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INFLUENCE OF THE TYPE OF MEMBRANE-FORMING POLYMER ON THE MEMBRANE FOULING

The effect of the membrane-forming polymer (PES, PAN and PVDF) on the fouling phenomenon has been investigated occurring on the surface of the ultrafiltration membranes used for the polishing of industrial wastewater pre-treated by biological methods. The activated sludge method in SBR reactor was used to treat dairy wastewater mixed with 10 vol. % of landfill leachate. The susceptibility assessment of polymeric membranes to the fouling phenomenon was carried out using the plate-and-frame membrane module SEPA CF-NP produced by GE Osmonics. The following properties of the membrane were determined: the dependence of the volumetric flux of the permeate on the process duration, the transport properties of deionized water, the relative permeability of the membrane for the flux of deionized water and for the wastewater flux, as well as the contact angle of the membranes. It can be concluded that the kind of membrane-forming polymer had an influence on the fouling phenomenon occurring on the ultrafiltration membranes used for the polishing of industrial wastewater treated in a SBR reactor.

1. INTRODUCTION

In recent years, pressure membrane techniques have become very popular because they allowed the reduction of the number of unit processes in sequential technological systems used hitherto for wastewater treatment. They were considered to be an attractive alternative to conventional processes due to their inherent advantages such as selective separation, purification without the need for additional chemicals, the ability to easily scale-up and a small volume [1]. However, as it is well known, these processes are accompanied by the inherent phenomena contributing to the reduction of the membrane

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performance due to the increase of the resistance of the filtration system, especially in the case of porous polymer membranes, this is, microfiltration and ultrafiltration membranes. They include the fouling phenomenon. There are many studies reported in literature that aimed at reducing the fouling process by selecting suitable membranes and their properties [2–8].

Membrane clogging and selectivity of membrane processes depend on properties of feed water (i.e. concentration of individual pollutants, feed temperature and pH) and those of the polymer membrane (hydrophilic/hydrophobic material, electrical surface charge, molecular weight cot off – MWCO), operational parameters (i.e. filtration mode, transmembrane pressure, linear flow velocity) [1–3]. Important factor influencing fouling is the type of membrane polymer. Wang et al. [7] investigated polyacrylonitrile (PAN) and polyvinylidene fluoride (PVDF) membranes. They have similar porosity however the PAN membrane had a slightly lower average pore size than the PVDF membrane. The PVDF membrane was more hydrophobic than the PAN one. Results showed that reversible fouling was dominant for both types of membranes. More susceptible to irreversible fouling was the PVDF membrane, due to higher pore size and more hydrophobic character. Furthermore, membranes demonstrated different surface interactions with individual organic compounds; the PAN membrane was less susceptible to proteins deposition, while the surface of the PVDF membrane was coated with carbohydrates at a lesser extent.

Choi and Ng [9] compared three microfiltration membranes made of polytetrafluoroethylene (PTFE), track-etched polycarbonate and polyethylene terephthalate (PETE) with the pore size of 0.1 μm. They found that increase in the filtration resistances can be caused by membrane roughness and applied pressure (the higher pressure the higher flux decline upon time was). Pollutant deposition on the membrane surface was not dependent on its hydrophobicity. Similar studies were carried out by Zhang et al. [10]. They studied effect of extracellular polymeric substances, released by activated sludge microoorganisms, on ultrafiltration performance. Three types of membranes (polyethersulfone – PES, PAN, PVDF) were examined in this study. It was found that the PAN membrane has the lowest susceptibility to adsorption of micropollutants while the PES one – the highest.

The aim of this study was to examine how the type of membrane polymer (polyethersulfone – PES, PVDF, and PAN) affects fouling intensity and behavior of ultrafiltration membranes. In co-treatment of wastewater, capillary ultrafiltration module installed in a membrane bioreactor was exposed to deposition of suspended particles, colloids and dissolved high molecular weight compounds on the surface or in pores of capillaries that caused the decrease in permeability of capillary membranes. The most favorable polymer could be used as membrane casting material for capillary membranes working in submerged membrane bioreactor for co-treatment leachate with dairy wastewater.

