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THE MEMBRANE–CLEANERS INTERACTION EFFECT IN ULTRAFILTRATION

The effects of cleaning agents on the properties of ultrafiltration membranes made from polysulfonamide and polyvinylchloride were considered based on their immersion in cleaners. The membranes were exposed to the reagent solutions of various concentrations during different time intervals (one hour, one day, three days and seven days). The results were shown as function of water and protein flux, versus time, reagent concentration and pressure. Changes in water flux at each interval of immersion were owing to the increasingly soaking effect shown by solutions above their crucial micelle concentrations. The fouling index, I, was determined based on changes in flux of the used ultrafiltration membranes. The calculated β and R values (compressibility factor and membrane resistance) from the experimental results were considered as means of examining the membrane physical structure.

LIST OF SYMBOLS

β — compressibility factor,
R_i — resistance of the incompressible membrane during UF of pure solvent (Pa·s/m),
R_s — resistance due to compressibility of the membrane (Pa·s/m),
R_m — membrane resistance (Pa·s/m),
R_a — resistance owing to solute adsorption or adhesion in membrane (Pa·s/m),
PSA — polysulfonamide membrane,
PVC — polyvinylchloride membrane,
L_p — membrane hydraulic permeability (m/Pa·s),
ΔP_{tr} — transmembrane pressure (MPa),
$\Delta \pi$ — osmotic pressure (MPa),
J — permeate flux (m³/m²·s),
J_0 — permeate flux of pure solvent (m³/m²·s),
J_1 — permeate flux of pure solvent through the compressible UF membrane (m³/m²·s),
J_* — water flux prior to immersion in cleaners (m³/m²·s),
$J_{(a-d)}$ — water flux after immersion in cleaners at different periods of time (m³/m²·s),
$J_\&$ — protein flux (m³/m²·s),
J_s — water flux measured after ultrafiltration of protein (m³/m²·s),

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I – total fouling index,
S – interval (immersion time),
PWP   – pure water permeability (m/Pa·s),
t – current time (s),
f – friction coefficient (kg·Pa·s/m²·kmol),
C_b – solute concentration in feed (kg/m³),
C_p – solute concentration in permeate (kg/m³).

1. INTRODUCTION

Ultrafiltration (UF) is a widely accepted unit operation in a variety of industries. In principle, in the UF-operation, anisotropic membranes are mainly used and a pressure difference, as the driving force, is applied for the separation or concentration of components of differing molecular weights. The economy of the operation is highly dependent on maximizing the flux rate and the membrane life (durability). So the best way to create these conditions is the removal of membrane foulants by an in place cleaning procedure. These cleaning methods aim to restore the flux rates to the values observed at the beginning of UF process. Generally, water flux is taken into account in classifying the degree of cleaning that took place during the membrane contact with the cleaning agents, while the study of membrane cleaning is supposed to deal with fouled membrane–cleaners interactions. However, investigating the effect of cleaners on clean membrane seems still a very good way of understanding any kind of interactions occurring during membrane cleaning. This is because some of the assumptions accepted in the case of both cleaning and sanitizing agents were based on the experiments with the agents whose interaction with the membrane was not so significant as to affect membrane performance. Intriguing, a study of the literature indicates that this assumption is questionable. For example, during ultrafiltration of a cationic surfacant solution through Amicon UM-05 membrane, a comparatively large, irreversible reduction in flux was observed. Ultrafiltration of 1000 ppm solution of the anionic sodium dodecylbenzenesulfonate destroyed the membrane [3]. The use of a 1% Terg-a-zyme solution with Amicon PM membrane termed to be questionable by the membrane manufacturer, whereas the detergent producer recommends the use of 0.75% Terg-a-zyme. Furthermore, 0.002M Triton X-100 solution is considered to be compatible with Amicon PM membranes, while a 0.001M Triton X-100 solution resulted in a decrease in flux. Application of chlorine in the case of DDS GR6P membrane caused an increase in water flux but decreased drastically the whey flux [4]. It is self-evident that cleaning reagents influence the membrane performance and membrane life in different degrees. This fact called for an extensive study on any foreseeable phenomenon in determining the influence of cleaners in a given process. So monitoring closely both the flux and stress of the membrane soaked firstly in cleaning agents will be a better way in observing any changes that occur in membrane during the ultrafiltration

operation. Although much has been written on flux decline and membrane fouling but, to the best of my knowledge, there has not been a study of this kind, involving several times immersion of the same membranes in cleaners followed by its sequential runs of flux and stress measurements. The objective of this paper is to present one possible method in using fresh ultrafiltration membrane to search for any possible change in membrane structural behaviour owing to cleaning agents used.

2. THEORY

2.1. CHANGES IN THE PHYSICAL STRUCTURE OF THE MEMBRANE MATRIX

It is clearly understood that mechanical properties and physicochemical transformation of the membrane are highly dependent on polymer type as well as the membrane structure. Membrane resistance towards the driving force (pressure) has sometimes a negative effect on its performance. During ultrafiltration process membrane structure could be subjected to change at pressure. This in effect changes the supposed linear functions of permeate flux versus pressure or time during UF-operation. So long as the solvent is pure (e.g. distilled water), its flux J, passing through a membrane and induced by an applied pressure difference ΔP is given by Darcy's law:

$$J = L_p \Delta P \tag{1}$$

where L_p – the membrane hydraulic permeability, which could be defined as the reciprocal of the intrinsic hydraulic resistance to pure solvent R_m:

