

Synthesis of polymer membranes of different porosity and their application for phenol removal from liquid phase

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(Received 19 April 2013 • accepted 27 October 2013)

Abstract—Preparation of polymeric membranes based on polyethersulfone (PES) modified by adding different amounts of a pore-forming agent (PVP) is presented, and potential application of the membranes obtained for removal of phenol from the liquid phase is examined. The addition of various amounts of PVP has been shown to bring about changes in the content of the surface oxygen groups, but has no significant effect on the chemical character of the groups and acidic groups dominate. Filtration by phenol solution leads to significant changes in the total content of surface oxides; however, the acidic groups remain dominant. Membranes characterized by higher porosity exhibited more stable and higher rejection ratio for phenol removal. Although all the membranes were characterized by similar rejection ratios for phenol removal, the cake resistance (R_c) and pore resistance (R_p) values were found to depend significantly on the structure and porosity of the membrane applied for filtration.

Keywords: Polyethersulfone Membranes, Phase Inversion, Porosity, Surface Chemistry, Phenol Removal

INTRODUCTION

Recently, rapid development of processes involving the use of membranes has been observed. Progress in membrane technology has permitted their effective employment in the tasks related to environmental protection, which is both economically and ecologically beneficial. The use of membranes permits separation of pollutants in the size of particles and separation of molecules or ions [1,2].

The choice of membrane depends on the type of process in which it is to be employed. The components separated on membranes do not undergo thermal, chemical or biological transformations, so they can be reused [3]. Interesting organic membranes are the polymer ones made of such materials as cellulose acetate, polysulfone or polyamide [1,4]. Although these membranes have found widespread use, they show a serious drawback, which is a limited chemical stability in aggressive systems such as water solutions of low or high pH and solutions of organic solvents [3,4].

From among polymer membranes of much interest have recently become those made of polyethersulfone (PES) because of their specific properties [4-6]. They show high thermal resistance, high chemical resistance to acids, petrol, oils and oxidizing substances such as fluorine and hydrogen peroxide, are relatively insensitive to UV radiation and are physiologically neutral [4,6-8].

Most of the polymeric membranes used for micro- and ultrafiltration of liquids are prepared by phase inversion via immersion precipitation [2,3]. The increase in the use of membrane technology is driven by spectacular advances in membrane development, wider acceptance of the technology in preference to conventional separation processes, increased environmental awareness and, most importantly, strict environmental regulations and legislation. Various

membrane processes are currently applied in the chemical (including petrochemicals), pharmaceutical, food and beverage industries [2,3,5]. Particularly strong development and growth of membrane technology can be observed in the purification of wastewater and the production of drinking water [5,9].

Excessive presence of phenol and its derivatives in natural water sources is a serious threat to human health and general water quality [10,11]. These compounds are introduced into water with industrial waste water and garbage. Most of them are in the forms of mono and dihydric phenols. However, monohydric phenols are particularly hazardous because of their volatility with steam [11-13]. Phenolic compounds are harmful to organisms even at low concentrations due to their toxicity and carcinogenic properties. In addition, they cause unpleasant smell. Therefore, constant monitoring and control of the content of phenols (and other contaminants) in surface water as well as groundwater is fully recommended [14].

Membrane processes have also been considered to remove some organic pollutants from wastewater [15,16]. The use of membranes to remove phenolic compounds has been commonly investigated. The types of membranes that have been used to remove phenol from wastewater include liquid membranes [17,18], anion exchange membranes [19], nanofiltration/reverse osmosis membranes [20,21] and pervaporation membranes [22,23].

The main aim of this study is to obtain polymer membranes of different porosity that could be applied for removal of phenol from the liquid phase. Membranes were obtained by the method of phase inversion and modified by incorporation of different amounts of porous factor (PVP) into their structures.

EXPERIMENTAL

1. Materials

Polyethersulfone (Ultrason E 6020 PES) was purchased from BASF and used as a membrane material. 1-Methyl 2-pyrrolidone

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(NMP) was purchased from POCh and used without further purification. Polyvinylpyrrolidone (PVP, 10,000 g/mol) as a pore former was supplied by Sigma Aldrich.