2. MATERIALS AND METHODS

The feed used in the presented study was biologically treated (in a sequential batch reactor, SBR) mixture of dairy wastewater and 10 vol. % of municipal landfill leachate. Table 1 presents the physicochemical characteristics of the treated wastewater subject to pressure membrane filtration.

Table 1

Physicochemical characteristics
of the treated wastewater subjected
to pressure membrane filtration

Parameter	Value
COD, mg/dm^3	120
BOD_5, mg/dm^3	9
N_{tot}, mg/dm^3	6
NH_4^+-N, mg/dm^3	1.9
NO_3^--N, mg/dm^3	1.5
PO_4^{3-}-P, mg/dm^3	2.9
Total suspended solids, mg/dm^3	38
pH	8.3
Conductivity, mS/cm	2.3

Apparatus. The determination of the susceptibility of polymer membranes to fouling was carried out in a plate-and-frame membrane module SEPA CF-NP (Osmonics, USA) The experimental installation was operated in a batch mode as a cross-flow system. The permeate was continuously collected from the setup, thus feed was progressively concentrated. The filtration surface area of the membrane was 155 cm^2, and the effective filtration surface area was 144 cm^2. The experimental setup is shown in Fig. 1.

Fig. 1. The experimental setup for ultrafiltration polishing of biologically treated wastewater

Ultrafiltration of biologically treated wastewater was carried out using three commercially available ultrafiltration membranes: PES, PVDF, PAN, with the cut-off values of 50 000 Da. Their transport properties were determined using deionized water in the range of transmembrane pressure 0.1–0.5 MPa. Then the membranes before the filtration of wastewater were subject to conditioning in order to stabilize the flux of deionized water. The processes of pressure filtration of deionized water and wastewater were carried out under the transmembrane pressure of 0.2 MPa. The linear flow velocity of filtered wastewater above the surface of the membrane was 1 m/s, and the temperature was equal to 17 °C. After each filtration, membranes were washed mechanically with deionized water. The characteristics of the membranes provided by the manufacturers are presented in Table 2.

Table 2

Characteristics of the commercially-available polymer ultrafiltration membranes [11 , 12]

Symbol	Type	MWCO [Da]	ΔP_{max} [MPa]	pH	Membrane thickness [mm]	Maximum temperature [°C]	Contact angle [deg]
MQ	PES	50 000	–	1–10	0.20	90	71
BN	PVDF	50 000	–	1–10	0.22	95	59
MW	PAN	50 000	0.7	2–9	–	80	4

The time dependences of volumetric flux before and after pressure filtration were also studied. The results allowed determining the following parameters:

Volumetric flux of the permeate

$$J_v = \frac{V_V}{s + t} \tag{1}$$

where: V_v – volume of permeate, m^3, s – surface area of the membrane, m^2, t – time, s.

The relative permeability of the membrane for the flux of deionized water:

$$\alpha_w = \frac{J_{wp}}{J_w} \times 100\% \tag{2}$$

where: J_{wp} – volumetric flux of deionized water after wastewater filtration, m^3/(m^2·s), J_w – volumetric flux of deionized water prior to wastewater filtration, m^3/(m^2·s).

The relative permeability of the membrane for wastewater flux:

$$\alpha_v = \frac{J_v}{J_w} \times 100\% \tag{3}$$

A percentage of fouling (R_f) which is the sum of reversible (R_{rf}) and irreversible fouling (R_{if})

$$R_f = R_{rf} + R_{if} \tag{4}$$

$$R_{rf} = \frac{J_{wp} - J_v}{J_w} \times 100\% \tag{5}$$

$$R_{if} = \frac{J_w - J_{wp}}{J_w} \times 100\% \tag{6}$$

$$R_f = \left(1 - \frac{J_v}{J_w}\right) \times 100\% \tag{7}$$

The total hydraulic resistance (R_c)consists of the membrane resistance (R_m) and the resistance caused by reversible (R_{rf}) and irreversible (R_{if}) fouling. The resistance connected with the polarization layer was classed as the resistance activated by reversible fouling. The permeate flux can be defined based on the Darcy equation:

$$J_v = \frac{\Delta P}{\eta R_c} \tag{8}$$

where: ΔP – transmembrane pressure, Pa, R_c – total resistance, m^{-1}, η – dynamic viscosity of the medium, Pa·s.

