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Membrane characterization by microscopic methods: Multiscale structure

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ABSTRACT

A great number of studies have been carried out to obtain a better understanding of membrane fouling so as to be able to limit its effects. The parameters studied are many and can be classified into membrane structure parameters (porosity, roughness, pore size, pore shape, pore size distribution) and membrane/effluent coupling parameters (material, surface charge, hydrophobicity, etc. . .). In the case of the membrane structure parameters, three types of techniques can be used: displacement techniques, tracer retention techniques and microscopic techniques. In this paper, first microscopy observation methods are reviewed, and then the potential of three different techniques is studied. Scanning Electron Microscopy (SEM) provides information on surface porosity and layer thickness. The pore sizes measured with this technique were in agreement with the membrane cut off values given by the manufacturers. Atomic Force Microscopy (AFM) and White Light Interferometry (WLI) provide surface RMS roughnesses that depend on the observation scale. The RMS roughnesses that were obtained ranged between 100 and 4000 nm. For 4 unused ceramic membranes of different cut-offs and for 3 different scan sizes, the passage from one scan size to another is continuous in terms of information provided.

1. Introduction

Membrane processes are the industrial processes whose development has been the fastest (12% growth per year) but membrane filtration is impeded by a major drawback: membrane fouling. The fouling can be either reversible or irreversible, depending on whether the membrane can be regenerated or not. This phenomenon entails a reduction in the production, a decline in the permeate flux, and a possible reduction in the performance of the membrane in terms of selectivity. Either a backwashing or a chemical wash will thus be necessary for the membrane to recover its initial performances. A great number of studies have been carried out in order to gain a better understanding of this phenomenon of membrane fouling so as to be able to limit its effects [1–3]. The parameters studied are many and can roughly be classified into: membrane structure parameters (porosity, roughness, pore size, pore shape, pore size distribution) and membrane/effluent coupling parameters (membrane material, surface charge, hydrophobicity, etc. . .). Only membrane structure parameters will be considered in this paper. The previous studies carried out in this domain have focused on three types of techniques: displacement techniques [4,5], techniques of tracers' retention and microscopic techniques [4,6]. The displacement techniques require high pressures as they are used on membranes with pore sizes of about 10 nm (ultrafiltration). The tracer retention techniques have been widely used, especially for defining membrane cut-offs. Polyethylene glycols and proteins are the most often used tracers in the case of ultrafiltration, but they are sensible to operating conditions. Advances in the study of membrane structure have been made possible thanks to microscopic techniques such as Scanning Electron Microscopy (SEM) [7], Transmission Electron Microscopy (MET) [8], near-field microscopy (Atomic Force Microscopy, (AFM) [9]) and Scanning Tunnelling Microscopy (STM) [10]). Among these various techniques, the most widely used are SEM and AFM. The SEM applications are varied and focus on membrane structure characterization [11], hollow fiber membrane fabrication [12] and the study of the fouling process [13]. Hwang and Lin [14] used observations made using SEM to qualify the nature of the pores of 3 microfiltration membranes with a cut-off of 0.1 μm. They also observed the fouling of these membranes after filtration of a solution containing model particles of polymethyl methacrylate (mean diameter = 0.4 μm). The major drawback of this technique is the sample preparation by gold metallization, which entails a less accurate pore size determination. Atomic Force Microscopy (AFM) is a quite recent technique dating back from 1986 [15]. It was first used in 1988 to study the structure of polymeric membranes [16]. This technique can be used in three different modes: contact [17], non-contact [18] and tapping mode [19] and can be applied to all membranes, from microfiltration to reverse osmosis [20–22], for organic [23,24]

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as well as inorganic [25,26] membranes. However, using contact mode AFM can damage reverse osmosis membranes [17,22,27]. This technique makes it possible to represent no conducting surfaces with a resolution of the order of the nanometer in either dry or wet environments [28–31]. Therefore, using AFM makes it possible to avoid drying the sample under vacuum. The AFM measurements give access to the roughness, pore size, pore density and pore size distribution of a membrane [32]. They can also provide information on the surface electrical properties of a membrane, its fouling potential towards a specific colloid [33] and its filtration performance as a function of its roughness [34]. All this can help to predict fouling without process measurements [35–37].

Vrijenhoek et al. [38] characterized 4 commercially available polyamide composite membranes for surface morphology, surface chemical properties and surface charge. Contact AFM measurements allowed them to show that the rougher the membranes, the more colloid particles deposited on them. Some drawbacks of the AFM technique were pointed at: due to the size of AFM scanning probe tips, there are some limitations to the scanning depth; also, AFM may distort membrane pore size due to rounded corners near pore entrance [39]. Boussu et al. [40] compared the results obtained using contact and non-contact mode AFM. It was concluded that when comparing surface roughnesses for different membranes the same AFM method and the same scan size must be used. Boussu et al. [40] also tested tapping mode AFM to characterize membranes with respect to their hydrophobicity, using phase shift measurements. Norberg et al. [41] performed bench-scale tests on membranes used for the treatment of brackish surface water. They evaluated membrane roughness by contact AFM (Root Mean Square roughness, RMS), surface charge by measuring the zeta potential and hydrophilic character by measuring the contact angle. Based on these results, 4 RO membranes (13.1 nm < RMS roughness < 67.4 nm) with a good resistance to fouling were selected for use in the pilot study. Al-Jeshi and Neville [42] studied the influence of the length of soaking time on RO membranes. Using contact mode AFM, they showed that surface roughness increased by 35% after 2 h of soaking in a NaCl solution at pH 4.3.