2. Preparation of PES Membranes

Casting solutions of PES 14 and 18 wt% and 1, 2, 3 or 4 wt% of PVP were prepared by mixing the ingredients in a flask. The casting solution obtained was left to rest for about 12 h to allow complete release of bubbles. After that, it was cast onto a glass plate using a stainless-steel knife to get a casting film of 300 μm thickness, exposed to the atmosphere for 40 s, and then immersed into a coagulation bath of pure water. The as-prepared cast solution films were immersed in a deionized water bath conditioned at 25 °C and kept there for 24 h, and then the membranes formed were washed for additional 24 h using deionized water.

3. Membrane Structure Characterization

3-1. Porosity and Equilibrium Water Content

The membrane porosity was determined by the mass loss of wet membrane after drying. The membrane sample was mopped with water on the surface and weighed under wet status. Then, the membrane sample was dried until a constant mass. The membrane porosity ε was evaluated from Eq. (1):

$$\varepsilon = \frac{W_w - W_d}{\rho \cdot v} \quad (1)$$

where W_w is the mass of a wet membrane sample, W_d is the mass of dry state membrane sample; ρ pure water density and v is the volume of a membrane in wet state.

The equilibrium water content (EWC) was determined by Eq. (2):

$$\text{EWC} = \frac{W_w - W_d}{W_w} \cdot 100\% \quad (2)$$

3-2. Contact Angle

The contact angle between water and membrane was directly measured using a contact angle measuring instrument G10, KRUSS, Germany. For evaluation of the membrane hydrophilicity deionized water was used as a probe liquid in all measurements. To minimize the experimental error, the contact angle was measured at five random locations for each sample and then the average was reported.

3-3. Surface Oxygen Groups

The surface properties were characterized using potentiometric titration experiments using 809 Titrand equipment manufactured by Metrohm. The instrument was set at the mode when the equilibrium pH was collected. Materials studied in the amount of about 0.100 g in 50 mL 0.01 M NaNO_3 were placed in a container thermostated at 25 °C and equilibrated overnight with the electrolyte solution. To eliminate the influence of atmospheric CO_2 , the suspension was continuously saturated with N_2 . The carbon suspension was stirred throughout the measurements. Volumetric standards NaOH (0.1 M) or HCl (0.1 M) were used as titrants [24].

4. Membrane Performance Characterization

Water permeability of the membranes prepared was measured in a stainless steel cell, holding the effective membrane area of 19.6 cm^2 . The membranes were initially subjected to deionized water of 3 bar for about 1.5 h before testing. Then, the pure water flux was measured at 3 bar, 23 \pm 1 °C and 0.22 m/s cross-flow velocity. The pure water flux was calculated from the following equation:

$$J_w = \frac{V}{A \cdot \Delta t} \quad (3)$$

where J_w ($\text{L}/(\text{m}^2 \text{ h})$) is the pure water flux, V (L) is the volume of permeated water, A (m^2) is the effective membrane area and Δt (h) is the permeation time.

The experiments were conducted using compressed nitrogen gas and phenol solutions of different initial concentrations (5, 10, 15 or 25 mg/L) and all measurements were made at 3 bar, in triplicate. The final concentration of phenol in the solution was analyzed with a double beam UV-Vis spectrophotometer (Varian Cary 100 Bio) at 510 nm wavelength. The phenol rejections (%R) were calculated from Eq. (4):

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \cdot 100 \quad (4)$$

where C_p and C_f (mg/mL) were phenol concentrations in the permeate and the feed solutions, respectively.

