



Removal of Iron and Copper Ions from the Liquid Phase by Modified Polymeric Membranes

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Abstract

Preparation of polymeric membranes based on cellulose acetate and modified by adding different amounts of a pore generating agent, which was polyvinylpyrrolidone (PVP), is presented and potential application of the membranes obtained for the removal of iron and copper ions from liquid phase is examined. Addition of various amounts of PVP has an impact on the physical (porosity, equilibrium water content and permeability) and chemical (content of the surface oxygen group, pH) properties of the membranes obtained. Filtration of iron and copper solution leads to significant changes in the total content of surface oxygen groups, however the acidic oxygen groups remain dominant. With the content of PVP increasing within a certain range, the membrane permeability is improved. The membranes obtained show higher efficiency in removal of Fe^{3+} than Cu^{2+} ions, but with increasing content of PVP the efficiency in iron ions removal decreases and the total filtration resistance decreases after filtration of iron ions solutions.

Keywords Cellulose acetate membrane · Phase inversion · Copper and iron ions removal · Physical and chemical properties · Surface chemistry

Introduction

Dynamical development of economy and industry taking place over the last few decades has brought about the need of searching for more effective methods for dealing with increasing industrial waste and environmental pollution. Not only the contaminants generated in the process of production of certain materials and products, but also those forming as side effects of using the ready products must be removed. One of the most promising methods is that based on the use of membrane processes. These processes have been used in chemical industry (including petrochemical), pharmaceutical industry, production of food and drinks [1–3]. Numerous membrane installations are used for gases separation in chemical and petrochemical industry. They permit separation of volatile hydrocarbons from the stream of air or separate monomers from the stream of exhaust gases in

polymeric installations and direct them to the next stage of the process [4–7].

Membrane processes do not require dosing of chemical agents and do not involve transformations of pollutants, which saves resources, energy and labor, permitting rational water management and utilization of industrial waste. Modern membranes are effective in removal of pollutants from liquid phase [8–11], which is important from the point of view of the environment protection, and offers a possibility of recovery of valuable components, which is economically important.

A pressing problem is the pollution of water environment with heavy metals. Their increased content deteriorates the quality of drinking water and is hazardous to human health [12, 13]. Many methods have been proposed to curb their amount or to eliminate them from water, like e.g. extraction with solvents, coagulation and flocculation, electrocoagulation, adsorption on various materials or membrane separation. The latter method has been increasingly often applied because of high efficiency and low cost of the process [14–17]. There is one more important benefit from using membrane processes, by appropriate membrane modification it is possible to obtain membranes highly selective towards certain compounds [18].

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The membranes used for removal of pollutants from liquid phase are mainly made of polymers such as polypropylene, polysulfone, polyethersulfone, polycarbonates, polyamides and cellulose esters, including cellulose acetate [19–21]. The membranes made of cellulose acetate have found wide application in the pressure separation techniques, e.g. ultrafiltration or reversed osmosis [22, 23]. The efficiency of separation is determined not only by the type of polymer of which a given membrane is made, but also by the type of additive polymers stimulating pore generation [24]. A well-known and widely used method for the production of synthetic membranes is the inversion of phases, in which the scattering phase becomes the scattered phase and vice versa [25–27]. A mixture of the polymer, solvent and pore-generating agent is spread out on a substrate, e.g. glass, by a special knife, then the solvent is evaporated and the polymer is immersed in a bath with a non-solvent, e.g. distilled water [28–30].

The aim of this paper was the synthesis and characterization of membranes based on cellulose acetate and containing different amounts of pore generating agent (polyvinylpyrrolidone, PVP), in particular, determination of their ability to remove copper and iron ions from liquid phase.

Experimental

Materials

Cellulose acetate (CA, average $M_n \sim 30,000$) and polyvinylpyrrolidone (PVP, average wt% 10,000) were purchased from Sigma Aldrich. CA was used as a membrane polymer and PVP was used as a pore-generating agent. *N,N*-dimethylformamide (DMF, >99.8%) was purchased from Avantor Performance Materials Poland S.A. and used as a solvent.

