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INFLUENCE OF NATURAL ORGANIC MATTER ON FOULING AND ULTRAFILTRATION MEMBRANES PROPERTIES – AFM ANALYSIS

WPŁYW NATURALNYCH SUBSTANCJI ORGANICZNYCH NA FOULING ORAZ WŁAŚCIWOŚCI MEMBRAN ULTRAFILTRACYJNYCH – ANALIZA AFM

Abstract: Low pressure membrane processes *ie* microfiltration and ultrafiltration are widely applied in water and wastewater treatment. The main exploitation problem connected with those technologies is the decrease of membrane capacity during the process caused by blocking of membrane pores with organic and inorganic substance (so-called fouling). The performance of atomic force microscopy analysis enables quantitative determination of membranes roughness and allows to characterize membrane surface before and after fouling. The paper discuss results of filtration of three surface waters differ in properties, mainly in specific UV absorbance ($SUVA_{254}$).

Keywords: fouling, ultrafiltration, natural organic matter, atomic force microscopy

Ultrafiltration is one of the low pressure membrane techniques applied in drinking water production. The method allows to remove colloids and high molecular weight substances from treated medium. However, a decrease of the permeate flux during the membrane filtration is one of the most important operating problems. *Natural Organic Matter* (NOM) interacts with membrane surface and pores and induces its fouling [1]. Except for organic substances, the type of a membrane also has a significant influence on fouling extent. Both, adsorption properties connected with hydrophobicity and electrostatic repulsion forces resulted from membrane material and foulant charges are considered [2].

Specific UV absorption (SUVA) can be used as a parameter describing hydrophobicity or aromaticity of NOM present in water [3]. However, chemical parameters of

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water *ie* pH, ionic strength and concentration of calcium ions can affect SUVA value [4]. The low value of SUVA indicates the greater concentration of non-humic fraction of organic matter present in water. The high value of SUVA indicates the greater concentration of aromatic compounds [5, 6].

To determine the structure of a membrane various microscopic techniques are used [7, 8] *eg Scanning Electron Microscope* (SEM), *Transmission Electron Microscope* (TEM), *Field Emission Scanning Electron Microscopy* (FESEM) and *Atomic Force Microscopy* (AFM). By means of those techniques the actual picture of membrane morphology can be obtained. AFM technique gives the picture of non-conductive structures with the resolution of 1 nm in both, air or liquid environment. Moreover, the sample does not require drying, thus, it is not deformed as in case of TEM or SEM [8]. The performance of atomic force microscopy analysis enables quantitative determination of *membranes mean roughness* (R_a) and *mean square roughness* (R_q). It allows to characterize membrane surface before and after fouling occurrence. AFM analysis is performed using electrons beam and sharp tip. The sample of membrane does not need to be coated with any extra material, however the obtained data can be deformed according to differences between shapes of either pore or support tip of microscope probe [9].

The wettability with distilled water is the significant membrane parameter. Hydrophobicity/hydrophilicity can be described by the measurement of the contact angle between the water drop and the membrane surface [5]. It is stated that the membrane is highly hydrophilic if the contact angle equal to 0^o (complete wetting) and highly hydrophobic for the contact angle above 90^o (no wetting) [10, 11]. To sum up, the greater contact angle the more hydrophobic membrane.

The aim of the study was to determine the influence of NOM on both, ultrafiltration membranes properties and the intensity of fouling. The effect of NOM on the retention coefficients of organic contaminants was also investigated.

Materials and methods

Experiments were carried out in MilliporeCDS10 (Millipore&Amicon), dead-end type stirred UF cell, using a feed volume of 2000 cm^3. The process pressure was maintained at 0.1 MPa and temperature was 20 ^oC. The diameter of the membrane disc was 76 mm. The experiments were conducted using *polyether-sulphone* (Millipore) (PES), *polyacrylonitrile* (PAN), *polysulphone* (PS), *poly(vinylidene fluoride)* (PVDF) (KOCH Membrane Systems) and *cellulose acetate* (GE Osmonics Labstore) (CA) membranes. The nominal *molecular weight cut off* (MWCO) was 10, 20, 10, 30 and 20 kDa for PES, PAN, PS, PVDF and CA, respectively.