Membrane resistance was evaluated according to Darcy's law by the resistance in the series of models as follows:

$$J = \frac{\Delta P}{\mu R_t} \quad (5)$$

where J ($\text{L}/(\text{m}^2 \text{ h})$) is the permeate flux, ΔP is the transmembrane pressure (TMP), μ is the dynamic viscosity of permeate, and R_t is the total filtration resistance. The resistance in the series of models combines various resistances causing flux decline as follows:

$$R_t = R_m + R_p + R_c \quad (6)$$

where, R_t is the total filtration resistance composed of various resistances including that of the membrane itself R_m , pore blocking R_p , cake resistance R_c . The intrinsic membrane resistance (R_m) can be estimated from the initial pure water flux (3). Fouling resistance (R_p) is caused by pore plugging and irreversible adsorption of foulants on membrane pore wall or surface. Cake resistance (R_c) induced by cake layer formed on the membrane surface was calculated from the water flux after pure water washing [2,17].

The detailed membrane fouling behavior was studied as follows. First, pure water flux of the membrane J_{w1} ($\text{L}/(\text{m}^2 \text{ h})$) was tested at 3 bar. Then, an aqueous solution of phenol (5-25 mg/L) was fed into the ultrafiltration system. After filtration for 30 min, the membrane was flushed with pure water for 10 min, and then pure water flux of the membrane J_{w2} ($\text{L}/(\text{m}^2 \text{ h})$) was measured. The flux recovery ratio (FRR) was calculated by using Eq. (5) to evaluate membrane antifouling property:

$$\text{FRR}(\%) = \frac{J_{w2}}{J_{w1}} \cdot 100 \quad (7)$$

RESULTS AND DISCUSSION

1. Membrane Characterization

Structural properties of the membranes studied, presented in Table 1, were determined to evaluate the influence of the amount of a porous factor on their hydrophilicity and surface properties.

For the series of membranes of low content of polymer PES14, an increase in porosity was observed with increasing amount of the pore-forming agent. The membranes PES-18 containing 2 and 3%wt

PVP (samples PES18-PVP2 and PVP3) show lower porosity than the other membranes of this series (PES18-PVP1, PES18-PVP4). Sample PES18-PVP4 has the highest porosity of all membranes studied. The equilibrium water content (EWC) is strictly dependent on the amount of the pore-forming agent in the membrane. For both series of membranes PES14 and PES18, the value of EWC increases with increasing amount of pore-forming agent (PVP). For the samples of series PES14, EWC values are in general higher than those for the samples of series PES18. The above observations are inter-

preted in relation to the amount of polymer used in the synthesis of membrane films in the samples of both series. The membranes with 18%wt of the polymer have more compact structure, which can result in lower EWC values.

The wetting abilities of the membranes were evaluated on the basis of measurements of the contact angle. As shown in Table 1, the two surfaces of membranes have different contact angles, which is attributed to the differences in morphologies between the top and the bottom membrane surfaces. The contact angles measured on the bottom side of the membrane are smaller than those measured on the top side. For PES14 membranes no relations were noted between the amount of PVP and the contact angle. From among the membranes from series PES14, the highest hydrophilicity was found for PES14-PVP-3, while the lowest for PES14-PVP1. For the membranes from series PES18, with increasing amount of pore-forming agent a small decrease in the hydrophilicity of membrane surface was observed. The smallest contact angle was measured for PES18-PVP-1 and PES18-PVP2, and these membranes are also characterized by the highest hydrophilicity from among all membranes studied in this work.

2. Membrane Performance

Tables 2 and 3 give the contents of acidic and basic oxygen groups in the membranes studied, determined before and after the filtration. Analysis of these data does not reveal any direct relation between

Table 1. Porosity (ϵ), equilibrium water content (EWC) and contact angle θ of investigated membranes

Membrane	ϵ (%)	EWC (%)	Contact angle	
			Top	Bottom
PES14-PVP1	41.4	78.3	80.3±3.7	75.5±12.7
PES14-PVP2	45.9	78.8	78.9±5.5	73.6±4.5
PES14-PVP3	50.7	80.0	77.8±6.1	72.1±3.9
PES14-PVP4	54.2	81.9	78.5±3.9	70.9±3.5
PES18-PVP1	50.4	75.2	76.0±5.1	71.2±4.9
PES18-PVP2	45.2	76.1	76.1±3.4	71.6±2.2
PES18-PVP3	47.4	76.5	76.9±3.2	71.7±1.9
PES18-PVP4	65.9	78.7	77.2±3.6	71.8±1.6

