

Membranes obtained on the basis of cellulose acetate and their use in removal of metal ions from liquid phase

Joanna Krason, Robert Pietrzak*

Adam Mickiewicz University in Poznań, Faculty of Chemistry, Laboratory of Applied Chemistry, Umultowska 89b, 61-614 Poznań, Poland

*Corresponding author: e-mail: pietrob@amu.edu.pl

The polymer membranes containing 18 wt% of cellulose acetate and different amounts of polyvinylpyrrolidone (PVP) as a cross-linker agent were used in the process of iron and copper ions removal from liquid phase. Depending on the content of PVP (changed from 1 to 4 wt.%) the membrane surfaces were characterised by different hydrophilic character and showed the dominant presence of surface oxygen-containing groups of acidic character. Irrespectively of the concentrations of solvents from which the metal ions had to be removed, the membranes showed better ability to remove Fe³⁺ ions than Cu²⁺ ones, and the membrane resistances decreased with increasing content of PVP. After the filtrations of solutions with iron ions the flux recovery ratio took rather high values; this ratio increased with increasing PVP content in the membrane.

Keywords: cellulose acetate membrane, phase inversion, physical and chemical properties, Cu and Fe ions removal.

INTRODUCTION

An important problem of our times that needs urgent and coordinated solution is increasing pollution of the natural environment. Until recently people have not been aware of the scale of degradation caused by modern technologies leading to poisoning of water, soil and air¹⁻³. Particularly dangerous is the presence of post-production waste in water, as it affects not only plants and animals but is also hazardous for health and life of people⁴⁻⁶. Since the danger was realised, much effort has been devoted to improve the technologies and to finding effective methods for the separation of pollutants from liquid phase. The methods proposed for this purpose include removal on block copolymers, flocculation, adsorption on activated carbons and carbon nanotubes, membrane methods of separation, including the method of separation under pressure⁷⁻¹⁵. From among many methods proposed, the use of membranes has enjoyed particular interest because of the low cost and simple application and these methods have been increasingly used for removal of different kind pollutants^{16, 17}. Depending on the type of pollutant to be removed (metal ions, proteins, emulsions, dyes), different pore size membranes are used and according to the size pores the filtration methods have been divided into microfiltration, ultrafiltration, nanofiltration and reversed osmosis¹⁸⁻²².

The membranes used in the pressure methods of separation are obtained in the processes of phase inversion, sintering and stretching of polymer films²³⁻²⁵. The process of phase inversion is commonly used for the preparation of membranes from polymers such as poly(vinyl alcohol), polyethersulfone, polypropylene or cellulose acetate²⁶⁻²⁹. A mixture of a polymer, non-solvent and solvent is spread over glass, the solvent is evaporated and the mixture on the glass is immersed in the coagulation bath. As a result asymmetric porous membranes are obtained³⁰⁻³². An often met problem is the presence of iron and copper ions in water. Too high content of these ions in human organisms is associated with cancer, nervous system disturbances, cardiovascular conditions and metabolic problems³³⁻³⁶.

This paper reports results of a study on characterisation and performance (in removal of iron and copper ions) of membranes obtained on the basis of cellulose acetate. The membranes studied differed in the content of polyvinylpyrrolidone used the cross-linker polymer.

EXPERIMENTAL

Material

Cellulose acetate (CA) was purchased from Sigma Aldrich and used as a membrane material. *N,N*-dimethylformamide (DMF) was purchased from POCh and used as a solvent. Polyvinylpyrrolidone (PVP, 10 000 g/mol) as a pore former was supplied by Sigma Aldrich.

Preparation of CA membranes

Casting solutions of CA 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 24 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 and kept for 24 h in a deionised water bath conditioned at 25°C to complete the exchange between the solvent and non-solvent.

Methods

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):

$$\varepsilon = \frac{W_w - W_d}{\rho \cdot v} \cdot 100\% \quad (1)$$

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):

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

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.

The surface properties were characterised 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 0.05 g in 50 mL 0.01 M NaNO₃ were placed in a container thermostated at 25°C and equilibrated overnight with the electrolyte solution. To eliminate the influence of atmospheric CO₂, the suspension was continuously saturated with N₂. The suspension was stirred throughout the measurements. Volumetric standards NaOH (0.1 M) or HCl (0.1 M) were used as titrants³⁷. Directly prior to use, each electrode was washed with a small amount of deionised water.

Water permeability of the membranes prepared was measured in a stainless steel cell, holding the effective membrane area of 19.6 cm². The membranes were initially subjected to deionised water of 3 bar for about 1.5 h before testing. Then, the pure water flux was measured at 3 bar, 23 ± 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 (L/(m² h)) is the pure water flux, V (L) is the volume of permeated water, A (m²) is the effective membrane area and Dt (h) is the permeation time.

