, the approach taken in this study is based on two choices: (i) contact between the membrane and the cleaning solution was performed in a continuous manner and (ii) only chemical ageing has been studied.

### 3.1. Membranes and procedure

The membranes studied were especially prepared for this series of experiments. They were inner skinned hollow fibers ($D_{int} = 0.96 \, mm$ and $D_{ext} = 1.70 \, mm$) made of a blend of polysulfone (PSf) and polyvinylpyrrolidone (PVP, 5%, w/w), the latter being added to make the final material more hydrophilic. The nominal cut-off deduced from filtration of dextrans is $40 \, kg \, mol^{-1}$.

In a first series of experiments, the hollow fiber membranes were soaked in sodium hypochlorite solutions containing various ratios of HClO to ClO$^-$ concentrations with a constant HClO concentration at 100 ppm (these conditions correspond to various pH's 5, 7, 8 and 10). One more experiment was performed with a solution containing only ClO$^-$ (pH 12).

In a second series of experiments different components have been added to the sodium hypochlorite solution: (i) an antioxidant (tertiobutanol) in order to validate the hypothesis of radical oxidation of the membrane material and (ii) metal ions ($Cu^{2+}$, $Fe^{3+}$) in order to verify their catalytic effect on the radical oxidation.

The tank used for this soaking stage was made of high-density polyethylene in order to avoid contamination of the solution by metal dissolution. Moreover, the tank was closed with a lid during the soaking period so as to protect the solution from the light. The volume of hypochlorite solution was 50 L and the volume ratio of the membrane to chemical solution was $1.5 \times 10^{-2}$.

All the experiments were performed at 25 °C.

Fibers were sampled from the tank after 1, 2, 4, 8 and 16 days. Before further analysis, membranes were rinsed by soaking in RO-treated water for 48 h. The volume ratio of the membrane to the rinsing water was $6 \times 10^{-4}$.

After this exposure to chlorine solution, mechanical properties (elongation, El and tensile strength, Ts at break point) were measured on fibers under wet conditions using an Instron 4301 (stretching speed = 200 mm min$^{-1}$ for a sample of 200 mm). As

already mentioned, these properties were chosen for monitoring as a function of soaking time because in a previous paper [7] we showed that they are the ones most sensitive to membrane degradation. All the values of elongation El and tensile strength Ts at break point reported in this paper come from an average of 14 measurements. The standard deviations of the experimental data were 0.5% for elongation and 0.2 N for tensile strength. In a first experiment, fibers were soaked in pure water as blank samples. No variation in mechanical properties was observed over 60 days soaking.

Results are reported in relative values, compared to the initial membrane characteristics: $El_0 = 37\%$ and $Ts_0 = 7.3$ N.

For cleaning experiments using fouled membranes, the membrane samples were flat sheets made of the same material as the hollow fibers (PSf–PVP) with the same nominal cut-off of $40 \, kg \, mol^{-1}$. Filtration of surface water, of cleaning solution, as well as measurements of membrane permeability, were performed with a 50 mm diameter stirred ultrafiltration cell (Model 8050, Amicon) connected to a 2 L tank. The transmembrane pressure drop was set by air pressurization of the tank. The pressure on the filtrate side was approximately atmospheric under all conditions. The stirring rate in the cell was 300 rpm. The filtrate flux was measured by timed collection using an Ohaus balance with accuracy of $\pm 0.01$ g. All experiments were performed at room temperature.

The cell contains a membrane sample with an effective area of $1.45 \times 10^{-3} \, m^2$. Before the first use, pure water was passed through the new membrane under 200 kPa for 1 h and then the membrane was cleaned with the hypochlorite solution at the selected pH in order to reach a reference state for the membrane structure. As already mentioned, hypochlorite pre-treatment is reported to enhance the flux of MF/UF membranes made of a blend of PVP and hydrophobic polymer. This change can be attributed to the removal of residual PVP from the membrane matrix [1–4].