Table 2. Acidic properties of investigated adsorbents before and after filtration with 15 mg/L phenol solution [mmol/g]

Membrane	pKa												Acidic groups		Total content of surface oxides	
	<3		3-5		5-7		7-9		9-11		>11		A	B	A	B
	A	B	A	B	A	B	A	B	A	B	A	B				
PES14-PVP1	-	-	1.27	0.90	-	-	0.07	0.94	-	-	2.69	1.46	4.03	3.30	5.88	5.47
PES14-PVP2	-	-	0.44	1.29	-	-	0.07	0.16	0.73	3.07	1.67	3.05	2.91	7.57	3.27	11.96
PES14-PVP3	0.29	-	1.48	1.72	-	-	0.07	0.07	-	0.90	2.18	1.61	4.02	4.30	5.82	6.98
PES14-PVP4	-	-	0.98	1.11	-	-	0.12	0.11	1.04	1.05	0.56	1.15	2.70	3.42	3.63	4.71
PES18-PVP1	-	-	3.86	0.55	1.32	1.49	0.14	0.16	-	-	1.72	1.47	7.04	3.67	8.98	4.99
PES18-PVP2	-	-	0.55	0.33	-	-	0.06	0.05	0.66	-	0.87	1.09	2.14	1.47	3.04	3.10
PES18-PVP3	-	1.08	0.58	1.49	0.98	-	0.21	0.11	-	0.80	1.54	0.50	3.31	3.98	5.19	6.03
PES18-PVP4	-	0.71	2.14	0.66	-	0.49	0.09	0.11	0.81	0.67	1.30	0.48	4.34	3.12	6.40	6.16

A- before filtration, B- after filtration

Table 3. Basic properties of investigated adsorbents before and after filtration with 15 mg/L phenol solution [mmol/g]

Membrane	pKa										Basic groups		Total content of surface oxides	
	3-5		5-7		7-9		9-11		>11		A	B	A	B
	A	B	A	B	A	B	A	B	A	B				
PES14-PVP1	-	0.98	0.24	0.20	1.32	-	-	0.65	0.29	0.34	1.85	2.17	5.88	5.47
PES14-PVP2	-	0.54	0.04	0.38	0.09	0.35	0.23	3.12	-	-	0.36	4.39	3.27	11.96
PES14-PVP3	0.23	0.77	0.28	0.27	-	-	1.02	1.35	0.27	0.29	1.80	2.68	5.82	6.98
PES14-PVP4	-	-	0.20	0.14	-	-	0.55	0.91	0.18	0.24	0.93	1.29	3.63	4.71
PES18-PVP1	0.27	0.23	0.30	0.20	-	-	0.99	0.89	0.38	-	1.94	1.32	8.98	4.99
PES18-PVP2	0.13	-	0.10	0.18	0.05	0.05	0.62	1.40	-	-	0.90	1.63	3.04	3.10
PES18-PVP3	0.26	0.23	0.24	0.28	0.18	-	0.87	1.18	0.33	0.36	1.88	2.05	5.19	6.03
PES18-PVP4	0.26	1.14	0.31	0.32	-	-	1.12	1.22	0.37	0.36	2.06	3.04	6.40	6.16

A- before filtration, B- after filtration

the content of PVP and the amount and type of surface oxides identified on the membrane surfaces. For almost all samples of PES14 series, after filtration of a phenol solution the total content of surface oxygen groups increased. The exception was sample PES14-PVP1, for which a small decrease in the content of surface oxygen groups was noted, from 5.88 mmol/g prior to filtration to 5.47 mmol/g after the process.

For PES18 series membranes, after filtration the total content of acidic groups increases on the surface of PES18-PVP1, PES18-PVP2 and PES18-PVP4, while for PES18-PVP3 it increases from 3.31 mmol/g before filtration to 3.98 mmol/g after this process.