$$J = \Delta P_{tr}/R_m. \tag{2}$$

If the solution used contains solutes which are rejected by the membrane, then the proportion between the cause and the effect (e.g. changes in the pressure and exerted resistances) will no longer be true as in eq. (2). The reason of that is the concentration of macrosolutes near the membrane surface or their adhesion to the membrane, etc:

$$J = \Delta P_{tr}/R_m + R_s. \tag{3}$$

Because the solute concentration on the low-pressure side of the membrane is extremely low, some authors [8], [10]–[12] consider the existence of osmotic pressure based on the concentration difference across the membrane. This phenomenon caused the reduction of the pressure applied, and the permeate flux (eq. (2)) becomes:

$$J = (\Delta P_{tr} - \Delta \pi)/R_m. \tag{4}$$

Despite the fast increase of osmotic pressure with the wall concentration C_m this osmotic model does not explain the occurrence of a real limiting flux J. Thus, a decrease in mass transfer coefficient is invoked by some authors [16], [17] in order

to justify the limiting flux. Furthermore, various authors (e.g. LIGHTFOOT and KOZINSKI [5]) observed that the hydraulic resistance of a membrane is different before and after an UF operation, depending on the operating conditions and time. Therefore, eq. (3) becomes:

$$J = (\Delta P_{tr} - \Delta \pi)/(R_m + R_a) \tag{5}$$

where membrane resistance R_m is assumed to be stable

$$R_m = 1/[dJ/d(\Delta P_{tr})]_{\Delta P_{tr}}, \tag{6}$$

J increases proportionally with the increase in pressure, while membrane resistance R_m will hopefully increase, depending on the operating conditions and time [6]. At minimum value of applied transmembrane pressure ΔP_{tr} (approximately equal to zero), the membrane resistance R_m in eq. (2) is equal to incompressible membrane resistance R_i during ultrafiltration of a pure solvent:

$$R_i = \lim R_m \tag{7}$$

where $\Delta P_{tr} \to 0$.

And the value of R_i as this point is observed to have no effect on the membrane structure.

According to many authors [5], [9], the flux during membrane filtration could be defined by the following equation:

$$J = J_0 \cdot (\Delta P_{tr})^m \tag{8}$$

where $1 \leq m < 0$. This relationship is illustrated in figure 1.
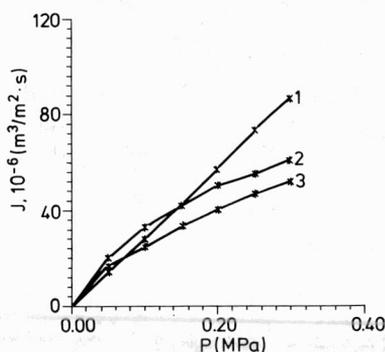
Fig. 1. Membrane permeability versus transmembrane pressure
1 – linear function, 2 – power function, 3 – membrane exponential function

Equation (8) does not meet physical conditions [6]. The better approximation of flux gives the following equation:

$$J = \Delta P_{tr}/R_i \cdot \exp(-\beta \Delta P) \tag{9}$$

where β is a compressibility factor (membrane deformation coefficient). The value of parameter β is an indication of a stable membrane structure. The stable structure means that the supposed resistance due to immersion in a given solution should be the sum of stable or normal membrane resistance, $R_m = R_i$, as well as the resistance exerted due to solution effects on membrane structure R_s:

$$R_s = R_i[\exp(\beta \varDelta P_{tr}) - 1]. \tag{10}$$

Therefore permeate flux of a solvent can be defined as follows:

$$J_i = \varDelta P_{tr}/[R_i + R_s]. \tag{11}$$

2.2. DETERMINATION OF FOULING INDEX

In the study of membrane performance, e.g. MWCO, a comparison of water fluxes before and after immersion in reagents is made. The ratio of the water flux before sampling (processing) to the water flux after sampling was defined as a convenient index of membrane fouling [7]. While absence of membrane fouling was indicated as a ratio of 1.0, the greater the fouling, the higher the ratio and vice versa.

The above mentioned index could be very helpful in observing the changes that took place during the ultrafiltration process. Possible determined fouling indexes, which may be anticipated during the ultrafiltration process, are listed below as follows:

$I_1 = J_*/J_{(a-d)}$ – membrane fouling effect due to stress, where $J_{(a-d)}$ are permeate fluxes after immersion for one hour (*a*), one day (*b*), three days (*c*) and seven days (*d*) (see table 4).

$I_2 = J_d/J_\&$ – membrane fouling effect coming from the membrane–reagent interactions plus the decline in flux caused by possible protein adsorption on the membrane.

$I_3 = J_\&/J_s$ – membrane fouling effect caused by interaction, degradation or shrinkage of the membrane.

$I = J_*/J_s$ – the total sum of membrane fouling effect that took place during the UF-operation ($I = I_1 + I_2 + I_3$).

3. EXPERIMENTAL

In the experiment, two types of membranes were used: 1) polyvinylchloride membranes made in the Technical University of Szczecin and 2) polysulfonamide membranes UMA-50 made by Waldipore (currently known as Waldi–Sartorious). Ultrafiltration tests for characterization of membrane performance were carried out in laboratory-scale unstirred batch cell with a volumetric capacity of 200 cm^3 and

filtration area of $1.194 \cdot 10^{-3}$ m^2. After filling with solution, the cell was pressurized by nitrogen gas delivered from a compressed gas cylinder through a pressure regulator. The pressure range was between 0 and 0.3 MPa. The cell was made of stainless steel and consists of two inlet channels for the feed solution and driving force (pressure) and one outlet channel for the permeate. The cleaners commonly used were applied as test materials (96% C_2H_5OH, 0.25M EDTA, 3% H_2O_2, 1% $Na_2S_2O_3 \cdot 5H_2O$). Water flux, as function of time, was studied at constant pressure 0.1 MPa prior and after stress measurements (J_* and $J_{(a-d)}$, respectively) of clean membranes.

