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Spatial localization of membrane degradation by *in situ* wetting and drying of membranes in the scanning electron microscope

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ABSTRACT

Flat sheet microfiltration membranes are often based on PES/PVP (polyethersulfone/polyvinylpyrrolidone), because of their wide range of applications and their excellent resistance to many physical and chemical treatments. Nevertheless, regular cleaning of the membranes is necessary, which often leads to membrane degradation and thus a gradual reduction in performance. This study investigates the impact of three typical cleaning agents (NaClO, NaOH and CA) on multilayered PES/PVP membranes used for water filtration by *in situ* wetting and drying experiments in an environmental scanning electron microscope (ESEM). It has been proven that this method enables the detection of membrane degradation and is able to identify the layer which is most affected by these chemical treatments. The results were verified by Fourier transform infrared spectroscopy (FT-IR) and a method based on the imbibition of water droplets at the membrane surface. But the ESEM based method is the only method that involves a large sample volume and can thus provide statistically significant results.

1. Introduction

Sustainable development is a major challenge in all fields of technology, including water treatment and health management, leading to progressive innovations in separation membrane development and production [1–4]. Widely used membrane types are polymer membranes such as microfiltration (MF), nanofiltration (NF), reverse osmosis (RS) or ultrafiltration (UF) membranes to name but a few. A comprehensive compilation of different types of polymer membranes and their fields of application can be found in Ref. [5]. A widely used material for micro- and ultrafiltration membranes is polyethersulfone (PES) [6]. One of the great advantages of PES is its stability against a variety of chemical and physical attacks [7]. Irrespective of their application, microfiltration membranes must be cleaned regularly to avoid membrane fouling, bacterial contamination and for disinfection [8]. One of the most common disinfection agents is sodium hypochlorite (NaClO), because it forms hypochlorite acid (HClO) and sodium hydroxide (NaOH) in an aqueous solution. The former is widely known as a good disinfectant due to its high oxidation potential in comparison with other cleaners [9]. Several studies have been performed to investigate the impact of different cleaning agents on different types of membranes [10,11]. They give a comprehensive overview of the effects of such cleaners in terms of changes in the strength, permeability and selectivity of PES based membranes [12]. But these are all macroscopic parameters and for a deeper insight into the ramifications of such treatments, a more profound knowledge of changes happening in the individual membrane layers would be a major advantage.

Membrane manufacturers routinely use a great variety of methods for the measurement of a multitude of membrane properties. The parameters obtained with these methods often result from integrations across the whole membrane. In addition, more specialized test procedures have been developed which can provide information at which location in the membrane degradation or fouling has taken place. These are mainly useful in membrane research, because they are often more time consuming, cannot be easily automated and thus cannot be applied directly in the production line. Water contact angle measurements for membrane characterization were applied by Zhang et al. [13]. First investigations of wetting properties of microporous polymer membranes in an ESEM were performed as early as 1993 by de la Parra [14]. The shapes of the droplets formed at the surface provide information about the surface tension and the hydrophilicity of the material, but also the influence of surface roughness on the wetting process. Additionally, hydrophobic spots at surfaces which became hydrophilic after chemical modification can be found. These methods do not provide information about the inner membrane structure, however, nor about the interaction between pore walls and water.

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Recording images of membrane cross-sections by electron microscopy will provide data about the inner structure of the membrane. But results obtained from images of cross-sections must always be regarded with caution due to the poor statistics and they also shed no light on the interaction between the water and the pore walls. To obtain reliable information concerning both of these issues, Staude et al. recorded drying rates for wet membranes as a function of time using an analytical balance in a specially designed drying apparatus [15]. The membrane weight was essentially recorded as a function of time. The shapes of these drying characteristics are dependent both on the inner membrane structure and the interactions between the liquid and the membrane material. They change with different manufacturing parameters or types of membrane used, or if different surfactants are added to the bath.

The measurement of the temperature changes at membrane surfaces wetted with water at a temperature substantially lower than that of the environment is similar to the measurement of the drying rate. The drying of different membrane layers is accompanied by steps in the temperature/time characteristic. The vital point is that the temperature of the dry membrane is much higher than that of the wetted membrane. The respective temperature characteristics reflect the internal membrane structure, but are also influenced by properties of the pore walls and thus the interaction of the pore walls with the water. H. Reingruber et al. designed and built an experimental setup for such measurements that can be mounted and operated in an ESEM [16]. This makes it possible to directly observe both the drying and wetting of the surfaces at high magnification and to simultaneously record the temperature/time characteristics. The correlation of both results provides comprehensive information about the structure and behavior of the membrane. It could be shown that different types of membranes definitely differ in their temperature/time characteristics.

