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ASSESSMENT OF THE POSSIBILITIES OF USING ATOMIC FORCE MICROSCOPY (AFM) FOR CHARACTERISATION OF POLYMERIC NANOFILTRATION MEMBRANE SURFACES

Key words

Atomic force microscopy, nanofiltration, polymeric membranes, surface roughness.

Abstract

In this study, the possibility of using an atomic force microscopy to analyse the surface structure of the polymeric nanofiltration membranes was investigated. Analysis of the obtained results allowed one to conclude that the size of the scanned surface directly affects the measurement result of both the average and root-mean-square roughness of tested membranes. Therefore, it is necessary to compare the results obtained for the same size of the scanned surface.

Introduction

Nanofiltration is a membrane pressure technique, which can be successfully applied for treatment of both surface water and ground water [1–4] and

separation of metal ions from industrial wastewaters [5–7]. However, still a major limitation on the widespread use of nanofiltration is a decrease in the efficiency of this process caused by fouling and/or scaling of membranes [8, 9]. These phenomena are primarily dependent on the properties of the nanofiltration membranes [10,11]. The main role played by the membranes charge, for which the presence of responsible functional groups present in their structure [12–14]. The charge of nanofiltration membranes is dependent on pH and the composition of the solution (mainly on the concentration and type of salt) [12–17]. It can be changed under the influence of the conditions prevailing in the treated solutions [18, 19] and cleaning baths [20–22]. The type and charge density of the membrane is also an important factor in determining the fouling and/or scaling tendency of the membrane is the surface structure. In recent years, atomic force microscopy (AFM) [11, 23, 25] and scanning electron microscopy (SEM) [22, 23] became the most common methods used to analyse changes in the surface structure of the membrane.

Atomic force microscopy (AFM) allows the determination of the average surface roughness, thereby determining the parameters such as the maximum and minimum value of the unevenness and the arithmetic mean deviation of the profile from the mean line or to determine roughness. The average roughness is determined based on the topographic image, which is a kind of map, where each point is assigned to a certain height. If all these values are averaged, it achieves an average height of the image. The difference between the average height of the image and the height at each point is a measure of the roughness of the surface [11, 23, 24].

Scanning electron microscopy (SEM) enables visual observation of surface and the structural changes of the analysed membrane samples. This technique gives the quantitative analysis on the investigated samples and a direct determination of details of the investigated objects [25–28].

The aim of the study was to analyse the surface structure of nanofiltration membranes using an atomic force microscopy (AFM). As part of the study, topographic images of nanofiltration membranes were made to determine the average roughness (R) and the root-mean-square (RMS) roughness.

Experimental

The AFM images of the tested membranes were performed with SollverBio Instruments NT-MDT. The cantilever was made out of Si with a spring of a 4.4 N/m and a nominal tip apex radius of 10 nm. The membrane surfaces were analysed in a scan size of 2 µm x 2 µm and 5 µm x 5 µm. The average surfaces roughness (R) and the root-mean-squared roughness (RMS) of tested membranes were calculated with equations (1–3) from AFM images using Nova SPM software.

$$R = \frac{1}{N} \sum_{i=1}^{N} |z_i - z| \tag{1}$$

$$RMS = \sqrt{\frac{1}{N} \sum_{i=1}^{N} |z_i - z|^2} \tag{2}$$

$$z = \frac{\sum_{i=1}^{N} z_i}{N} \tag{3}$$

where N – number of data points in the surfaces, z_i – height of each point in the scanning image, z – average height.

Two kinds of commercial nanofiltration flat sheet membranes (under symbol DL and HL) provided by GE Osmonics were analysed by AFM. The tested nanofiltration membranes had an active layer made of the poly(piperazine-amide) on the polysulfone support [18, 19]. The detailed of tested membranes were presented in our previous work [29].

