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Separation of organic compounds by reverse osmosis and diafiltration

Theses of the Doctoral Dissertation

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References

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Abstract

The dissertation is focused on the separation of organic compounds by reverse osmosis and diafiltration. The theoretical part is devoted to a detailed description of reverse osmosis and factors that can affect the separation process. In the experimental part of the work, the influence of process parameters, such as the applied pressure difference ΔP and the concentration of compounds, on membrane performance, was studied. The knowledge gained was further applied in experimental work and diafiltration. Another topic of the experimental part was the investigation of membrane stability in binary mixtures and mathematical modelling there of. A solution diffusion model was performed to verify its feasibility for reverse osmosis separation of organics in binary mixtures.

Abstrakt

Disertační práce je zaměřena na separaci organických látek s využitím reverzní osmózy a diafiltrace. Teoretická část je věnována detailnímu popisu reverzní osmózy a faktorů, které mohou ovlivňovat separaci organických látek. Experimentální práce se zabývala vlivem vybraných procesních parametrů, aplikovaný tlakový rozdíl ΔP a koncentrace látek, na výkon membrány. Nabyté znalosti byly aplikovány v průběhu dalších experimentů a diafiltrace. Část práce byla také věnována stabilitě membrány v roztocích organických látek a matematickému modelování, konkrétně ověření vhodnosti základního modelu rozpouštění-difuze pro separaci organických látek z binárních směsí.

Keywords

Reverse osmosis, separation of organic compounds, dealcoholisation, membrane stability, diafiltration, solution-diffusion model

Klíčová slova

Reverzní osmóza, separace organických látek, dealkoholizace, stabilita membrány, diafiltrace, model rozpouštění–difuze

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1. INTRODUCTION

Reverse osmosis is a well-known process within the desalination industry. With increased necessity for wastewater treatment, the interest in the removal of micropollutants from water streams is also growing. Micropollutants are different organic compounds that are used on daily basis e.g., pharmaceuticals, hormones, pesticides. The concentration of these compounds is, in many cases, under the detection limit and thus the emergency of their presence in water was underestimated for a long time [1].

Despite being used in wastewater treatment, reverse osmosis is also applied as an alternative in the food and beverage industry, especially in the field of preserving thermosensitive compounds with high added value such as aromas, flavors, or bioactive functional extracts [2]. The main interest can be divided into the following areas:

- Production of nonalcoholic beverages.

- Product concentration.

- Recovery of bioactive compounds.

Within the past decades a tremendous effort has been made in the production of nonalcoholic beverages (e.g. beer and wine). The main challenge is the preservation of compounds responsible for aroma and taste profile. Whereas these compounds were damaged using thermal processes, RO achieved satisfying results, especially in diafiltration mode [3].

Besides nonalcoholic beverage production, RO is also utilized in juice concentration. This process is focused on the removal of water from juice where the final concentrated product should still contain the full spectrum of aroma and flavor. Concentration reduces the need for special storage and transport, thus reducing production and shipping costs. [4]

The third major application area of RO is focusing on the recovery of bioactive compounds and natural botanic extracts. Often these high-added-value compounds are gained from waste streams, where special processing can make reuse possible [5].

The various uses of RO in different fields is highly attractive, however, the application itself is One of the main challenges is the separation of organic compounds and their retention by the membrane. Conventional mathematical models describing RO were tested but no satisfactory results could be observed [6]. This is mainly caused by the immense complexity of applied separation mechanisms during the treatment of water-organic solvent solutions.

The focus of this work is to gain a more detailed understanding of the separation of organic substances from aqueous solutions using reverse osmosis and the study of parameters that influence the separation process.

2. THE AIM OF THE THESIS

The conducted research focused on the feasibility of the separation of organic substances using reverse osmosis. Organic solvents (e.g. lower alcohols and ethyl acetate) are substances that are used in chemical and pharmaceutical production.

It is noteworthy that the exact mechanism of separation is still not known, despite the number of studies dealing with this topic [7]. The main reason is the fact that the separation process is very complex and is influenced by a large number of factors. These are primarily process parameters (pressure, temperature, concentration of substances), physical and physicochemical properties of both the separated components and the membrane itself [8].

So far, most published studies worked with only one organic substance and often in low concentration in an aqueous solution. The influence of substance concentration on the rejection factor R and permeate flux J_p has not been investigated in more detail [9], and few works were also devoted to the separation of multicomponent systems and especially to diafiltration [10].

The aim of this work is therefore to study the separation of selected organic substances on spiral wound reverse osmotic membranes. In addition, the work focused on following sub-objectives:

- Choose suitable model systems of organic substances and verify the possibility of their separation in reverse osmosis.

- Investigate the influence of the applied pressure difference ΔP and the concentration of the compound in the binary system on the permeate flux J_p and the observed rejection R for different membranes. For the selected membrane, test multi-component systems and compare the rejection of individual components.

- Assess the influence of the physicochemical properties of the substance on the actual separation process.

- Assess the suitability of the basic solution-diffusion model for describing the separation of binary mixtures.

- Based on previous measurements, choose suitable conditions, and perform diafiltration of a multi-component mixture with a constant volume in the tank.

3. THEORETICAL PART

Pressure driven membrane processes use a difference in applied pressure between feed and permeate side of the membrane as driving force. This group of membrane processes includes microfiltration, ultrafiltration, nanofiltration and reverse osmosis, where the applied pressure difference ΔP, type of membrane and applied separation mechanism are varied.

The main performance parameters studied for pressure driven membrane processes are rejection factor R (equation 1) and permeate flux J_p (equation 2).

$$R = 1 - \frac{c_P}{c_F} \tag{1}$$

Where c_P is the concentration of the compound in the permeate and c_F is the concentration of the compound in feed.

$$J_P = \frac{1}{S}\frac{V_P}{\tau} \tag{2}$$

V_P is the volume of permeate obtained per unit of time τ related to the area of the membrane S [11].

The solution-diffusion model

The basic solution-diffusion model was applied for the modelling of binary mixtures. The actual mechanism is realized in three steps: sorption of the substance on the membrane surface, diffusion and desorption on the permeate side.

The following assumptions apply to the above model:

- Membrane is non-porous.
- Immediate formation of equilibrium between the liquid and the membrane on the feed and permeate side.
- The phenomenon of absorption and desorption prevails over diffusion.
- The pressure in the membrane is constant and the chemical potential of the component is expressed only as a concentration gradient [12].