Based on the filtration resistance, we have:

$$J_v = \frac{\Delta P}{\eta\left(R_m + R_{rf} + R_{if}\right)} \tag{9}$$

The value of clean membrane resistance (R_m) can be determined from Eq. (8). In this case, the total resistance is equal to the membrane resistance, thus the following equation can be used:

$$R_m = \frac{\Delta P}{\eta + \vartheta_w} \tag{10}$$

The irreversible-fouling resistance can be determined from Eq, (10), where the volumetric flux of deionized water after filtration of wastewater can be deducted from the resistance of clean membrane [4, 8]:

$$R_{if} = \frac{\Delta P}{\eta J_{wp}} - R_m \tag{11}$$

The reversible-fouling resistance can be determined from:

$$R_{rf} = \frac{\Delta P}{\eta J_v} - R_m - R_{if} \tag{12}$$

The zeta potential was determined from the measurements of the streaming potential. They were made with a SurPASS electrokinetic analyzer (Anton Paar, Austria). The Helmholtz–Smoluchowski equation was used:

$$\zeta = \frac{dI}{dp} \frac{\eta}{\varepsilon\varepsilon_0} \frac{L}{A} \tag{13}$$

where: ζ – electrokinetic potential, mV, dI/dp – slope of the streaming potential versus pressure, η – viscosity of the solution, kg/(m·s), ε – electric permittivity, F/m, ε_0 – electric permittivity of vacuum, F/m, L – length of the measurement tunnel, m, A – the cross-section area of the measurement tunnel, m^2.

0.01 M KNO_3 was used as an electrolyte. pH during titration was adjusted by addition HNO_3 or KOH (0.1 M). The samples (20×10 mm^2) were adhered by double-sided tape to the measurement channel where the electrolyte with an appropriate pH was provided. Then the dependence of the current in the flow cell and applied pressure (dI/dp) was determined, allowing one to compute the zeta potential according to the Helmholtz –Smoluchowski equation.

The value of the contact angle is a measure of hydrophilic/hydrophobic properties. It was measured wth using a goniometer.

The evaluation of the efficiency of the treatment process was based on the change of wastewater quality indicators before and after UF. Tollowing parameters were controlled: COD, BOD_5, NO_3^--N, NH_4^+-N, PO_4^{3-}-N. Nitrate and ammonium nitrogen as well as COD and phosphate phosphorus were measured by the method given by Merck company. The BOD_5 was determined by the respirometric method using an OXI Top WTW analyzing set.

3. RESULTS AND DISCUSSION

3.1. ULTRAFILTRATION OF LEACHATE CO-TREATED WITH THE DAIRY WASTEWATER

The efficiency of the membrane process was assessed based on the membrane productivity and on the degree of removal of contaminants from the wastewater. No significant differences were observed in terms of permeate quality. A slight reduction (5–10%) of organic compounds was observed for all tested membranes. The average values of COD and BOD_5 were 105 mg/dm^3 and 8 mg/dm^3, respectively. Next, the change of concentration of nutrition compounds i.e. ammonium nitrogen, nitrate nitrogen and phosphate phosphorus were analyzed. The concentrations of nutrients in treated wastewaters also slightly varied during the process. However, the result of the (UF) wastewater treatment was total removal of solids. Obtained results of the study are presented in Table 3.