The same membranes were immersed in cleaners at intervals of one hour, one day, three days and seven days. This was followed by a study in the range of 0–0.3 MPa (intervals S) with sequential runs of stepwise increase and decrease in pressure through the membrane as a stress test. After the above procedure the ultrafiltration of 0.1% bovine serum albumin at 0.1 MPa was carried out in order to measure the protein flux $J_\&$. Then the same membranes were cleaned by dilute solution of 0.1 n NaCl, 0.1 n HCl and 0.5 M NaCl for 30 minutes, respectively. Finally, the water flux was measured again for one hour and its value denoted by J_s. All the experiments were carried out at room temperature (21–23°C). It should be pointed out that before the ultrafiltration of 0.1% bovine serum albumin was carried out, the values of water flux and the stress flux were determined by both least square and Eureka computer program basing on the dependence of output quantities on the input variables for the entire region. The effect of membrane–cleaners interaction was verified by "including" the values of flux prior and after immersion in reagents, thereby introducing logarithmic equation of nonlinear function of flux J (eq. (9)) versus pressure difference ΔP_{tr}:

$$\ln[\Delta P_{tr}/J] = \ln R_i + \beta \Delta P_{tr}. \tag{12}$$

Graphical presentation of eq. (12) will indicate membrane resistance R_i to be an integral part of the membrane structure that can be affected by cleaners, if there exists an interaction between membrane, reagents and the solution treated. This actually prompted the investigation of influence of cleaners on membrane performance. Therefore any changes in membrane resistance exerted due to membrane–cleaning agents contact becomes:

$$R_s = R_i[\exp(\beta \Delta P_{tr}) - 1]. \tag{10a}$$

The additional membrane resistance during ultrafiltration of 0.1% bovine serum albumin was defined as follows:

$$R_a = \frac{\Delta P}{J_{min}} - (R_i + R_s + R_m). \tag{13}$$

This, in addition, was compared with the fouling index [7] values calculated from the variations of flux J and stress procedure as a control test of changes that took place during the operation

$$I = J_*/J_s. \tag{14}$$

4. RESULTS AND DISCUSSION

The effect of different cleaners on membrane performance was explicitly considered. Generally, the delay observed in flux J versus time due to continuous increase and decrease in the pressure applied at each step of the ultrafiltration was neglected due to an interval of 3 to 5 minutes for each flux measurement [6].
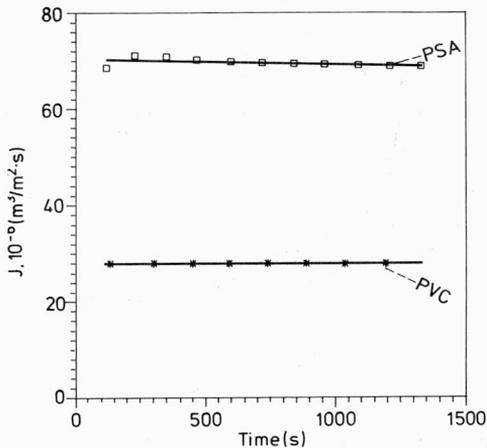
Fig. 2. Water flux versus time for the chosen membranes before contact with various cleaning agents

PSA – polysulfonamide membranes, PVC – polyvinylchloride membranes; applied pressure: 0.1 MPa
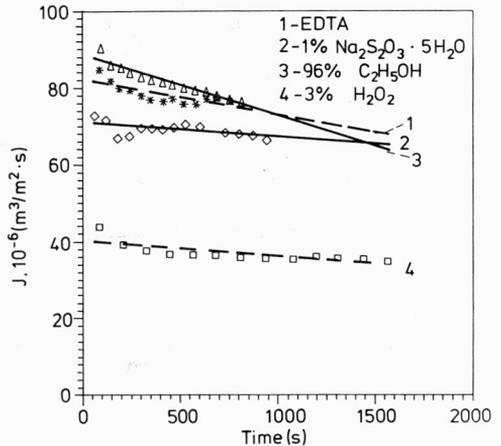
Fig. 3. Water flux versus time of ultrafiltration at 0.1 MPa for a PSA membrane being in contact with various cleaning agents for one hour

Measurements performed after stress test

Figure 2 shows the water flux versus time for the polysulfonamide and polyvinylchloride membranes (before immersion in cleaners). From figure 3 it can be seen that 96% ethanol and 0.25 M EDTA solutions caused a comparative increase in flux of the PSA membrane being 27.8% and 18.1%, respectively, while 3% hydrogen peroxide brought a 57% decrease in flux. For the same membrane immersed in 1% anhydrate thiosulphate solution no changes in flux were indicated. The reason for these changes (figure 3) could be an attack of the reagents on the amide bonds in the polysulfonamide membrane structure. In polysulfone, the aromatic groups are highly resistant to oxidation because the sulfur atom is in its highest oxidation state and the sulfone group tends to draw the electrons from the adjacent benzene rings which allows their stabilization and thus protection against oxidation. There also occur the oxygen molecules from this group, each having two unshared electrons to donate to strong hydrogen bonding of solute or solvent molecules [15].

