Rapid characterization of ultrafiltration membranes by scanning electron microscopy

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Physicochemical properties of ultrafiltration membranes were studied by scanning electron microscopy. The membrane elemental composition (carbon, oxygen, and sulfur) was determined by energy dispersion analysis. The elements were shown to be homogeneously distributed along the membrane. A homogeneous pore distribution on the membrane surface was found after covering it with a thin gold layer. The pore sizes are ~50 nm. The topographic analysis of the permeate-side of the membrane indicated its anisotropy.

Key words: ultrafiltration membranes, scanning electron microscopy, topographic analysis, elemental analysis.

In recent years, the progress in development of membranes for the treatment of aqueous solutions has attracted much interest to this technology. Membrane separating processes are widely used in biotechnology and wastewater decontamination. For application in membrane separating processes, the membrane composition is an important factor for the optimization of the process operation.[1]

The most usual membranes are produced from polysulfone (PSF), polyethersulfone (PES), and cellulose. The first two polymers are nonhydrophilic and possess a relatively high adsorptivity. They are stable chemically, mechanically, and thermally and are commonly used as supports in mixed membranes for ultrafiltration (UF) or as hemodialysis membranes. Aromatic polyamide membranes are used in desalting due to their selective permeability and thermal and chemical stability. However, the amide group is susceptible to oxidation, particularly by chlorine.[2] Polyacrynitrile (PAN) is also used in the UF membranes. It is less hydrophilic than the above polymers, however it doesn't possess a selective permeability and it is not used for reverse osmosis (RO).[1]

The IUPAC (1985) classifies the porous membranes as macroporous (> 50 nm), mesoporous (2—50 nm), and microporous (< 2 nm), which are used for microfiltration (MF), UF, and nanofiltration (NF), respectively.[3] In nonporous membranes, for example, in RO membranes, diffusion occurs in the free space between the macromolecular chains of the membrane material. The ion-exchange membranes are nonporous, and they bear a positive or negative charge.

The properties that influence the penetration process, are directly related with the elemental composition of the membrane and their pore size and distribution on the surface, as well as the properties of the treated fluid. All these characteristics are important for understanding the nature of the filtration surface and optimization of the UF process.[4]

The separation efficiency is based primarily on the size of the species in the liquid relative to the size of the membrane pores (such as in a simple sieving process). Meanwhile, the geometries of the pores and the separated species, the electric charge, and the membrane surface chemistry are also important. In the separation size spectrum, UF falls between nanofiltration (NF, membrane pore sizes < 0.01 μm) and MF (pore sizes > 1.0 μm).[5]

Scanning electron microscopy (SEM) is an important tool that allows a rapid analysis of all types of solid samples of industrial importance. Submicron particles, 0.00005 μm to 0.05 μm in size, are only visible with a scanning electron microscope or transmission electron microscope (TEM). Ultrafiltration polysufone membranes have a molecular weight cut off of 800—100000. Particles of this size are filtered using crossflow membrane technology (*viz.*, RO, NF, and UF)*.

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* M. Torok, 1994: http://osmonics.com/products/

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Studies focused at determination of the structure of membranes are scarce, however, some authors[2] mention the importance of these analyses for the search and development of new materials. In this work, we studied by SEM the elemental composition and topographic characteristics of a typical ultrafiltration membrane.

Experimental

Sample preparation. Membrane samples from a spiral module system designed for treatment of effluents with high protein and fat concentration were studied. The membranes were washed with distilled water before analyses. Samples were weighted on an analytical balance Mettler AE240 and dried at 60 °C for 3 h in an oven Quincy, Model 12-140. The membranes were separated into their components: membrane (M), support of the membrane (SM), and permeate re-collector.

Elemental analyses. The membranes were analyzed by an analyzer of dispersed energy, model EDAX marks Dxprime, with a CDU leap detector. For the analysis of samples an electron microscope JSM-5800LV (JEOL) was used.

Topographic analyses. Samples were coated with a fine electrically conducting layer of gold in order to remove electrons and avoid a load effect that could be reflected as too much shine, mainly in more marked areas. A microscope JSM-5800LV (JEOL) was used. When the primary electron beam interacts with the sample, secondary electrons that form the morphology image are formed, while back-scattered electrons bring the information of the sample composition. Hence, analyzing the topography images and the secondary X-ray emitted, we obtain the elemental composition of the area under study. In this way it is possible to perform the local elemental analysis of certain microparticles and in some cases to find superficial contamination.

Results and Discussion

Energy-dispersion analysis of the secondary X-ray emitted by the sample exposed to the electron beam showed the presence of C, O, and S on the surface (Fig. 1). These data revealed that the membrane material contains C (74.89%), O (21.53%), and S (3.59%), whereas the membrane support contain C (58.62%) and O (41.28%). On the basis of these data, we can conclude that the analyzed membrane was fabricated from PSF or PES. As expected, the main constitutent of the membrane and support is carbon.

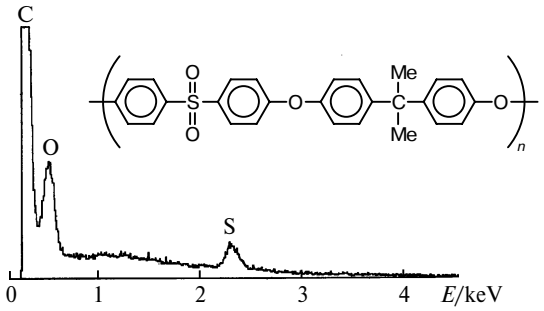

Fig. 1. Elemental composition of the membrane surface determined by X-ray differential emission.