Measurements of contact angle were performed using the goniometer (Pocket Goniometer PG-1) and the sessile drop method was applied. The angle between drop of water, membrane surface and air was measured according to Yoon et al [12]. The obtained contact angles were 73.1 ± 5.0^o, 65.7 ± 4.5^o, 63 ± 2.4^o, 49.6 ± 4.9^o and 39.1 ± 5.0^o for PES, PAN, PS, PVDF and CA, respectively. This allowed to classify membrane materials as ranging between strongly hydrophobic and strongly hydrophilic.

CA membrane was found to be the most hydrophilic and PES membrane as the most hydrophobic.

Pictures of membranes surface were made using contact atomic force microscope. Membranes, after preliminary drying were placed on a metal plate which was next placed in the microscope. Pictures were registered for sectors of dimensions 50 × 50 μm and 5 × 5μm. The setpoint varied at ranges 5.725––2.725, –4.65––2.5, –2.475–0, –4.075––3.050 and –3.875––3.3V for CA, PVDF, PS, PAN and PES membranes, respectively. The scan rate was equal to 5.086 Hz for all membranes.

Prior to the first use, the membranes were conditioned according to the manufacture protocol using Milli-Q water. The new membrane was used for each filtration. Fluxes of distilled water J_m ($t = 20\ ^oC$) were 98.7–311.2, 52.4–81.0, 39.92–105.72, 44.6–70.71 and 32.7–39.6 $dm^3/m^2 \cdot h$ for PES, PAN, PS, PVDF and CA, respectively.

In the membrane filtration three different surface water samples were used. Zabie Doly – "Zabie D" ("Frog Ditches") is a nature and landscape protected area in the centre of the highly-urbanized region of Upper Silesia (Poland). Many centuries of human activity, in particular underground mining and metal smelting, left the area covered with unused water retention pools, post-mining sinkholes, tailings and slag heaps. The second water "Lasek S" was sampled from a lake located in the forest (Piasniki district in Swietochlowice, Upper Silesian Region). The third water sample "Las P" originated from a lake located in the forest in the town of Poraj (near City of Czestochowa, Poland). The lake is a hydrographic basin of the surrounding forest.

The concentration of NOM in the feed and permeate was measured as TOC (Total Organic Carbon), DOC (Dissolved Organic Carbon) and by UV absorbance at $\lambda = 254$ nm (UVA_{254}). TOC and DOC were measured using a TOC Analyzer (HiPerTOC), while UVA in an UV/VIS spectrophotometer (CECIL 1021). Prior to the UV and DOC measurements the samples were subsequently filtered with 0.45 μm cellulose filters (Sartorius Stedim Biotech S.A.). SUVA was calculated as the ratio of UVA to DOC. The conductivity and pH were measured using a Microcomputer pH/conductivity meter CPC-551. The pH, UVA, DOC and SUVA of natural waters are shown in Table 1.

Table 1

Feed water characteristics

Sample	pH	k [μS/cm]	DOC [mg/dm^3]	TOC [mg/dm^3]	UVA_{254} [1/cm]	SUVA [m^2/gC]
Zabie D	6.90 ± 0.02	907.7 ± 2,5	13.40 ± 0.22	13.40 ± 0.31	0.099 ± 0.000	0.74
Lasek S	6.96 ± 0.03	260.8 ± 2.5	10.65 ± 0.24	12.67 ± 0.07	0.240 ± 0.001	2.25
Las P	6.52 ± 0.03	82.6 ± 2.5	8.90 ± 0.24	18.10 ± 0.35	0.304 ± 0.002	3.43

Moreover, in order to measure the particulate fouling potential of feed waters for low pressure membranes, the *unified membrane fouling index* (UMFI) was determined. UMFI value can be assigned from the dependence between normalized membrane specific flux and unit permeate capacity, regardless of hydrodynamic process conditions [13, 14].

Results and discussion

In the present work five different UF membranes were tested. The water from Las P (SUVA values close to 4) indicated that NOM was dominated by high molecular weight, hydrophobic humic acid fractions. For water form Lasek S, SUVA ratio was in the range 2–4. Water of such qualities is normally dominated by a mixture of hydrophobic and hydrophilic fractions of different molecular weights, humic and fulvic acids. For raw waters with SUVA below 2 (Zabie D), NOM is normally dominated by mostly non-humic, low molecular weight substances of low hydrophobicity [3].

