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Membrane characterization by optical methods: Ellipsometry of the scattered field

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ABSTRACT

The fouling phenomenon is the major drawback of membrane processes. To be able to localize membrane fouling could be a real progress in the fouling understanding and the optimization of membrane regeneration step. For that, the membrane structure parameters must be taken into account. Classical techniques; such as displacement, tracer retention and microscopy; provides only information about the pore size of the skin layer and the thickness of the successive layers. The angle-resolved light scattering technique and the analysis of the scattered wave polarization state via ellipsometry of angle resolved scattering (EARS) are used to characterize more accurately membrane structure and to discriminate microfiltration and ultrafiltration ceramic membranes. The main objective of this study is to show the potential of these recent optical techniques that are very little known in the domain of membrane processes. First, the techniques of light scattering and ellipsometry will be reviewed, and then the results obtained for several unused ceramic membranes with different cut-offs will be detailed. The low resolution analysis clearly shows that the observed light scattering comes essentially from the bulk, but fails to differentiate between cut-offs. High resolution angle-resolved measurements make it possible to obtain a specific signature to each cut-off. The higher the porosity, the greater the angular variations of the polarimetric phase shift. Simulations performed by applying a rigorous method for the resolution of Maxwell's equations will validate these observations.

1. Introduction

The application of membrane processes in the industrial world is impeded by a major drawback: membrane fouling. During the filtration steps, this fouling can occur either on the surface or within the pores of the membrane. Where this fouling occurs not only affects the permeate flux and/or the selectivity but is also of crucial importance for the membrane regeneration step. A great number of studies have been carried out in order to gain a better understanding of this fouling phenomenon so as to be able to limit its effects. To study structure parameters, three types of techniques are generally used [1–4]: displacement techniques, tracer retention techniques and microscopic techniques. Displacement techniques include the bubble point method, liquid/gas displacement and biliquid porometry. These techniques require high pressures as they are used on membranes with pore sizes of about 10 nm (ultrafiltration membranes). They give the values of the maximum pore radius and of the mean pore radius, and also the pore size distribution. The tracer retention techniques have been widely used, especially for defining membrane cut-offs. Dextranes, polyethylene glycols and proteins are the most often used tracers in the case of ultrafiltration. Unfortunately, due to their sensitivity to pressure effects, they give different values according to the protocol used [5]. The study of the structure of membranes has been made possible thanks to various microscopic techniques: scanning electron microscopy (SEM [6]), transmission electron microscopy (TEM [7]), near-field microscopy (atomic force microscopy, AFM [8]) and scanning tunnelling micrsocopy (STM [9]). Among these various techniques, the most widely used are without any doubt SEM and AFM.

SEM applications are varied: qualification of the nature of the pores for a same cut-off [10], measurement of the thickness of the deposit that forms during the fouling of the membrane [11]. AFM is a quite recent technique dating back from 1986 [12]. It was applied to the study of membrane structure in 1988 [13]. This technique can be used in three different modes: contact, non-contact and tapping mode [14]. It makes it possible to represent surfaces with a resolution of the order of the nanometer and gives access to information such as membrane roughness, pore size, pore density and pore size

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distribution [15]. However, there are some limitations to this technique, due to the size of the scanning probe tips, the depth to which these tips can penetrate the pores [16], the possible distortion of the size of the pores through distortion of their rounded corners [17] and the fluctuations of the information obtained depending on the observation window size [4,14].