The sources of copper and iron ions were copper(II) sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and ammonium iron(III) sulfate ($(\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O})$), from Avantor Performance Materials Poland S.A.

Preparation of CA Membranes

At the first stage of membrane preparation, the so-called membrane film was obtained by mixing appropriate amounts of reagents. Glass flasks were charged with 1, 2, 3 or 4 wt% of PVP and 85, 84, 83 or 82 wt% of DMF. Then each flask was placed on a magnetic stirrer and stirred at 600 rev./min. Then CA was added in portions, to the final content of 14 wt%. and then the flask was placed in a water bath and heated at 60 °C for 24 h, upon continuous stirring to release bubbles. After careful stirring of the components, the solutions were left on the magnetic stirrer to cool down to room temperature and then the films were prepared by

spreading the contents on a glass plate using a special knife Elcometer 3580 made by Sterlitech Corporation and left for 40 s to evaporate the solvent. The plate with the film was immersed in a coagulation bath of deionized water, to obtain membranes in the form of plane sheets of 300 μm in thickness. The particular samples were labelled as CA14 PVP1, CA14 PVP2, CA14 PVP3 and CA14 PVP4. The membranes obtained were washed for additional 24 h using deionized water bath conditioned at 25 °C.

Membrane Structure Characterization

Porosity and Equilibrium Water Content

Porosity of the membranes obtained was characterized on the basis of the membrane mass loss after drying. The membranes taken out of the deionized water were weighted and then placed in a drier at 60 °C for 24 h. After this time the membranes were weighted again and their porosity was calculated from Eq. (1):

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

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

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

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

Contact Angle

The contact angle between water and membrane surface was directly measured using a measuring instrument G10, KRUSS, Germany. Deionized water was used as a probe liquid (sessile drop technique) in all measurements. The contact angle between water and membrane was measured five times at random places for each sample and then the average was calculated.

Surface Oxygen Groups

The surface oxygen groups were characterized using potentiometric titration experiments with the help of 809 Titrando, Metrohm. The instrument was set in the mode of equilibrium pH measurement and recording. Membranes in the amount of about 0.05 g in 50 mL 0.01 M NaNO_3 were placed in a vessel thermostated at 25 °C and equilibrated for 1 h with the electrolyte solution. The suspension was stirred throughout the measurements. The volumetric standards NaOH (0.1 M) or HCl (0.1 M) were used as titrants [31].

Membrane Performance Characterization

Water permeability of the membranes prepared was measured in a stainless steel membrane module, for the effective membrane area of 19.6 cm². 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 Eq. (3):

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

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 Δt (h) is the permeation time.

The experiments were conducted with 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). All measurements were carried at 3 bar, in triplicate. The final concentration of iron or copper in the solution was determined using a double beam UV–Vis spectrophotometer Varian Cary 100 Bio. Measurements were made at 487 nm wavelength for iron solutions and at 620 nm wavelength for copper solutions. The amount of metal ions removed (in %) was found from the following equation:

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

where C_p is the concentration in the permeate (mg/L) and C_f is the concentration in the feed solution (mg/L).

Membrane resistance was calculated from Eq. (5):

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

where J is the permeate flux [L/(m²h)], ΔP is the transmembrane pressure, μ is the dynamic viscosity of permeate [Pa·s], and R_t is the total filtration resistance [m/s]. The total filtration resistance comprises three terms: resistance of the membrane (R_m), resistance of the pores that undergo blocking (R_p) and that of the filtration cake (R_c). The total filtration resistance was calculated from Eq. (6):

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

The flux recovery ratio (FRR) was studied as follows. Firstly, pure water flux of the membrane J_{w1} (L/(m²h)) was tested at 3 bar. After filtration of metal ions solution, the membrane was rinsed with deionized water for 10 min and then pure water flux of the membrane J_{w2} (L/(m² h)) was measured. The FRR was calculated from Eq. (7):