When describing the solution-diffusion model, a binary mixture of solvent (water) i and solute j is considered. As already mentioned above, the pressure on the injection side and in the membrane is constant, while the change only occurs on the permeate side.

The flux of i-compound and j-compound is described by equations (3) and (4).

$$J_i = A * (\Delta p - \Delta \pi) \tag{3}$$

Where A is the permeability of solvent (water), Δp is the applied pressure difference and $\Delta \pi$ is the difference in osmotic pressure of feed and permeate. In case of J_j, the B expresses the permeability of dissolved species (organic compound). The diffusion coefficient D_j, sorption coefficient K_j and thickness of membrane is included in this

parameter. The concentration of organic compound in membrane on feed side is described by $c_{j,M,0}$, whereas the concentration of j-compound in permeate is $c_{j,p}$.

$$J_j = J_i c_{j,p} = B * (c_{j,M,0} - c_{j,p}) = \frac{D_j^M K_j}{\Delta x} (c_{j,M,0} - c_{j,p}) \qquad (4)$$

Rejection of j-compound normally is calculated by eqaution (1), but a relation between water flux J_p and parameter B was found (equation 5).

$$R_j = \frac{J_i}{J_i + B} \qquad (5)$$

Estimation of parameter B from experimental data

Parameter B was determined by the MS Office Excel tool with the solver function. The minimization of the root mean square deviation of the experimental and calculated rejection values was selected (equation 6) to optimize the estimation of parameter *B* (equation 5). The determination of the parameter B was considered for each substance, specific concentration, and each membrane.

$$\sigma_{n-1} = \sqrt{\frac{\sum_{i=1}^{n}(R_{exp,i} - R_{model,i})^2}{n-1}} = min \qquad (6)$$

Estimation of parameter B from experimental data

The concentration polarization at the membrane surface can be specified by using the parameter β [11]. The β factor is equal to the ratio of the compound concentration on the surface of the membrane and the concentration of the substance in feed (equation 7).

$$\beta = \frac{c_{j,M,0}}{c_{j,F}} \qquad (7)$$

The parameter β can be determined based on the knowledge of parameter *B*, experimentally measured compound concentration in the permeate and flux J*p*. It was calculated for all substances, different concentrations and applied pressure difference *ΔP*.

$$\beta * c_{j,F} = \frac{\frac{c_{j,P} J_p}{B} + c_{j,P}}{c_{j,F}} \qquad (8)$$

Estimation of concentration j-compound in the permeate

The predicted values of concentration *j*-compound in the permeate can be calculated by knowing parameters *A*, *B*, *β*,. The constant k_{osm} applies to different osmotic pressure equations and equals the expression of the constants included in equation.

To solve equation (9), the MS Excel and the Solution Search tool were used to calculate the concentration $c_{j,p}$. The goal was to minimize the function (9) and thus find the concentration $c_{j,p}$) [13].

$$c_{j,p}^2 + \left(\frac{\Delta P}{k_{osm}} + \frac{B}{k_{osm} * A} - \beta * c_{j,F} \right) c_{j,p} - \frac{B}{k_{osm} * A} \beta * c_{j,F} = 0 \qquad (9)$$

Osmotic pressure calculation

The osmotic pressure of feed and permeate solution was calculated by two Van´t Hoff equations - the general Van´t Hoff equation (10) and a modified Van´t Hoff equation (11).

$$\pi = -\frac{RT}{v_i} \ln a_w \qquad (10)$$

Where v_i described water molar volume, a_w is activity of water, R is universal gas constant and T is thermodynamic temperature.

$$\pi = c_i RT \qquad (11)$$

The physicochemical properties of molecules

Several recent studies have investigated the transport mechanisms of organic solutes through NF/RO membranes [3, 8, 9, 14]. The comprehensive study [15], where neural a network technique was used, focused on the determination of important parameters affecting organic solute rejection. The parameters can be divided into several groups:

- Solute description – molecular weight, length, equivalent molecular width, log Ko/w.

- Membrane characteristics – MWCO, sodium chloride and magnesium sulfate rejection, contact angle, zeta potential.

- Operational conditions – pH, pressure, and recovery.

Therefore, a fundamental understanding of the chemical and physical mechanisms of the RO membrane rejection is of great importance.

This study is focused on the separation of selected organic compounds which are used in the beverage or pharmaceutical industry, specifically alcohols in homologous order and maltose. These compounds were studied in binary, ternary, and multicomponent model solutions at relatively high concentrations and compared to published studies. The impact of each selected solute on the process performance permeate flux J_p and solute's rejection R was studied. The knowledge gained was used in a diafiltration process.

4. EXPERIMENTAL PART

Three different spiral wound reverse osmosis membranes were studied, their specification is shown in Table 1.

Table 1 Membrane specification [16-18]

	M1	M2	M3
Producer	GE Power&Water	Hydranautics	Hydranautics
Model	SG2540F30	ESPA2	ESPA4
Area	2.6 m^2	2.3 m^2	2.3 m^2
R$_{NaCl}$	98.5%	99.6%	99.2%

Model solutions

The composition of model solutions was designed according to the aims presented previously. Binary, ternary and multicomponent solutions. were prepared as a mixture of organics and demineralized water with conductivity 8.0 ± 1.0 µS cm^{-1}. The experiments were focused on the work with the following substances: ethanol, *n*-propanol, *i*-propanol, butanol, ethyl acetate and maltose. These compounds were selected as representatives of basic ingredients in beverages (aroma compounds in beer, wine, juices) and industry (e.g., solvents in pharmaceutical industry).

The presence of the organic compounds and their concentrations are listed in the Table 2-4.