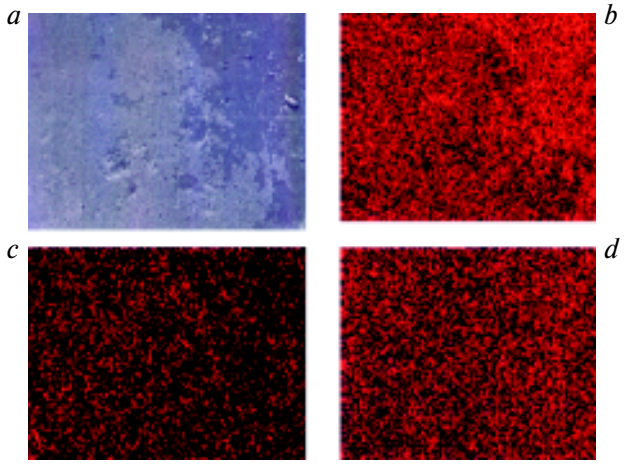

Fig. 2. Electronic mapping of elemental composition determined by secondary (back-scattered) electrons: *a*) source region, *b*) carbon, *c*) sulphur, and *d*) oxygen distribution on the membrane (magnification of ×15).

According to the SEM analysis data, all three elements are homogeneously distrubuted along the membrane (Fig. 2). This result is in agreement with the data[6] on the physicochemical mechanism of membrane fouling. The authors[6] concluded that the chemical composition of the UF membrane surface is of primary importance in determining the potential fouling, which depends on the chemical nature of the membrane, effluent, and the membrane pores.

The electron micrograph of the membrane recorded at the 10 kV voltage and amplification ×20000 (Fig. 3) gives a view of the topographic characteristics, where a rough surface is observed, with protuberances of ~200 nm in size on which pores with a diameter of ~50 nm are located, and the latter were visualized with amplification of ×200000. On the back of the membrane (Fig. 4) the pores with different sizes from 0.5 to 1.6 μm are seen. Therefore, the membrane can be classified as an

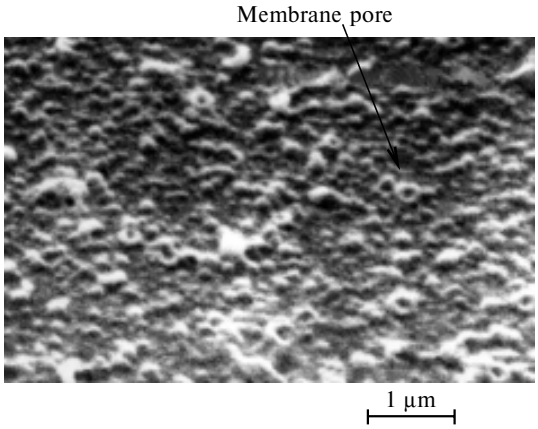

Fig. 3. Topographic overview of the membrane surface using a magnification of ×20000. Pores are seen on the membrane surface.

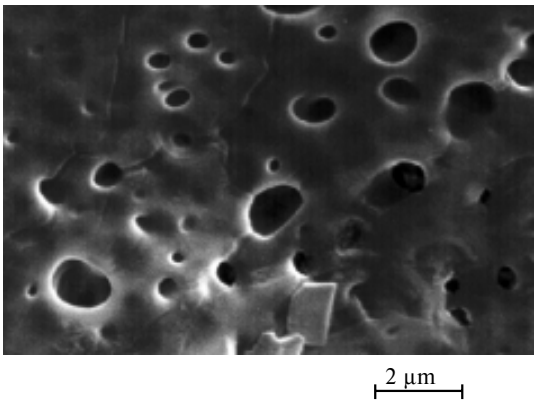

Fig. 4. Topographic analysis of the back side of the membrane with a magnification of ×10000.

anisothropic structure with a gradation of the cell size from small at the feed-side to large at the permeate-side of the membrane. These data are decisive for membranes used for filtration of fluids containing particles of different sizes.[1] Earlier[4] the performance of the UF and RO membranes has been studied as function of basic parameters such as particle size, concentration, cross-flow velocity, and trans-membrane pressure. However, such a procedure is time-cosuming, expensive, and requires repetitive experiments under different conditions. Electron microscopy analyses take advantage because it can give a rapid and clear information of what is happening during ultrafiltration process.

The electron microscopy analyses can be used to determine the relationship between the surface membrane topography and biofouling processes. The permeability efficiency for wastewaters with different compositions treated by UF membranes can be varied by selection of a specific membrane composition.[3]

Thus, the SEM—dispersed energy analysis technique was proved to be a rapid and simple method for analysis of the type, elemental structure, and topography of the membrane. These data for the used membranes allow one to increase their efficiency during operation and to enlarge its application range, as well as to monitor the structure changes during the preparation of membranes, particularly the ratio of the pore area to the membrane area.

References

1. W. Reimann, *Desalination*, 1997, **109**, 51.
2. E. Roth, M. Kessler, B. Fabre, and A. Accary, *Desalination*, 1999, **121**, 183.
3. D. Balley, T. Asano, R. Bhamidimarri, K. K. Chin, W. O. K. Grabow, S. Ohgaki, D. Orhon, A. Milburn, C. D. Purdon, and P. T. Nagle, *Water Quality International 96, Part 5: Innovative Treatment Technologies; Membrane Technology*, 1996, **34**, 215.
4. S. G. Yiantsios and A. J. Karabelas, *Membranes in Drinking and Industrial Water Production*, Elsevier-Science BV, Amsterdam, 1998, **118**, No. 1—3, 143.
5. M. Cheryan, *Ultrafiltration Handbook*, Technomic Publishing Co., Inc., Lancaster, PA, 1986.
6. K. Khatib, J. Rose, O. Barres, W. Stone, J.-Y. Bottero, and C. Anselme, *J. Membrane Science*, 1997, **130**, 53.

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