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

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

| Membrane | ϵ (%) | EWC (%) | Contact angle |
|-----------|----------------|---------|---------------|
| CA14 PVP1 | 46.08 | 83.09 | 65.4 ± 3.00 |
| CA14 PVP2 | 43.23 | 82.50 | 52.6 ± 7.68 |
| CA14 PVP3 | 52.93 | 83.40 | 53.5 ± 8.34 |
| CA14 PVP4 | 52.93 | 83.70 | 54.4 ± 2.98 |

Table 2 Acidic and basic properties of membranes [mmol/g]

| Membrane | Acidic groups | Basic groups | Total content of oxygen groups |
|-----------|---------------|--------------|--------------------------------|
| CA14 PVP1 | 4.58 | 2.61 | 7.19 |
| CA14 PVP2 | 4.51 | 1.72 | 6.23 |
| CA14 PVP3 | 4.60 | 1.70 | 6.30 |
| CA14 PVP4 | 4.42 | 1.65 | 6.07 |

Results and Discussion

Characterization of Membranes

Table 1 presents the structural parameters and contact angles determined for the series of membranes studied. Analysis of these results reveals that the values of these parameters are not directly related to the content of PVP in the membrane. The porosity of membrane CA14 PVP1 is 46.08%, while that for the membrane with 2% addition of PVP is 43.23%. Much higher values were obtained for membranes CA14 PVP3 and CA14 PVP4, of 52.93% for each of them. The differences in these values follow from the fact that pore distribution in the membrane is inhomogeneous. All membranes were characterized by similar values of EWC; for CA14 PVP1 it was 83.09%, for CA14 PVP2 it was 82.50%, for CA14 PVP3 and CA14 PVP4 the values of EWC were 83.40 and 83.70%, respectively. The highest contact angle value of 65.4 was found for the membrane with the lowest content of PVP. For the other membranes, the contact angle values were similar 52.6 for CA14 PVP2, 53.5 for CA14 PVP3 and 54.4 for CA14PVP4 with the highest content of PVP, which can be related to the hydrophilic properties of this polymer.

Membrane Performance

Table 2 presents the contents of acidic and basic oxygen groups on the surfaces of the membranes studied. The amounts of acidic oxygen groups are similar on the

surfaces of all membranes, on CA14 PVP1 their content was 4.58 mmol/g, on CA14 PVP2 – 4.51 mmol/g, on CA14 PVP3 and CA14 PVP4 their amounts were 4.60 and 4.42 mmol/g, respectively. The acidic surface oxygen groups were dominant on all membranes. The basic oxygen groups were present in much smaller amounts. They occurred in the greatest amount of 2.61 mmol/g on the surface of CA14 PVP1, while on the surfaces of the other membranes their amounts were smaller, varying from 1.65 to 1.72 mmol/g. Also the total content of oxygen groups on the surface of the membranes was the greatest, 7.19 mmol/g, on CA14PVP1 with the lowest content of PVP. The total content of oxygen surface groups on the other three membranes was 6.23 mmol/g for CA14 PVP2, 6.30 mmol/g for CA14 PVP3 and 6.07 mmol/g for CA14PVP4 with the greatest content of PVP.

The data on permeability of CA14 series membranes are presented in Fig. 1. The highest permeability after the filtration of iron solution of 165.58 L/m²h, is found for the membrane with 3 wt% of PVP, which is interpreted as related to the fact that this membrane shows the highest porosity. For the membrane with 4 wt% of PVP, the permeability of pure water flux is a little lower, 161.71 L/m²h. For membranes CA14 PVP1 and CA14 PVP2 the permeability increased with increasing content of PVP and took the values 54.95 and 78.25 L/m²h. After the filtration of copper ions solution, the highest permeability was measured for membrane CA14 PVP3 (168.74 L/m²h). For sample CA14 PVP4 the permeability was 138.45 L/m²h, while for the other two membranes the permeability was much lower 60.90 L/m²h for CA14 PVP1 and 35.22 L/m²h for CA14 PVP2.