Results and discussion

Performing measurements with an atomic force microscopy assigned topography of selected areas of the polymeric nanofiltration membranes. The AFM images of tested membranes for two different scanned areas are illustrated Fig. 1 and 2. The effect of the size of the scanned area of the membrane on the results of measurements of the average (R) and root-mean-square (RMS) roughness were analysed. The obtained results are summarized in Tables 1 and 2. From these results, it appears that the scanned area plays a significant role. The expansion of the area scanned contributes to the greater roughness. The phenomenon of increasing roughness with increasing scan area can be related to the dependency of the roughness on the spatial wavelength of the scanned area or the frequency [11]. For a small surface area, only the roughness of the "higher" frequencies is measured. When a larger surface area is scanned, the roughness caused by additional lower frequencies also has to be taken into account. This results in a larger roughness value when a larger surface area is scanned. According to Boussu et al. [11] another explanation for the increasing roughness with increasing scan size may be the formation of a fractal structure on the membrane surface when polymers are assembled to nodules or aggregates of nodules. Therefore, when the scan size is changed, it is possible to get a

different surface topography, resulting in a different roughness. Therefore, it is crucial that the same scan size range is used when comparing the surface roughness for different samples. Similar results were obtained in the works [23, 24].
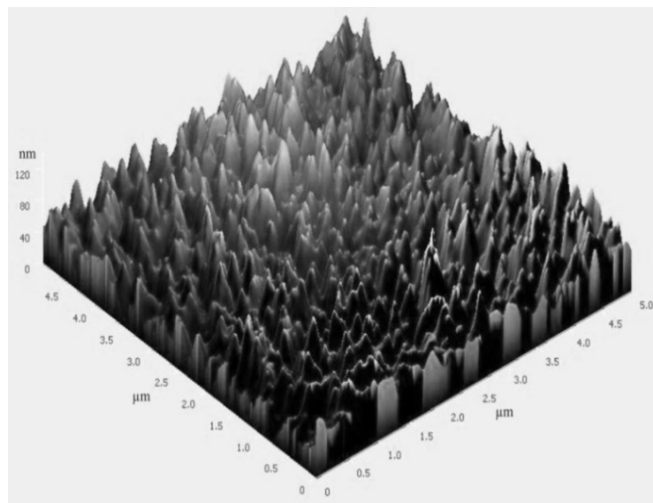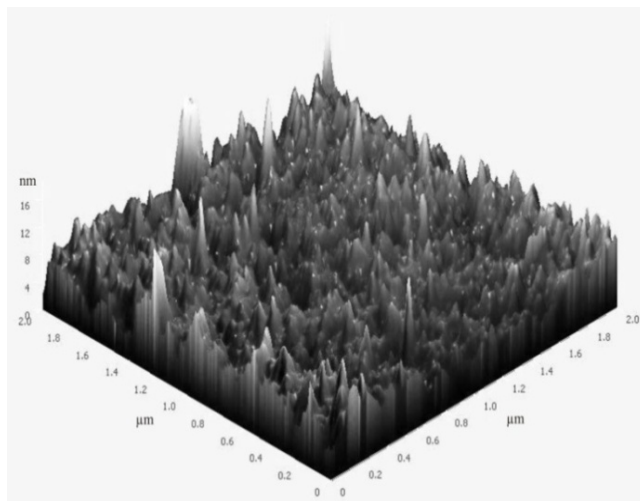
(a)
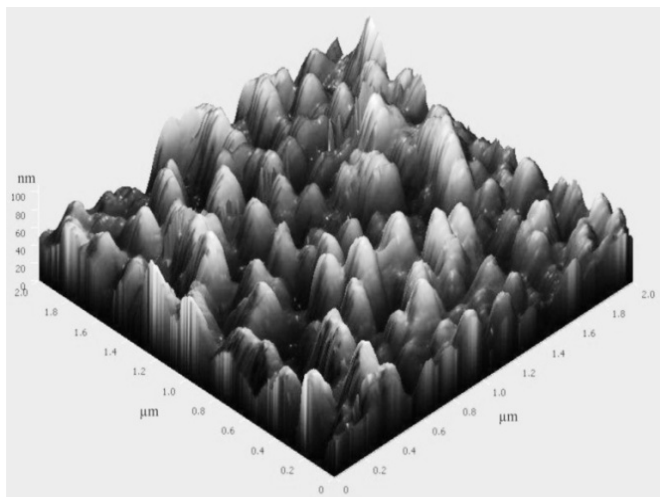
(b)