The experiments were conducted using compressed nitrogen gas and iron or copper solutions of different initial concentrations (12 or 20 mg/L for iron solution and 800 or 1000 mg/L for solution of copper) and all measurements were made at 3 bar, in triplicate. The final concentration of iron or copper in the solution was analysed using a double beam UV-Vis spectrophotometer (Varian Cary 100 Bio) at 487 nm wavelength for iron solutions and at 620 nm wavelength for copper solutions. The iron or copper 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 iron or copper 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 (L/(m² 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 contaminants 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^{38, 39}.

The detail membrane fouling behaviour was studied as follows. Firstly, pure water flux of the membrane J_{w1} (L/(m² h)) was tested at 3 bar. Then, aqueous solution of iron or copper (12–1000 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} (L/(m² h)) was measured. The flux recovery ratio (FRR) was calculated using Eq. (5) to evaluate membrane antifouling property:

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

RESULTS AND DISCUSSION

Membrane characterisation

The values of structural parameters and contact angles for the series of membranes studied are given in Table 1.

As follows from these data, the porosity of the membranes does not depend on the content of the cross-linker agent. The porosity values obtained for the membranes containing 1, 3, or 4 wt.% PVP are similar and change from 43.55 to 44.54%. For CA18 PVP2 the value of porosity is much higher, reaching 50.31%. The values of equilibrium water content are similar for all membranes and change from 75 to 77%. Difference between values of porosity and EWC follows fact that the pore distribution in the membrane is not symmetrical. Because of that values of porosity and equilibrium water content can sometimes differ. The contact angle measurements show that the membrane with a 3% content of PVP was characterised by the highest value of this parameter. For the other membranes the difference between values of contact angle is not significant and may be caused by roughness of membrane surface.

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

Membrane	ε [%]	EWC [%]	Contact angle
CA18 PVP1	44.13	75.57	61.9 ± 2.41
CA18 PVP2	50.31	76.74	62.8 ± 1.47
CA18 PVP3	43.55	76.93	58.0 ± 3.43
CA18 PVP4	44.54	76.89	61.1 ± 3.08

Membrane performance

Tables 2 and 3 present the contents oxygen-containing acidic and basic groups on the surfaces of the mem-

Table 2. Content of acidic surface sites on investigated membranes before and after filtration with 20 mg/L iron solution [mmol/g]

Membrane	pH												Acidic groups		Oxygen-containing groups	
	<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				
CA18 PVP1	–	–	0.50	1.21	0.91	–	0.09	0.10	1.08	1.31	1.79	2.25	4.37	4.87	5.89	6.50
CA18 PVP2	–	–	1.59	0.73	–	–	0.09	–	1.27	1.99	0.74	2.11	3.69	4.83	5.35	7.55
CA18 PVP3	0.16	–	1.32	1.56	–	–	0.12	0.10	1.27	1.23	1.13	1.25	4.00	4.14	5.63	6.82
CA18 PVP4	–	–	1.53	0.58	–	0.99	0.10	0.12	1.72	1.15	0.76	2.60	4.11	5.44	6.87	7.22

A – before filtration, B – after filtration.

Table 3. Content of basic surface sites on investigated membranes before and after filtration with 20 mg/L iron solution [mmol/g]

Membrane	pH										Basic groups		Oxygen-containing groups	
	3–5		5–7		7–9		9–11		>11		A	B	A	B
	A	B	A	B	A	B	A	B	A	B				
CA18 PVP1	–	–	0.19	0.17	–	1.28	1.33	0.18	–	–	1.52	1.63	5.89	6.50
CA18 PVP2	–	1.18	0.19	0.19	1.24	–	0.23	1.35	–	–	1.66	2.72	5.35	7.55
CA18 PVP3	–	1.15	0.18	0.18	1.45	1.15	–	0.20	–	–	1.63	2.68	5.63	6.82
CA18 PVP4	1.13	–	0.20	0.21	1.24	1.36	0.19	0.21	–	–	2.76	1.78	6.87	7.22

A – before filtration, B – after filtration.

branes studied before and after the filtration of Fe³⁺ ion solution of the concentration 20 mg/l.

Prior to filtration, the highest amount of acidic oxygen-containing groups (4.37 mmol/g) was found on the membrane with the lowest content of PVP. Somewhat lower values were obtained for membranes CA18 PVP3 and CA18 PVP4, 4.00 and 4.11 mmol/g, respectively. The lowest amount of such groups, of 3.69 mmol/g, was on the surface of the membrane containing 2 wt.% of PVP. The highest amount of basic oxygen functional groups before filtration was 2.76 mmol/g on the surface of the membrane with the greatest content of PVP. The contents of these groups on the other membranes were much smaller and equal to 1.52, 1.66 and 1.63 mmol/g.

After the filtrations of iron ion solutions, the amount of acidic oxygen-containing groups increased on the surfaces of all membranes. The highest amount of acidic oxygen-containing groups of 5.44 mmol/g, was noted for the membrane of the highest content of PVP. For membrane CA18 PVP1 after the filtration the amount of acidic surface oxygen-containing functional groups was smaller, 4.87 mmol/g and a similar value was obtained for CA18PVP2. The lowest content of these groups after filtration was on the surface of CA18 PVP3.