Figure 2 presents results illustrating the efficiency of iron ions removal from the solutions of different iron concentrations by the membranes synthesized with different contents of PVP. Irrespective of the initial concentration of the solution, the most effective in iron ions removal were the membranes with the lowest contents of PVP, which removed 53 and 47% of iron ions. High capacity for iron ions removal

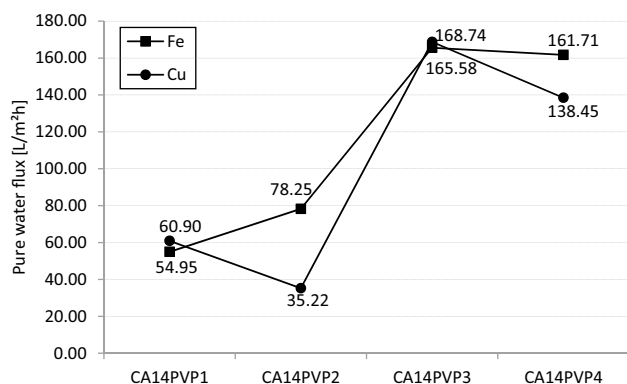


Fig. 1 Pure water flux of the membranes studied

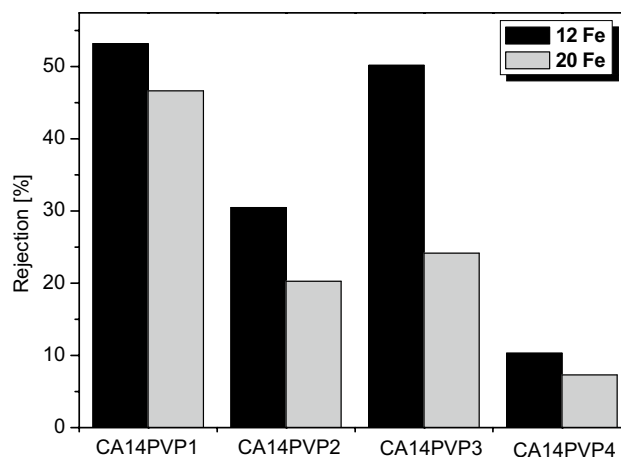


Fig. 2 Iron rejection of CA14 series membranes after filtration of an iron solution

(50%) was noted for membrane CA14 PVP3 when used for filtration of iron ions from the solution of 12 mg/L. The capacities for iron removal observed for the other two membranes were much smaller, of 30 and 10%. When filtration was performed from the solution of 20 mg iron ions/L, only sample CA14 PVP1 showed relatively good capacity for iron ions removal, while the other ones containing 2, 3 and 4 wt% of PVP were much less effective and their capacities for iron ions removal were 20, 24 and 7%. The most efficient in iron ions removal were the membranes with the lowest content of PVP, while the least efficient was that with the highest content of this pore generating polymer. It means that with increasing amount of pores the membranes lose the ability of effective removal of iron ions. The results also show that irrespective of the type of membrane the most effectively purified are the solutions of lower concentration of Fe³⁺ ions.

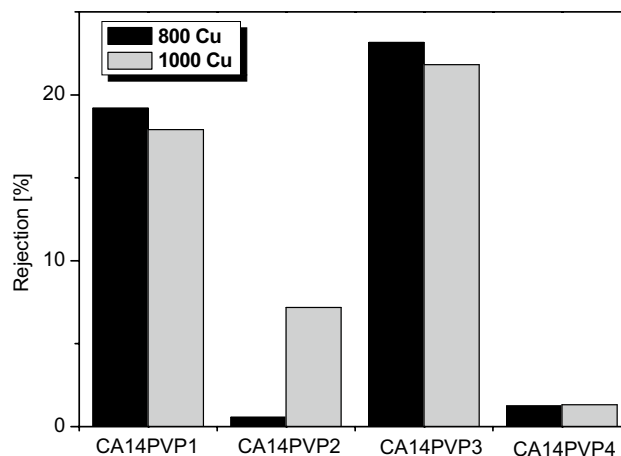


Fig. 3 Copper rejection of CA14 series membranes after filtration of a copper solution