Figure 4 shows 15.6% and 30.6% decline in flux for PVC membrane after immersion in 0.25 M EDTA and 96% ethanol solutions. 28.4% and 21.3% increase in flux for the 1% anhydrate thiosulfate and 3% hydrogen peroxide solutions was

observed. The membranes after immersion in hydrogen peroxide and anhydrate thiosulfate were found to be thicker and rolled together like toilet paper.

Results shown in figures 5 and 6 indicate that macrosolutes of bovine serum albumin form sediments on the membrane surface. The fact that some of these
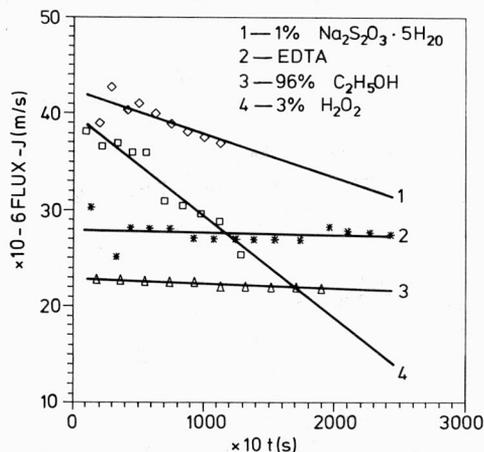
Fig. 4. Water flux versus time of ultrafiltration at 0.1 MPa for a PVC membrane being in contact with various cleaning agents for one hour
Measurements performed after stress test
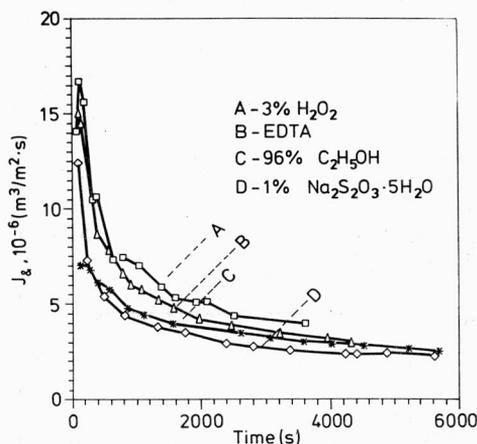
Fig. 5. Protein flux versus time for PSA membranes after their contact with various cleaning agents
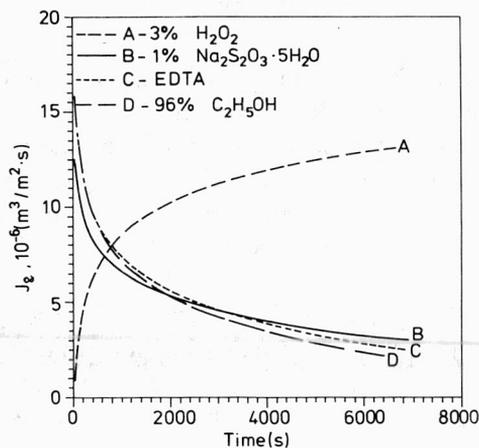
Fig. 6. Protein flux versus time for PVC membranes after their contact with various cleaning agents
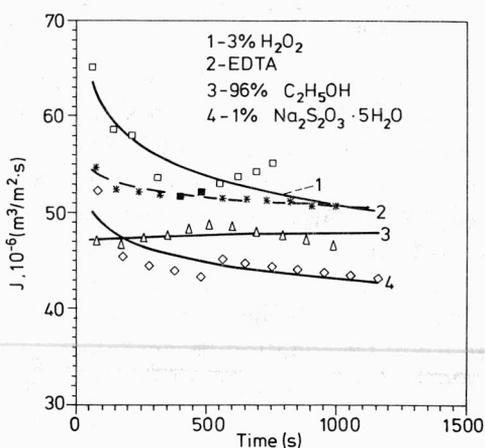
Fig. 7. Water flux versus time for the PSA membrane after the protein measurement and rinsing the membrane with cleaners (0.1 n NaOH, 0.1 n HCl and 0.5 M NaCl)
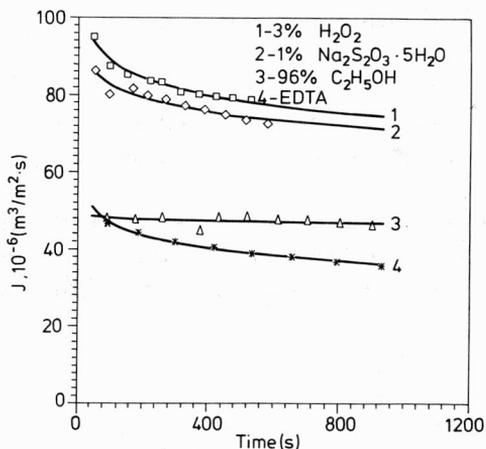
Fig. 8. Water flux versus time for the PVC membrane after the protein measurement and rinsing the membrane with cleaners (0.1 n NaOH, 0.1 n HCl and 0.5 M NaCl)
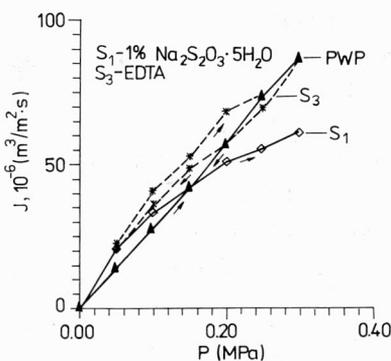
Fig. 9. Dependence of flux on pressure for the PVC membrane immediately after its contact with 0.25 M EDTA and 1% $Na_2S_2O_3 \cdot 5H_2O$ for one hour