Table 2

Retention coefficients of TOC and DOC

Sample	ZABIE D					LAS S					LAS P				
Membrane	PES	PAN	PS	PVDF	CA	PES	PAN	PS	PVDF	CA	PES	PAN	PS	PVDF	CA
R_{TOC} [%]	7.79	22.95	10.99	9.00	12.51	37.43	27.53	37.18	32.68	26.04	58.92	48.02	58.37	64.30	45.98
R_{DOC} [%]	8.13	23.23	11.32	8.75	12.84	18.55	21.08	21.34	18.11	19.46	12.41	8.55	11.24	4.16	29.30

The highest retention of organic compounds was obtained for Las P water regardless the membrane applied, next for Las S water and the lowest for Zabie D water. It was probably caused by the highest difference between TOC and DOC concentration of Las P water (Table 1). The retentions of DOC did not exceed 30%. Similar values were obtained during filtration of Las S water (characterized with the most heterogenic composition) regardless the membrane used. Moreover, these were the greatest values of R_{DOC} obtained for particular membranes. The only exception was the retention of DOC obtained for Las P water during filtration with CA membrane. The highest value of retention coefficient was probably caused by the adsorption of positively charged particles on negatively charges membrane surface.

The main advantage of using UMFI over other fouling indices is its universality *ie* it is independent of filtration scale or mode [14]. Figure 1 depicts the values of UMFI for each filtration. In case of Zabie D and Las S waters the fouling of membranes follows the trends: PES > PS > PVDF > CA. This is in agreement with pervious consideration of Zularisam et al [13] for membrane–foulant interactions. The hydrophobic membranes (PES) tended to foul more than hydrophilic membrane (CA). It was ascribed to the electrostatic adsorption occurring between negatively charged functional group of NOM and the membrane (positively) charged polymer [15, 16] of hydrophobic membrane (PES, PAN). Natural organic matter present in Las P water caused the smallest fouling of intensity comparable for all membranes. It could result from a significant share of non-dissolved organic compounds, which deposited on the membrane and acted as a protective layer for membrane pores. The highest fouling was observed in all cases for Las S water. The SUVA value obtained for this water indicated the content of both aromatic and aliphatic substances, what confirmed the significant influence of foulant--foulant interaction on fouling.

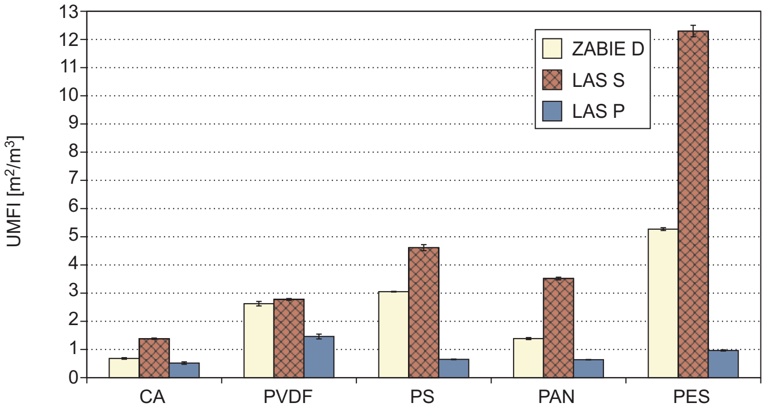

Fig. 1. Calculated UMFI indexes

Mean roughness (R_a) and *mean square roughness* (R_q) of clean and used membranes measured for both sectors *ie* a) 50 × 50 μm, b) 5 × 5 μm are shown in Fig. 2. The highest values of both, mean roughness and mean square roughness were obtained for PAN membrane. Its surface was the most diversified considering geometry, thus the smaller membrane sectors showed unrealistic pictures (Fig. 3). For this reason,