Table 3

Physicochemical characteristics of the treated wastewater for the tested membranes (PAN, PVDF, PES)

Parameter	SBR effluent	UF effluent
COD, mg/dm^3	120.0	105.0
BOD_5, mg/dm^3	9.0	8.0
NH_4^+-N, mg/dm^3	1.9	1.9
PO_4^{3-}-P, mg/dm^3	2.9	2.2
NO_3^--N, mg/dm^3	1.5	1.4

3.2. TRANSPORT PROPERTIES OF THE MEMBRANES

The PAN membrane was characterized by the lowest volumetric flux of deionized water in the entire range of the studied pressure values. The greatest volumetric flux of deionized water was observed for PVDF membrane. For the transmembrane pressure equal to 0.2 MPa, the volumetric water fluxes (J_w) for the PVDF and PES membranes were higher by 47% and 33% as compared to the PAN membrane, respectively. Figure 2 shows the dependences of the fluxes of deionized water on the transmembrane pressure of each membrane. The differences in capability of the membranes were likely to define by membrane-forming polymers, their structure and thickness [20].

3.3. THE EFFECT OF FOULING ON MEMBRANE SURFACE PROPERTIES

The fouling is a phenomenon associated with pressure membrane techniques, and it has a measurable impact on decreasing the capability of the membrane. The impurities adsorbed on the membrane surface can often change hydrophilic/hydrophobic properties, contact angle, acidity and basicity.

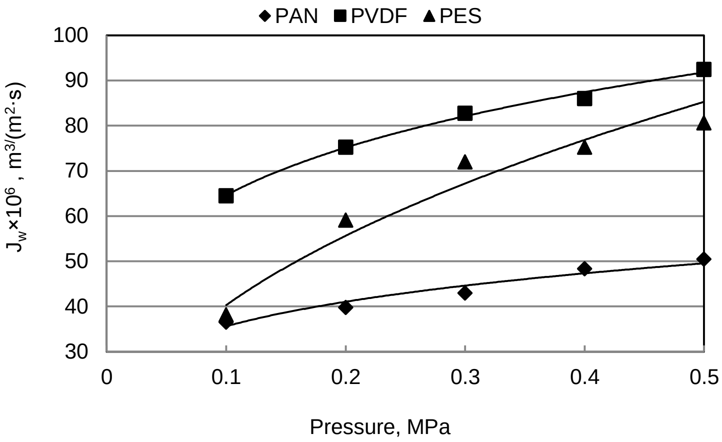

Fig. 2. Dependence of the volumetric flux of deionized water on the transmembrane pressure of the studied membranes

Figure 3 shows contact angles (θ) of both clean and post-pressure filtration membranes. It was found that the PAN membrane (θ = 4°) was characterized by the highest hydrophilicity. On the other hand, the PES membrane (θ = 71°) was the most hydrophobic.