The direction of measurements is indicated by arrows

Table 1

Experimental flux before and after the PVC and PSA membrane immersion in cleaners
(BS – before stress, PF – protein flux, APF – after protein flux)

Type of membrane	Cleaner	Flux $J \times 10^6$ $(m^3/m^2 \cdot s)$						
		BS	1 h	1 day	3 days	7 days	PF	APF
PVC 29.09	0.25 M EDTA	32.98	27.83	16.02	8.17	27.88	19.18	68.76
	3% H_2O_2	32.98	31.34	38.92	30.23	39.99	2.61	117.5
	1% $Na_2S_2O_3 \cdot 5H_2O$	32.98	21.35	17.78	18.11	42.35	19.85	105.5
	96% ethanol	32.98	17.50	20.25	18.20	22.88	15.27	50.52
PSA UAM-450	0.25 M EDTA	70.56	61.22	58.81	30.17	11.90	8.08	56.69
	3% H_2O_2	70.56	48.13	52.68	46.68	40.86	19.85	71.24
	1% $Na_2S_2O_3 \cdot 5H_2O$	70.56	68.43	49.27	24.28	70.89	17.50	54.60
	96% ethanol	70.56	70.98	77.26	68.65	88.74	16.57	46.65

macrosolutes can be deposited or finally adhered to membrane pores might be true owing to variation in rate of protein flux decline of the same membranes. Furthermore, there are the membrane cleaning agents which can dissolve, sequester or disperse these macrosolutes, thereby allowing their passing through the membrane pores. An exception from the supposed sedimented macromolecules (as shown

in figure 6) was the immersion of PVC membrane in 3% hydrogen peroxide solution. This, in fact, showed a total defect of the PVC membrane with visible holes in the membrane after the operation.

The repeated pure water flux measurements (figures 7 and 8) show a further failure or decline in flux. The explanation could be that in determining the membrane performance a longer contact time is needed in the case of the cleaning agents applied.

Table 1 presents the results of membrane compressibility test for the entire parameters. Membrane contact with commonly used reagents affected the water flux of clean membranes. This test procedure allows us to establish a proper cleaner for a given membrane.
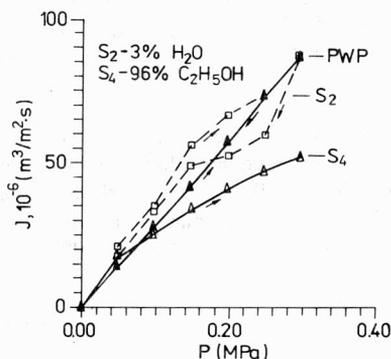
Fig. 10. Dependence of flux on pressure for the PVC membrane immediately after its contact with 96% C$_2$H$_5$OH and 3% H$_2$O$_2$ for one hour
The direction of measurements is indicated by arrows
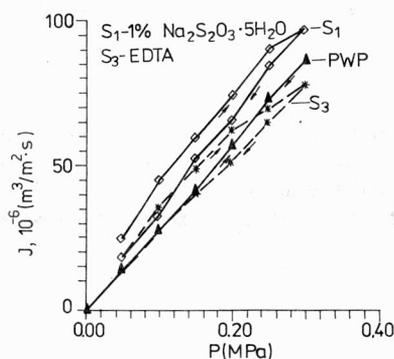
Fig. 11. Dependence of flux on pressure for the PVC membrane immediately after its contact with 0.25 M EDTA and 1% Na$_2$S$_2$O$_3\cdot$5H$_2$O for 7 days
The direction of measurements is indicated by arrows