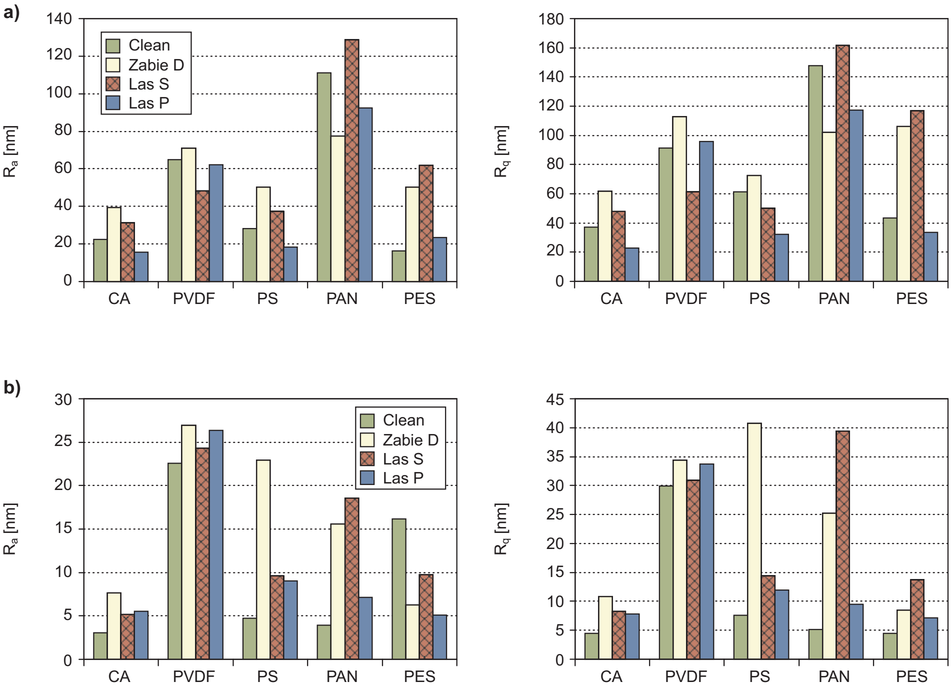

Fig. 2. R_a and R_q of new and used membranes: a) sector 50 × 50 μm, b) sector 5 × 5 μm

