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# THE PERMEABILITY OF THE NANOFILTRATION MEMBRANES USING FOR CHROMIUM CONCENTRATION IN THE MODEL SOLUTIONS

**Key words:** nanofiltration membrane, permeability, salts, chromium.

**Abstract:** In the paper, the permeability of polymer nanofiltration membranes was analysed. The studies were carried out for the model wastewater chromium (III) solutions at pH 4. The model wastewater chromium (III) solutions were included different concentrations of $NaCl$, $Na_2SO_4$, and $CrCl_3$. It was found that on the membrane permeability is influenced by their morphology and electrostatic properties, regardless of the composition of the feed. The negative charge of the DL membrane was limited by the polarization of the membrane and the osmotic effect. This had a beneficial effect on the permeability of the DL membrane. It positively influenced the permeability of the membrane. For the HL membrane, it does not have a surface charge under the process conditions, and the electrostatic effect is not observed. The formation of the polarization layer and the osmotic effect is limited only to a small extent by the Donnan effect. Thus, a significantly higher permeability drop for the separated salt of solutions was observed for the HL membrane, despite its looser structure. In the case of the CK membrane, it increased the polarization of the membrane, because, under the process conditions, the membrane was positively charged. This caused a reduction in membrane permeability, practically excluding its use as a nanofiltration membrane for concentrating chromium in salt solutions. The presence of small amounts of chromium in the solution containing a fixed concentration of chlorides and sulphates resulted in a slight increase in the permeability of the DL membrane to the solutions of the salts themselves. In the case of the HL membrane, this relationship was not observed. In the case of both membranes, an increase in chromium concentration caused a constant, slow decrease in permeability.

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## Przepuszczalność membran nanofiltracyjnych stosowanych do zatężania chromu z roztworów modelowych

**Słowa kluczowe:** membrana nanofiltracyjna, przepuszczalność, sole, chrom.

**Streszczenie:** W pracy przeanalizowano przepuszczalność polimerowych membran nanofiltracyjnych. Badania przeprowadzono dla modelowych roztworów ścieków chromowych o pH 4, zawierających różne stężenia $NaCl$, $Na_2SO_4$ oraz $CrCl_3$. Stwierdzono, że bez względu na skład nadawy, przepuszczalność membran zależy od ich morfologii oraz właściwości elektrostatycznych. Ujemny, w warunkach procesu, ładunek membrany DL ograniczał polaryzację membrany oraz efekt osmotyczny, co korzystnie wpływało na jej przepuszczalność. W przypadku membrany HL, w warunkach procesu nie posiada ona ładunku powierzchniowego, więc nie obserwuje się efektu elektrostatycznego. Powstawanie warstwy polaryzacyjnej i efektu osmotycznego tylko w nieznacznym stopniu jest niwelowane przez efekt Donnana. Zatem w przypadku membrany HL, mimo jej otwartej struktury, obserwowano znacznie wyższy spadek przepuszczalności dla separowanych roztworów soli. W przypadku dodatnio naładowanej w warunkach procesu membrany CK występowało zwiększenie polaryzacji membrany oraz obniżenie jej przepuszczalności. Praktycznie wykluczające użycie membrany CK jako membrany nanofiltracyjnej do zatężania chromu w roztworach soli. Obecność niewielkich ilości chromu w mieszaninie zawierającej ustalone stężenie chlorków i siarczanów powodowała nieznaczny wzrost przepuszczalności membrany DL w stosunku do roztworów samych soli. W przypadku membrany HL takiej zależności nie obserwowano. W przypadku obu membran wzrost stężenia chromu powodował stały, powolny spadek przepuszczalności.

## Introduction

The popularity of pressure membrane processes has increased significantly in the last few years. The increase is due to the advantages of using pressure membrane processes, which include the following: low energy consumption, modular construction operate in continuous or batch feeds, there is no need to apply additional chemical reagents, and the possibility of using streams obtained during the separation [1, 2]. Pressure membrane processes are used in water treatment, wastewater treatment, and the concentration and recovery of substrates. Nanofiltration (NF) is one of the most popular membrane processes used for the purpose of treatment and purification of surface and underground waters, but also for the separation of mono– and multivalent ion solutions.