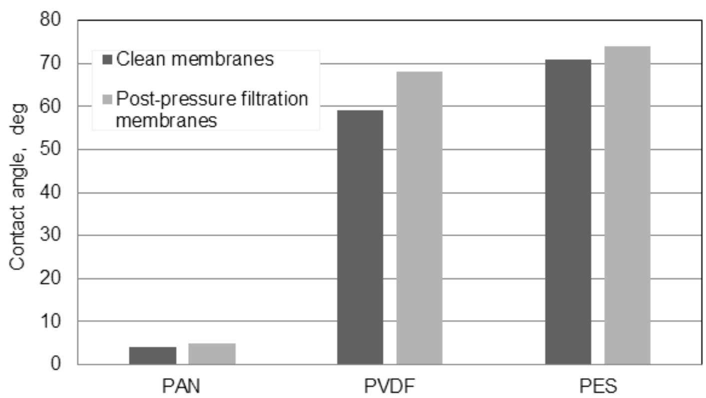

Fig. 3. Contact angles of clean and post-pressure filtration membranes

The membrane has highly-hydrophilic properties if the contact angle using deionized water is lower than 45°, intermediate properties for the angle of 45–90°, whereas highly hydrophobic if the contact angle exceeds 90° [3]. It was found that the PAN membrane was typically hydrophilic (θ = 4°) but PVDF and PES membranes had intermediate hydrophilic/hydrophobic properties, whereas a higher contact angle was observed for PES membranes (θ = 71°) in comparison to PVDF (θ = 59°). The differences can result not only from the polymer properties (most of commercial membranes as PVDF, PES, PAN are hydrophobic) but also from the membrane preparation methods including surface modification. The main aim of the modification is improving the transport properties and gaining high resistance to fouling [16–19]. The contact angle of the membranes increased after wastewater filtration to 74° and to 68° for the PES and for the PVDF membrane, respectively. It was caused by hydrophobic substances present in the wastewater which likely affect sorption on the membrane surface. For PAN membranes, any important change of their hydrophilic properties was observed. Highly-hydrophilic properties of membranes are connected with their surface charge whose measure can be the zeta potential [13–15]. Its value and sign are characterized by the presence of dissociated functional groups of membrane-forming polymer and adsorbed organic and inorganic pollutants. The reactive groups on the surface intensify the impact of water molecules. As a result, the surface is more hydrophilic.

Before the contact with wastewater, all membranes were characterized by low value of the isoelectric point (IEP) corresponding to pH with the zeta potential equal to zero. PES and PVDF membranes had the isoelectric point at pH = 3.0, PAN membrane at pH = 3.5. Upon increasing pH, the zeta potential varied from –58 mV (PAN) to –87 mV (PVDF). The result suggests that all membrane surfaces have strong acidic properties. The properties of PES membranes might originate from the sulfonic group occurring in the polymer structure. However, in the case of the other membranes, the properties might be a result of surface modification using hydrophilic groups to reduce susceptibility to fouling. As can be seen in Figs. 4–6, under conditions of ultrafiltration (pH 8.5) the surfaces of membranes have a high negative charges which enable adsorption of cationic pollutant.

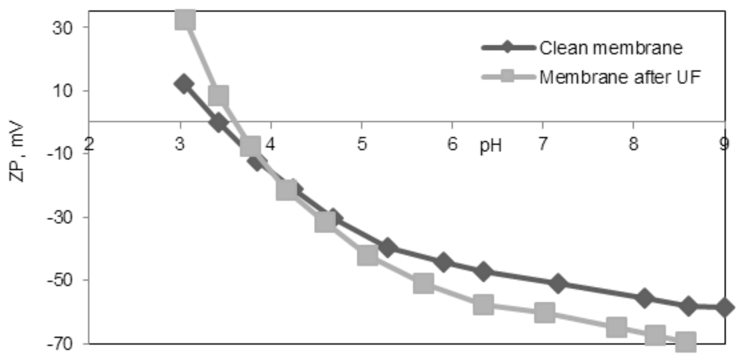

Fig. 4. Dependence of the zeta potential (ZP) of PAN membrane on pH, for a clean membranes and membrane after filtration of wastewater

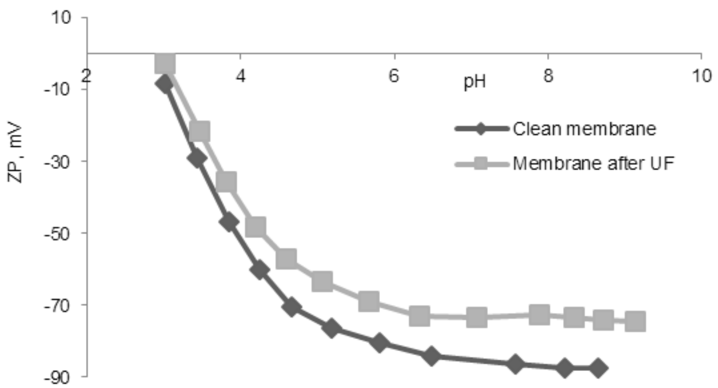

Fig. 5. Dependence of the zeta potential (ZP) of PVDF membrane on pH for a clean membrane and membrane after filtration of wastewater