The highest number of acidic oxygen-containing groups after filtration occurs for the pH range above 11. In this pH range, the amount of acidic groups increased significantly for all membranes from the CA18 series. The highest amount of acidic oxygen-containing sites of 2.60 mmol/g was determined for CA18PVP4, (with 4% content of PVP). The amounts of acidic oxygen-containing groups in the range pH = 3–5 decreased for membranes CA18PVP2 and CA18PVP4, while increased for CA18 PVP1 and CA18 PVP3. In this pH range, the contents of acidic oxygen-containing groups on the surfaces of membranes with 1 and 3% of PVP are 1.21 and 1.56 mmol/g, respectively, while on the membranes containing 2 and 4% of PVP the corresponding values are 0.73 mmol/g and 0.58 mmol/g, respectively. For membrane C18PVP4, the acidic oxygen-containing

groups appeared in the pH range 5–7. For membrane CA18 PVP1 observed increase caused a disappearance of acidic oxygen-containing group from the pH range 5–7. For membranes CA18PVP1 and CA18PVP2, the number of acidic oxygen-containing groups increased for pH = 9–11, while for membrane CA18 PVP4 it decreased in this pH range. Similarly as for the membranes with 14% content of CA, also for the CA18 series after filtration, no acidic groups were detected below pH = 3.

The amount of basic oxygen-containing surface sites after the filtration of Fe³⁺ ions solution increased for membranes with 1, 2 and 3 wt.% of PVP, while for membrane CA18PVP4 it decreased. The highest increase in the amount of basic oxygen-containing groups was observed for membranes CA18PVP2 and CA18PVP3. For these samples after the filtration the basic groups appeared in the pH range 3–5. Only for membrane CA18PVP2, the basic groups in the pH range 7–9 disappeared, while their number significantly increased in the pH range 9–11. For membrane CA18PVP3 a small decrease in the number of basic oxygen-containing groups was noted for pH = 7–9, while for pH = 9–11 a small number of basic oxygen-containing groups appeared. For membrane CA18PVP1, the number of basic oxygen-containing groups decreased in the pH range 9–11, but the basic groups appeared in the pH range 7–9. For membrane CA18PVP4, the basic oxygen-containing groups in the pH range 3–5 disappeared. After filtration of iron ion solutions, in the extreme pH ranges, below 3 and above 11, no presence of basic oxygen-containing groups was detected.

Tables 4 and 5 present the data on the contents of acidic and basic oxygen-containing groups on the series of membranes studied before and after the filtration of copper ions solution of the concentration 1000 mg/L.

The total amount of acidic oxygen-containing surface groups after the filtration was the highest for membranes with 2 and 3 wt.% of PVP and equal to 5.16 and 5.67 mmol/g, respectively. For membranes CA14 PVP1 and CA14 PVP4, this amount was lower than 5 mmol/g,

Table 4. Content of acidic surface sites on investigated membranes before and after filtration with 1000 mg/L copper solution [mmol/g]

Membrane	pH												Acidic groups		Oxygen-containing groups	
	<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
CA18 PVP1	-	-	0.50	1.42	0.91	-	0.09	0.11	1.08	1.57	1.79	1.01	4.37	4.11	5.89	5.84
CA18 PVP2	-	-	1.59	1.57	-	-	0.09	0.11	1.27	1.19	0.74	2.29	3.69	5.16	5.35	6.72
CA18 PVP3	0.16	-	1.32	0.59	-	-	0.12	1.10	1.27	-	1.13	3.98	4.00	5.67	5.63	8.34
CA18 PVP4	-	-	1.53	0.59	-	0.91	0.10	0.12	1.72	1.30	0.76	1.64	4.11	4.56	6.87	6.18

A – before filtration, B – after filtration.

Table 5. Content of basic surface sites on investigated membranes before and after filtration with 1000 mg/L copper solution [mmol/g]

Membrane	pH										Basic groups		Oxygen-containing groups	
	3-5		5-7		7-9		9-11		>11					
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
CA18 PVP1	-	-	0.19	0.20	-	1.17	1.33	0.36	-	-	1.52	1.73	5.89	5.84
CA18 PVP2	-	-	0.19	0.22	1.24	1.34	0.23	-	-	-	1.66	1.56	5.35	6.72
CA18 PVP3	-	1.08	0.18	0.19	1.45	1.24	-	0.16	-	-	1.63	2.67	5.63	8.34
CA18 PVP4	1.13	-	0.20	0.22	1.24	-	0.19	1.40	-	-	2.76	1.62	6.87	6.18