The NF process consists in retaining multivalent ions and organic compounds with a molecular weight higher than 200 Da on the membrane; whereas, monovalent ions and water are permeated through the membrane. Separation mechanism characteristic of the NF process includes both the effect of the sieve and the electrostatic effect [3]. Separation is possible due to the presence on the surface and in the internal structure of the membrane of "active centres" endowed with an electric charge. Charge on the surface of the membrane has a large influence on the separation of mono – and multivalent ions. The density and type of charge on the NF membrane is strongly dependent on the material of the membrane and the pH of the solution [4]. Depending on the pH, the membrane may have a negative charge, with a pH above the isoelectric point (IP) of the membrane, or a positive charge, with the pH below the IP of the membrane. When the pH value is equal to IP of the membrane, the membrane has no surface charge. In this case, there is a sieve separation mechanism.

The results of research available in the literature are mostly focused on the ability of nanofiltration membranes to separate components [5,6]. Based on the obtained results, it has been proved that, in addition to the pH of the solution, the important factors affecting the final composition of individual streams are the type and size of the separated ions, and the concentrations and the ratio between them [4,6,7]. A side element of the study is a problem of the efficiency of nanofiltration membranes. The analysis of the presented results allows one to state that the permeability of the membranes becomes different depending on the process conditions. At the same time, the nature of these changes varies.

The aim of the study was to determine the nature of changes in the permeability of nanofiltration membranes used in the concentration of chromium in salt solutions.

## 1. Materials and methods

Three different nanofiltration membranes with an active area of 0.0155 m² were tested. The exact characteristics of the membranes are shown in Table 1. The DL and HL membranes were made of polyamide, whereas the CK membrane was made of cellulose acetate.

**Table 1. Characteristics of nanofiltration membranes used in research [8,9,10,11,14]**

| Characteristic | Membrane | | |
|---|---|---|---|
| | DL | HL | CK |
| Surface material | Polyamide | Polyamide | Cellulose acetate |
| Type of membrane | Thin film | Thin film | Integrally asymmetric |
| Cut – off [g/mol] | 150 – 300 | 150 – 300 | 2 000 |
| pH | 2 – 11 | 3 – 9 | 2 – 8 |
| Max. pressure [bar] | 40 | 40 | 31 |
| Max. temperature [°C] | 90 | 50 | 50 |
| Isoelectric point [pH] | 3.0 | 3.3 | 4.4 |
| Zeta potential [mV] pH = 4 | – 13.0 [8,10] – 14.0 [8] | – 4.0 [8,10] 0.0 | – |
| The MgSO$_4$ rejection [%] | 98 [11] | 98 [11] | 94 [11] |

In order to determine changes in the permeability of nanofiltration membranes used for chromium concentration in salt solutions, studies were carried out on a laboratory scale, which was described in [12]. The research was carried out in three stages. The first stage of the research was to determine the permeability of membranes for deionized water. The second stage of the research was the determination of the permeability of membranes for solutions containing the following:

10 g Cl⁻/L and 10 g $SO_4^{2-}$/L;

10 g Cl⁻/L and 15 g $SO_4^{2-}$/L;

10 g Cl⁻/L and 20 g $SO_4^{2-}$/L;

20 g Cl⁻/L and 10 g $SO_4^{2-}$/L;

20 g Cl⁻/L and 15 g $SO_4^{2-}$/L;

20 g Cl⁻/L and 20 g $SO_4^{2-}$/L.