Table 2 Selected organics and their concentration in the model solution – binary solution

		Binary mixtures				
		compound – concentration				
	Mixture	**0**	**1**	**2**	**3**	**4**
		2 g l^{-1}	0,15 mol l^{-1}	0,30 mol l^{-1}	0,45 mol l^{-1}	0,60 mol l^{-1}
1	Ethanol	-	M1-M3			
2	*n*-propanol	-				
3	*i*-propanol	-				
4	butanol	-	M1-M3	M1-M2		
5	ethylacetate	-				
6	maltose	M3	-			

Table 3 Selected organics and their concentration in the model solution – ternary solution

Ternary mixtures M3				
	compound – concentration			
Mixture	Maltose	ethanol	*n*-propanol	*i*-propanol
7	2 g l^{-1}	0,6 mol l^{-1}		
8	2 g l^{-1}		0,6 mol l^{-1}	
9	2 g l^{-1}			0,6 mol l^{-1}

Table 4 Selected organics and their concentration in the model solution – multicomponent solution

Multicomponent mixture M3				
	compound – concentration			
Mixture	maltose	Ethanol	*n*-propanol	*i*-propanol
10	2 g l^{-1}	0,15 mol l^{-1}	0,15 mol l^{-1}	0,15 mol l^{-1}
11	2 g l^{-1}	0,6 mol l^{-1}	0,6 mol l^{-1}	0,6 mol l^{-1}

Analytical methods

Several analytical methods were applied for determination of compounds in the studied model solutions. The analytical methods are listed in Table 5.

Table 5 Selected analytical methods for compounds determination in the samples

Analyzed substances	Origin of the sample	Analytical method
Organics	Feed, permeate	GC chromatography
Maltose	Feed, permeate	Polarimetry; UV-VIS
Content of salts	Feed, permeate	Conductivity measurement

Process conditions and apparatus

Several process parameters were used during the experiments:

- Transmembrane pressure (abv. TMP): 10, 15, 20, 25, 30 bar.
- Retentate flow: 500 L h^{-1}.
- Temperature was maintained constant at value of 20±1.0°C.

The experimental setup as depicted in the Figure 1 was used for the experiments.
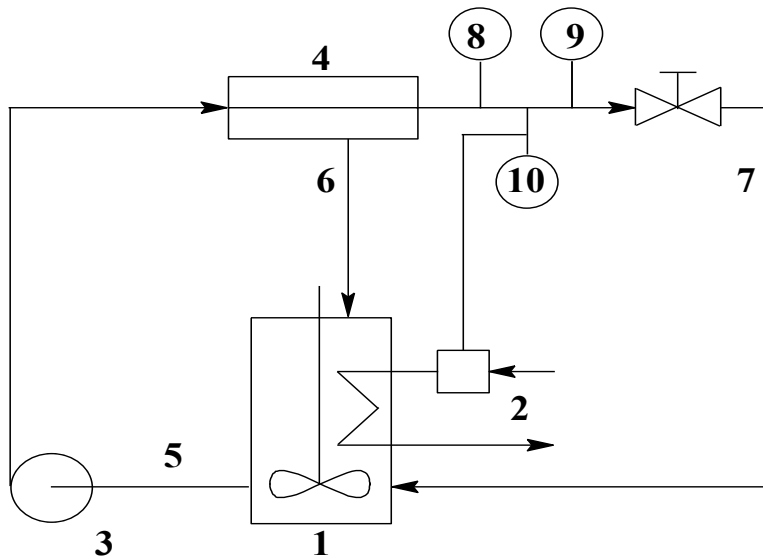

Figure 1 Diagram of experimental setup; 1-stirred tank; 2-water cooling system; 3-diaphragm pump; 4 membrane module; 5-feed; 6-permeate; 7-retentate; 8-flow meter; 9-pressure transducer; 10- thermometer.

The mentioned model solutions were individually prepared according to Table 2-4. Each model solution was pumped from the stirred tank (1) to the membrane module (4). Operating pressures were adjusted by a reducing valve. After setting the parameters and stabilization of the process, time needed to obtain 0.2-0.5 kg of permeate (depending on model solution) was measured. The measurement was repeated three times for each setting. Samples were taken from feed and permeate. The conductivity of the samples was measured directly during the experiment. The content of volatile organic compounds and maltose was analysed after finishing the experiment. The membrane was rinsed with demineralized water after the experiment until conductivity and permeate flux J_p remained stable. If a decline of flux was observed, the membrane was cleaned by a solution of sodium hydroxide (pH=11) and citric acid (pH=2.5).

5. RESULTS AND DISCUSSION

5.1 MEMBRANE CHARACTERISTICS

Pure water permeation

The basic method of membrane characterization is the determination of pure water permeability.

Based on the results of the mentioned experiments, it was observed that membrane M1 achieved the lowest permeate flux J_p compared to membranes M2 and M3. In the case of ESPA type membranes, a deviation from the expected values was noted at a lower applied pressure difference, namely 10 and 15 bar.

Sodium chloride rejection for the studied membranes reached values higher than 98.7% at an applied pressure difference of 10 bar. The experimentally obtained values were compared with the values specified by the manufacturer, while the deviation was no more than 0.3%. It can therefore be concluded that the separation properties of the membranes were not affected by transport or storage.
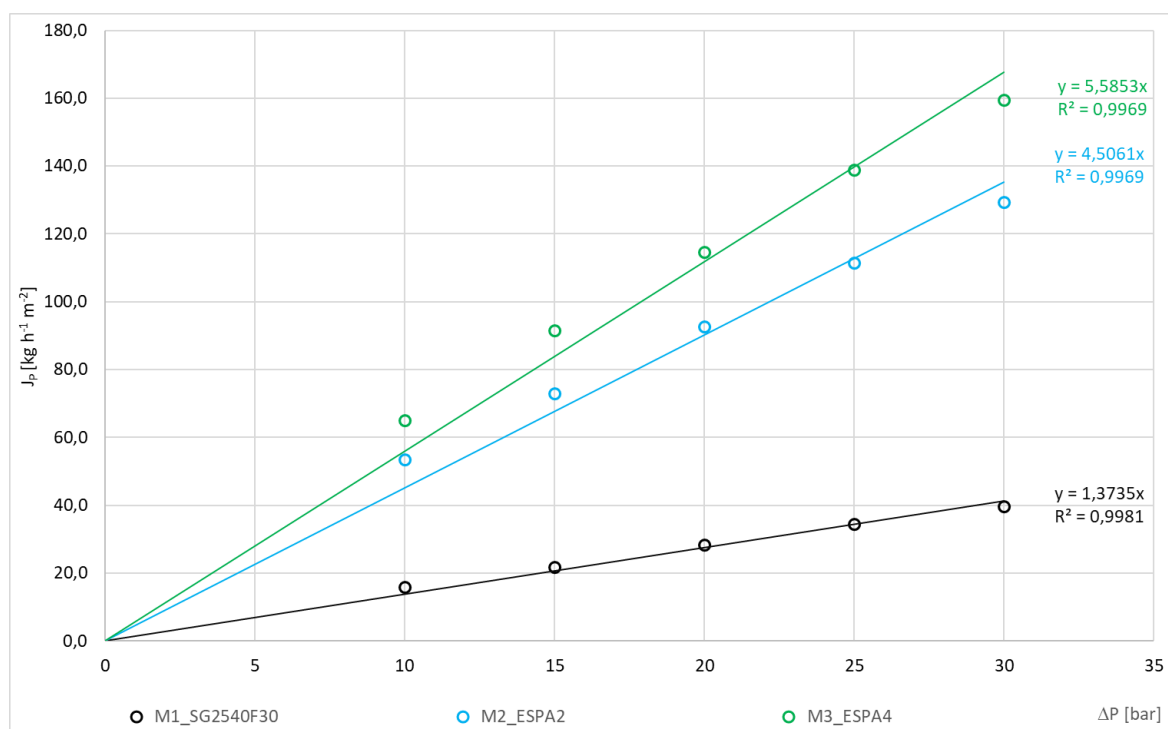