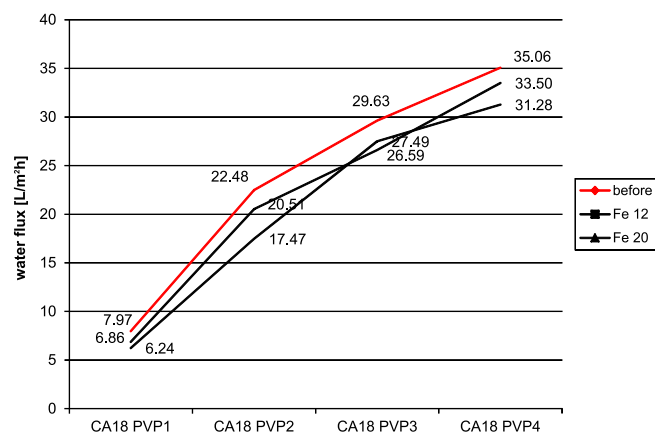
A – before filtration, B – after filtration.

that is 4.11 and 4.56 mmol/g. For the membrane of the lowest content of PVP, in the pH range 3–5, the amount of acidic oxygen-containing groups increases, but they disappear in the next pH range (pH 5–7). For CA18 PVP3 after the filtration, in the pH range 9 – 11, the acidic oxygen-containing groups disappear and above 11 their amount significantly increases up to 3.98 mmol/g. For the same membrane, in the pH range 3–5 the amount of acidic oxygen-containing groups considerably decreases, although it decreases even more for CA18 PVP4. After the filtration of copper ions solution, on the surface of CA18 PVP4 the acidic groups appear in the pH range 5–7, while in the range 9–11 their content decreases. Above pH 11, on the surface of membrane CA18 PVP4, the amount of acidic oxygen-containing groups increases from 0.76 to 1.64 mmol/g. For pH below 3, no presence of acidic oxygen-containing groups was detected on the surface of all membranes.

After the filtration, the total amount of surface oxygen-containing groups of basic character decreases for CA18 membranes with 2 and 4% wt. of PVP, and the decrease is more pronounced for CA18 PVP4 from 2.76 to 1.62 mmol/g. For membranes CA18 PVP1 and CA18 PVP3 their amount increases. The greatest amount of basic oxygen-containing groups of 2.67 mmol/g was determined for membrane CA18PVP3. For membrane CA18 PVP4 a considerable number of basic oxygen-containing groups disappeared in the pH range 3–5 and 7–9. For CA18 PVP2 a small number of basic oxygen-containing groups disappeared in the pH range 9–11. For CA18 PVP3 after filtration a large number of basic oxygen-containing groups, close to 1.08 mmol/g, appeared in the pH range 3–5 and a small amount of about 0.16 mmol/g appeared in the pH range 9–11. For membrane CA18 PVP1, the presence of basic oxygen-containing groups on the surface in the number of 1.17 mmol/g

was detected only after filtration in the pH range 7–9. For the same membrane, in the pH range 9–11, the amount of basic oxygen-containing groups decreased from 1.33 to 0.36 mmol/g after filtration. On the surface of membrane CA18 PVP4 the number of basic oxygen-containing groups increased from 0.19 to 1.40 mmol/g. In the extreme ranges of pH, below 3 and above 11, no presence of basic oxygen-containing groups was found.

Figure 1 presents value of determined before and after the filtration of Fe^{3+} ions solutions.

**Figure 1.** Metal ions removal by polymer membranes obtained on the basis of cellulose acetate

For all membranes, water flux increase with increasing content of the cross-linker agent. For membrane CA18 PVP1 before filtrations water flux was 7.97 L/m² h, while for CA18PVP4 the value increases to 35.06 L/m² h. Irrespectively of the content of PVP in membrane, the value of water flux before filtrations are higher than after the processes, which is a result of membrane pore blocking. For the majority of membranes, the water flux were higher after the filtration of Fe^{3+} solution of the

concentration 20 mg/L than those after the filtration of the solution of the concentration 12 mg/L. Only for CA18 PVP3, the value of water flux was higher after the filtration of iron ions solution of the concentration 12 mg/L than after the filtration of the solution of higher concentration.

Figure 2 presents the water flux values determined before and after the filtrations of Cu^{2+} ions solutions.

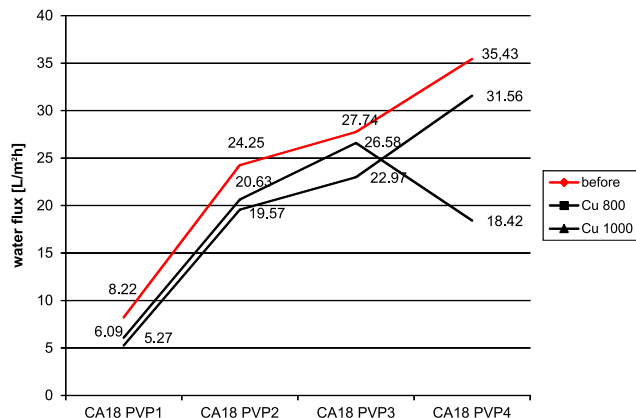


Figure 2. Metal ions removal by polymer membranes obtained on the basis of cellulose acetate

For all membranes, the values before filtration increase with increasing content of the PVP. The lowest value of 8.22 L/m² h was obtained for CA18 PVP1, while for CA18 PVP2, CA18 PVP3 and CAPVP4, the water flux were 24.25, 27.74 L/m² h and 35.43 L/m² h, respectively. The values of water flux after the filtration of copper ions solution of the concentration 1000 mg/L were for the majority of membranes higher than those obtained after the filtration of the solution of lower copper ions concentration. The only exception was CA18 PVP4 for which the water flux after the filtration of the copper solution of 1000 mg/L was much lower than that after the filtration of 800 mg/L solution. The higher value before than after the filtrations are a consequence of membrane pore blocking.