The third stage of the research was to determine the effect of chromium (III) concentration on membrane permeability for the following solutions:

10 g Cl⁻/L, 20 g $SO_4^{2-}$/L and 1.0 g/L $Cr^{3+}$;

10 g Cl⁻/L, 20 g $SO_4^{2-}$/L and 1.5 g/L $Cr^{3+}$;

10 g Cl⁻/L, 20 g $SO_4^{2-}$/L and 2.0 g/L $Cr^{3+}$;

10 g Cl⁻/L, 20 g $SO_4^{2-}$/L and 4.0 g/L $Cr^{3+}$;

20 g Cl⁻/L, 10 g $SO_4^{2-}$/L and 1.0 g/L $Cr^{3+}$;

20 g Cl⁻/L, 10 g $SO_4^{2-}$/L and 1.5 g/L $Cr^{3+}$;

20 g Cl⁻/L, 10 g $SO_4^{2-}$/L and 2.0 g/L $Cr^{3+}$;

20 g Cl⁻/L, 10 g $SO_4^{2-}$/L and 4.0 g/L $Cr^{3+}$.

The solutions were prepared from the following reagents: pure NaCl (Chempur®), pure Na2SO4 (Chempur®), pure CrCl3·6H2O (Chempur®), and deionized water. The pH of each prepared solution was 4. In order to define to the membrane permeability, the dependence of the permeate flux on pressure was determined. The studies were carried out for pressures of 10 bar, 12 bar, 14 bar, and 16 bar. The measurements were made at a constant temperature T = 20°C and velocity V = 0.01 m · s⁻¹. The permeate flux was determined by measuring the reception time of 10 cm³ of permeate after establishing the equilibrium in the system.

## 2. Results and discussion

### 2.1. The permeability of nanofiltration membranes for deionized water

The studies show that the HL membrane has highest permeability, and the DL membrane has slightly lower permeability. The lowest values of water permeability of the membrane were observed for CK. Such results
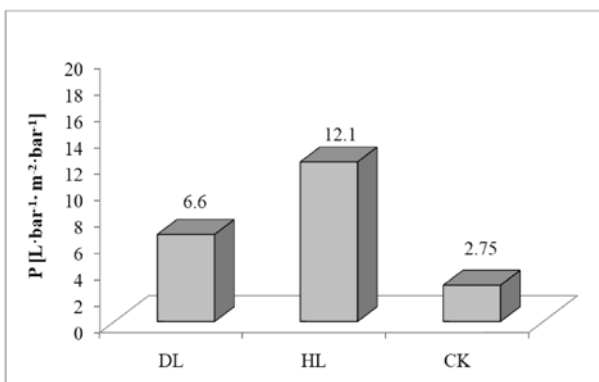
are attributed to the structure of the membrane. The integrally asymmetric CK membrane has a compact and relatively thick active layer, which significantly impedes solvent permeation through the membrane. In the case of composite DL and HL membranes, the active layers are much thinner. Wherein the active layer of the HL membrane consists of two polymer sublayers, and the DL membrane active layer consists of three polymer sublayers. Such a structure of membranes made of the same polymer – polyamide – shows observable differences in the permeability values. Similar results were obtained in a previous work [8]. The results of the studies are presented in Fig. 1.

### 2.2. Permeability of nanofiltration membranes for solutions with a constant sodium chloride concentration and variable sulphate concentration

During the studies conducted for the DL membrane, it was observed that, as the concentration of sulphates in the solution increases, the permeability of the membrane decreases (Fig. 2). Differences in the permeability of the membrane were in the range of 30–60%. Similar results for chloride and sulphates (salts) carried out for the DL membranes were observed by Yan et al. [13]. The decrease in the permeability of the membrane with the increase in salt concentrations can be explained by the formation of a polarization layer and the occurrence of an osmotic effect. Large sulphate ions are retained by the membrane. These ions begin to form a polarization layer near the membrane surface, which inhibit the flow of smaller chloride ions. The result is a reduction in liquid flow through the membrane and a decrease in its permeability.