Figure 2 Dependency of permeate flux J_p on applied pressure difference ΔP

Scanning electron microscopy

The method of scanning electron microscopy (SEM) was applied for inspection of the membrane surface. The typical structure of reverse osmotic membranes, the so-called *"ridge-and-valley"*, was observed. In the case of the M3 membrane, the individual structural protuberances were larger and less curved. In general, both samples were similar without major differences (see Fig. 3).
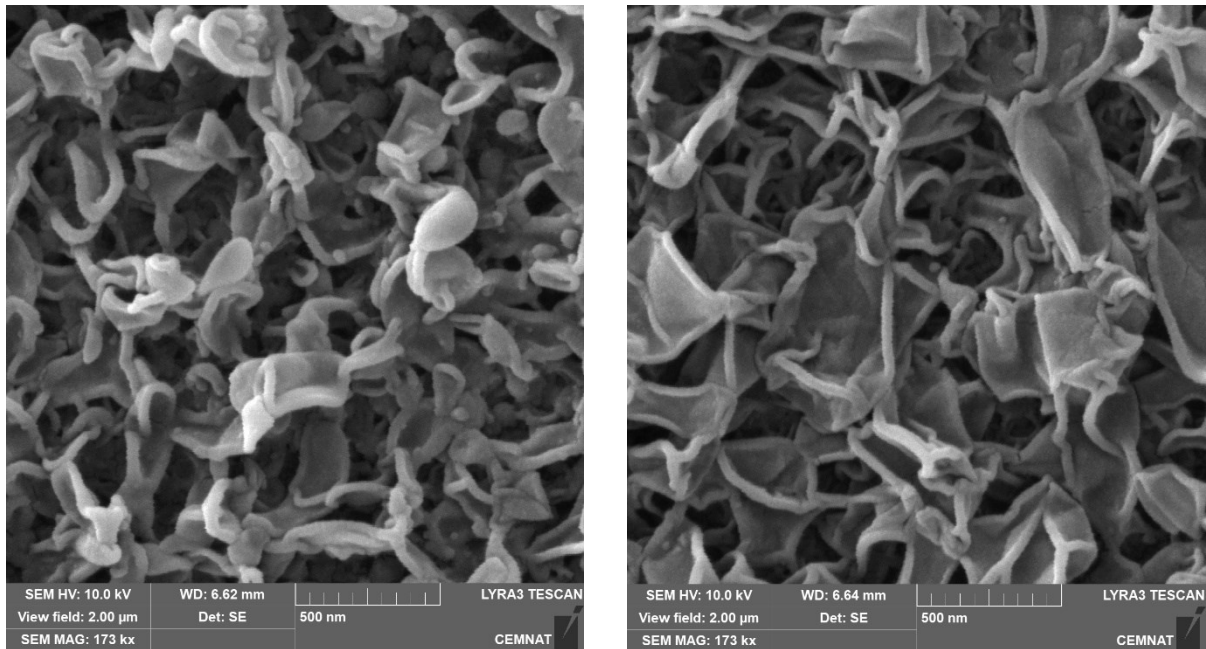

Figure 3 SEM picture of M2 and M3 surface in resolution 2.0µm

5.2   MODEL SOLUTION

5.2.1   Binary mixtures

The first part of the experimental work was focused on the separation of selected organic substances from binary mixtures.

The permeate flux J_p and the rejection of substances R depending on the applied pressure difference ΔP and the concentration of compounds were studied. In the following section, the results obtained for the M2 membrane, which was considered in a wider range of experiments for binary mixtures, are evaluated. The studied substance concentrations were 0.15-0.3-0.45-0.6 mol l^{-1}. The selected range of concentrations was chosen due to the applicability of the research to several areas, not only to the food industry. In this way, the actual analysis of the samples was also simplified and made more precise.