Figure 3 presents the data characterizing sorption abilities of the membranes used for filtration of copper ions. The highest sorption capacity was obtained for membrane CA14 PVP3 which removed 23% of copper ions from a solution of the concentration 800 mg/L and 22% of copper ions from a solution of the concentration 1000 mg/L. The sorption capacity of membrane CA14 PVP1 was a bit lower, it removed 19% of copper ions from the solution of the initial concentration 800 mg/L and 18% of copper ions from the solution of 1000 mg/L. Membrane CA14 PVP2 removed 7% of copper ions from the solution of 1000 mg/L, while only 0.6% of copper ions from the solution of 800 mg/L. Membrane CA14 PVP4 showed very low sorption capacity towards copper ions, within 1%, irrespective of the solution initial concentration.

Figure 4 presents the degree of recovery of the membranes after filtrations of iron and copper ions, expressed in terms of the flux recovery rate (FRR). The value of this parameter informs about the membranes efficiency and about the theoretical possibility of their reuse for the filtration of solutions. After filtration of iron solutions, the values of FRR were the highest for CA14 PVP1 and CA14 PVP2, (Fig. 4a). FRR for CA14 PVP4 was lower and for CA14 PVP3 it was the lowest. After filtration of copper ions,

the highest FRR values were measured for CA14 PVP1 and CA14 PVP3 (Fig. 4b), while the lowest FRR was obtained for CA14 PVP4. No effect of the PVP content in the membrane on the FRR value was noted. When filtering copper solutions, for the majority of samples higher FRR values were obtained for the samples of lower initial concentration. The values evidence high effectiveness of the membranes studied. Moreover, the FRR values indicate the theoretical possibility of reuse of the membranes for removal of liquid phase pollutants. High FRR values mean that after filtration the membranes are effectively cleaned so the blocking of their pores and surfaces by the removed compounds is relatively small.

Table 3 presents the data on filtration resistance of the membranes used for the filtration of iron ions solutions. As follows from these data, the total filtration resistance R_t decreases with increasing content of the pore generating agent PVP, so from CA14 PVP1 to CA14 PVP4. The value of R_t for CA14 PVP1 was 8.37×10^{13} L/m²h, it was twice lower, 4.08×10^{13} L/m²h for CA14 PVP2, and for CA14 PVP3 and CA14 PVP4 it was 2.34 and 2.31×10^{13} L/m²h, respectively. The values of individual components of the total filtration resistance also decreased with increasing content of PVP, the exception was the membrane resistance which was a bit higher for CA14 PVP4 than for CA14 PVP3.

The values of different types of resistance determined for the membranes studied after filtration of copper ions are collected in Table 4. The highest components of resistance were measured for CA14 PVP2 whose total resistance is 12.82×10^{13} L/m²h and is much higher than the values obtained for the other membranes. The components of total resistance for this membrane were as follows: membrane resistance 2.99×10^{13} L/m²h, pore resistance 4.94×10^{13} L/m²h and cake formation resistance 4.89×10^{13} L/m²h.