In order to observe explicitly the physical changes in membrane structure, the membranes were subject to increasing and decreasing pressures. Figure 9 shows dependence of flux on pressure for the PVC membrane after its contact with 1% Na$_2$S$_2$O$_3\cdot$5H$_2$O and 0.25 M EDTA for one hour. This relationship shows that the PVC membrane flux versus pressure up to the value of 0.2 MPa for the curve S_1 is a straight line intersecting the origin of coordinate system with no hysteresis, whereas for the curve S_3 a slight increase in flux above the pure water permeability (PWP) curve with negligible hysteresis was observed. A similar experiment for PVC membrane having been in contact with 96% ethanol and 3% hydrogen peroxide for one hour proves that the curve S_4 after reaching the pressure of 0.15 MPa (fig. 10) is almost straight lying quite below the pure water permeability (PWP) curve, while for the curve S_2 a straight line intersecting the origin of coordinate system was observed (up to the value of 0.18 MPa). However, further increase in pressure up to 0.3 MPa and then decrease up to 0.05 MPa occurred simultaneously with both hysteresis and deviation in curves S.
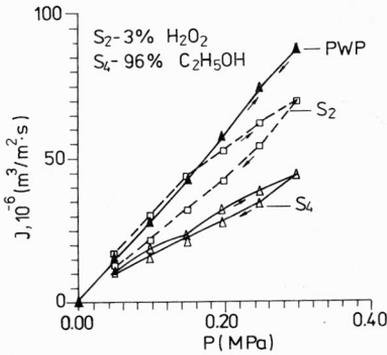
Fig. 12. Dependence of flux on pressure for the PVC membrane immediately after its contact with 96% C_2H_5OH and 3% H_2O_2 for 7 days
The direction of measurements is indicated by arrows
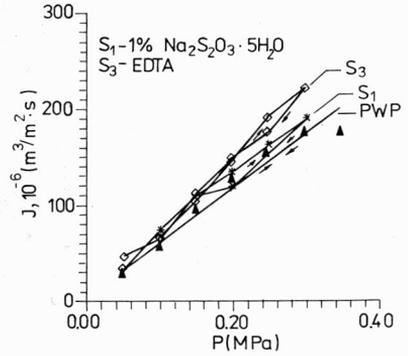
Fig. 13. Dependence of flux on pressure for the PSA membrane immediately after its contact with 0.25 M EDTA and 1% $Na_2S_2O_3 \cdot 5H_2O$ for one hour
The direction of measurements is indicated by arrows
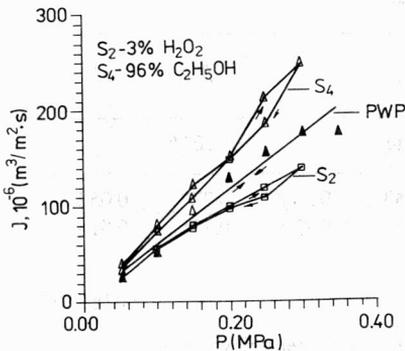
Fig. 14. Dependence of flux on pressure for the PSA membrane immediately after its contact with 96% C_2H_5OH and 3% H_2O_2 for one hour
The direction of measurements is indicated by arrows
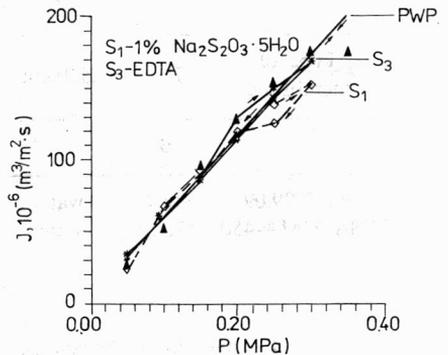
Fig. 15. Dependence of flux on pressure for the PSA membrane immediately after its contact with 0.25 M EDTA and 1% $Na_2S_2O_3 \cdot 5H_2O$ for 7 days
The direction of measurements is indicated by arrows

In figures 11 and 12, the same parameters and conditions as in figures 9 and 10 are presented, with one exception only which concerns the contact time, being 7 days instead of one hour. This gives examples of the flux variation with pressure for curves S_1 and S_3 as compared to figure 9 with a higher value of flux than the pure water permeability (PWP) value. For the curve S_4 as compared to figure 10, the flux versus pressure was the same after immersion for 7 days, while for the curve S_2 a comparatively slight change in flux was observed.
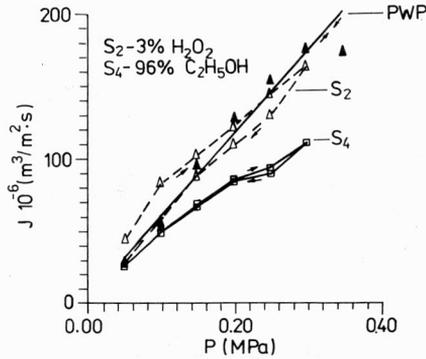
Fig. 16. Dependence of flux on pressure for the PSA membrane immediately
after its contact with 96% C_2H_5OH and 3% H_2O_2 for 7 days
The direction of measurements is indicated by arrows

Table 2a

Changes in membrane resistance $R_{(o, o')}$ and its tangential value β after immersion of
membrane in water. BS – water flux before immersion in cleaning agents,
β value here is constant

Type of membrane	Flux	Solvent	R_o	$R_{o'}$	β	β'	$\Delta\beta$
	BS		$\times 10^9$ (Pa·s/m)			$\times 10^{-6}$	
PVC 29.09	32.98	water	3.249	3.253	0.685	0.737	0.052
PSA UMA-450	70.56	water	1.760	1.727	0.270	0.285	0.015

Table 2b

Changes in membrane resistance $R_{(o, o')}$ and its tangential value β
after immersion of membrane in cleaning agents for one hour

Type of membrane	Cleaner	R_o	$R_{o'}$	β	β'	$\Delta\beta$
		$\times 10^9$ (Pa·s/m)			$\times 10^{-6}$	
PVC 29.09	0.25 M EDTA	2.270	2.849	1.587	1.104	0.483
	3% H_2O_2	2.175	2.594	1.369	0.771	0.598
	1% $Na_2S_2O_3 \cdot 5H_2O$	3.098	4.154	1.457	0.831	0.626
	96% ethanol	2.881	4.009	2.458	1.478	0.980
PSA UMA-450	0.25 M EDTA	1.736	2.070	0.683	0.260	0.423
	3% H_2O_2	1.367	1.553	0.463	0.221	0.242
	1% $Na_2S_2O_3 \cdot 5H_2O$	1.250	1.380	0.354	0.464	−0.110
	96% ethanol	1.275	1.499	0.143	0.557	−0.414

Changes in membrane resistance $R_{(o, o')}$ and its tangential value β
after immersion of membrane in cleaning agents for one day