The successive steps of the procedure were:

(1) compaction;
(2) filtration of hypochlorite solution at the selected pH (duration 15 min, pressure 50 kPa);
(3) measurement of the initial membrane permeability deduced from water flux (method: filtration of RO-treated water – measurement of permeation flux at five different transmembrane pressures in the range 20–100 kPa – calculation of the membrane hydraulic permeability from the slope of the plot of permeation flux versus pressure according to Darcy's law);
(4) filtration of surface water (from the Canal du Midi, Toulouse, France, average characteristics: $UV_{254}$ 7.2 $m^{-1}$, turbidity 20 NTU, COD 4 $mg \, L^{-1}$) (filtration duration 1 h, transmembrane pressure 50 kPa);
(5) measurement of the fouled membrane permeability: calculation of the percentage of loss in permeability;
(6) back-flushing with hypochlorite solution at the selected pH (duration 15 min, transmembrane pressure 50 kPa); for this step the membrane was placed back-to-front in the cell (permeate face in contact with the feed);

Table 1
TFC, HClO and ClO⁻ concentrations in hypochlorite solutions vs. pH

| pH | [TFC] (ppm) | [HClO] (ppm) | [ClO⁻] (ppm) |
|---|---|---|---|
| 5 | 100 | 100 | ~0 |
| 7 | 130 | 100 | 30 |
| 8 | 400 | 100 | 300 |
| 10 | 29,914 | 100 | 29,814 |
| 12 | 400 | ~0 | 400 |

(7) Measurement of the cleaned membrane permeability: calculation of the percentage of recovery in permeability.

For each experiment at a selected pH a new sample of membrane was used.

### 3.2. Solutions and analysis

Solutions were prepared from sodium hypochlorite concentrates (Oxena, 36° in chlorine) diluted in RO-treated water. The total free chlorine TFC concentration was determined using a spectrophotometer at 530 nm (HACH 2400) with a specific reagent (DPD free chlorine reagent HACH 14070–14099 Pk/ 100) and standard samples for the calibration. The solutions were replenished every second day, so as to maintain a constant chlorine concentration. The pH was adjusted with sodium hydroxide and hydrochloric acid (1 $mol \, L^{-1}$) supplied by ACROS Organics. As previously mentioned, in a first step we aimed at using soaking solutions containing a constant [HClO] (100 ppm) and varying [ClO⁻]. Based on Eqs. (1) and (2), the following solutions have been prepared (Table 1).

In the second series of experiment, tertiobutanol (2-methyl-propan-2-ol, 99.5% supplied by ACROS Organics) was added to the chlorine solution at a concentration of $0.2\%_{vol}$ and $2.0\%_{vol}$ ($d = 0.78$). The other chemicals dissolved are ferric(III) chloride $FeCl_3$ (anhydrous 98%) and copper(II) chloride $CuCl_2$ (anhydrous 99%) supplied by ACROS Organics.

## 4. Results

### 4.1. Effect of the concentrations in HClO and ClO⁻: identification of the most probable reaction involved in the formation of $^{\bullet}OH$

We have shown in previous articles [7,15] that fiber degradation can only occur in the presence of HClO. This conclusion was drawn from the experiment performed with a chlorine soaking solution at pH 12 (i.e. containing only the ClO⁻ form of chlorine), conditions for which no change was observed in the mechanical properties of the membrane (results reported in Fig. 2).

Similar observations were reported by Gabelich et al. [6] who mention that chlorination reactions with polyamide membranes have been shown to be pH dependent, with greater chlorine sensitivity observed at lower pH. Therefore, they suggested that HClO is the active ion in polyamide chlorination.