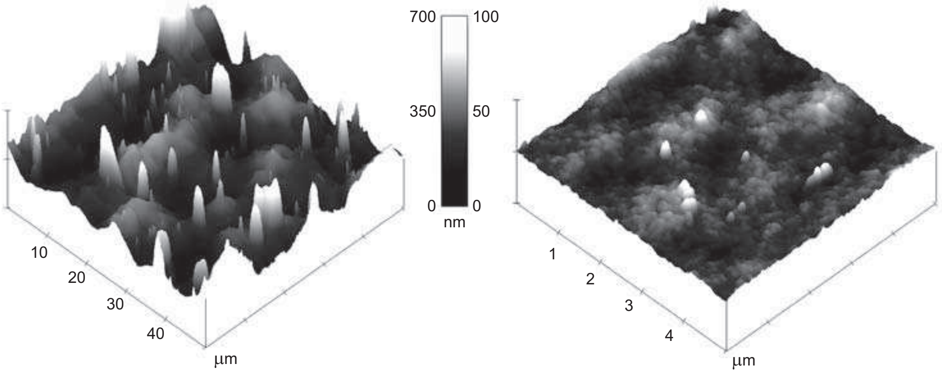

Fig. 3. The comparison of surface for different sectors of PAN membrane

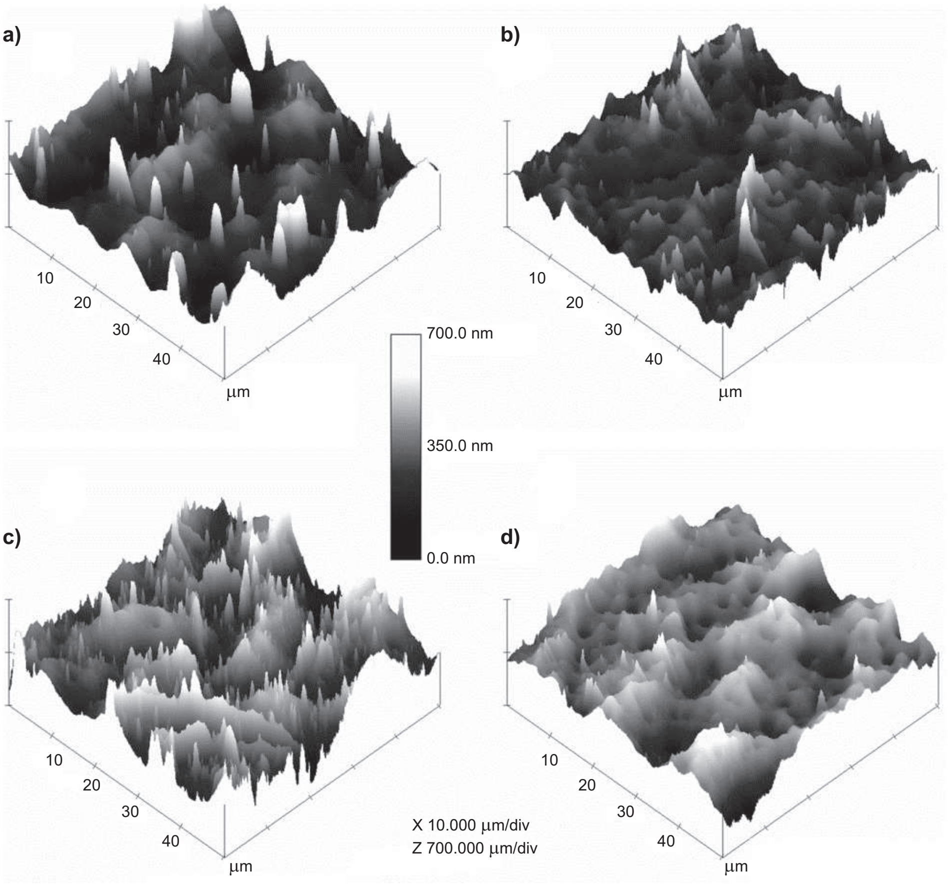

Fig. 4. The comparison of PAN membrane surface: a) clean membrane, b) after filtration of Zabie D water, c) after filtration of Las S water, d) after filtration of Las P water

membrane sectors of 50 × 50 μm were used for analysis. The smallest roughness was observed for PES membrane. However, irregularities sporadically appearing on its surface could have been seen.

The increase of both, mean roughness and mean square roughness was observed after filtration of Zabie D water for all membranes except for PAN membranes. Zabie D water characterized with high content of mineral substances (Table 1), which could partially crystallize on membranes surface increasing the roughness. In case of PAN membranes those compounds could penetrate its irregular surface and caused its smoothing. Moreover, non-aromatic organic compounds present in Zabie D water could also adsorb on membrane surface. The changes of PAN membrane surface are shown in Fig. 4.

The smoothing of membranes surface and the decrease of mean square porosity were observed after filtration of Las P water except for PES membrane. Non-dissolved organic compounds affected the irregularity of more rough membranes, on the other