To assess the effect of concentration, two border concentrations of organic compounds (0.15 and 0.6 mol $^{-1}$) were considered.
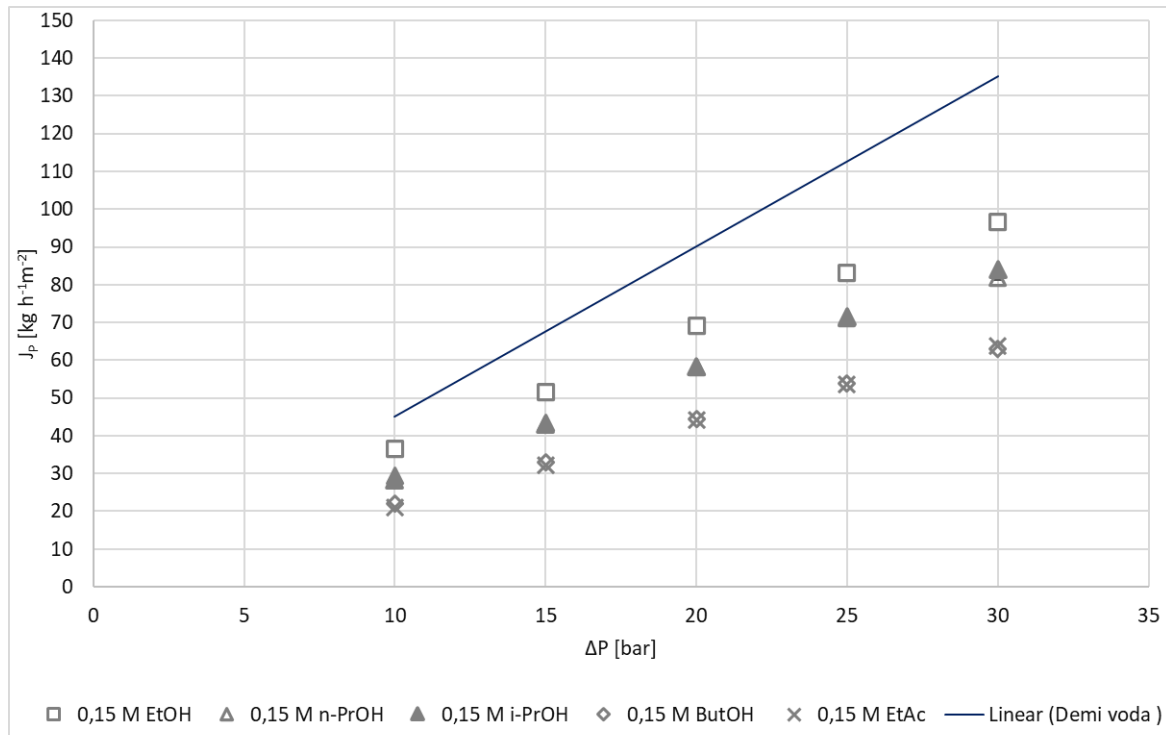
Figure 4 Dependency of permeate flux J_p on applied pressure difference ΔP, organic compounds at concentration 0,15 M (M2).

The presence of an organic substance already in a low concentration (see Fig. 4) led to a decrease in permeate flux J_p, on average by 37% for the ethanol solution compared to the permeate flux J_p of demineralized water. For the other substances studied, the decrease in the value of permeate flux J_p was even higher. As an example, for butanol a decrease in permeate flux J_p by 53% compared to demineralized water was observed.

A dependency of the decrease of permeate flux J_p with increase of organic compound concentration was found. A difference was seen especially between concentrations of 0.15 mol l^{-1} and higher. A similar trend was observed for all binary mixtures, where the difference was not prevalent for the concentration range of 0.3-0.6 mol l^{-1}. Apparently, at a concentration of 0.15 mol l^{-1}, the sorption of water in the membrane is still preferred, which leads to an easier transport of water through the membrane.

At the applied pressure difference of $\Delta P=10$ bar, the permeate flux J_p was similar to higher concentrations of substances, mainly due to the lower driving force and the prevailing phenomenon of diffusion.

An interesting trend observed for all studied substance concentrations was their sequence in decrease of permeate flux J_p. The ethanol solution reached the highest permeate flux J_p, whereas butanol and ethyl acetate solutions reached the lowest permeate flux J_p. The linearity or branching of the alkyl chain in the case of propanols had no effect on the permeate flux J_p. However, a decrease in permeate flux J_p was observed with increasing alkyl chain length. This trend appears to be independent of the osmotic pressure of the solution.

The second studied parameter was the rejection R of the substance and its dependency on concentration and applied pressure difference ΔP. In general, a decrease in rejection

can be observed with increasing concentration of substances in the system. The phenomenon is related to the intensity of permeate flux J_p.

For all substances, a non-linear dependence of rejection on the applied pressure difference ΔP was observed. For more polar substances (ethanol and ethyl acetate), the change in the observed rejection at the applied pressure difference $\Delta P =10$ bar was more evident, especially at a higher concentration. On the contrary, at higher applied pressure difference $\Delta P =20$ bar, rejection reached almost stable values.
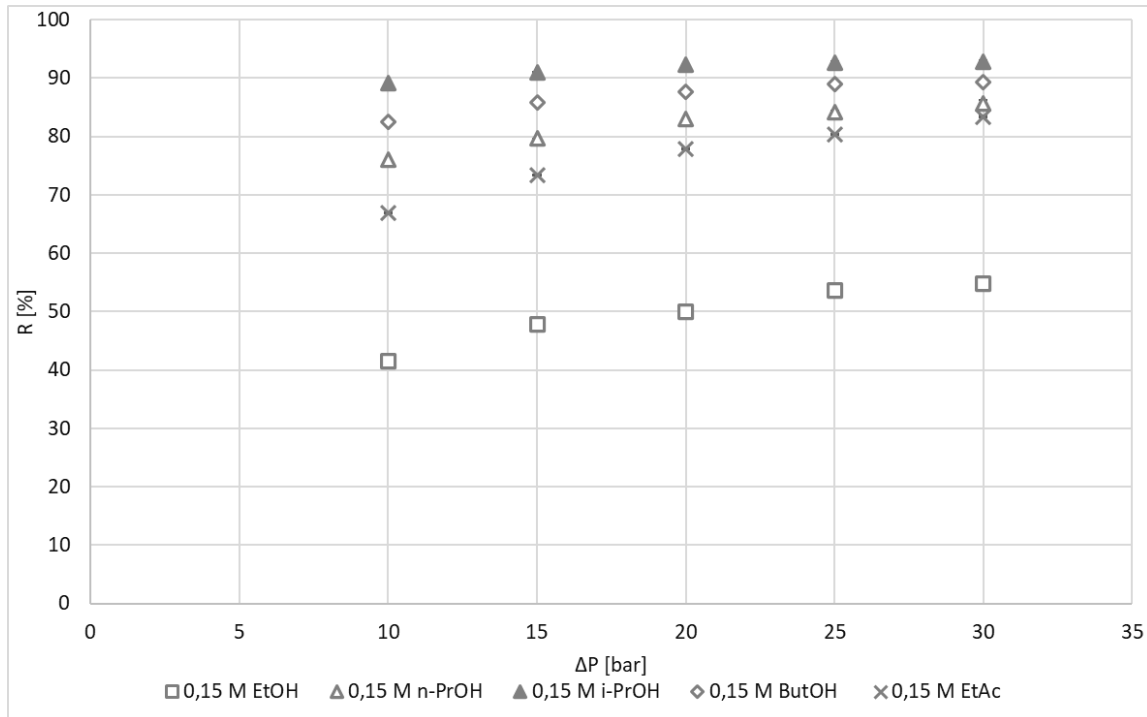

Figure 5 Dependency of rejection R on applied pressure difference ΔP, organic compounds at concentration 0,15 M (M2).