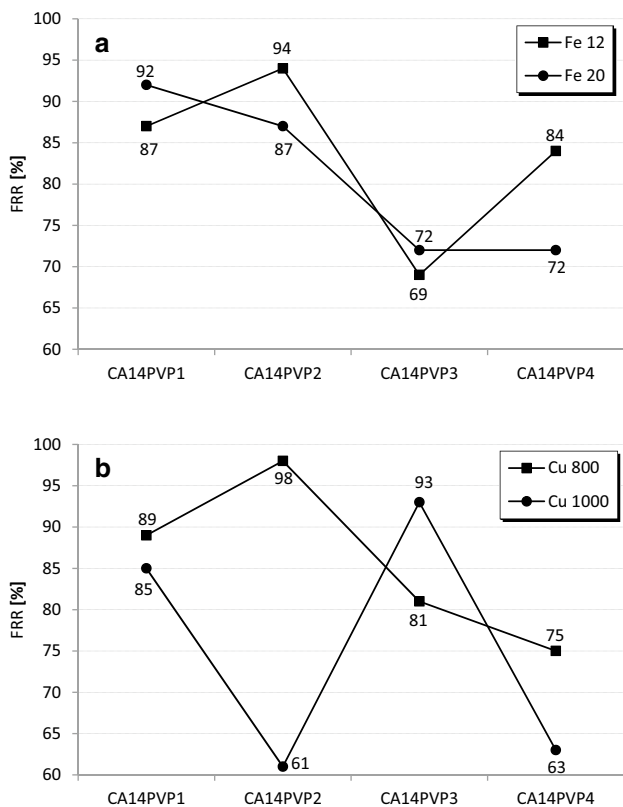


Fig. 4 Flux recovery ratio of membranes studied after filtration of a iron and b copper solution

Table 3 Filtration resistance of different membranes for iron solution

| Membrane | $R_m (\times 10^{13})$ | $R_p (\times 10^{13})$ | $R_c (\times 10^{13})$ | $R_t (\times 10^{13})$ |
|-----------|------------------------|------------------------|------------------------|------------------------|
| CA14 PVP1 | 2.70 | 2.93 | 2.74 | 8.37 |
| CA14 PVP2 | 1.25 | 1.43 | 1.40 | 4.08 |
| CA14 PVP3 | 0.64 | 0.89 | 0.81 | 2.34 |
| CA14 PVP4 | 0.68 | 0.85 | 0.78 | 2.31 |

Table 4 Filtration resistance of different membranes for copper solution

| Membrane | $R_m (\times 10^{13})$ | $R_p (\times 10^{13})$ | $R_c (\times 10^{13})$ | $R_t (\times 10^{13})$ |
|-----------|------------------------|------------------------|------------------------|------------------------|
| CA14 PVP1 | 1.64 | 1.91 | 1.93 | 5.48 |
| CA14 PVP2 | 2.99 | 4.94 | 4.89 | 12.82 |
| CA14 PVP3 | 0.63 | 0.67 | 0.63 | 1.93 |
| CA14 PVP4 | 0.68 | 1.07 | 0.99 | 2.74 |

Almost twice lower total resistance of 5.48×10^{13} L/m²h was measured for CA14 PVP1, while for CA14 PVP3 and CA14 PVP4 the values of total resistance were much smaller, 1.93 and 2.74×10^{13} L/m²h, respectively. It should be pointed out that after filtration of iron and copper ion solutions, the values of pore resistance and cake formation resistance are similar for all membranes and the membrane resistance brings the lowest contribution to the total resistance.

Conclusions

Analysis of the above presented results permits concluding that the amount of the pore generating polymer, PVP, used in the process of membrane syntheses, has a significant influence on the properties of membranes based on cellulose acetate. The addition of PVP causes an increase in porosity, equilibrium water content and is responsible for the fact that acidic oxygen groups dominate on the surfaces of the membranes. The content of PVP has a favorable effect on the membranes permeability. The membranes studied (CA14 PVP1–4) show better efficiency in removal of Fe³⁺ ions than Cu²⁺ ones, but with increasing content of PVP the efficiency of iron ions removal decreases. After the filtration of iron ions solutions the highest degree of recovery is observed for membranes CA14 PVP1 and CA14 PVP2, while after the filtration of copper ions solutions the highest recovery is measured for membranes CA14 PVP1 and CA14 PVP3. The total filtration resistance after the filtration of iron ions solutions decreases with increasing PVP content.

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