A detailed analysis of the content of acidic groups on the surface of PES14 series membranes has shown that after the filtration the number of acidic groups identified in the range $pK_a=3-5$ decreases only for PES14-PVP1, but increases for the other PES14 membranes. In the range $pK_a=7-9$, the number of acidic groups increases after the filtration for PES14-PVP1 and PES14-PVP2. Moreover, in the range $pK_a=9-11$, the number of acidic groups on PES14-PVP2 increases after the filtration. It should be emphasized that for PES14-PVP3 the filtration of phenol solution leads to generation of surface groups in the pK_a range 9-11, which is not observed on PES14-PVP1. For $pK_a>11$, the total content of acidic groups after the filtration increases on membranes PES14-PVP2 and PES14-PVP4, but decreases for the other two samples of this series. For PES18-PVP3 and PES18-PVP4, the filtration of a phenol solution leads to generation of acidic groups in the range $pK_a<3$ increases. In the range $pK_a=3-5$ the total content of acidic oxygen groups decreases for PES18 series membranes, except for sample PES18-PVP3 for which it increases. This membrane is distinguished by showing the highest content of acidic oxygen surface groups; the total content of such groups identified after the filtration in the ranges $pK_a<3$ and 3-5 is 2.57 mmol/g. Moreover, this membrane shows the disappearance of surface acidic oxygen groups after the filtration in the range $pK_a=5-7$, while samples PES18-PVP1 and PES18-PVP4 show an increase in their content. In the range $pK_a=9-11$, after the filtration, samples PES18-PVP2 and PES18-PVP4 show a decrease in the content of surface acidic oxygen groups, while on PES18-PVP2 the surface acidic oxygen group's disappearance. On membrane PES18-PVP3, after the filtration, the surface acidic oxygen groups appear in the range $pK_a=9-11$, while the number of these groups disappears in the range $pK_a>11$. Decrease in the content of the surface acidic oxygen groups in the range $pK_a>11$ after the filtration is also observed for PES18-PVP1 and PES18-PVP4, while only for PES18-PVP2 the content of these groups in this range shows a small increase.

For membranes of PES14 series, filtration of a phenol solution of leads to an increase in the total content of surface basic oxygen groups (see Table 3). The greatest increase in the content of these groups, from 0.36 mmol/g to 4.39 mmol/g, is observed for PES14-PVP2. For membranes of PES18 series a similar tendency is noted except for sample PES18-PVP1, on whose surface the content of basic oxygen groups decreases after the filtration. A detailed analysis of the content and type of surface basic oxygen groups shows that on membranes PES14-PVP1, PES14-PVP2 after the filtration of phenol solution the basic oxygen groups of $pK_a=3-5$ are generated. On membrane PES14-PVP3 the content of basic oxygen groups of $pK_a=3-5$ increases after the filtration, while on membrane PES14-

PVP4, no surface basic oxygen groups of pK_a from this range are detected. Moreover, on the latter membrane after the filtration the content of surface basic oxygen groups of $pK_a=5-7$ decreases. Small differences in the content of basic oxygen groups of pK_a from the same range can be noted for PES14-PVP1 and PES14-PVP3. Only for PES14-PVP2, after the filtration shows a higher content of surface basic oxygen groups of $pK_a=5-7$ and $pK_a=7-9$. Filtration of a phenol solution with membrane PES14-PVP1 leads to a total disappearance of surface basic groups of $pK_a=7-9$, on the other two membranes of this series no surface basic oxygen groups of $pK_a=7-9$ are detected either before or after the filtration. As a result of filtration of a phenol solution, on the surfaces of all membranes from PES-14 series the content of surface basic groups of $pK_a=9-11$ increases, while the content of those of $pK_a>11$ shows slight changes.

