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Morphological analysis of flat and hollow fiber membranes by optical and microscopic methods as a function of the fouling

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ABSTRACT

In order to provide a better understanding of the impact of flocculant used on membrane properties in drinking water production, a complete structural characterization of membranes was carried out from microscopic to macroscopic scale. New flat-sheet PES membranes with 10, 30 and 100 kDa MWCO were characterized by SEM, ellipsometry of angle resolved scattering (EARS), white light interferometry (WLI) and atomic force microscopy (AFM). It was shown that AFM is able to differentiate between membranes according to their MWCO and their manufacturing processes. The impact of flocculant filtration (PAX-XL 7A and Aqualenc F1) on flat-sheet PES 100 kDa membrane was studied. SEM and AFM characterizations revealed a modification of membrane surface state after flocculant filtration and cleaning step. AFM was finally used to characterize hollow fiber membranes after 1 and 2 years of water production. The results showed that AFM is a very interesting tool to investigate membrane ageing.

1. Introduction

Increasing needs for potable water and the evolution of regulations concerning its quality and reliability have been instrumental force behind the development of membrane filtration processes. One of the critical issues in the successful development of membrane processes is the understanding of the membrane fouling mechanisms. Fouling can be defined as the whole phenomena resulting from the crossing or non-crossing of the matter through the membrane. It results in the reversible and/or irreversible modifications of the membrane properties (permeability, selectivity, etc.), that can affect the productivity of membranes. Since a large number of factors must be taken into account, mechanisms associated with fouling are not yet well understood. Moreover, the nature of the organic fraction [1–3], the properties of the solution [4], the hydrodynamic conditions of the filtration system [5] and the membrane surface properties [6,7] also appear to play key roles in the fouling phenomenon. For a better understanding of the fouling phenomenon, the characterization of membrane structure, roughness and porosity, are of particular importance. There has been a wide range of techniques developed for this purpose, such as displacement [8,9], retention [10] and microscopic techniques. Among the microscopic techniques, Scanning Electron Microscopy (SEM) [11], Transmission Electron Microscopy (TEM) [12] and Atomic Force Microscopy (AFM) [13,14] are widely used. These tools allow the characterization of membrane properties like porosity and pore size distribution [15,16], deposit layer thickness [17] and roughness [18,19]. AFM is widely used to quantify membrane roughness because of its easy sample preparation. The sample can be imaged in either air or liquid medium and a high resolution image can be achieved. Apart from AFM, the literature dealing with the characterization of membrane surface refers to optical interferometry technique [20]. With this technique, it is possible to obtain a scan-size up to square millimeter with vertical resolution of approximately 0.1 Å. In this way, optical interferometry provides a more comprehensive analysis of membrane roughness, especially when it is jointly used with AFM for multi-scale analysis [21,22]. There are other non-invasive techniques that are also used for the characterization of membranes. Zator et al. applied confocal laser scanning microscopy to characterize fouled membranes and the cleaning step efficiency [23]. However, the main disadvantage of this technique is its weak resolution, which limits the characterization to microfiltration/ultrafiltration membranes. The use of optical microscope with a digital camera makes it possible to measure in situ the size of the

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filtration cake on the external surface of a hollow fiber [24]. However, like any other optical microscopy, the turbidity of the solution is a limiting factor for this application.

Despite the promising aspects of each of the above discussed characterization techniques, no individual technique seems to provide sufficient information for a thorough understanding of structural properties of membrane and fouling mechanisms. This necessitates a multi-technique approach which simultaneously accounts for multi-scale characterization of surface by using various microscopes, and bulk characterization by using light scattering techniques (optical). The first objective of this work is to study the structural properties of three new flat-sheet polyethersulfone (PES) membranes with MWCO of 10 kDa, 30 kDa and 100 kDa. To collect information about membrane surface, SEM was used to determine morphological properties of the membranes. The joint use of AFM and White Light Interferometry (WLI) highlights influences of the observation scale on the roughness determination. Light scattering measurements and ellipsometry of angle resolved scattering (EARS) were used to probe membrane bulk. The combination of optical and microscopic results allows a complete characterization of membrane structural properties. In a second part, the modification of the 100 kDa membrane structure will also be studied by filtration of a synthetic solution of flocculant used in pretreatment during the production of drinking water by membrane process. In a third part, this work will be extended to the study of the geometry of hollow fibers at different states: new hollow fibers, hollow fibers after 1 operating year and hollow fibers after 2 operating years.

2. Experimental

In order to access the question of fouling, both membrane surface and membrane bulk properties have to be characterized. The surface state is characterized at different scales with microscopic techniques: WLI, AFM and SEM as described below. Optical specific techniques are used in order to quantify the bulk properties of membranes. These techniques are based on light scattering measurement at different angular resolutions and on the study of polarization properties of light scattering [22,25,26].