Type of membrane	Cleaner	R_o	$R_{o'}$	β	β'	$\Delta\beta$
		$\times 10^9$ (Pa·s/m)			$\times 10^{-7}$	
PVC 29.09	0.25 M EDTA	1.917	2.511	1.391	6.001	−4.610
	3% H_2O_2	3.926	5.809	1.731	4.558	−2.827
	1% $Na_2S_2O_3 \cdot 5H_2O$	3.326	5.048	1.730	6.109	−4.379
	96% ethanol	3.119	4.230	2.030	8.430	−6.400
PSA UMA-450	0.25 M EDTA	1.806	1.930	1.174	1.850	−0.676
	3% H_2O_2	1.709	1.867	3.016	5.323	−2.313
	1% $Na_2S_2O_3 \cdot 5H_2O$	1.933	2.169	4.345	9.081	−4.736
	96% ethanol	0.831	1.267	1.537	1.733	−0.196

Changes in membrane resistance $R_{(o, o')}$ and its tangential value β
after immersion of membrane in cleaning agents for three days

Type of membrane	Cleaner	R_o	$R_{o'}$	β	β'	$\Delta\beta$
		$\times 10^9$ (Pa·s/m)			$\times 10^{-6}$	
PVC 29.09	0.25 M EDTA	1.818	2.820	2.473	1.135	1.338
	3% H_2O_2	6.224	9.878	2.477	1.174	1.303
	1% $Na_2S_2O_3 \cdot 5H_2O$	3.557	4.874	1.650	0.717	0.933
	96% ethanol	3.340	5.066	1.603	0.725	−0.878
PSA UMA-450	0.25 M EDTA	1.350	1.513	1.333	0.420	0.913
	3% H_2O_2	2.556	3.318	0.781	0.208	0.573
	1% $Na_2S_2O_3 \cdot 5H_2O$	2.317	4.807	1.254	1.234	0.020
	96% ethanol	1.300	1.527	0.818	0.378	0.445

The graphical results in figures 13–16 for the PSA membranes and the others not reported here (membranes immersed in reagents for 1 day and 3 days) showed that the shapes of lines and curves are similar.

The fact that the relationship between flux and pressure deviates from a straight line at a certain value of pressure proved critical pressure limit for the applied membrane reported by various authors [2], [5], [7]. Due to membrane contact with cleaning agents this limiting value can vary. Investigation of the same membranes after immersion in cleaners indicated quite a different deviation in relationship between flux and pressure, as in the case of PWP line representing the clean membrane.

Changes in membrane resistance $R_{(o, o')}$ and its tangential value β
after immersion of membrane in cleaning agents for seven days

Type of membrane	Cleaner	R_o	$R_{o'}$	β	β'	$\Delta\beta$
		$\times 10^9$ (Pa·s/m)			$\times 10^{-6}$	
PVC 29.09	0.25 M EDTA	2.910	4.276	1.284	1.225	0.059
	3% H_2O_2	2.445	3.619	1.433	2.028	−0.595
	1% $Na_2S_2O_3 \cdot 5H_2O$	1.882	2.746	1.629	3.218	−1.589
	96% ethanol	3.663	4.649	1.818	1.227	0.591
PSA UMA-450	0.25 M EDTA	1.736	2.320	0.155	0.752	−0.597
	3% H_2O_2	1.492	1.650	0.511	0.281	0.230
	1% $Na_2S_2O_3 \cdot 5H_2O$	1.776	1.690	0.055	0.329	−0.274
	96% ethanol	1.030	1.728	2.055	0.322	1.733

Table 3

Friction coefficient f and the rate of membrane flux decline Q of bovine serum albumin
after immersion of membrane in cleaning agents

Type of membrane	Mean pore diameter	Cleaner	R_a $\times 10^{-10}$	ΔP	$\Delta\pi$	C_b	C_p	Q	$f \times 10^{-8}$
	$r \times 10^9$ (m)		$\left(\dfrac{Pa \cdot s}{m}\right)$	$\times 10^{-1}$ (MPa)		(kg/m³)		$\left(\dfrac{1}{s} \cdot 10^3\right)$	$\left(\dfrac{Pa \cdot s \cdot kg}{m^2 \cdot kmol}\right)$
PVC 29.09	46.4	0.25 M EDTA	2.579	1.0	0.03	0.904	0.067	0.1138	0.9574
	46.4	3% H_2O_2	1.872	1.0	0.02	0.858	0.112	1.8801	0.0293
	46.4	1% anhy. thiosul.	3.810	1.0	0.02	0.805	0.391	0.7433	0.0297
	46.4	96% ethanol	3.862	1.0	0.03	0.878	0.359	0.4003	0.0677
PSA	39.8	0.25 M EDTA	1.926	1.0	0.03	0.934	0.038	3.5190	0.0109
UMA-450	39.8	3% H_2O_2	0.323	1.0	0.05	1.875	0.029	1.2601	0.3639
	39.8	1% anhy. thiosul.	1.775	1.0	0.05	1.876	0.050	1.4413	0.2494
	39.8	96% ethanol	2.057	1.0	0.05	1.995	0.065	1.7822	0.0574

Furthermore, the values of additional resistance R_a (table 3) indicate that the
phenomenon of concentration polarization is negligible. The test solution of memb-
rane-cleaning agent has no effect on adsorption layer that depends on the distance from
the leading edge of the membrane. In addition, one of the reasons of decrease in flux (as
earlier mentioned in this paper) could be shrinking effect (e.g. PSA-membrane in 1%
$Na_2S_2O_3 \cdot 5H_2O$ solution, fig. 3) and wearing effect (e.g. PVC membrane in 96%
ethanol, fig. 4).