For the membranes of PES18 series different relations are observed. On PES18-PVP1 and PES18-PVP3 after the filtration the content of surface basic groups of $pK_a=3-5$ is smaller, while on PES18-PVP2 they are no longer present. Only on PES18-PVP4, the filtration of a phenol solution leads to generation of new surface basic groups of pK_a from this range. On membranes PES18-PVP2 and PES18-PVP3 after the filtration the content of the surface basic groups of $pK_a=5-7$ increases. A small increase in their content is also observed for PES18-PVP4. On PES18-PVP3 the filtration leads to total disappearance of surface basic groups of $pK_a=7-9$, while on the other membranes from this series no change in their content is observed. On PES18-PVP2, PES18-PVP3 and PES18-PVP4, the filtration leads to an increase in the surface basic groups of $pK_a=9-11$, while on PES18-PVP1 the content of the surface basic groups of $pK_a=9-11$ slightly decreases. Moreover, on this membrane the surface basic groups of $pK_a>11$ disappear, while on PES18-PVP2 and PES18-PVP4 their content remains unchanged after the filtration and on PES18-PVP3 their content slightly increases.

The above observations imply that part of the phenol molecules from the permeate have been bonded to the groups present on the membrane surfaces, which can significantly affect the rate and effectiveness of phenol removal upon filtration. A layer blocking the membrane surface can be formed and inhibit further adsorption of phenol. Another phenomenon leading to a decrease in the filtration rate and changes in the separation performance of the membrane is the polarization of concentration, involving the formation of a layer in which the concentration of phenol is much greater than that in the bulk solution in direct vicinity of the membrane.

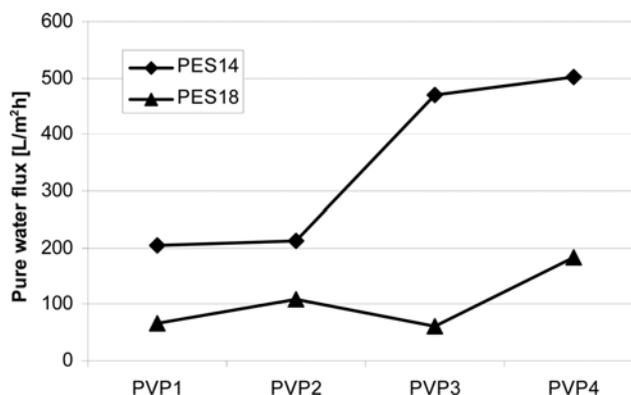


Fig. 1. Pure water flux of the membranes studied.

The pure water fluxes of the membranes prepared are shown in Fig. 1. Analysis of the data shows that the permeability values of membranes of the series PES-18 are much smaller, in particular for membranes PES18-PVP3 and PES18-PVP4, than those of PES-14 membranes. The reason for this difference is probably that a greater content of the polymer was used for the synthesis of PES18 series membranes, endowing them with much greater density. For membranes of the series PES14, with increasing content of pore-forming PVP from 1 to 4%wt, the pure water flux increases. For PES14-PVP1 and PES14-PVP2, the pure water flux is similar, but for PES14-PVP3 and PES14-PVP4 it significantly increases. These results are interpreted as arising from differences in the membrane porosities (Table 1). The pore contents of PES14-PVP1 and PES14-PVP2 are 41.43 and 45.9%, while those of PES14-PVP3 and PES14-PVP4 are 50.7% and 54.2%, respectively. Greater porosity permits greater water flux. The pure water flux for PES18-PVP1, PES18-PVP2 and PES18-PVP3 takes similar values, while for PES18-PVP4 the pure water flux is the highest from among the values for this series of membranes is 182 L/(m²h). Similarly as for PES14 series membranes, the highest pure water flux is measured for the sample of greatest porosity (Table 2). No correlation is found between the con-