2.1. Characterization techniques

2.1.1. White light interferometry and atomic force microscopy

White light interferential optical microscopy (WLI) was used for a non-contact surface topography measurement of the membranes. In this study, a commercial optical profilometer, with a Mirau interference objective (Talysurf CCI 3000) was used. This optical microscope allow to obtain image sizes ranging from 360 μm × 360 μm (with a ×50 objective) to 900 μm × 900 μm (with a ×20 objective), with a video camera providing images with 1024 × 1024 points. In the case of the ×50 objective, the accessible lateral resolution is about 0.4 μm; it is equal to 0.9 μm with the ×20 objective. In both cases, the expected vertical resolution is about a few angstroms. AFM images are performed in the tapping mode and non-contact mode with a commercial XE-70 instrument (Park system). Two different scan sizes were used: 10 μm × 10 μm and 40 μm × 40 μm with a same number of data points equal to 512 × 512. Cantilever was made out of silicon with a resonant constant frequency equal to 325 kHz, a constant force equal to 40 N m^{-1}, and a scan speed ranging from 0.3 to 0.7 Hz. The same tip (NCHR model) was used to scan all surfaces and all images obtained can be numerically processed in the same way. The accessible lateral resolution is about 80 nm (40 μm × 40 μm) and 20 nm (10 μm × 10 μm). These two microscopic techniques supply information at different scales, depending on the sampling step and the size of the measured area. It is important to identify performances and limits of each technique, and to understand in what way they complement each other for a multiscale analysis of the samples. The two types of microscopes presented above provide a profile of each membrane surface: $h(x, y)$. It is then possible to extract roughness parameters using the following equation:

$$\gamma(\vec{\sigma}) = \frac{4\pi^2}{S}\left|\tilde{h}(\vec{\sigma})\right|^2 \quad (1)$$

where $\sigma=(\sigma,\sigma_y)$: spatial pulsation, $\tilde{h}$: spatial Fourier transform of the $h(x, y)$ profile, $S=L^2$ (measured area).

2.1.2. High resolution scanning electron microscopy (HRSEM)

JEOL JMS-6320F is a high resolution scanning electron microscope with a cold field emission source and an in lens detection. The resolution can reach 1.2 nm at 15 kV and magnifications from ×25 to ×650.000 (at 8 mm WD) are possible. In this study, HRSEM is used to estimate the pore diameter and the surface porosity (equal to ratio between the total surface of the pores and the total surface of the SEM image). For that, each sample was coated with titanium with the use of a 4 magnetron sputtering apparatus. For each sample, 5 images were randomly taken and analyzed.

2.1.3. Light scattering measurements and ellipsometry of angular resolved scattering analysis at low and high (speckle) resolutions

The membrane is a porous material and it diffuses light in all directions when it is lighted up. The measurement of the angular scattering pattern, associated with the development of electromagnetic models, makes it possible to access the physical and geometrical properties of the object [27,28]. When the medium is highly scattering, it is very difficult to separate the surface and the volume effects. However, the dissociation of the different scattered sources is possible when working at high angular resolution, or by studying the polarization states of scattered waves [29–32]. This technique is called “Ellipsometry of angular resolved scattering”: EARS [33–35]. The scattered intensity is measured with an instrument called “scatterometer”. The principle and apparatus have been described previously [25].

2.2. Membranes and filtration protocol

Three commercially available flat-sheet PES ultrafiltration membranes from Millipore with different molecular weight cut-offs (10, 30 and 100 kDa) were investigated in this study. As any organic membrane is delivered generally packed with glycerin, a chemical cleaning and then a dynamic rinse are advised to remove glycerin without altering membranes. The chemical cleaning consists of three steps: a filtration with citric acid (pH=4) during one hour in dead-end mode with a constant transmembrane pressure (TMP) of 0.5 bar, a rinse with 250 mL ultrapure water and filtration with a sodium hydroxyde solution (pH=8). After the chemical cleaning, the membrane is thoroughly rinsed by filtration with ultrapure water (about 300 L m^{-2}). A measurement of the initial water permeability is then achieved in order to obtain a reference value to carry on the study.

The feed solution to filter is a polyaluminum hydroxychlorosulfate hydrolyzed in Evian water (100 mg L^{-1}). The use of Evian water (French natural water) gives reproducible results and it is as close as possible to the composition of a natural freshwater with an average mineral content. Two solutions of commercial polyaluminum hydroxychlorosulfate flocculants (PAHCS) “WAC HB” are used: PAX-XL 7A (Kemira, France) and Aqualenc F1 (Feralco, Italy). The empirical formula of the flocculant given by the supplier is $Al(OH)_a\ Cl_b(SO_4)_c$, ($a+b+2c=3$ with $a > 1.05$). The solution of