Figure 3 presents the abilities of CA18 series membranes to remove iron ions from liquid phase.

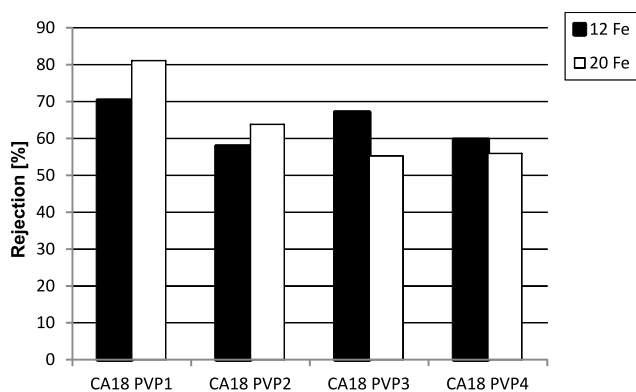


Figure 3. Metal ions removal by polymer membranes obtained on the basis of cellulose acetate

When the iron ions solution of 12 mg/L is used, the most effective in their removal, 70%, shows membrane CA18PVP1, a slightly lower value of 67% is found for CA18 PVP3, while the values of rejection for the other two membranes are 57 and 59%. After the filtration of iron solution of the concentration 20 mg/L, the effecti-

veness of iron ions removal decreased and this decrease was dependent on the PVP content. The highest value of R, of 81%, was obtained for CA18 PVP1, while for CA18 PVP2 this value decreased to 64%, and for the other two R was close to 55%. According to the results presented, membranes CA18 PVP1 and CA18 PVP2 are more effective in removal of Fe^{3+} ions from the 20 mg/L solution than from the 12 mg/L one, while the reversed tendency is observed for membranes CA18PVP3 and CA18PVP4.

The degree of copper ions removal for the 4 membranes studied is shown in Figure 4. The values of R for membranes CA18 PVP1 and CA18 PVP2 after the filtration from copper solution of the concentration 800 mg/L are similar and equal to 23 and 21%. For membrane CA18PVP3 this value decreases to 10%, while for CA18PVP4, rejection increases to 14%. Completely divergent values were effectiveness of copper ions removal were obtained after the filtrations of the copper solution of 1000 mg/L concentration. The highest effectiveness in copper ions removal showed membrane CA18 PVP1 (29%), while the effectiveness of CA18 PVP2 is 0.27% and CA18 PVP3 is 0.77%. The effectiveness of copper ions removal from the solution of 1000 mg/L was 10% for CA18 PVP4.

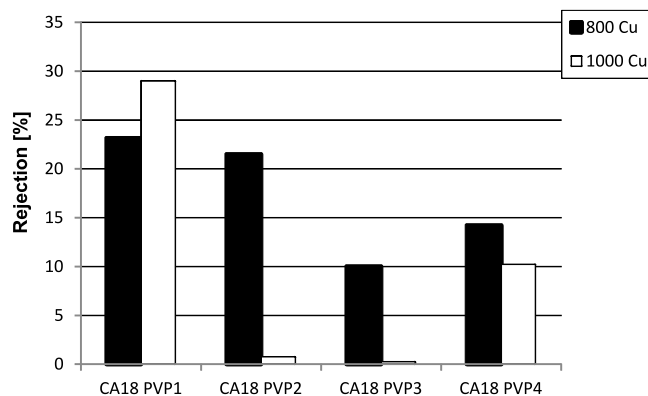


Figure 4. Metal ions removal by polymer membranes obtained on the basis of cellulose acetate

Figure 5 shows the flux recovery ratio (FRR) of the membranes studied for different solutions.

After the filtrations of iron ions solutions, the FRR value increased with increasing content of PVP. For membrane CA18 PVP1 the FRR value was 79%, for CA18PVP2 it was 85%, while for CA18 PVP3 and CA18 PVP4, the values of FRR were 91 and 93%, respectively. After the filtrations of copper ions solutions, the FRR

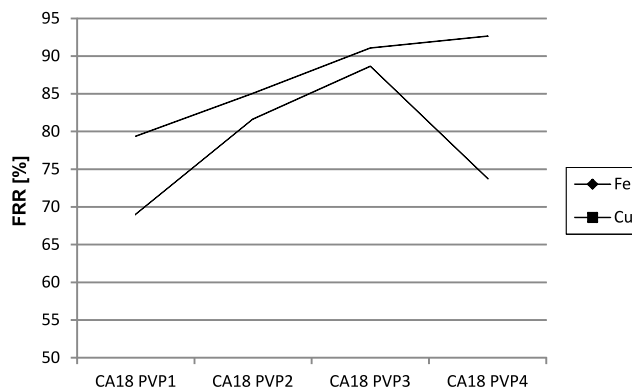


Figure 5. Metal ions removal by polymer membranes obtained on the basis of cellulose acetate

values at first increase with increasing PVP content and reach 69% for CA18 PVP1, 82% for CA18 PVP2 and 89% for CA18 PVP3, but significantly depart from this tendency for CA18PVP4, for which FRR is 74%. For the first 3 membranes FRR increases with increasing PVP content in membrane.