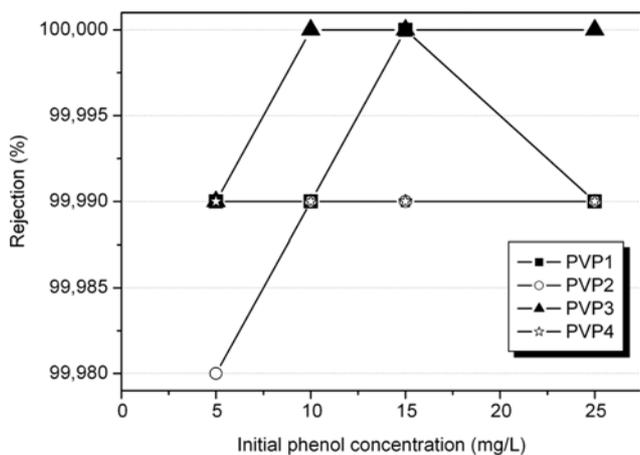


Fig. 2. Phenol rejection (R) versus the initial phenol concentration in the solution used for filtration with PES14 membranes.

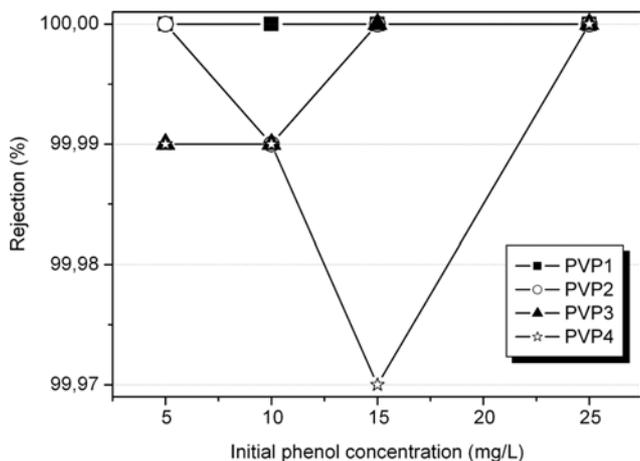


Fig. 3. Phenol rejection (R) versus the initial phenol concentration in the solution used for filtration with PES18 membranes.

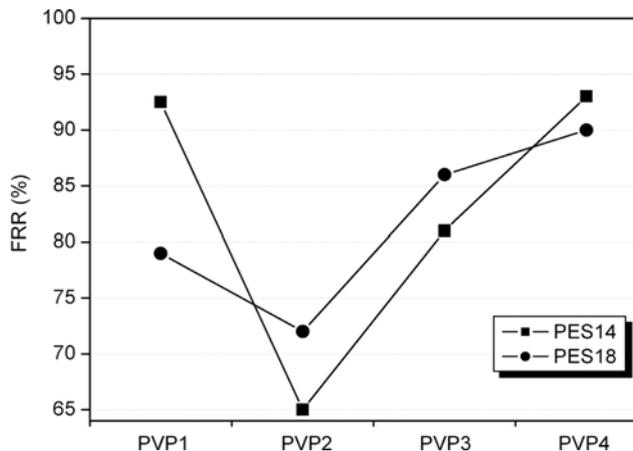


Fig. 4. Flux recovery ratio of PES-14 and PES-18 series membranes after filtration of a phenol solution.

tact angles of membranes and the pure water flux values. Thus, it can be concluded that alteration in the membrane morphology has a greater influence on the water flux compared to its hydrophilicity.

The prepared membranes were applied for phenol removal from solutions of different initial concentrations (5-25 mg/L). Figs. 2 and 3 present rejection values for phenol (R) versus the initial phenol concentration in the solution used for filtration for PES14 and PES18 membranes, respectively. As follows from the results, the effectiveness of phenol removal determined for the membranes of both series is similar and close to 100%. Figs. 2 and 3 were drawn in the narrow scale but in high accuracy to illustrate the small differences between the membranes studied.

The flux recovery ratio (FRR) depending on the starting phenol concentration was presented in order to evaluate the recycling ability of the membranes prepared (Fig. 4). The FRR values for membranes of both series show some small differences, but the character of the curves showing FRR versus the starting phenol concentration is the same. For all membranes, starting from those containing 2%wt of PVP, the FRR values increase with increasing content of PVP. The values of FRR determined for PES14-PVP1 and PES14-PVP4 are similar, of 92.5 and 93%, respectively and are the highest from among the values obtained for all membranes. Moreover, from among the PES18 membranes, only the two PES18-PVP2 and PES18-PVP3 show higher FRR values than the analogous PES14 membranes.