The ethanol solution was the least affected within both studied parameters. The substance with the highest achieved rejection was i-propanol whereas butanol and ethyl acetate showed the lowest measured permeate flux J_p.

Table 6 The compound sequence in terms of performance of membrane

Performance parameter	Compound's sequence The highest value → the lowest value
Permeate flux J_p	ethanol> n-propanol~ i-propanol> butanol~ ethyl acetate
Rejection R	i-propanol> butanol> n-propanol> ethyl acetate> ethanol

5.2.2 Binary mixtures – comparison of membranes

The performance characteristics of individual membranes for the studied binary mixtures were compared. As expected, a decrease in the intensity of permeate flux J_p was observed with the following sequence M3>M2>M1. As already mentioned in chapter 5.1, a change in the shape of the *"ridge-and-valley"* surface structure formations

was observed for M3. The protuberances were larger and less curved, which could contribute to higher mass transport through the membrane. At the same time as the intensity of the permeate flux J_p increased, the rejection of the substance decreased. The rejection of substances for M1 and M2 was similar, which shows that the membranes are similar.

5.2.3 Ternary and multicomponent mixtures

Based on the results of the previous measurements, the M3 membrane was selected as the membrane for the next experimental part.

The effect of maltose in ternary mixtures and the effect of other organic substances in a multicomponent mixture regarding their rejection and permeate flux J_p was evaluated. Only concentrations of 0.15 mol l^{-1} and 0.6 mol l^{-1} were considered.

Compared to the binary solution the ternary solution contains the same concentration of organic compound, but maltose (2 g l^{-1}) was added. Maltose rejection obtained stable values for all studied systems, i.e. values of 98.5±1.0%.

Such high maltose rejection was not expected. Compared to the literature, when a multicomponent system containing ethanol and a saccharide (glucose) was studied, the rejection of the saccharide decreased by almost 50% in presence of ethanol [19].

In the previous work [20], the presence of a saccharide (glucose) led to a decrease in permeate flux J_p. However, the concentration of maltose in the current system was apparently so low that it did not lead to a significant reduction in the permeate flux J_p of the studied systems.

The presence of maltose did not significantly affect ethanol rejection either. The rejection of *n*-propanol and *i*-propanol was affected especially at a lower applied pressure difference ΔP. In both cases, the addition of maltose led to an increase in the rejection of the substance. The maltose obviously created additional resistance to the transport of substances through the membrane.

The rejection of substances in multicomponent systems was significantly influenced by their concentration in the system. A different behavior of ethanol compared to other alcohols was observed with a change in the concentration of the substance. In the tests with organic compounds concentration 0.15 mol l^{-1}, ethanol rejection was on average 50% higher compared to binary and ternary system. In contrast, the rejection of *n*-propanol and *i*-propanol was not significantly affected.

Changes in rejection were observed for an organic substance concentration of 0.6 mol l^{-1}. A decrease in the rejection of all components of the mixture was observed. Ethanol rejection was the most affected, decreasing by 58%. The least affected was *i*-propanol, whose rejection was lower by 19%.

The rejection of alcohols in the multicomponent system was probably influenced by the interaction of the alcohols with the polyamide layer of the membrane. The alcohols can disrupt the hydrogen bonds formed between the water molecule and the membrane. At the same time, the free volume inside the polyamide layer is increased, which results in a lower retention of organic substances [21].

5.3 INFLUENCE OF PHYSICOCHEMICAL PROPERTIES

Table 7 Molecular descriptors [8, 9, 22, 23]

Compound	Molecular weight	Geometric properties			Lipophilicity	Substituent's effect	
	M_w	R_s	W	N_H	log K_{OW}	σ^*	E_s
	[g mol^{-1}]	[Å]	[Å]	[Å]	[-]	[-]	[-]
EtOH	46,1	1,98	1,99	22,94	-0.24	-0.100	-0.07
n-PrOH	60,1	2,13	2,05	22,99	0,42	-0.115	-0.36
i-PrOH	60,1	2,16	2,34	31,10	0.12	-0.190	-0.70
ButOH	74,1	2,41	2,0	28,4	0,96	-0,130	-0,39
EtAc	88,1	2,14	2,2	-	0,93	0	-

For the parameters mentioned above, no satisfactory correlation was found between an individual parameter and the rejection of the substance, including ethyl acetate as a representative with a different functional group. If only alcohols with a linear alkyl chain are considered, then the most suitable parameters for prediction are parameters describing the geometry of the molecule.

In the case of permeate flux J_p, the molecular weight of the substance M_w was determined as a suitable parameter.

The mechanism of substance rejection cannot simply be considered as a process dependent on one parameter. Agenson et al. [24] found a correlation between rejection and three parameters: molecular width, length, and n-octanol/water partition coefficient *log $K_{o/w}$*, where higher rejection was observed for substances with a higher partition coefficient and greater molecular length and width. This correlation could also be observed for the studied substances.

5.4 MEMBRANE STABILITY

Based on experience with studied compounds and knowledge from literature, no significant effect of the selected organic compounds on membrane integrity was expected. However, after exposing the M2 membrane to a solution of 0.6 mol l^{-1} ethyl acetate, performance characteristics of this membrane changed. A decrease in the intensity of the permeate flux J_p for demineralized water, a convex shape of the dependence of the permeate flux J_p on applied pressure ΔP for a solution of sodium

chloride and a decrease in the rejection of sodium chloride at a higher applied pressure were observed.

This shows that the membrane was affected by this solution and a damage to the chemical structure is suspected. The change in chemical structure can be specified by determining the IR-FTIR spectrum before and after exposure of the membrane to the solution. If the chemical structure is damaged, the degree of damage can be determined by comparing the area of selected absorption bands that correspond to selected bonds that are susceptible to degradation.

However, no significant change in IR-FTIR spectra was observed when comparing the virgin membrane and the membrane after 24 hour exposure to the binary solutions at highest concentrations.

The membrane samples were also subjected to contact angle measurements. Also here, no significant changes in the measured contact angle values were observed for alcohols with the maximum number of carbons in the alkyl chain and maltose.