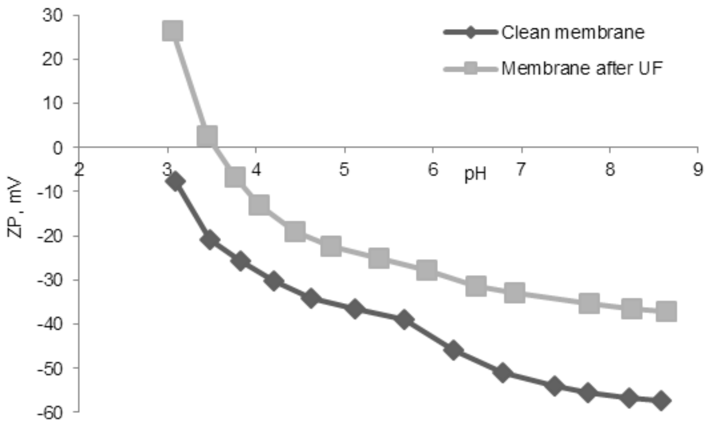

Fig. 6. Dependence of the zeta potential (ZP) of PES membrane on pH for a clean membrane and membrane after filtration of wastewater

After filtration, the specified plots of the zeta potential vs. pH moved towards the positive potential for more hydrophobic membranes (PVDF and PES). This reaction clearly indicated that the adsorption of compounds included the nature of cationic adsorption, which practically counteracted negative surface charge, observed in the whole range of pH studied. The greatest shift of the curve zeta potential vs. pH was observed for PES membranes in accordance with the results of analysis of irreversible fouling. On the other hand, the plot of the zeta potential vs. pH for PAN membrane shifted not only because of the contact with wastewater but also its character changed. When pH was lower than the isoelectric point (pH when the zeta potenial is 0), the zeta potential reached a higher value as was observed for a membrane with hydrophobic surface.

Moreover, the higher pH, the lower the reduction potential was. It means that after contact with wastewater, the effect of acid-base properties (responsible for electrical charge on the surface) have changed.

3.4. THE EFFECT OF THE FOULING ON THE VOLUMETRIC PERMEATE FLUX

In the course of the wastewater polishing process, the PAN membrane was characterized by the lowest volumetric permeate flux. Its initial value was $34.72 \cdot 10^{-6}$ $m^3/(m^2 \cdot s)$, and after 140 min it decreased by $13.97 \cdot 10^{-6}$ $m^3/m^2 \cdot s$ and it was $20.75 \cdot 10^{-6}$ $m^3/m^2 \cdot s$. In contrast, the highest efficiency of the process was found for the PVDF membrane, and after 140 min of filtration the volumetric flux was $26.00 \cdot 10^{-6}$ $m^3/m^2 \cdot s$ and was higher than for the PES membrane by $4.06 \cdot 10^{-6}$ $m^3/m^2 \cdot s$ and for the PAN membrane by $5.87 \cdot 10^{-6}$ $m^3/m^2 \cdot s$ [20].

To assess a degree of fouling and its nature (reversible, irreversible), deionized water was filtered through the membranes after the wastewater polishing process. The determined volumetric flux allowed the calculation of the relative permeability of the membrane for wastewater and deionized water. The PVDF membrane was characterized by lower flux of deionized water after filtration of wastewater (by 39.3% lower) as compared to the flux for the clean membrane. For PES and PAN membranes, the flux of deionized water was by 62.5% and 47.8% lower, respectively. Thus, the PVDF membrane was characterized by the highest relative permeability for the flux of deionized water (equal to 60.8%) as compared to the other membranes (52.1% for PAN and 37.7% for PES).