For all pH conditions investigated in this study (Table 1), it is shown in Fig. 2 that after an important drop in elongation over
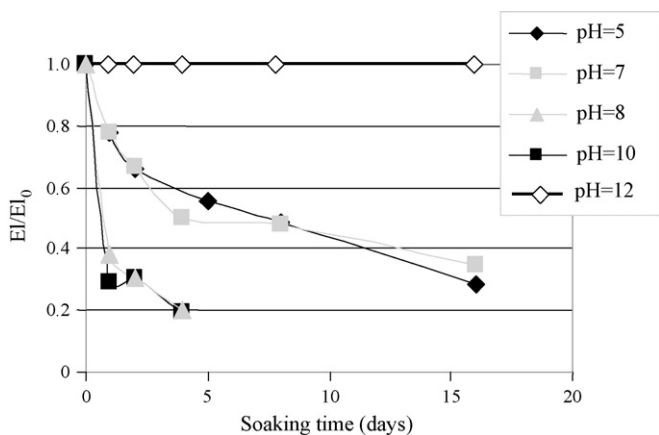
Fig. 2. Variation in time of relative elongation at break point of membranes soaked in 100 ppm HClO at various pH's (25 °C) [7].
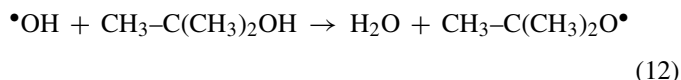
the first day, the mechanical properties of the membrane decline more slowly. Moreover, the results show that pH 8 and 10 are much worse conditions than pH 5 or 7 at constant HClO concentration: the mechanical resistance of membrane samples dipped in solutions at pH 8 and 10 was too low to be measured after 4 days. According to Table 1, the pH range 5–7 corresponds to a low $ClO^-$ concentration, whereas the pH range 8–10 corresponds to a high $ClO^-$ concentration. This shows that an increase in $ClO^-$ (and $OH^-$) concentration plays a role in membrane degradation.

If it is assumed that membrane degradation is due to radical oxidation, these results seem to show that the reaction leading to the formation of $^{\bullet}OH$ in chlorine solution corresponds to Eq. (6). According to this equation, for pH between 5 and 7, $ClO^-$ is the limiting species in radical formation: the quantity of $^{\bullet}OH$ formed in solution is low; the kinetics of membrane degradation is slow. For pH between 8 and 10, the ratio of $ClO^-$ to HClO concentrations is equal to or greater than 3 (see the stoichiometric coefficients in Eq. (6)), the limiting species is then HClO which is present at a constant concentration of 100 ppm. In this range of pH, almost the same quantity of $^{\bullet}OH$ radicals can be expected to be formed in solution and as a result the same level of membrane degradation, with faster kinetics than in the pH range 5–7. These tendencies are confirmed by our experimental observations.
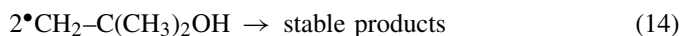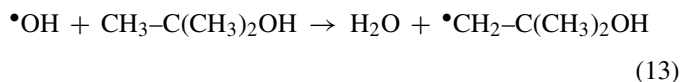
## 4.2. Effect on the variation of membrane properties of adding an antioxidant to the chlorine solution

In a second series of experiments, an antioxidant was added to the chlorine solution. Antioxidants are electron donors with which free radicals will preferentially react. Their activity depends mainly on the number and positions of hydroxyl groups within their structure. From a general point of view, antioxidants act by chain transfer or termination to prevent propagation reactions in any oxidation process, whatever the initiation mechanism. There are both hydrophobic antioxidants (vitamin E and carotenoids) and hydrophilic ones (ascorbic acid, glutathione and so on). Among the various hydrophilic antioxidants, 2-methylpropan-2-ol or tertiobutanol (TB) was chosen. In this
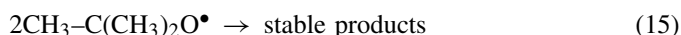
case, the reactions involved are thought to be

$$^{\bullet}OH + CH_3-C(CH_3)_2OH \rightarrow H_2O + CH_3-C(CH_3)_2O^{\bullet} \tag{12}$$