Fouling index values of the membrane (based on experimental results)

Type of membrane	Cleaner	Fouling index						
		$I_{(1a)}$	$I_{(1b)}$	$I_{(1c)}$	$I_{(1d)}$	I_2	I_3	I
PVC 29.09	0.25 M EDTA	1.052	0.847	1.091	0.825	−15.30	−45.00	0.281
	3% H_2O_2	1.185	2.059	4.037	1.183	1.454	3.585	0.480
	1% $Na_2S_2O_3 \cdot 5H_2O$	1.545	1.855	1.821	0.779	2.134	5.315	0.313
	96% ethanol	1.885	1.630	1.812	1.441	1.498	3.308	0.653
PSA	0.25 M EDTA	1.466	1.340	1.512	1.727	2.058	3.589	0.990
UMA-450	3% H_2O_2	1.153	1.200	2.339	5.955	3.734	7.016	1.245
	1% $Na_2S_2O_3 \cdot 5H_2O$	1.031	1.432	2.906	0.995	4.051	3.120	1.292
	96% ethanol	0.994	0.913	1.028	0.795	5.355	2.802	1.513

The increase in flux could be attributed to such factors as unblocking of the already existing pores by the cleaning solution or the contraction of the membrane molecular structure due to membrane–cleaning solutions interactions. Long time of immersion would be the cause of penetration of some solutes through the membrane, and/or their adhesion to the membrane pores should be suspected. However, this kind of interactions between the membrane and reagents depends much on hydrophilic nature of the membrane as well as critical micelle concentration of the cleaning agents. This will be one of the areas to be extensively investigated in next paper.

From the constants determined (table 2b–e), a relationship was developed to cover explicitly the changes that might have occurred during the membrane stress (e.g. different values of β and $R_{(o, o')}$ for the same membranes). This is caused by different reagents applied.

It could be admitted that the hystereses observed and the differences in PWP curves representing flux vs pressure before and after immersion of the membrane in cleaning agents (figures 9–16) indicate the effect of cleaners on membrane properties. While the same membranes tested in pure solvent (table 2a) exhibit no changes in membrane matrix (e.g. $R_o = R_{o'}$; $\beta = \beta'$). The changes in membrane friction factor f (table 3) are the sum of influence of cleaners and the solution treated on the membranes used.

The fouling index values, which indicate great changes in membrane flux behaviour, are presented in table 4. The index value higher than one ($I > 1$) provides evidence of increase in flux caused by reduction in normal membrane resistance due to unblocking of some blocked pores, increasing early existing pores or holes (e.g. PVC membrane contacted in 3% hydrogen peroxide, fig. 6). Index value lower than one ($I < 1$) indicates that decrease in flux is due to membrane–reagents interactions (e.g. damage or loss of quality of the membrane surface and reduction of the membrane-stress flux after immersion in alcohol for seven days, fig. 8).

5. CONCLUSIONS

Alcohol and EDTA brought about increase in flux for the PSA membranes, while the same reagents caused decrease in flux for the PVC membranes. There is a decrease in flux for PSA membrane caused by hydrogen peroxide, while a comparative increase in flux was observed with the same solution in the case of the PVC membrane. For this reason examining the membrane–cleaner contact prior to its usage, despite the already provided specifications, is highly recommended. The attempt presented will help in eliminating irregularities in membrane performance.

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WPŁYW ŚRODKÓW CZYSZCZĄCYCH NA WŁAŚCIWOŚCI MEMBRAN

Przedstawiono wpływ środków czyszczących na właściwości membran ultrafiltracyjnych. Membrany z polisulfonamidu i poli(chlorku winylu) były zanurzane w roztworach reagentów o różnych stężeniach. Czas płukania membran wynosił jedną godzinę, jeden dzień, trzy i siedem dni. Wyniki badań przedstawiono w formie zależności strumienia wody i białka przechodzącego przez membranę od czasu zanurzenia, stężenia środka płuczącego w kąpieli i ciśnienia. Zmiany wartości strumienia wody wraz z wydłużaniem czasu zanurzenia w kąpieli płuczącej spowodowane były wzmagającym się efektem nasiąkania membrany środkiem czyszczącym. Indeks blokowania membran został określony na podstawie zmian wartości strumieni cieczy przechodzących przez membranę ultrafiltracyjną. Na podstawie otrzymanych wyników wyznaczono wartości współczynników ściśliwości i oporności membran. Parametry te mogą być wykorzystane do oceny fizycznej struktury membran.

ВЛИЯНИЕ ЧИСТИТЕЛЬНЫХ СРЕДСТВ НА СВОЙСТВА МЕМБРАН

Представлено влияние чистительных средств на свойства ультрафилтрационных мембран. Мембраны из полисульфамида и поли(винилхлорида) погружали в растворах реагентов разных концентраций. Время промывания мембран составляло один час, один день, три дня и семь дней. Результаты исследований были представлены в виде зависимостей струи воды и проходящего через мембрану белка от времени погружения, концентрации промывающего средства в ванне и давления. Изменения значений струи воды вместе с продлением времени погружения в промывающей ванне были вызваны увеличивающимся эффектом промокания мембраны чистителным средством. Индекс блокирования мембран был определен на основе изменений значений струй жидкостей, проходящих через ультрафильтрационную мембрану. На основе полученных результатов определены значения коэффициентов сжимаемости и устойчивости мембран. Эти параметры можно использовать для оценки физической структуры мембран.