The values of particular type resistances determined for the CA18 series membranes after the filtration of iron ions are collected in Table 6.

Table 6. Filtration resistance of different membranes for iron solution

Membrane	CA18 PVP1	CA18 PVP2	CA18 PVP3	CA18 PVP4
$R_m (x 10^{13})$	13.40	5.45	2.91	3.52
$R_p (x 10^{13})$	16.60	6.06	3.17	3.71
$R_c (x 10^{13})$	16.80	5.54	2.99	3.48
$R_t (x 10^{13})$	46.80	17.05	9.07	10.71

The highest value of total resistance R_t of $46.80 \times 10^{13} \text{ L/m}^2 \text{ h}$ was determined for membrane CA18PVP1. The total resistance of CA18 PVP2 was much lower, of $17.05 \times 10^{13} \text{ L/m}^2 \text{ h}$, while for membranes CA18PVP3 and CA18PVP4 the total resistance was 9.07 and $10.71 \times 10^{13} \text{ L/m}^2 \text{ h}$. The partial resistances for particular membranes change following the same tendency as the total resistance of filtration. The values of resistances determined after the filtrations of copper ions solutions are presented in Table 7.

Table 7. Filtration resistance of different membranes for copper solution

Membrane	CA18 PVP1	CA18 PVP2	CA18 PVP3	CA18 PVP4
$R_m (x 10^{13})$	15.60	3.69	3.63	2.33
$R_p (x 10^{13})$	22.70	4.21	3.79	3.69
$R_c (x 10^{13})$	26.30	3.86	3.42	4.58
$R_t (x 10^{13})$	64.60	11.76	10.84	10.60

The highest value of R_t , reaching $64.60 \times 10^{13} \text{ L/m}^2 \text{ h}$ was obtained for CA18 PVP1 and is much different from the values obtained for the other membranes. The total resistance for the other membranes varied from $11.76 \times 10^{13} \text{ L/m}^2 \text{ h}$ for CA18PVP2 to $10.60 \times 10^{13} \text{ L/m}^2 \text{ h}$ for CA18PVP4, so are similar, while the value for CA18PVP1 is a few times higher.

CONCLUSIONS

Depending on the content of PVP, the membranes from the series studied showed negligible different degrees of surface hydrophilicity. The content of PVP added had no effect on the membranes porosities and equilibrium water content. Before and after the filtrations, the dominant presence of acidic oxygen functional groups was established. For the majority of membranes the number of these groups increased after the processes of filtration. The permeability of membranes of cellulose acetate increased with increasing content of PVP, and decreased after the processes of filtration as a result of pore blocking. Irrespective of the solvent concentrations, the membranes studied were more effective in removal of Fe^{3+} ions than Cu^{2+} ions from liquid phase. After the filtrations of iron ions, the values of FRR were high and increased with increasing PVP content in the membranes. The membrane resistance decreased with increasing PVP content.