or

$$^{\bullet}OH + CH_3-C(CH_3)_2OH \rightarrow H_2O + {}^{\bullet}CH_2-C(CH_3)_2OH \tag{13}$$

$$2^{\bullet}CH_2-C(CH_3)_2OH \rightarrow \text{stable products} \tag{14}$$

or

$$2CH_3-C(CH_3)_2O^{\bullet} \rightarrow \text{stable products} \tag{15}$$

In the case of a radical oxidation of PSf chains, the presence of this antioxidant should inhibit the effects of the radicals on the membrane material and have an impact on the changes in mechanical properties of the membrane during contact with chlorine solutions.

In our experiments, tertiobutanol was added at two different concentrations: $0.2\%_{vol}$ and $2\%_{vol}$ to a chlorine solution at 400 ppm TFC (100 ppm HClO) and pH 8. These conditions of chlorine concentration and pH were chosen because they lead to drastic membrane degradation, so higher sensitivity to the inhibitor effect of the antioxidant could be expected under these conditions.

The mechanical properties of the membrane after 1, 2 and 4 days of soaking in these solutions were determined and compared with those obtained with membranes exposed to chlorine alone and to water only (experiment used as a reference), at the same concentrations, pH and temperature. Results are reported in Figs. 3 and 4.

In the presence of antioxidant, whatever its concentration ($0.2\%_{vol}$ or $2.0\%_{vol}$), no loss in tensile strength was observed over 4 days of soaking.

As for elongation, a slow decline in this parameter was observed versus soaking time in the presence of antioxidant but this decline is weaker than without tertiobutanol. Again, under our experimental conditions, we observe no effect of tertiobutanol concentration on the variation of elongation.

From these results, we conclude that in the presence of an antioxidant the initial kinetics of elongation loss by a mem-
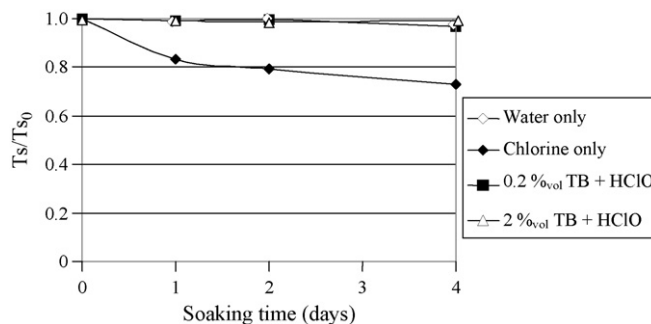


Fig. 3. Variation in time of relative tensile strength at break point for membranes soaked in 400 ppm TFC (100 ppm HClO) at pH 8 and $T = 25$ °C, in the presence or absence of tertiobutanol.
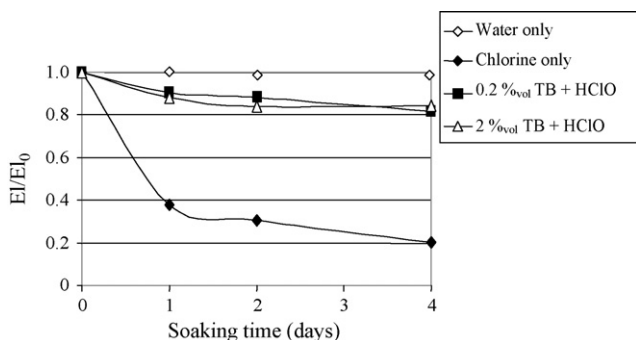
Fig. 4. Variation in time of relative elongation at break point for membranes soaked in 400 ppm TFC (100 ppm HClO) at pH 8 and $T = 25\,°C$, in the presence or absence of tertiobutanol.
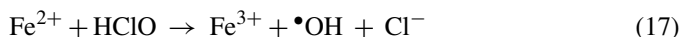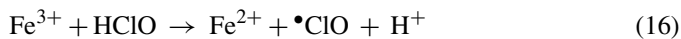
brane exposed to chlorine solution is slowed down by a factor of approximately 6, without being totally inhibited. It seems that under our experimental conditions, an optimum concentration in tertiobutanol could be found (below $0.2\%_{vol}$) above which no more would be gained in terms of degradation kinetics. This optimum was not investigated in the present work and the lower concentration of $0.2\%_{vol}$ was used in the following measurements.