As these characteristics are also influenced by the interaction between the water and the pore walls, membrane fouling or degradation caused by cleaning agents should also change the temperature/time characteristics. And in a layered system, it should be possible to figure out whether the degradation is homogeneous across the whole cross-section or, if this is not the case, to identify the layer which is most strongly affected by fouling or cleaning. The main aim of this work is to verify this assumption and to find values for the minimum concentrations and doses of cleaning agents necessary to detect changes in the temperature/time characteristics. The findings will be corroborated by FT-IR maps recorded at cross-sections of membranes and wettability tests at the surfaces by attachment of water droplets.

2. Materials and methods

Commercially available flat sheet PES microfiltration membranes were used in all experiments. Because PES is relatively hydrophobic, PVP (polyvinylpyrrolidone) is often added to make it more hydrophilic. In addition PVP influences the membrane structure, hence the pore number and pore area [17], but also the mechanical properties of the membrane [18]. This polymer blend enables the production of hydrophilic membranes with highly anisotropic cross-sections with different nominal pore sizes. The two membrane types used in this study were the DuraPES® 600 with 0.6 μm and the MicroPES® 2F with 0.2 μm nominal pore size (both from Membrana GmbH, Wuppertal, DE) [19]. Fig. 1 shows that the two membranes differ not only in nominal pore size, but also in the distribution of small and large pores across the cross-section. The DuraPES® 600 membrane consists of roughly three layers, the MicroPES® 2F membrane of four layers. But in both membranes the separation layer is close to the air side.

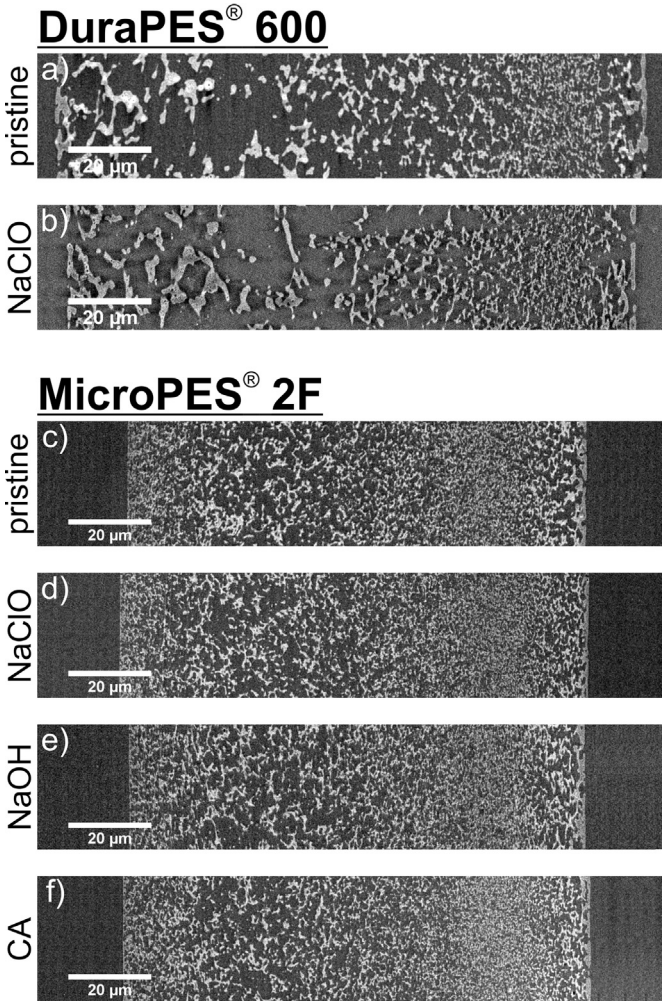

Fig. 1. SEM images of cross-sections of pristine and treated DuraPES® 600 ((a) pristine; (b) 30,000 ppm.day with 30,000 ppm NaClO) and MicroPES® 2F membranes ((c) pristine; (d) 30,000 ppm.day with 30,000 ppm NaClO; (e) 12,000 ppm.day with 3000 ppm NaOH; (f) 8000 ppm.day with 2000 ppm CA). The air side is at the right side.

2.1. Chemical treatment and aging protocol

In this study commonly used cleaning agents were utilized for the chemical treatment: sodium hypochlorite (NaClO) with 16% free chlorine, ≥99% sodium hydroxide (NaOH) and 99.9% citric acid (CA). These agents were diluted with ultrapure water (14.7 MΩ cm) generated by Barnstead™ NANOpure™ (ThermoFisher Scientific, Waltham, USA). Much higher concentrations than quoted in the literature were used to accelerate the treatment at ambient temperature and keep the exposure times short. Solutions with differing concentrations and pH values were prepared:

- NaClO: 4000 ppm, 15,000 ppm and 30,000 ppm (pH 9),
- NaOH: 3000 ppm (pH 10),
- CA: 2000 ppm (pH 3).

Strips of 5 × 15 mm^2 were cut from the membranes and soaked in the respective solution for varying lengths of time without any stirring. This differs from the procedures used in practice, like chemically enhanced backflush [20]. Furthermore, both the concentrations and doses are much higher than those used for on-site chemical cleaning. The main aim of this treatment, however, was