In contrast, the contact angle values for butanol and ethyl acetate increased. This can be attributed to the influence of the membrane surface change, as the contact angle measurement is also affected by the surface structure and humidity [25, 26].

Based on the above findings, the active layer of the membrane was not chemically damaged. However, changes in the behaviour of the membrane were noticeable during experiments. Physical changes in the shape of the membrane occurred when a solution of butanol and ethyl acetate was used.

After the membrane was exposed to the butanol solution, the membrane curled. This change was reversible by rinsing the membrane with demineralized water after which it returned to its original shape. After exposing the membrane to an ethyl acetate solution, the membrane was more prone to damage and the formation of cracks on the surface, which could also contribute to an increase in the measured contact angle. This phenomenon was dependent on the concentration of the substance in the solution. In general, this behaviour can be considered as mechanical stress which contributes to the reduction of membrane life.
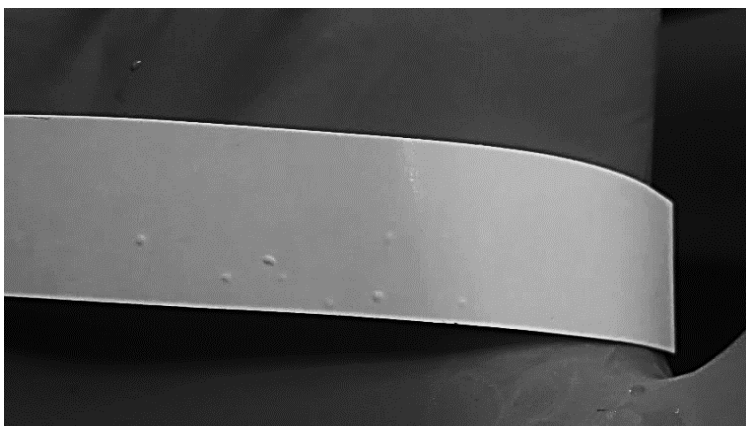

Figure 6 Detachment of polyamide layer from support layer

The critical phenomenon that was noted is shown in Fig. 6. Localized detachment of active layer was clearly visible on the surface of the membrane.

Based on the result of membrane stability tests, it can be concluded that the active layer of the M2 membrane was not damaged in chemical structure. The most likely reason for the change in performance parameters of the membrane and the deviation from normal behaviour is a mechanical damage of the membrane with detachment of the polyamide layer from the support.

5.5 SOLUTION-DIFUSION MODEL

The solution-diffusion model is most often used to describe the transport of substances in reverse osmosis. The aim of this study was to verify its suitability for describing the separation of the studied binary mixtures.

5.5.1 Estimation of parameter *B*

According to commonly considered assumptions, this parameter is independent of the applied pressure difference ΔP and the concentration of the substance, similar to parameter A [13].

However, it was found that the highest values of parameter *B* were achieved by ethanol, on the contrary, less polar substances, such as *i*-propanol and butanol, exhibited the lowest values.

From the data presented, it was not possible to simply determine whether parameter *B* showed a similar trend for all membranes. For this reason, data normalization was used. It was found that the normalized parameter *B* for individual substances was equivalent for all studied membranes.

5.5.2 Estimation of parameter *β*

With increasing applied pressure difference ΔP, the concentration polarization also increased. The effect of change in compound concentration was not observed. The lowest parameter value was found for ethanol; *β* below 1.1. For *n*-propanol and ethyl acetate, the *β* factor reached values of *β* lower than 1.2. For other substances and especially at a higher applied pressure difference ΔP, an increase up to *β*=1.6 was observed.

The calculated values of the parameter *β* for butanol and *i*-propanol indicate that concentration polarization had a greater impact for these substances. Both compounds are more hydrophobic and have lower diffusivity than the other studied substances. It can be assumed that due to the physicochemical properties and the size of the molecule, there is a slower transport of the substance through the membrane and thus also a more pronounced concentration polarization.

5.5.3 Permeate flux J_p

The permeate flux J_p was calculated from the basic equation of the solution-diffusion model (equation 3), using the experimentally determined water permeability A and the calculated difference of osmotic pressures for feed π_F and permeate π_P.

The calculated values were affected by selection of Van´t Hoff equation (10-11). The equation 11 provided better results, but still with observed divergence from measured data especially at higher applied pressure difference ΔP.

The accuracy of the data must also be considered, since even very small changes in activity affect the calculated value of the permeate flux intensity. For this reason, equation 11 was considered in the following calculations.

The model with the considered parameter β reflected the value of this parameter in the resulting calculated permeate flux J_p. In the case of ethanol, the β parameter could be neglected, and its effect was not observed. However, for i-propanol, its addition in the calculation had the effect of reducing the permeate flux J_p and thus also reducing the difference between the experimental and model values.

5.5.4 Rejection of compounds R

Similar to the evaluation of permeate flux J_p, several variants of the calculation were considered here as well.

A comparison of the experimentally obtained and model values of compound rejection R resulted in the following findings:

- The Van't Hoff equation is not satisfactory for calculation, especially equation 10.

- The mentioned model can only be applied to a certain range of concentrations and pressure difference ΔP, i.e. a higher concentration of the substance and the applied pressure difference up to 20 bar.

- The calculated rejection of the substance is dependent on the value of the parameter B. For higher concentrations of the substance a higher alignment with the experimentally determined rejection was achieved.

- From the knowledge of the parameter β, it was possible to determine the real rejection of the substance, which reached higher values at a higher applied pressure difference ΔP.

- The rejection of substances determined by equation (5) and with consideration of the estimated parameter B for individual concentrations were in the best fit with the measured data.

5.6 DIAFILTRATION

Diafiltration was applied to a multicomponent solution with an organic compound concentration of 0.6 mol l^{-1} and maltose of 2 g l^{-1}.

The permeate flux J_p increased during the duration of the experiment. This behaviour was non-linear and compared to previous work [20], the shape of the curve changed from concave to convex. The value of the permeate flux J_p at the end of the measurement was similar to the values of the permeate flux J_p for binary mixtures containing both types of propanol.

The change in intensity of permeate flux J_p during the experiment was related to the change in the concentration of substances in feed. A decrease of ethanol and other compounds in feed was observed. This phenomenon was expected because of incomplete rejection of substances. The compound's rejection of substances showed nonlinear behaviour.