LITERATURE CITED

- Zorita, I., Apraiz, I., Ortiz-Zarragoitia, M., Orbea, A., Cancio, I., Soto, M., Marigomez, I. & Cajaraville, M.P. (2007). Assessment of biological effects of environmental pollution along the NW Mediterranean Sea using mussels as sentinel organisms. *Environ. Pollut.* 148, 236–250. DOI: 10.1016/j.envpol.2006.10.022.
- Guo, G., Wu, F., Xie, F. & Zhang, R. (2012). Spatial distribution and pollution assessment of heavy metals in urban soils from southwest China. *J. Environ. Sci.* 24(3), 410–418. DOI: 10.1016/S1001-0742(11)60762-6.
- Seinfeld, J.H. & Pandis, S.N. (2006). *Atmospheric Chemistry and Physics* (2nd ed.). New Jersey, USA: John Wiley & Sons.
- Lewis, M. & Pryor, R. (2013). Toxicities of oils, dispersants and dispersed oils to algae and aquatic plants: Review and database value to resource sustainability. *Environ. Pollut.* 180, 345–367. DOI: 10.1016/j.envpol.2013.05.001.
- Camargo, J.A. & Alonso, A. (2006). Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment. *Environ. Int.* 32, 831–849. DOI: 10.1016/j.envint.2006.05.002.
- Khan, S., Shahnaz, M., Jehan, N., Rehman, S., Shah, M. T. & Din, I. (2013). Drinking water quality and human health risk in Charsadda district, Pakistan. *J. Clean. Prod.* 60, 93–101. DOI: 10.1016/j.jclepro.2012.02.016.
- Ostolska, I. & Wiśniewska, M. (2015). Investigation of the colloidal Cr_2O_3 removal possibilities from aqueous solution using the ionic polyamino acid block copolymers. *J. Hazard. Mater.* 290, 69–77. DOI: 10.1016/j.jhazmat.2015.02.068.
- Wiśniewska, M., Nosal-Wiercińska, A., Dąbrowska, I. & Szewczuk-Karpisz, K. (2013). Effect of the solid pore size on the structure of polymer film at the metal oxide/polyacrylic acid solution interface – Temperature impact. *Micropor. Mesopor. Mater.* 175, 92–98. DOI: 10.1016/j.micromeso.2013.03.032.
- Wiśniewska, M., Ostolska, I., Szewczuk-Karpisz, K. & Nosal-Wiercińska, A. (2015). Adsorption and Stability Properties of Aqueous Suspension of Chromium (III) Oxide in the Presence of Synthetic and Natural Polymers: Possibilities of Solid Removal. *Adsorpt. Sci. Technol.* 33, 639–700. DOI: 10.1260/0263-6174.33.6.693.
- Nowicki, P., Kazmierczak-Razna, J. & Pietrzak, R. (2016). Physicochemical and adsorption properties of carbonaceous sorbents prepared by activation of tropical fruit skins with potassium carbonate. *Mater. Design.* 90, 579–585. DOI: 10.1016/j.matdes.2015.11.004.
- Nowicki, P., Bazan, A., Kazmierczak-Razna, J. & Pietrzak, R. (2015). Sorption Properties of Carbonaceous Adsorbents Obtained by Pyrolysis and Activation of Pistachio Nut Shells. *Adsorpt. Sci. Technol.* 33(6–8), 581–586. DOI: 10.1260/0263-6174.33.6-8.581.
- Nowicki, P., Supłat, M., Przepiórski, J. & Pietrzak, R. (2012). NO_2 removal on adsorbents obtained by pyrolysis and physical activation of cardboard. *Chem. Eng. J.* 195–196, 7–14. DOI: 10.1007/s10450-015-9729-x. DOI: 10.1016/j.cej.2012.04.073.
- Nowicki, P., Szymanowski, W. & Pietrzak, R. (2015). Textural, surface, thermal and sorption properties of the functionalized activated carbons and carbon nanotubes. *Pol. J. Chem. Technol.* 17(4), 120–127. DOI: 10.1515/pjct-2015-0078.
- Jasiewicz, K. & Pietrzak, R. (2013). The influence of pore generating agent on the efficiency of copper and iron ions removal from liquid phase by polyethersulfone membranes. *Chem. Eng. J.* 228, 449–454. DOI: 10.1016/j.cej.2013.05.005.
- Wei, P., Zhang, K., Gao, W., Kong, L. & Field, R. (2013). CFD modeling of hydrodynamics characteristics of slug bubble flow in a flat sheet membrane bioreactor. *J. Membr. Sci.* 445, 15–24. DOI: 10.1016/j.memsci.2013.05.036.
- Matos, M., Suarez, M.A., Gutierrez, G., Coca, J. & Pazos, C. (2013). Emulsification with microfiltration ceramic membra-

nes: A different approach to droplet formation mechanism. *J. Membr. Sci.* 444, 345–358. DOI: 10.1016/j.memsci.2013.05.033.

17. Han, J., Cho, Y.H., Kong, H., Han, S. & Park, H.B. (2013). Preparation and characterization of novel acetylated cellulose ether (ACE) membranes for desalination applications. *J. Membr. Sci.* 428, 533–545. DOI: 10.1016/j.memsci.2012.10.043.

18. Qdais, H.A. & Moussa, H. (2004). Removal of heavy metals from wastewater by membrane processes: a comparative study. *Desalination* 164, 105–110. DOI: 10.1016/S0011-9164(04)00169-9.

19. Lee, K.J., Mower, R., Hollenbeck, T., Castelo, J., Johnson, N., Gordon, P., Sinko P.J., Holme, K. & Lee, Y.H. (2003). Modulation of Nonspecific Binding in Ultrafiltration Protein Binding Studies. *PHrm. Res.* 7, 1015–1021. DOI: 10.1023/A:1024406221962.

20. Lobo, A., Cambiella, A., Benito, J.M., Pazos, C. & Coca, J. (2006). Ultrafiltration of oil-in-water emulsions with ceramic membranes: Influence of pH and crossflow velocity. *J. Membr. Sci.* 278, 328–334. DOI: 10.1016/j.memsci.2005.11.016.

21. Purkait, M.K., DasGupta, S. & De, S. (2004). Removal of dye from wastewater using micellar-enhanced ultrafiltration and recovery of surfactant. *Sep. Purif. Technol.* 37, 81–92. DOI: 10.1016/j.seppur.2003.08.005.