Contrary to SEM, AFM can be used in an aqueous environment [43]. However, the observations are made on small surfaces and depend on the size and shape of the tips used. The information obtained using AFM are often confronted to the results obtained with electron microscopy techniques in order to better understands the fouling mechanism. With this in view, Elimelech et al. [44] used the contact mode AFM/SEM coupling to demonstrate the influence of the roughness of RO membranes on fouling by a colloidal suspension of silica. They compared the fouling behavior of cellulose acetate and polyamide composite membranes, the former being smoother than the latter. Results showed a higher permeate flux and a slower flux decline for the cellulose acetate membranes (the smoothest) compared to those for the polyamide composite membranes. For polysulfone membranes, Kim et al. [19] obtained with SEM smaller pore size than with tapping AFM. To determine pore size, AFM is more precise than SEM which needs a sample preparation step of gold metallization [45–47]. Hirose et al. [48] and Warczock et al. [49] studied by SEM and AFM the relationship between the skin layer surface structure of, respectively, RO and NF membranes and their filtration performances. It was shown that the roughest membranes provided the best performances in terms of flux, the flux increases quasi-linearly with the roughness.

Although SEM and AFM are the two most popular techniques for characterizing membrane structure and fouling, there are other techniques that can be used for the same purpose. Koyuncu et al. [50] showed that the roughness values obtained by white light interferometry (scanned area = 64 μm^2 and 0.05 mm^2) were higher than those obtained by tapping mode AFM (scanned area = 100 μm^2). This can be accounted for, to some extent, by the fact that membrane surface roughness increases with increasing scan size, until a critical scan size of 250,000 μm^2 is reached. The area that can be scanned by AFM is relatively small, well below this critical value, and so the results obtained using this technique can be misleading [50]. Today, new characterization techniques, as Confocal Scanning Laser Microscopy (CSLM) [51–56], provide a 3D representation of the membranes and of their fouling. By means of a fluorescent contrast agent, this non-destructive technique reveals the presence in the porous structure of defects that do not propagate to the membrane surface. This is a clear advantage of CSLM over SEM, which provides only 2D representations. Ferrando et al. [57] and Zator et al. [58] developed this technique to characterize the fouling of flat microfiltration membranes with fluorescent probes. This technique provides information on the fouling at the surface of the membrane and also inside the porous matrix as well as on the origin of the fouling and on the quantification of the blocked pore surface. However, the resolution of this technique is low, and thus it has so far been applied only to microfiltration. Another technique, also using fluorescence labelling, was developed by Hugues et al. [59] to give a 3D representation of flat membranes fouling. With this optical technique – namely two-photon femtosecond near infrared non-linearoptical imaging – they were able to show the influence of the concentration of a yeast fouling solution on the cake formation. The use of modern synchrotron radiation sources provides 3D visualization of the membranes using 2D images. Remigy and Meireles [60] applied this technique – which does not require any membrane preparation – to study the influence of the nature of the polymer (polysulfone or PVDF-HFP) for hollow fiber membranes. They were able to describe the geometry of the pores and the 3D architecture of the hollow fibers. However, using 2D images to obtain this 3D representation requires quite advanced data processing software and this technique is limited to the study of microfiltration membranes.

Each microscopic technique has its advantages and disadvantages. We are going to compare the information obtained on ceramic membranes as a function of the cut-off using three different techniques: SEM, WLI and AFM. The range of membranes studied goes from the mere membrane support to ultrafiltration membranes. In particular, it will be shown that the roughness values depend on the scan size and that the passage from one scan size to another provides continuous information on the roughness. This not only confirms the importance of the scan size but also shows that some coherence exists between the surface roughness values obtained using two different techniques. This study was performed on unused ceramic membranes that had not been fouled. Previous studies had already showed the influence of the roughness–fouling relationship [34,38].

2. Material and methods

Surface analysis can be done with different tools, each one with its own specificity with regard to the conditions of use and to the information it provides. In our study, we used a Scanning Electron Microscope (SEM), a White Light Interferometer (WLI) and an Atomic Force Microscope (AFM). In this section, the operating principle of each tool will be presented, so that the complementarity of the three techniques can be better understood. This study deals with the investigation of three ceramic membranes (cut-offs: 300 kDa, 0.1 and 0.45 μm) and the corresponding support. The membranes, supplied by Novasep Company, are 27 channels tubular KERASEP membranes with a TiO_2/ZrO_2 skin. The membrane samples were obtained using a diamond saw and only the plane part of the channels was used.