Fig. 1. AFM images of DL membrane for scan areas: 2 µm x 2 µm (a) and 5 µm x 5 µm (b)

(a)

(b)
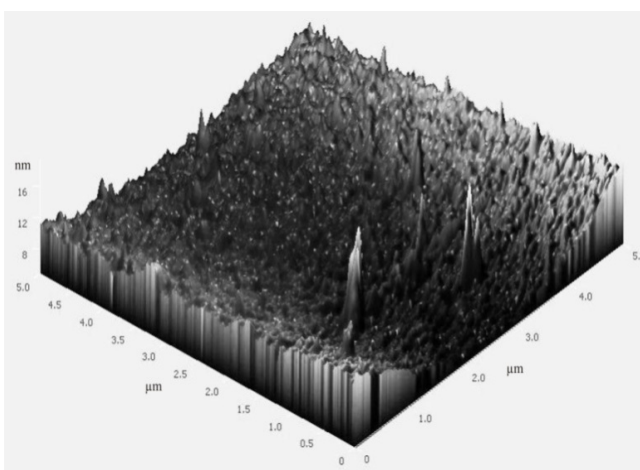
Fig. 2. AFM images of HL membrane for scan areas: 2 µm x 2 µm (a) and 5 µm x 5 µm (b)

Table 1. Average (R) and root-meat-square (RMS) roughness values for DL membranes for different scan areas (2 µm x 2 µm, 5 µm x 5 µm)

Area	R roughness nm	RMS roughness nm
2 µm x 2 µm	14.4	18.0
5 µm x 5 µm	15.4	18.8

Table 2. Average (R) and root-mean-square (RMS) roughness values for HL membranes for different scan areas (2 µm x 2 µm, 5 µm x 5 µm)

Area	R roughness nm	RMS roughness nm
2 µm x 2 µm	1.4	1.9
5 µm x 5 µm	6.0	7.4

It was also noted that the tested nanofiltration membranes produced a significantly different result of average and root-mean-square roughness. When analysing the scanned surface area, it was found that the HL membrane was characterized by a lower value of the average and root-mean-square roughness than was the DL membrane (Table 1 and 2). According to Boussu et al. [23], it is most likely caused by the construction of the top active layer. The top active layer of DL membrane consists of three sub-layers, while the HL membrane has a top active layer composed of two-sub layers [21, 30]. Additionally, according to Vrijenhoek et al. [8] and Nanda et al. [9], the membranes characterized by lower roughness of an active layer have less tendency to fouling and scaling. It is due to the fact that both the organic and inorganic particles favouring accumulation in the "valley" presented on the membrane surface is characterized by higher surface roughness [28, 31].

Conclusions

Based on the obtained results, it was found that atomic force microscopy provides valuable information about the shape of the surface layer of polymeric nanofiltration membranes, and the results contribute to the selection of a suitable membrane for a particular application.

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Ocena możliwości wykorzystania mikroskopu sił atomowych w badaniach powierzchni polimerowych membran nanofiltracyjnych

Słowa kluczowe

Mikroskopia sił atomowych, nanofiltracja, membrany polimerowe, chropowatość powierzchni.

Streszczenie

W pracy zbadano możliwość zastosowania mikroskopu sił atomowych do analizy struktury powierzchni polimerowych membran nanofiltracyjnych. Analiza uzyskanych wyników pozwoliła na stwierdzenie, że wielkość skanowanej powierzchni bezpośrednio wpływa na wynik pomiaru zarówno chropowatości średniej arytmetycznej, jak i kwadratowej testowanych membran. Konieczne jest zatem porównywanie wyników uzyskanych dla takich samych wielkości skanowanej powierzchni.