One possible explanation is the time required for conditions to stabilize. In a specific case, the permeate was taken every 10 minutes and during this time the diafiltration liquid was gradually added so that the feed volume in the tank was maintained. Probably, this time was insufficient for the conditions to stabilize and thus deviations of the observed rejection occurred.

6. CONCLUSION

The work presented focused on the separation of organic substances using reverse osmosis and diafiltration, with emphasis on dealcoholization. Following model organic substances were used: ethanol, *n*-propanol, *i*-propanol, butanol, ethyl acetate and maltose. These substances can be found in a wide range of applications. In beverages, they contribute to the organoleptic properties of the product and in the chemical industry they are used as organic solvents. Understanding their effect on the membrane and their impact on the separation process is therefore key to the applicability of reverse osmosis in industry.

As part of the experimental work, the influence of applied pressure difference ΔP and concentration of the substance on permeate flux J_p and rejection of substances R, was studied in binary, ternary and multicomponent systems.

The knowledge obtained was then used in a diafiltration process, which was studied as a potential process for dealcoholization. Attention was paid to membrane stability in binary mixtures with the highest possible concentration of separated substances.

The theoretical part of the work focused on the evaluation of the relationship between the physicochemical properties of the substances and membrabe performance, as well as on the assessment of the suitability of the basic solution-diffusion model for binary mixtures. Three reverse osmotic membranes were studied: M1 (SG2540F30), M2 (ESPA2) and M4 (ESPA4), which differed both in sodium chloride rejection and pure water flux J_p.

Experimental work with binary, ternary and multi-component mixtures with different concentrations of the studied substances was carried out in recirculation mode, when the applied pressure difference of 10, 15, 20, 25 and 30 bar was gradually adjusted.

It was found that the permeate flux J_P increased linearly with increasing applied pressure difference ΔP. Both the flux J_P and the rejection of substances R in binary mixtures decreased with increasing concentration of the substance.

For all membranes, the same trend was observed for the separation of substances in binary systems (from the highest measured values to the lowest):
- Permeate flux intensity J_P: ethanol> n-propanol~ i-propanol> butanol~ ethyl acetate
- Rejection of substances R: i-propanol > butanol > n-propanol > ethyl acetate > ethanol

The addition of maltose did not significantly affect permeate flux J_P, but an increase in the rejection of organic compound was observed for less polar substances, especially at lower applied pressure differences ΔP.

In the case of multi-component mixtures, a further decrease in permeate flux J_P was observed for both studied concentrations of organic substances, i.e. 0.15 mol l^{-1} and 0.6 mol l^{-1}. The presence of other organic substances in the system did not significantly affect the rejection of substances at low concentrations (except for ethanol, for which an increase in rejection was observed). However, for higher concentration values, a decrease in rejection of all substances in the system was observed.

As part of the membrane performance study, a non-linear behaviour of the intensity of the permeate flux J_P and a decrease in sodium chloride rejection was found after exposure of the membrane M2 to ethyl acetate solution with a concentration of 0.6 mol l^{-1}. Based on this observation, the research was expanded to include a study of membrane stability in model solutions. After exposure of the membrane sample for 24 hours and subsequent analyses, no degradation of its chemical structure was observed. However, the membrane showed a change in mechanical properties for butanol and ethyl acetate solution, which was also reflected in a change in contact angle for these specific samples. It is also important to mention the local detachment of the polyamide layer in the case exposure to an ethyl acetate solution. Based on these findings, ethyl acetate and butanol solutions were no longer used for the M3 membrane.

Prediction of separation of organic substances is one of the key areas of interest. An effort has been made to identify the parameters of the separated substances, to simplify predictions, i.e. for example, that as the molecular weight of the substance increases, so does its retention factor, or rejection. Four groups of parameters were studied - molecular weight, geometric properties of substances, lipophilicity of the substance and the effect of substituents on the reactivity of the substance.

No linear dependence was observed between the mentioned parameters and the rejection of substance R. In most cases, it was a non-linear dependence It can therefore be stated that the prediction of the separation of substances by a membrane is not possible with

the knowledge of only one parameter, i.e. that separation is a complex phenomenon in which many more parameters participate.

Another possibility of predicting the separation of organic substances is the use of mathematical modelling. In the presented work, it was primarily investigated whether it is possible to consider the basic solution-diffusion model for the separation of binary mixtures. As part of the process of estimating individual parameters, it was found that the parameter B, which represents the permeability of the membrane for the organic substance, is not constant, i.e. its value depends on the concentration of the substance.

Parameter B was estimated for each concentration of the substance as well as for the entire range of concentrations. The best results in predicting substance rejection were achieved in the case of using parameter B specific to the considered concentration. Based on normalized data, it was found that the behaviour of the membranes is similar for the selected substances, even though the values of parameter B were different (due to the dependence on the measured intensity of the permeate flow J_P).

The influence of concentration polarization factor β was also determined. The increase of concentration polarization was observed for less polar substances. On the contrary, in the case of the separation of the ethanol solution, no effect of concentration polarization was detected even with increasing concentration of the substance. In general, the concentration polarization was dependent on the applied pressure difference ΔP. Based on the findings, it has to be noted that the basic solution-diffusion model can be applied to the separation of the mentioned organic substances only in a limited range of the applied pressure difference, $\Delta P = 10$–20 bar.

Diafiltration of the multicomponent mixture was performed at a constant volume of the mixture in the tank. The permeate that was removed during the experiment (duration of the process approx. 150 minutes) was replaced with diafiltration liquid (demineralized water) in a total amount of 96 liters. During the diafiltration, an increase in the intensity of the permeate flow J_p was observed due to a change in the concentration of substances in the injection and due to a decrease in the osmotic pressure of the solution.

The dealcoholisation process of the studied model mixture was successful, i.e. ethanol was the substance that was removed the most by the addition of diafiltration liquid. However, other substances concentration decreased, to a greater extent than expected and desired.

In conclusion, it can be stated that the complexity of the given work also pointed to the complexity of the studied topic, i.e. the implementation of dealcoholisation of solutions of organic substances using reverse osmosis. In the case of further work, it would be appropriate to focus on the study of multi-component systems and also on the separation of a real injection (i.e. beer or wine). It would also be advisable to optimize the diafiltration process. A further study of the prediction of the separation of substances using mathematical models could contribute to a better understanding of the influence of selected parameters of solutions of organic substances on the course of their separation process.

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