On the other hand, the DL membrane has an IP value of 3.0, which according to the isoelectric point theory, indicates that the membrane has negative charge on its surface (Table 1) [14]. The charge of the membrane interacts with the positive ions contained in the solution, making them easier to transport. In addition,



**Fig. 1.** Changes in membrane permeability DL, HL, CK for water, temperature T = 20°C and velocity V = 0.01 m·s⁻¹, pressure: 10 bar, 12 bar, 14 bar, and 16 bar

the system containing monovalent cations and mono and multivalent anions seeks to preserve the electro–neutrality of the Donnan effect. Growth in the $SO_4^{2-}$ ion solution leads to a decrease in $Cl^-$ ion retention by the negatively charged membrane. These effects partially limit the unfavourable changes in the permeability of the DL membrane due to osmotic phenomena.

During the tests of the HL membrane, a reduction in its permeability was also observed in the presence of chloride and sulphate salts, as compared to the results obtained for deionized water (Fig. 3). These changes were very clear and amounted to 75–80%.
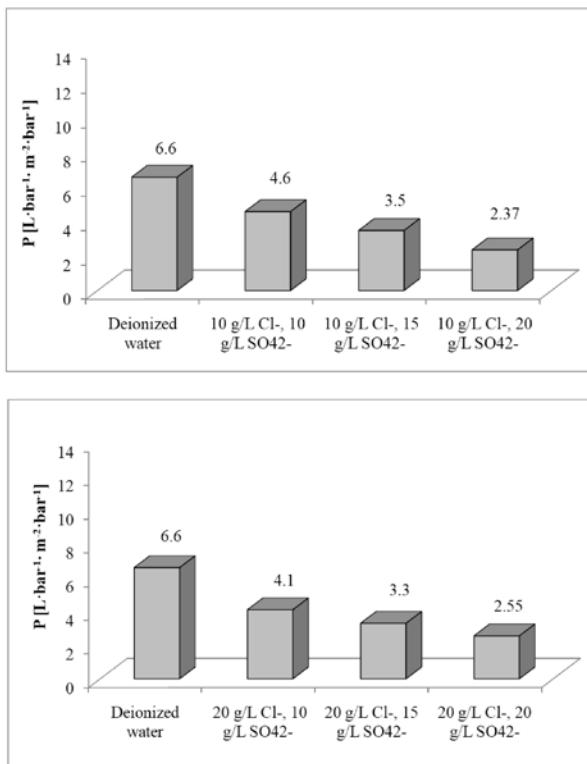




Fig. 2.   Changes in membrane DL permeability during filtration of the salt mixture with a constant concentration of chloride and various concentrations of sulphate, temperature T = 20°C and velocity V = 0.01 m·s⁻¹, pressure: 10 bar, 12 bar, 14 bar, and 16 bar

The studies for the HL membrane, as for the DL membrane, were carried out for a pH of 4. The HL membrane is inert in the process conditions (Table 1). There are no favourable electrostatic effects in this case. During the particle separation process on the HL membrane, the sieve effect dominates, which, as in the case of the DL membrane, leads to the formation of a polarization layer and an osmotic effect. This unfavourable phenomenon, from the point of view of the permeability of the membrane, is only slightly offset by the Donnan effect. Thus, in the case of the HL membrane, despite its looser structure, a significantly
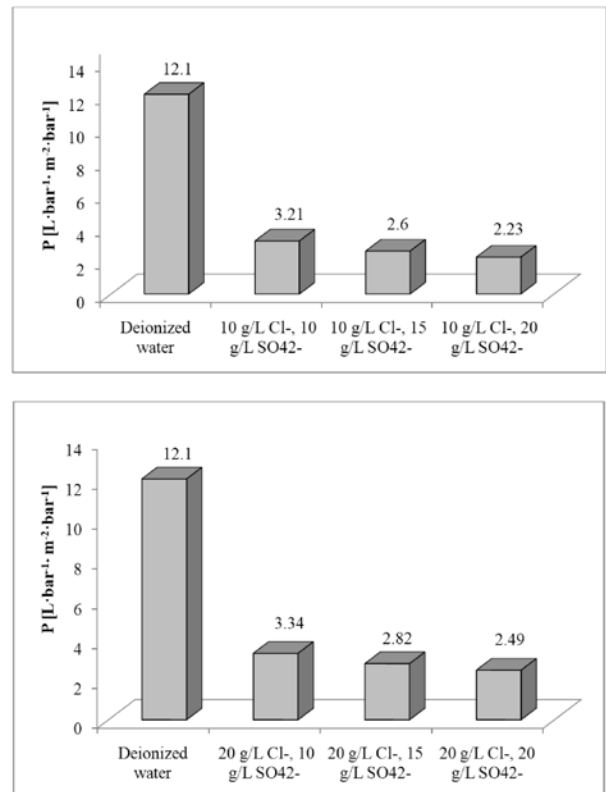