Moreover, these results confirm that elongation at break point is more sensitive to membrane degradation than tensile strength. For this reason only elongation variation will be presented in the following sections.

### 4.3. Effect on the variation in membrane properties of the presence of dissolved metal ions in chlorine solutions

Dissolved metal ions are likely to be present in water sources, possibly at low concentrations. As opposed to antioxidants, transition metal ions act as effective catalysts in the production of hydroxyl radicals as mentioned in Section 2. To study the effect of these ions on the variation in properties of membranes exposed to chlorine solutions, the ferric ion $Fe^{3+}$ and the copper ion $Cu^{2+}$ were selected to be added to soaking solutions.

Some researchers investigating the use of the Fenton reaction in advanced oxidation processes have used ferric rather than ferrous ions to avoid the handling problems raised by the highly air-sensitive $Fe^{2+}$ (hygroscopic character, easy oxidation) and to reduce the demand in $H_2O_2$ as $Fe^{3+}$ acts as a true catalyst [16]. By similarity with the system $Fe^{3+}/H_2O_2$, we propose the following reaction between $Fe^{3+}$ and hypochlorite producing radical species and $Fe^{2+}$:

$$Fe^{3+} + HClO \rightarrow Fe^{2+} + {}^\bullet ClO + H^+ \qquad (16)$$

$$Fe^{2+} + HClO \rightarrow Fe^{3+} + {}^\bullet OH + Cl^- \qquad (17)$$

Moreover, we mentioned in the background section that the kinetics of reaction between $Fe^{2+}$ and HClO is very fast. So the use of the ferrous ion in our experiments would lead to membrane degradation too fast to be monitored over time. Again on the assumption that $Fe^{3+}/HClO$ and $Fe^{3+}/H_2O_2$ systems exhibit similar behavior, we can expect a much slower rate of decomposition of HClO by $Fe^{3+}$ than by $Fe^{2+}$ [17].

Finally, one can assume that the reduction of HClO in the presence of $Cu^{2+}$ may result in ${}^\bullet OH$ radical formation following a mechanism similar to $Fe^{3+}/HClO$ redox chemistry:

$$Cu^{2+} + HClO \rightarrow Cu^+ + {}^\bullet ClO + H^+ \qquad (17)$$

$$Cu^+ + HClO \rightarrow Cu^{2+} + {}^\bullet OH + Cl^- \qquad (18)$$
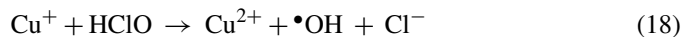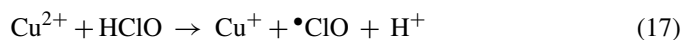
Several studies, e.g. [17,18], have shown that the reaction system $Fe^{3+}/H_2O_2$ is also effective in oxidation processes despite a slower kinetics than the $Fe^{2+}/H_2O_2$ system for which hydroxyl radicals are immediately formed (Eq. (10)).

Our experiments tried to approach the conditions met in water production plants, so ion concentrations were chosen equal to or below the limit allowed in drinking water by French legislation: 0.2 ppm for $Fe^{3+}$ and 1 ppm for $Cu^{2+}$. For the same reason, the pH was adjusted to the natural water pH of 7 and the TFC concentration lowered from 130 to 13 ppm (conditions used during back-flushing). Experiments lasted 8 days and samples were taken after 1, 2, 4 and 8 days. The temperature was always $25\,°C$.

The first experiment was performed with a soaking solution containing 130 ppm TFC (100 ppm HClO) at pH 7, with or without the presence of dissolved $Fe^{3+}$ and $Cu^{2+}$ ions at two different concentrations.