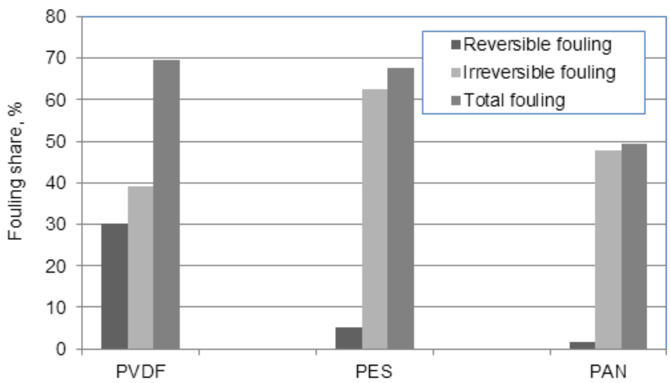

Fig. 7. Percentage share between reversible and irreversible fouling

Based on Equations (5)–(7), the percentage of reversible and irreversible fouling was determined (Fig. 7). In the first case, pollutants on the surface can be removed and it allows reverting to its initial productivity. If deposition, accumulation of contaminants occurs within pores, the fouling is irreversible. Thus, mechanical and chemical purification did not re-form the initial transport properties.

Based on the obtained results it can be observed that PVDF membranes had the greatest fouling. It was equal to 69.5%. Despite this, they were characterized by the highest contribution in reversible fouling (30.5%) and the lowest in irreversible one (39.25%). Thus the membrane reached the highest relative permeability for the flux of deionized water (α_w) among the other membranes and was characterized by the greatest initial transport properties on deionized water. For the other membranes irreversible fouling was the dominant phenomenon. It means that the coating process was permanent and blocking occurred within the pores. The hydrophobic surface significantly facilitated fouling (PVDF and PES). For PAN membranes, the adsorption of the pollutants was less intense due to the hydrophilic properties of the membrane-forming polymer. The main reason for the fouling was the effect of a molecular sieve.

Considering both the hydrophilic/hydrophobic properties and the lowest hydraulic permeability, it can be suggested that the structure of the PAN membrane must have been compact in relation to the other membranes. The pollutants transported by the membrane caused irreversible pore blocking, reducing the productivity of the process. That fact can be confirmed by the membrane resistance (R_m), which was equal to 4.52×10^{12} m^{-1}. The value was almost twice as high as it was for PVDF and PES membranes (2.16×10^{12} m^{-1} and 2.65×10^{12} m^{-1}, respectively). The presented data correlates well with the conclusions. Each of tested membranes was characterized by similar resistance caused by irreversible fouling. However, considering reversible fouling, the lowest resistance was determined for PAN membrane which was equal to 2.71×10^{11} m^{-1} (Table 3).

Table 3

Hydraulic resistances of filtration
for the membranes [m^{-1}]

Membrane	R_m	R_{if}	R_{rf}
PAN	4.52×10^{12}	4.14×10^{12}	2.71×10^{11}
PVDF	2.16×10^{12}	4.10×10^{12}	3.56×10^{12}
PES	2.65×10^{12}	4.42×10^{12}	1.14×10^{12}

4. CONCLUSIONS

- The kind of membrane-forming polymer had an influence on the fouling phenomenon in the ultrafiltration membranes used for the polishing of industrial wastewater treated in SBR reactor. More hydrophobic membranes were characterized by a similar value of total fouling varying from 67% to 69%, while the fouling of hydrophilic membrane was by 20% lower.

- The PAN membrane was characterized by the lowest volumetric flux of deionized water whereas the PVDF membrane by the highest one. The volumetric flow of the permeate during wastewater filtration constantly decreased, which was the result of the fouling phenomenon occurring on the surface.
- The contact angle of PES and PVDF membranes increased after wastewater filtration, so their respective values were higher by 3° and 9°. It was caused by sorption of hydrophobic substances on the surface.
- The zeta potential after wastewater filtration decreased for PAN membrane, whereas it increased for PVDF and PES membranes.
- Each of tested membranes was characterized by similar resistance, caused by irreversible fouling. On the other hand, based on reversible fouling, PAN was characterized by the lowest resistance. It was equal to 2.71×10^{11} m^{-1}.