Fig. 3.   Changes in HL membrane permeability during filtration of a salt mixture with a constant concentration of chlorides and various sulphate concentrations, temperature T = 20°C and velocity V = 0.01 m·s⁻¹, pressure: 10 bar, 12 bar, 14 bar, and 16 bar

higher permeability drop is observed for the separated salt solutions.

In the case of conducting processes for the CK membrane in a system containing salts of various concentrations, a very high drop in its permeability was observed in the tested pressure range (Fig. 4). This result is attributed to the structure of the CK membrane, which has a much thicker, dense separating layer, which significantly impedes the permeation. Furthermore, under the process conditions, a positive charge is present on the surface of the CK membrane. In the salt solutions tested, this causes repulsion of the positive (sodium) ions from the membrane, and causes negative ions (chlorides and sulphates) to accumulate at its surface. As a consequence, this increases the membrane's polarization and reduces the permeability of the membrane. Based on these studies, it was found that the CK membrane has the properties of the RO membrane than the NF membrane.

On the basis of the obtained results, a DL and HL membrane was chosen for further testing. These membranes are characterized by a looser structure and favourable electrostatic characteristics, which has a positive effect on their permeability.
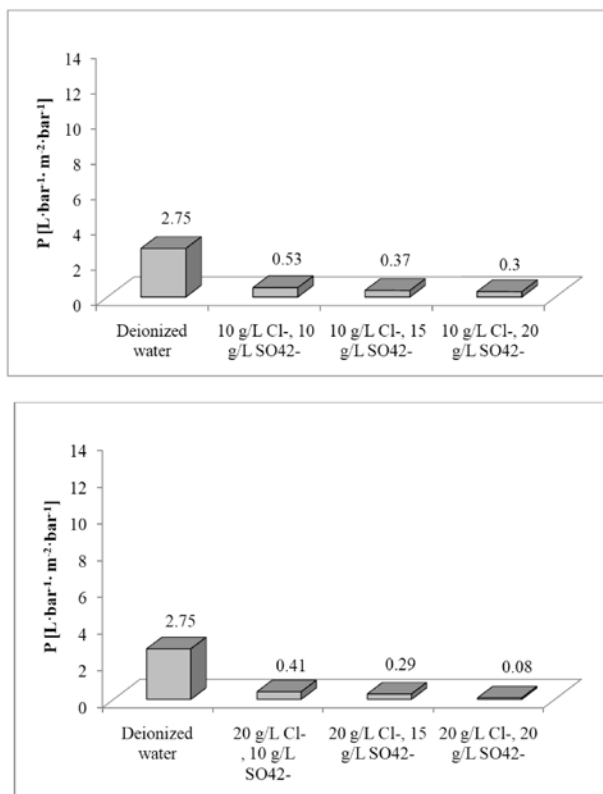
**Fig. 4.** Changes in the permeability of the CK membrane during filtration of a salt mixture with a constant concentration of chloride and various sulphate concentrations, temperature $T = 20°C$ and velocity $V = 0.01$ m·s$^{-1}$, pressure: 10 bar, 12 bar, 14 bar, and 16 bar

## 2.3. Permeability of DL and HL membranes for solutions with a constant concentration of sodium chlorides and sodium sulphates, with various concentrations of chromium

During the studies, for the DL membrane, it was observed that the presence of chromium in the mixture containing a fixed concentration of chlorides and sulphates does not reduce the permeability of the membrane. This affects a slight increase compared to solutions containing a fixed concentration of chlorides and sulphates. (Fig. 5).