Fig. 5 shows the time variation of elongation at break point of the membranes exposed to these solutions.

It was observed that the loss in membrane elongation is approximately four times faster in the presence of $Fe^{3+}$ or $Cu^{2+}$ ions over the first 2 days. After 2 days of soaking, elongation at break point almost levels off at a plateau value about twice as low as that obtained without metal ions.

These results prove the strong catalytic effect of metal ions on mechanical degradation of the membrane. The loss in elongation seems to be almost independent of the type of ion, $Fe^{3+}$ or $Cu^{2+}$, and of ion concentration in the range studied in this work.

The effect of TFC concentration in the chlorine solution containing 1 ppm $Cu^{2+}$ is presented in Fig. 6. As expected, it is shown that in the presence of $Cu^{2+}$ at 13 ppm TFC the kinetics of membrane degradation is slower over the first 4 soaking
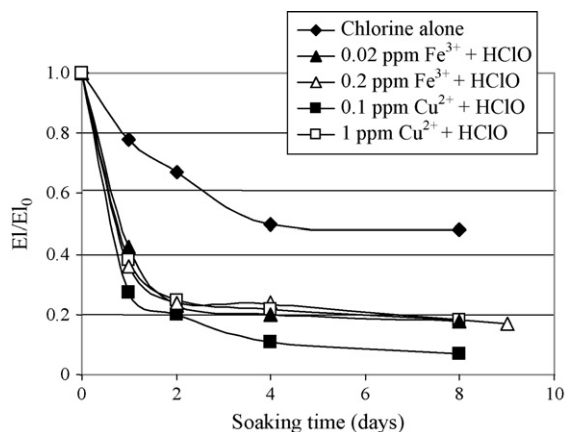


Fig. 5. Variation in time of relative elongation at break point of membranes soaked in 130 ppm TFC (100 ppm HClO) at pH 7, with or without the presence of dissolved metal ions.
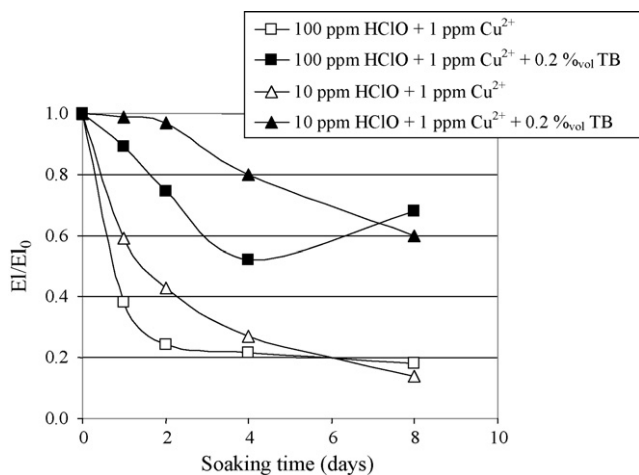
Fig. 6. Variation in time of relative elongation at break point of membranes soaked in 130 and 13 ppm TFC (100 and 10 ppm HClO) at pH 7, with 1 ppm $Cu^{2+}$ and with or without tertiobutanol.

days than at 130 ppm TFC. However, after 8 days of soaking, the relative elongation at break point of the membranes reaches almost the same value, whatever the TFC concentration 13 or 130 ppm (open triangles and open squares). The same conclusion can be drawn from the results obtained if tertiobutanol is added to $Cu^{2+}$/chlorine solution (black triangles and black squares). Moreover, it can be seen that the inhibitor effect of tertiobutanol at a concentration of $0.2\%_{vol}$ is also effective in the presence of metal ion: the addition of an antioxidant in solution leads to a decrease in the impact of dissolved metal ions on mechanical degradation of the fiber.