Fouling of investigated membranes has been quantified by the resistance appearing during filtration. Various filtration resistances, such as intrinsic membrane resistance (R_m), which reflects the membrane intrinsic resistance characterized by mainly the pore shape and size and membrane thickness, cake resistance (R_c) of the cake layer formed on the membrane surface, fouling resistance caused by pore plugging and irreversible adsorption of foulants on the membrane wall or surface (R_p) and total filtration resistance (R_t) were calculated. The values obtained for the starting phenol concentration of 15 mg/L as a representative are summarized in Table 4. The pore resistance as well as cake resistance values for membranes PES18 are much higher than those obtained for analogous membranes of lower content of the polymer (PES14 series). For the samples of this series, the cake resistance (R_c) decreases with increasing con-

Table 4. Filtration resistance of different membranes for 15 mg/L phenol solution

Membrane	$R_m (\times 10^{13})$	$R_p (\times 10^{13})$	$R_c (\times 10^{13})$	$R_t (\times 10^{13})$
PES14-PVP1	0.87	0.96	0.95	2.78
PES14-PVP2	0.21	0.47	0.66	1.34
PES14-PVP3	0.20	0.22	0.24	0.66
PES14-PVP4	0.24	0.28	0.34	0.86
PES18-PVP1	32.00	50.50	52.20	134.70
PES18-PVP2	0.51	0.94	15.20	16.65
PES18-PVP3	7.10	7.22	6.72	21.04
PES18-PVP4	0.52	0.84	0.95	2.31

tent of PVP, from PES14-PVP1 through PES14-PVP2 to PES14-PVP3. For PES14-PVP4 this value is a bit higher than for PES14-PVP3, but still this resistance brings a greater contribution to total pore resistance of this membrane. For the membranes of PES18 series, the cake resistance decreases with increasing amount of PVP used for the synthesis. Note that the cake resistance values for most of the membranes are higher than those of R_m and R_p . The above results suggest that the cake formation was a more significant fouling mechanism for this membrane. The high pore-fouling can be attributed to the straight through pore structure and/or the surface chemistry of modified membranes. If the aggregates enter to a pore in a straight through channel, the permeate flow cannot pass through the pores as it may be the case for interconnected membranes, causing higher pore resistance. With increasing content of PVP, the values of particular types of resistances decrease. This indicates that the surface antifouling property of the membranes was improved with increasing amount of PVP in the casting solution. Only for PES14-PVP4, containing the highest amount of PVP, the values of the resistances fall off the trend and are slightly higher than that for the membrane containing 3%wt PVP. Furthermore, the total filtration resistance (R_t) of PES18-PVP1, PES18-PVP2 and PES18-PVP3 membrane, which is the sum of R_m , R_c and R_p , is much higher than for the other membranes. This fact can be related to the compact structure of these membranes, which is confirmed by, e.g., a low value of EWC calculated for these materials (Table 1). It can be concluded that modification of casting solution by adding different amount of PVP is a method for surface modification and fouling mitigation of PES-based membranes.

CONCLUSIONS

Modification of PES polymer membrane by the use of different amount of the polymer and pore forming agent in their syntheses leads to significant changes in porosity and equilibrium water content. It has been shown that addition of various amounts of PVP brings about changes in the content of the surface oxygen groups, but has no significant effect on the chemical character of the groups and does not change the domination of acidic groups. Filtration of phenol solution leads to significant changes in the total content of

surface oxygen groups; however, the acidic groups remain dominant. In the phenol concentration range used, the membranes characterized by higher porosity exhibit more stable and higher rejection ratio for impurities removal. Although all membranes studied show similar rejection, the values of their cake resistance (R_c) and pore resistance (R_p) significantly depend on the structure and porosity of the membranes applied for filtration.

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