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C. Regula, Emilie Carretier, Yvan Wyart, M. Sergent, Geneviève Gésan-Guiziou, et al.. Ageing of polysulfone ultrafiltration membranes for drinking water production in contact with sodium hypochlorite or formulated detergents. *Procedia Engineering*, 2012, 44, pp.1038-1040. 10.1016/j.proeng.2012.08.668 . hal-01026337

HAL Id: hal-01026337

<https://hal.science/hal-01026337>

Submitted on 29 May 2020

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Ageing of polysulfone ultrafiltration membranes for drinking water production in contact with sodium hypochlorite or formulated detergents

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In water drinking production plants using membrane processes, contact with chemicals is supposed to play an important role in membrane ageing. Indeed, the main drawback is that organic membranes are sensitive to chemical exposure and to mechanical stress involved in cleaning and disinfection sequences. So, this raises the problem of the necessary optimization of the cleaning/disinfection procedures which have to take into account the best cleaning efficiency as well as the less detrimental procedures for the membranes. That is why ageing is becoming the new bone of contention between end users, membrane manufacturers and chemical product suppliers. Nevertheless, in spite of numerous scientific researches realized on the subject, several gaps can be underlined:

- First, to make ageing experiments easier and to shorten the experimental times involved by the ageing mechanisms, the commonly used parameter “concentration × time of exposure” ($c \times t$) is used. This way of thinking would suppose that strong concentrations for short times of exposure could be considered equivalent to low concentrations for long times of exposure. This approach remains questionable and the major issue of the current membrane ageing researches would be to define consistent and representative ageing protocols.

- Secondly, the studies performed until now are focused on the use of chlorine, while hypochlorite is not universally applied and the use of chlorine-based reagents is expected to be restricted in the next years. Some new membranes are not chlorine tolerant and the use of chlorine was shown to generate chlorinated organics with detrimental effects on health and environmental impacts. So, alternative detergents could be significantly used in the future. However very few works have been focused on the membrane ageing resulting from the use of formulated detergents (such as enzymatic detergents, less detrimental oxidants).

Experiments were realized in order to get a better understanding of changes in membrane properties, or at least a better understanding in the mechanisms behind the changes, so as to be able to take them into account in optimizing cleaning procedures. Polysulfone hollow fibers membranes were used to simulate the industrial ageing in static conditions in NaOCl and in five detergents: P3-Ultrasil 75 (acidic), P3-Ultrasil 110 (alkaline), P3-Ultrasil 67/P3-Ultrasil 69New (Enzymatic/buffer), P3-Oxysan ZS (composed of peracetic acid) and Microcare 2730 (biocide). The macroscopic changes were monitored by permeability measurements and mechanical strength tests coupled with a microscopic characterization by ATR-FTIR (to identify the functional groups affected by ageing) and SEM (to visualize qualitatively the surface modifications and deteriorations).

First, preliminary experiments were realized (only with NaOCl) for a same value of $c \times t$ parameter, but with a simultaneous variation of concentration and of time of exposure. The results emphasized that the macroscopic ageing as well as the microscopic ageing are not equivalent for a high concentration/short time of exposure and low concentration/long time of exposure. For the ultrafiltration membranes and for the experimental conditions tested, the permeability deterioration in function of $c \times t$ parameter has been shown to be not homogeneous according to the temperature. At 5°C and 20°C, it seems to have a minimal time of contact for the membrane degradation. Moreover, the use of $c \times t$ parameter significantly underestimates the degradations caused by NaOCl contrary to what happens at 40°C where the

$c \times t$ parameter overestimates the degradations. This is clearly visible on the SEM images obtained for the same $c \times t$ parameter corresponding to 18,000 ppm.day (Fig. 1).

In order to achieve a relevant establishment of an ageing pattern without using an accelerated ageing protocol with high concentrations and short contact times, further experiments were realized using an approach based on methodological tools with several concentrations, around the industrial concentrations commonly used for all the compounds, several temperatures (from 5°C to 40°C, and several soaking times (from 7 days to 180 days) defined by experimental designs. The results achieved let to consider high deteriorations involved by NaOCl (increase of permeability, decrease of strength at break, modifications of surface properties, apparition of crackles, and disappearance of specific peaks from ATR-FTIR spectra). The comparison of results at 20°C of hollow fibers aged in NaOCl and P3-Oxysan ZS at their respective industrial concentration show that degradations of membrane permeabilities are far more detrimental with NaOCl than with P3-Oxysan ZS in spite of possible extreme cleaning pH and/or time of exposure. The same tendencies can be observed on mechanical properties and polymer deteriorations observed on SEM images and ATR-FTIR spectra. Concerning the other detergents tested, and considering the long ageing duration applied in this study, it could be concluded that the formulated detergents are quite harmless for the membrane for a time corresponding to the effective cumulated industrial time of contact. These results would help operators to optimize the cleaning conditions and to avoid the worst combinations concentration/temperature/time of contact in order to maintain the best performances of membranes in place without degradation of them.