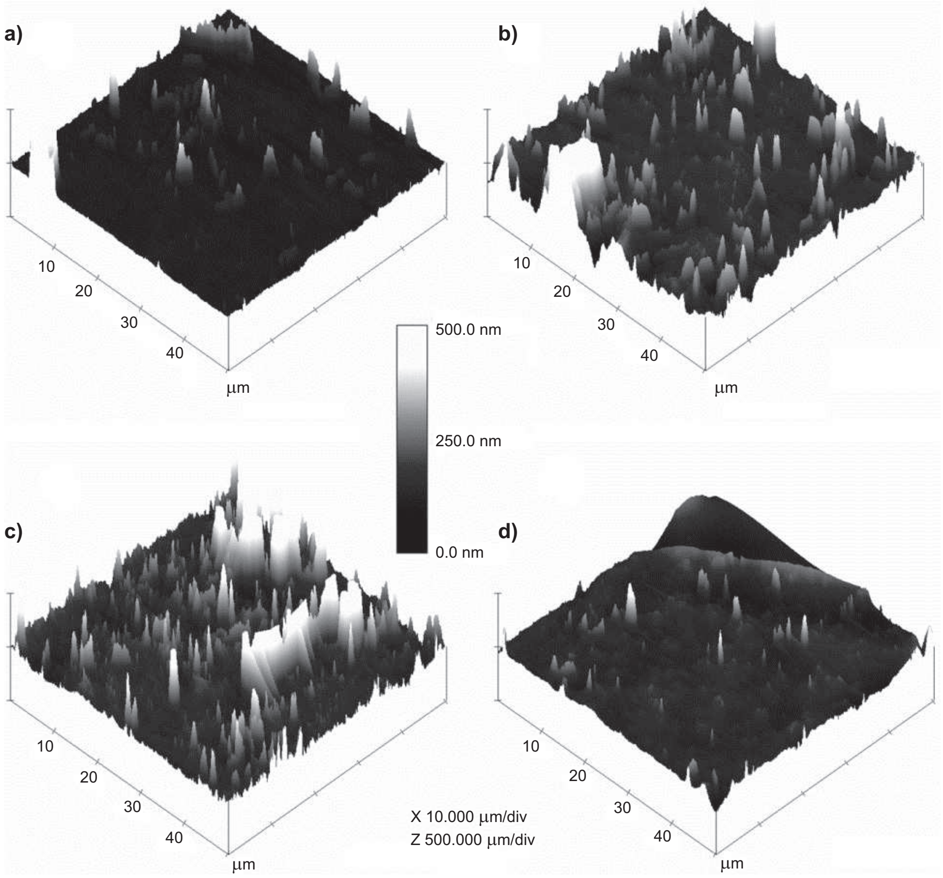

Fig. 5. The comparison of PES membrane surface: a) clean membrane, b) after filtration of Zabie D water, c) after filtration of Las S water, d) after filtration of Las P water

hand caused the roughness increase of the smoother membrane (PES), thus its surface became more uniform (lower R_q). The changes of PES membrane surface are shown in Fig. 5.

The filtration of Las S water resulted in the increase of R_a and R_q of CA, PAN and PES membranes. The changes of CA membrane surface are shown in Fig. 6. The increase of R_a was also observed for PS membranes, however its surface became more uniform than before the filtration (lower R_q). The surface of PVDF membrane became smoother and more uniform. The differences between changes in membranes surface can result from water heterogeneity.

Fouling affected also membranes wettability. The observed changes in contact angle values are shown in Fig. 7. The increase of hydrophobic character of membranes for which the initial contact angle was below 50° was stated regardless the water type. Opposite phenomenon was observed for membranes of contact angle above 63°.