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REFERENCES

[1] GUOA W., NGOA H., LI J., *A mini-review on membrane fouling*, Biores. Technol., 2012, 122, 27.
[2] AMY G., *Fundamental understanding of organic matter fouling of membranes*, Desalination, 2008, 231, 44.
[3] BODZEK M., PŁATKOWSKA A., *Fouling of semi-permeable membranes during the purification of water by ultrafiltration and microfiltration. A review*, Inż. Ochr. Środ., 2009, 12 (1), 1 (in Polish).
[4] DREWS A., *Membrane fouling in membrane bioreactors. Characterization, contradictions, cause and cures*, J. Membrane Sci., 2010, 363, 1.
[5] DUAN L., JIANG W., SONG Y., XIA S., HERMANOWICZ S., *The characteristics of extracellular polymeric substances and soluble microbial products in moving bed biofilm reactor-membrane bioreactor*, Bioresource Technol., 2013, 148, 436.
[6] KATSOUFIDOU K., YIANTSIOS S.G., KARABELAS A.J., *A study of ultrafiltration membrane fouling by humic acid and flux recovery by backwasching. Experiments and modeling*, J. Membrane Sci., 2005, 266, 40.
[7] WANG P., WANG Z., WU Z., MAI S., *Fouling behaviours of two membranes in a submerged membrane bioreactor for municipal wastewater treatment*, J. Membrane Sci., 2011, 382, 60.
[8] ZHANG J., ZHOU J., LIU Y., FANE A., *A comparison of membrane fouling under constant and variable organic loadings in submerge membrane bioreactors*, Water Res., 2010, 44, 5407.
[9] CHOI J.H., NG H.Y., *Effect of membrane type and material on performance of a submerged membrane bioreactor*, Chemosphere, 2008, 71, 853.
[10] ZHANG G.J., JIA S.L., GAO X., LIU Z.Z., *Adsorptive fouling of extracellular polymeric substances with polymeric ultrafiltration membranes*, J. Membrane Sci., 2008, 309, 28.
[11] *Specification of flat membranes BN i MQ Synder Filtration*, www.synderfiltration.com
[12] Technical Bulletin GE Power and Water, http://www.gewater.com/

[13] LAWRENCE N., PERERA J., IYER M., HICKEY M., STEVENS G., *The use of streaming potential measurements to study the fouling and cleaning of ultrafiltration membranes*, Sep. Purif. Technol., 2006, 48, 106.
[14] SALGIN S., SALGIN U., SOYER N., *Streaming potential measurements of polyethersulfone ultrafiltration membranes to determine salt effects on membrane zeta potential*, Inter. J. Electrochem. Sc., 2013, 8, 7073.
[15] NYSTROM M., LINDSTROM M., MATTHIASSON E., *Streaming potential as a tool in the characterization of ultrafiltration membranes,* Colloids Surf. 1989, 36, 297.
[16] WANG D., LI K., TEO W.K., *Preparation and characterization of polyvinylidene fluoride (PVDF) hollow fiber membranes,* J. Membrane Sci., 1999, 163, 211.
[17] XU A., YANG A., YOUNG S., DEMONTIGNY D., TONTIWACHWUTHIKUL P., *Effect of internal coagulant on effectiveness of polyvinylidene fluoride membrane for carbon dioxide separation and absorption*, J. Membrane Sci., 2008, 311, 153.
[18] YEOW M.L., LIU Y., LI K., *Preparation of porous PVDF hollow fibre membrane via a phase inversion method using lithium perchlorate ($LiClO_4$) as an additive*, J. Membrane Sci., 2005, 258, 16.
[19] ZHANG M., ZHANG A.Q., ZHU B.K., DU C.H., XU Y.Y., *Polymorphism in porous (polywvinylidene fluoride) membranes formed via immersion precipitation process*, J. Membrane Sci., 2008, 319, 169.
[20] ŚWIERCZYŃSKA A., BOHDZIEWICZ J., *The effect of the type of membrane-forming polymer on the occurrence of the fouling phenomenon*. *Membranes and Membrane Processes in Environmental Protection*, Monographs of the Environmental Engineering Committee Polish Academy of Sciences, 2014, 119, 209.