In general terms, the results show that NaOCl causes the worst ageing deteriorations on membranes after extended exposure and changes (in membrane chemical groups, hydraulic performances, mechanical properties and physical structure) which was well known for a long time. The added value of our working lies in the broad field of ageing conditions tested and mostly in the rigorous ageing methodology applied. Indeed, the $c \times t$ parameter which was though significant revealed not significant and this study clearly demonstrated this point. That is how new visions thrive as well as the new detergents tested. However, for all detergents, deterioration of PVP is obvious and unavoidable, as it can be observed on the spectra obtained at 40°C over 180 days to concentrations equal to the half and the double of the effective industrial concentration applied (Fig. 2). Regarding to the microscopic deteriorations obtained no obvious correlation can be established with the permeability variation and the deterioration of the mechanical properties. Even if the deterioration mechanism has been well established in previous works, other deterioration mechanisms seem to occur and have to be studied.

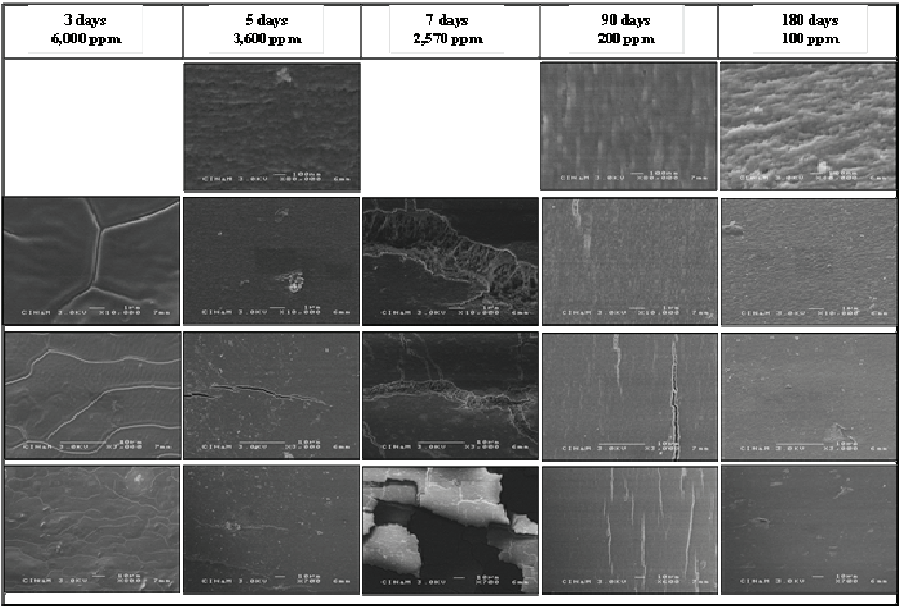


Fig 1: SEM pictures of membranes aged in accelerated conditions in NaOCl for a same product concentration $\times t = 18,000 \text{ ppm.day}$ at 40°C

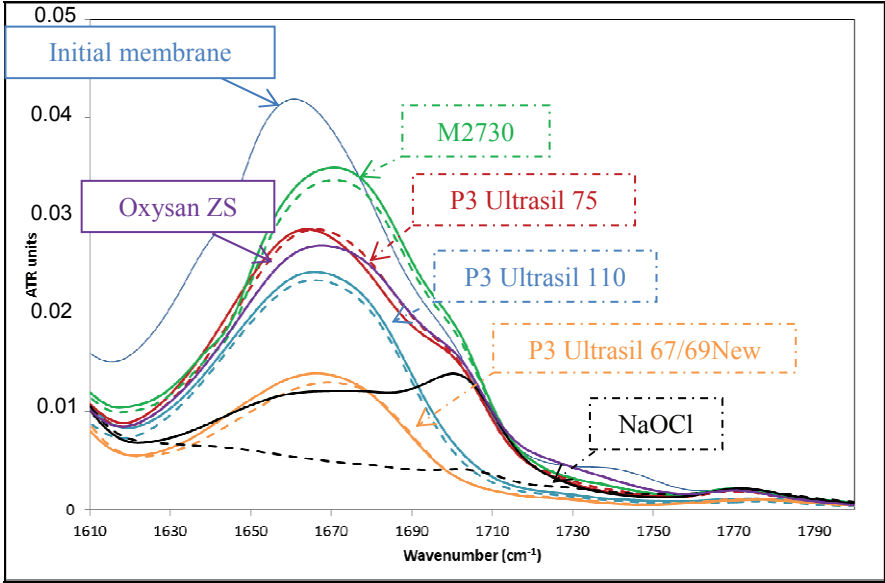


Fig. 2: Comparison of the deterioration of the amide bond of PVP by all the chemicals tested at $0.5^\circ\text{C}/40^\circ\text{C}$ and $2^\circ\text{C}/40^\circ\text{C}$ for 180 days

Keywords: polysulfone, macroscopic and microscopic characterisation, hypochlorite and formulated detergents, experimental design