The obtained results indicate that, for the tested solutions, the presence of chromium at the level of 1.0–4.0 gCr$^{3+}$/L, only to a small extent contributes to the increase of membrane polarization. The positive charge of chromium ions is much more important. This contributes to an increase in the transport of small positive sodium ions, which results from the electrostatic interaction with the negatively charged membrane, and they maintain the electro-neutrality principle separated by a membrane solution (Donnan effect). Easier transport of small, positive sodium ions results in easier transport of small, negative chloride ions. The decrease in chloride

ion retention in solutions containing chromium ions was observed by Gomes et al. [5]. As a consequence, the polarization of the membrane decreases, which leads to an observed increase in its permeability.
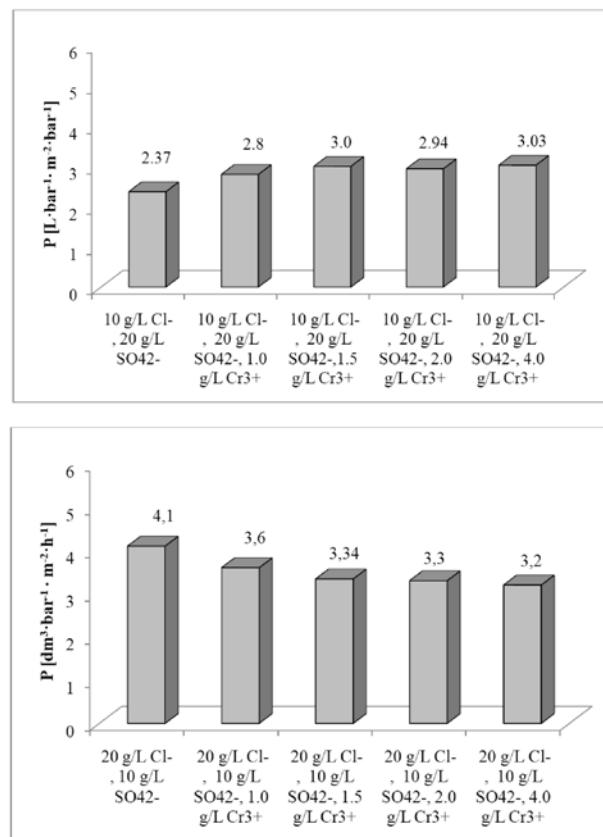




**Fig. 5.** Changes of DL membrane permeability during filtration of a mixture of chlorides and sulphates with various concentrations of chromium (III), temperature $T = 20°C$ and velocity $V = 0.01$ m·s$^{-1}$, pressure: 10 bar, 12 bar, 14 bar, and 16 bar

In carrying out the study on the HL membrane for a system containing predetermined proportions of chlorides and sulphates, while the variable chromium concentration was observed to decrease, its permeability compared to the system containing only salts (Fig. 6).