22. Zarebska, A. et al. Anna Narebska, Piotr Adamczak, Stanisław Koter, Wojciech Kujawski, Andrzej Warszawski, Marek Staniszewski, Grzegorz Sionkowski (1997). *Membrany i membranowe techniki rozdzielania* (in Polish). Toruń, Polska: Wydaw. UMK.

23. Hendrix, K., Vaneynde, M., Koeckelberghs, G. & Vankelecom, I.F.J. (2013). Synthesis of modified poly(ether ether ketone) polymer for the preparation of ultrafiltration and nanofiltration membranes via phase inversion. *J. Membr. Sci.* 447, 96–106. DOI: 10.1016/j.memsci.2013.07.006.

24. Wu, Z., Faiz, R., Li, T., Kingsbury, B.F.K. & Li, K. (2013). A controlled sintering process for more permeable ceramic hollow fibre membranes. *J. Membr. Sci.* 446, 286–293. DOI: 10.1016/j.memsci.2013.05.040.

25. Tabatabaei, S.H., Carreau, P.J. & Aji, A. (2009). Microporous membranes obtained from PP/HDPE multilayer films by stretching. *J. Membr. Sci.* 345, 148–159. DOI: 10.1016/j.memsci.2009.08.038.

26. Li, N., Xiao, C., An, S. & Hu, X. (2010). Preparation and properties of PVDF/PVA hollow fiber membranes. *Desalination* 250, 530–537. DOI: 10.1016/j.desal.2008.10.027.

27. Rahimpour, A., Madaeni, S.S. & Mansourpanah, Y. (2010). Nano-porous polyethersulfone (PES) membranes modified by acrylic acid (AA) and 2-hydroxyethylmethacrylate (HEMA) as additives in gelation media. *J. Membr. Sci.* 364, 380–388. DOI: 10.1016/j.memsci.2010.08.046.

28. Lalia, B.S., Kochkodan, V., Hashaikeh, R. & Hilal, N. (2013). A review on membrane fabrication: Structure, properties and performance relationship. *Desalination* 326, 77–95. DOI: 10.1016/j.desal.2013.06.016.

29. Sairam, M., Sereewatthanawut, E., Li, K., Bismarck, A. & Livingston, A.G. (2011). Method for the preparation of cellulose acetate flat sheet composite membranes for forward osmosis-Desalination using MgSO₄ draw solution. *Desalination* 273, 299–307. DOI: 10.1016/j.desal.2011.01.050.

30. Hořda, A.K., Aernouts, B., Saeys, W. & Vankelecom, I.F.J. (2013) Study of polymer concentration and evaporation time as phase inversion parameters for polysulfone-based SRNF membranes. *J. Membr. Sci.* 442, 196–205. DOI: 10.1016/j.memsci.2013.04.017.

31. Cao, J.H., Zhu, B.K., Ji, G.L. & Xu, Y.Y. (2005). Preparation and characterization of PVDF-HFP microporous flat membranes by supercritical CO₂ induced phase separation. *J. Membr. Sci.* 266, 102–109. DOI: 10.1016/j.memsci.2005.05.015.

32. Ren, J., Zhou, J. & Deng, M. (2010). Morphology transition of asymmetric flat sheet and thickness-gradient membranes

by wet phase-inversion process. *Desalination* 253, 1–8. DOI: 10.1016/j.desal.2009.12.001.

33. Foy, S.P. & Labhasetwar, V. (2011). Oh the irony: Iron as a cancer cause or cure? *Biomaterials* 32, 9155–9158. DOI: 10.1016/j.biomaterials.2011.09.047.

34. Walter, U. (2010). Transcranial Sonography in Brain Disorders with Trace Metal Accumulation. *Int. Rev. Neurobiol.* 90, 166–178. DOI: 10.1016/S0074-7742(10)90012-3.

35. Kang, Y.J. (2011). Copper and homocysteine in cardiovascular diseases. *PHarmacol. Ther.* 129, 321–331. DOI: 10.1016/j.pharmthera.2010.11.004.

36. Rines, A.K. & Ardehali, H. (2013). Transition metals and mitochondrial metabolism in the heart. *J. Mol. Cell. Cardiol.* 55, 50–57. DOI: 10.1016/j.yjmcc.2012.05.014.

37. Hofman, M. & Pietrzak, R. (2011). Adsorbents obtained from waste tires for NO₂ removal under dry conditions at room temperature. *Chem. Eng. J.* 170, 202–208. DOI: 10.1016/j.cej.2011.03.054.

38. Li, N. N., Fane, A.G., Winston, Ho, W.S. & Matsuura, T. (2008). *Advanced membrane technology and applications*. New Jersey, USA: John Wiley & Sons.

39. Basile, A. & Gallucci, F. (2011). *Membranes for Membrane Reactors. Preparation, Optimization and Selection*. Chichester, UK: John Wiley & Sons.