The last experiment was performed with a mixture of 1 ppm $Cu^{2+}$ and 0.2 ppm $Fe^{3+}$ added to a chlorine solution 13 ppm TFC, at pH 7. The objective was to tell whether the catalytic effect of the two metal ions was additive when they are simultaneously present in solution. The results are shown in Fig. 7, with and without the presence of tertiobutanol.

The results obtained without tertiobutanol seem to show no additive effect of the simultaneous presence of the two types of ions: the loss in membrane elongation is almost the same with
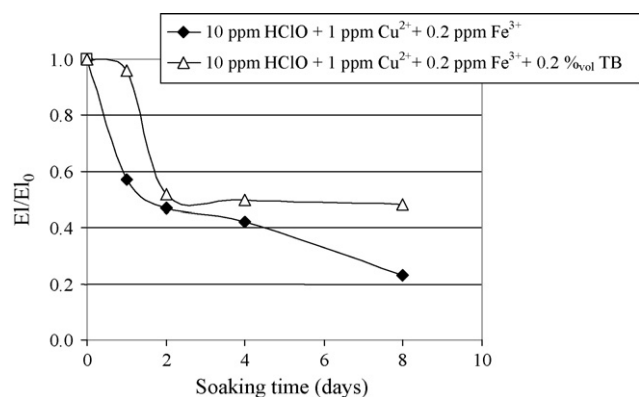


Fig. 7. Variation in time of relative elongation at break point of membranes soaked in 13 ppm TFC (10 ppm HClO) at pH 7, with the presence of the mixture 1 ppm $Cu^{2+}$ + 0.2 ppm $Fe^{3+}$ and with or without tertiobutanol.
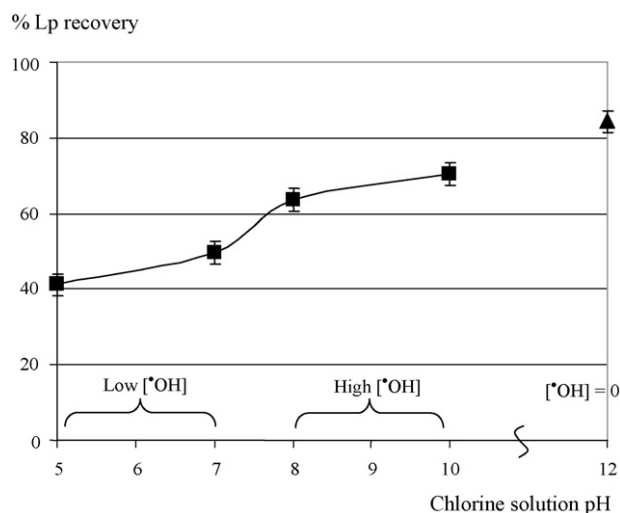


Fig. 8. Variation of percentage permeability recovery for different pH's of the chlorine solution (Table 1) used during back-flushing.

the mixture $Cu^{2+}$ + $Fe^{3+}$ (black symbols in Fig. 8) as with $Cu^{2+}$ alone (open triangles in Fig. 7).

On the other hand, the inhibitor effect of the tertiobutanol is less effective over the first soaking days in comparison with the results obtained with $Cu^{2+}$ alone.

The results obtained in the present study confirm the catalytic effect of $Fe^{3+}$ and $Cu^{2+}$ in the reaction between hypochlorite and polysulfone membranes, as is demonstrated by the greater loss in mechanical properties of the membrane.

As a conclusion from these results, dissolved metal ions likely to be present in water sources have a catalytic effect in the formation of hydroxyl radicals with a strong impact on the lifetime of the membrane and can dramatically shorten it. Introducing an antioxidant into the system could slow down membrane degradation. Of course numerous parameters: composition of the water source, concentrations of ions, chlorine and antioxidant, pH, and temperature, membrane material and structure and so on, all determine the overall reaction kinetics. In each particular case, an experimental study is necessary to understand the relationships between these parameters in terms of production and consumption of hydroxyl radicals.