Even if these microscopic techniques are coupled with other techniques such as surface potential measurement and/or contact angle measurement [18], the results obtained concern only the structure of the skin layer [19,20] of the membrane and the values of the thicknesses of the successive layers that constitute the membrane. Very few studies have focused on the in-depth characterization of membranes. From the 1990s, impedance spectroscopy was applied to the characterization of the membrane structure as well as the membrane fouling. This method, based on the measurement of electrical properties of membrane, allows to monitor the separation performance of synthetic membranes [21,22]. It was also used to estimate the porosity of ultrafiltration membranes [23] and to follow in real time the fouling phenomenon of electrodialysis membrane [24]. Applying confocal scanning laser microscopy (CSLM) in fluorescence mode, Bonilla et al. [25] characterized zeolite membranes. By using a fluorescent contrast agent, they were able to reveal the presence in the porous structure of defects that do not propagate to the membrane surface, such as internal cracks. This is a clear advantage of CSLM over SEM, which provides only 2D representations. Ferrando et al. [26] and Zator et al. [27] developed this technique to characterize the fouling of flat microfiltration membranes by proteins. The addition of fluorescent probes (fluorescine, Texas red, rhodamine B, tetramethylrhodamine) to the proteins gives access to information such as the characterization of the fouling at the surface of the membrane and within the porous matrix, the origin of the fouling and the quantification of the surface of the pores that are blocked. Another technique, also using fluorescence labeling, was developed by Hughes et al. [28] to give a 3D representation of the fouling of flat millipore membranes. The characterization of the fouling layer can also be achieved by using small angle neutron scattering (SANS). This technique was performed to characterize the protein fouling in ceramic membranes [29] and the clay fouling in organic membranes [30]. The use of modern synchrotron radiation sources provides 3D visualization of the membranes from 2D images [31]. This technique provides visualization of the membrane material as a whole by visible light absorption difference. Remigy et al. [32] applied this technique – which does not require any membrane preparation – to the study of the influence of the nature of the polymer (polysulfone or PVDF-HFP) for microfiltration hollow fiber membranes formation. They were also 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 optical technique has its advantages and disadvantages, and it is obviously very difficult to obtain information on the membrane bulk using a non-destructive technique. The techniques that have been developed up to now make it possible to obtain values for the roughness, porosity and/or size distribution or possibly layer thicknesses. However, even though the light can easily pass through a porous structure, it is scattered in all directions due to a phenomenon of scattering generated by the porous structure. In these conditions, any imaging technique is difficult to apply to access to bulk information. Light scattering is a topic that has long been studied by optics researchers. Indeed, through the development of sophisticated experimental techniques and the exploitation of measurement results by using electromagnetic codes, it is possible to develop an approach to the problems of the reconstruction, and use the light as a probe for the non-destructive evaluation of heterogeneous materials. In our study, the angle resolved scattering technique and the analysis of the scattered wave polarization state using the technique of ellipsometry of angle resolved scattering are used to characterize ultrafiltration and microfiltration membranes and discriminate between them. The main objective of our work is to show the potential of these recent optical techniques that are very little known in the domain of membrane processes [33]. The information, obtained for ceramic membranes, is compared for different cut-offs.

In particular, it will be showed that to each membrane corresponds a specific signal and that it is possible, by coupling several optical techniques, to distinguish between surface and bulk information. This study was carried on unused membranes that had never been fouled.

2. Material and method: light scattering and ellipsometry of angular resolved scattering

Generally speaking, and because it provides information linked either to the surface topography or to the bulk heterogeneities, the study of elastic light scattering is an extremely powerful characterization tool, often the only one capable of probing or scrutinizing in a non-destructive way the components of inert or living organisms in various domains: optical gauging of objects or of far-field scenes, electromagnetic reconstruction, reduction of losses in modern optical systems, cosmetics, teledetection, visualization, observation of living organisms. This scrutation is done in far field, which may have many instrumental advantages. The measurement of the angular scattering pattern (Fig. 1) associated with the development of electromagnetic models [28–35] usually makes it possible to have access to the statistical physical and geometrical properties of the object. It has recently been shown that the study of the polarization state of the scattered wave is a good complement to that technique, as it discriminates between the different scattering sources (surface or volume) [36–39]. This technique is called "ellipsometry of angular resolved scattering": EARS [40–42].

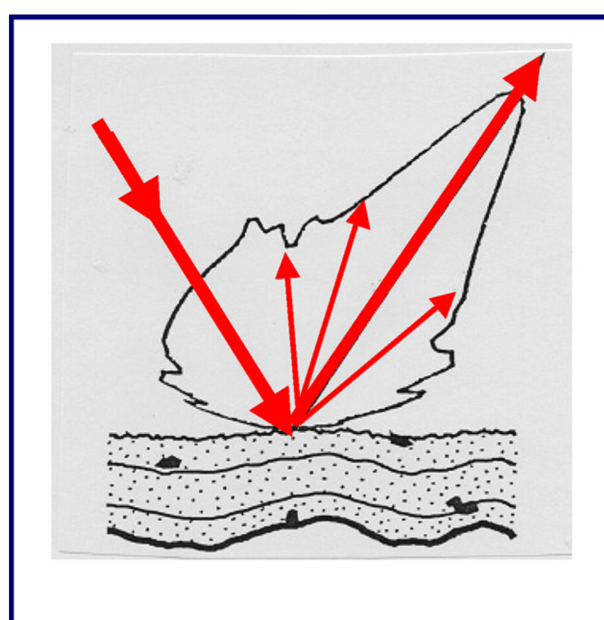

Fig. 1. Light scattering for a sample with rough interfaces and heterogeneous bulks.