The HL membrane in solutions with pH = 4 does not have a surface charge. This means that the HL membrane is dominated by the sieve effect, not the electrostatic effect. Consequently, an increase in the concentration of large chromium ions in the solution causes a formation in the polarization layer and a decrease in the permeability of the membrane. Apart from the permeability, another important parameter characterizing the nanofiltration membrane is selectivity. The selectivity of the membranes is expressed as the retention of chlorides and chromium (III). For the studied mixtures of chlorides, sulphates, and chromium, for the HL membrane with a "looser" structure, the chromium (III) retention was 95–97%. The chloride retention for the HL membrane was 15–22%. For the DL membrane, chromium (III)
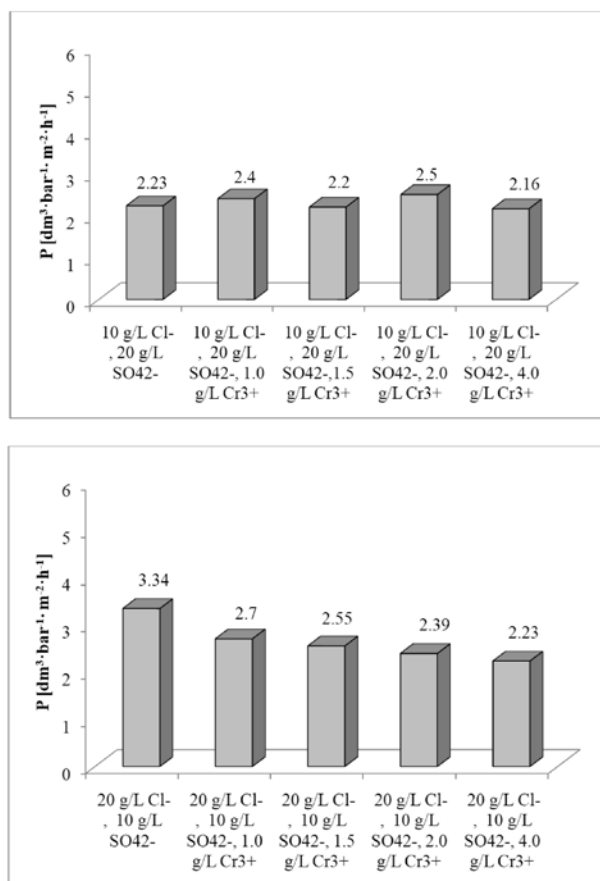
**Fig. 6.** **Changes in HL membrane permeability during filtration of a mixture of chlorides and sulphates with various concentrations of chromium (III), temperature T = 20°C and velocity V = 0.01 m·s⁻¹, pressure: 10 bar, 12 bar, 14 bar, and 16 bar**

retention was 93–97%. The chloride retention for the DL membrane was 5–10%.

When analysing DL and HL membranes for a system containing a constant concentration of chloride salts and sulphates, while a variable chromium concentration, we can see that the HL membrane has a lower permeability than the DL membrane. The active layer of the HL membrane has a "looser" structure with easier permeation than the "thicker" DL membrane. Such differences for the tested HL and DL membranes indicate the importance of the presence or absence of a surface charge.

## Conclusions

An important element in the membrane permeability is the construction of the active layer. The integrally asymmetric CK membrane has a compact and relatively thick active layer, which significantly impedes solvent permeation through the membrane. The CK membrane has low permeability. In the case of composite DL and

HL membranes, the active layers are much thinner. The filtration layer of the HL membrane is "looser" than the active layer of the DL membrane. This structure of membranes made of the same polymer shows observable differences in the permeability values. The "looser" active layer produces a higher water permeability of the membrane. In the tested solutions, the electrostatic properties of the membrane have a significant influence on their permeability. In the case of process conditions producing a negative charged, the DL membrane formation of the polarizing layer and the occurrence of the osmotic effect is partially limited by the electrostatic and the Donnan effect. In the HL membrane, the process conditions do not produce a surface charge. There are no favourable electrostatic effects in this case. During the particle separation process, the sieve effect dominates the HL membrane. It leads to the formation of a polarizing layer and an osmotic effect. Both of these phenomena are disadvantageous from the point of view of the permeability of the membrane, and they ae only slightly compensated by the Donnan effect. Thus, in the case of the HL membrane, despite its looser structure, a significantly higher permeability drop is observed for the separated salt solutions. In the case of a positively charged CK membrane during the process condition, it increases the membrane polarization and reduces the permeability of the membrane, which excludes its use as a nanofiltration membrane was observed.

The presence of chromium in a mixture containing a fixed concentration of chlorides and sulphates does not reduce the permeability of the negative DL membrane, and even causes a slight increase in relation to the individual salt solutions. Chromium ions reduce the polarization of the membrane by strengthening the electrostatic and the Donnan effect. In the case of the HL membrane, neutral under the process conditions, this relationship is not observed.

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