Moreover, the present study was run using clean membranes. In the presence of fouling, a demand in chlorine can be generated by the fouling material, and therefore reduce the TFC available in solution. This probably slows down the ageing process.

### 4.4. Cleaning experiments on fouled membranes

Besides the question of membrane ageing, hydroxyl radicals could possibly be involved in the cleaning mechanisms for fouled membranes: their presence probably leads to a better efficiency of the in-place chemical cleaning procedures for membranes. In order to illustrate this, an additional series of experiments was performed to quantify the gain in permeability when a membrane fouled by real surface water was back-flushed using hypochlorite solution at different pH's.

Because of the short duration of the surface water filtration step (1 h) and as a new sample of membrane was used for each experiment (one per pH selected), membrane fouling was caused by natural organic matter, colloids and particles. This fouling causes a permeability loss of approximately 65%.

We report the variation of the permeability recovery as a function of the pH of the back-flushing solution (Table 1) in Fig. 8.

Whatever the pH of the chlorine solution, some residual fouling remains on the membrane surface and/or in its structure after back flushing, since a maximum of only 84% of the permeability is restored. The results show that the more alkaline the solution, the greater is the permeability recovery.

Concerning the experiments performed at constant hypochlorous acid concentration (pH 5–10), it is found (in agreement with the comments in Section 4.1) that the conditions that favor the production of $^{\bullet}$OH seem to be also those that enhance cleaning. This is in accordance with literature that reports that hydroxyl radicals show powerful oxidizing ability in degrading organic compounds RH by abstracting a hydrogen atom and then initiating a radical chain oxidation as shown in the following reaction [10]

$$^{\bullet}OH + RH \rightarrow R^{\bullet} + H_2O \qquad (19)$$
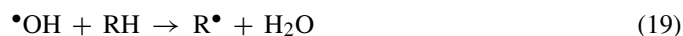
Organic radicals produced $R^{\bullet}$ are highly reactive and can be further oxidized, reduced or dimerized.

Considering now the experiment performed with a chlorine solution at pH 12 (where [HClO] $\sim$ 0) our results show that this cleaning procedure is the most effective with a permeability recovery of 84%, even though $^{\bullet}$OH is not expected in solution under this condition. This last result underlines the fact that cleaning mechanisms involve numerous complex reactions other than the ones mentioned above, depending on the chemical properties of the cleaning solution and of the filtered water source. In these mechanisms it seems that not only radicals must be considered: hydroxyl ions $OH^-$ certainly play an important role in cleaning efficiency. So reducing the presence of $^{\bullet}$OH by adding an antioxidant does not necessarily reduce the efficiency of cleaning agents. In this context, an area of interest would be a more thorough study of both membranes ageing and cleaning when an antioxidant is added to the cleaning solution.

## 5. Conclusion and perspectives

Exposure of polysulfone polymer to sodium hypochlorite produces chain breakage which is clearly reflected in changes in the membrane mechanical properties. It has been shown that the degradation mechanism involves radical oxidation by hydroxyl radicals $^{\bullet}$OH and this can be catalyzed by the presence of some metal ions, such as $Fe^{3+}$ and $Cu^{2+}$, thus suggesting that the reaction is Fenton-like. According to the mechanisms proposed and to the experimental results presented in this paper, the consumption of $^{\bullet}$OH by an antiradical, tertiobutanol, added to chlorine solution inhibits oxidation of the polysulfone chains in membrane material. This could allow an increase in mem-

brane lifetime. A strategy to adapt cleaning procedures to the ionic profile of the water cannot be proposed without further studies to understand the interactions between reagent conditions ([ion] [chlorine]) and the reaction characteristics (pH, temperature and the quantity of organic and inorganic constituents) in terms of hydroxyl radical production and consumption.

## Appendix A. Nomenclature

El      elongation at break point (%)
Ts      tensile strength at break point (N)
Lp      hydraulic permeability of the membrane (m)

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