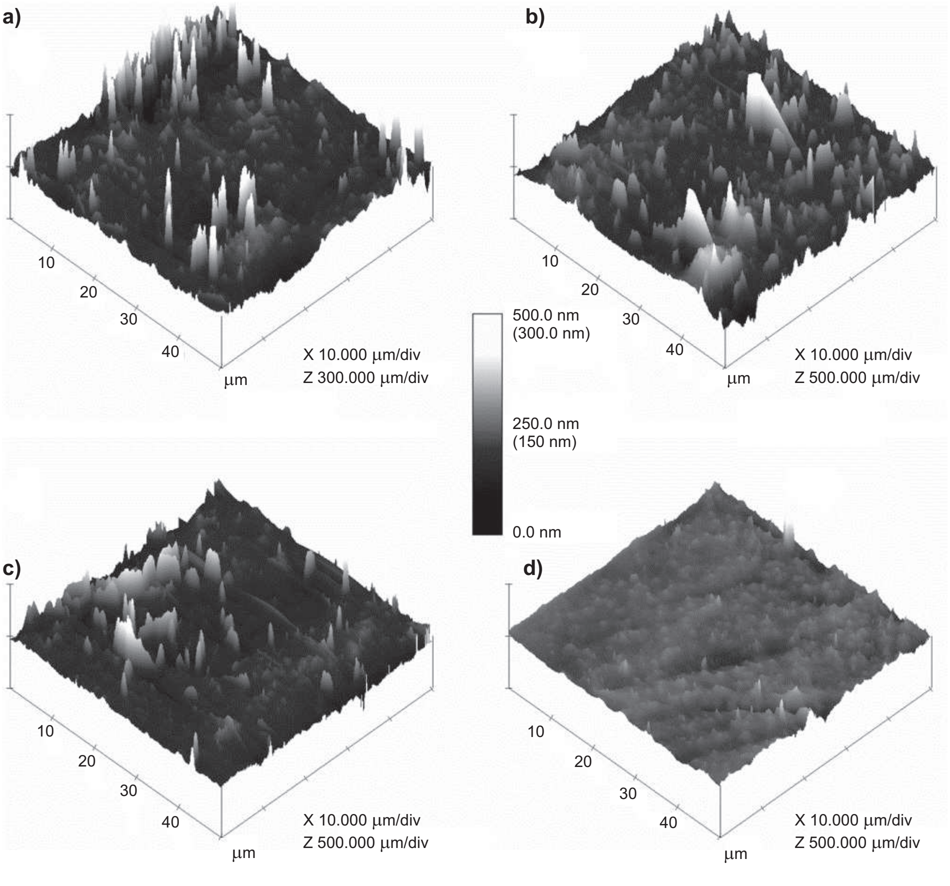

Fig. 6. The comparison of CA membrane surface: a) clean membrane, b) after filtration of Zabie D water, c) after filtration of Las S water, d) after filtration of Las P water

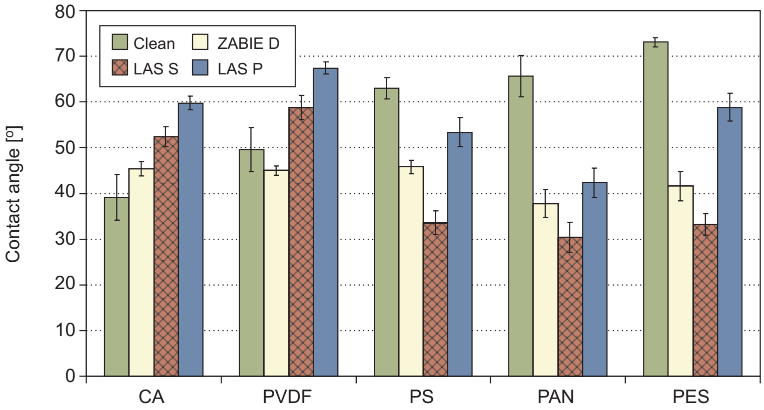

Fig. 7. Changes of contact angle of the new and used membranes

Conclusions

The mechanism of spherical exclusion is significant during TOC removal, while for DOC removal foulant-foulant interaction and adsorption on the membrane are of the greatest importance.

Hydrophobic membranes (*eg* PES) tends to foul more than hydrophilic ones (*eg* CA). Such a tendency is not observed for waters in which the difference between TOC and DOC content is high. Such waters caused smaller fouling as non-dissolved particles deposit on membrane surface forming a protective layer for membrane pores. The highest fouling is caused by water for which SUVA value indicates the presence of both aromatic and aliphatic substances, what confirmed the significant impact of foulant-foulant interactions on fouling.

Substances stopped on a membrane significantly affect its properties *ie* wettability and roughness. Depending on water and initial membrane properties the roughness can increase or decrease. Membranes of small roughness reveal the greatest ability to foul during filtration of low and medium SUVA value waters. In case of Las P water the difference between TOC and DOC content seems to be the more important property than the type of organic substance. This water causes the greatest fouling of membrane of high mean roughness and medium mean square roughness.

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WPŁYW NATURALNYCH SUBSTANCJI ORGANICZNYCH NA FOULING ORAZ WŁAŚCIWOŚCI MEMBRAN – ANALIZA AFM

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Abstrakt: Niskociśnieniowe techniki membranowe, ultrafiltracja i mikrofiltracja, stosowane są do oczyszczania i uzdatniania wody. Głównym problem eksploatacyjnym jest zmniejszanie wydajności membrany w trakcie procesu, związane z blokowaniem porów przez substancje organiczne i nieorganiczne (tzw. fouling). Analiza mikroskopem sił atomowych (AFM) umożliwia ilościowe określenie chropowatości powierzchni membrany, co pozwala scharakteryzować powierzchnię membran przed i po foulingu. W artykule przedstawiono wyniki filtracji trzech wód powierzchniowych różniących się głównie specyficzną absorbancją w nadfiolecie ($SUVA_{254}$).

Słowa kluczowe: fouling**,** ultrafiltracja, naturalne substancje organiczne, mikroskop sił atomowych