The Effect of Mineral Salt on Reactive Dye Removal from Aqueous Solutions by Ultrafiltration

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ABSTRACT
The effect of mineral salt on the reactive dye removal was evaluated by using flat ultrafiltration (UF) membranes made of polyethersulfone (PES) and regenerated cellulose (C). Five reactive dyes varied in molecular weight (Reactive Orange 16, Remazol Brilliant Blue R, Reactive Orange 20, Reactive Black 5, Reactive Red 120) were used in the UF experiments. The applied membranes were characterized by the cut-off value equal to 10 kDa. The ultrafiltration process was performed in a dead-end mode under the transmembrane pressure of 0.2 MPa. Dye concentration in model solutions was equal to 100 mg/dm³. Two various mineral salts (NaCl and Na₂SO₄) were chosen to simulate the composition of dye-house baths. The concentration of monovalent and divalent salt in model dye solutions amounted to 1–2 g/dm³. Transport and separation properties of the UF membranes towards reactive dyes and mineral salts were evaluated. It was found that the separation efficiency of all tested dyes was dependent on the mineral salt presence. The effect of mineral salt on dye retention was more pronounced for membrane made of regenerated cellulose (C) than for polyethersulfone membrane (PES). In the case of the C membrane the dye retention coefficients varied in the wide range – from 55 to 83%, whereas for PES membrane the degree of dye separation was less diverse and amounted to 81–96%. The presence of mineral salt in water and dye solutions generally worsen the membrane permeability due to osmotic pressure increase as well as enhancing adsorptive fouling of dye particles in membrane matrix.

Keywords: reactive dye, ultrafiltration, dye rejection, flux, mineral salt.

INTRODUCTION

Reactive dyes are commonly used in the textile industry for dyeing cotton fibres and fabrics. The exhausted dye baths after dyeing processes may contain, among others, unfixed dyes and mineral salts. The colour of dye effluents usually exceeds the allowable discharge limits, thus it is obvious that reactive dyes should be removed from dye effluents before entering water bodies. What is more, taking into account the economic point of view, it is advisable to recovery the unfixed dyes together with other auxiliary substances as well as water for reuse. Conventional treatment methods applied to the decolourization of dye containing effluents do not always assure satisfactory dye removal efficiencies. The application of membrane techniques to the treatment of dye-house wastewater provides opportunities for efficient colour removal, reuse of water and recovery of some valuable substance.

The research on dye solution treatment by membrane processes has been performed for more than 20 years, however the high-pressure membrane processes (i.e., reverse osmosis, RO, nanofiltration, NF) have been mainly proposed. Rashidi et al. (2015) performed a comprehensive study on the removal of reactive dyes by tight NF membranes (cut-off equal to 200 Da). The dye retention was quite satisfactory (90–97%) and was dependent on the structure, size and electrical charge of dyes. However, the NF membranes still
have the drawback of high rejection of Na$_2$SO$_4$ salt, which is a common salt present in dye baths. Thus, the NF process with conventional membranes seems to be unsuitable for salt recovery from textile wastewater. To overcome this disadvantage new loose NF membranes were developed. Zhang et al. (2017) fabricated the NF membrane with hybrid polymer-nanoparticle active layer and obtained high rejection (>95%) of azo dye (Congo Red) with rather low separation of sodium sulphate salt (about 17%). Application of the modified polyvinylidene fluoride (PVDF) loose NF membrane to fractionation of dye-salt mixtures resulted in 99.9% removal of Congo Red with simultaneous low salt rejections (NaCl by 1.7%, MgCl$_2$, by 4.5%, and MgSO$_4$, by 1.2%) (Kang et al., 2021). However, these new loose NF membranes were still characterized by rather low water permeability.

Recently, a variety of novel ceramic membranes and integrated membrane processes have been developed and described. Jiang et al. (2018a) used a tight ceramic UF membrane and obtained excellent separation (>98.12%) of reactive dyes varied in molecular weight from 626 to 1025 Da. Due to application of an integrated UF-diafiltration process, it was also possible to concentrate Reactive Blue 19 up to 140 g/dm$^3$, whereas mineral salt (Na$_2$SO$_4$) passed simultaneously to the permeate. It was concluded that tight ceramic UF membranes have high potential in reactive dyes and Na$_2$SO$_4$ salt fractionation. Ma et al. (2017) also showed that tight UF ceramic membranes had good performance in reactive dye (Reactive Brilliant Blue KN-R, Reactive Black 5, Reactive Red HE-7B) removal from multicomponent solutions containing NaCl/Na$_2$SO$_4$, salts. The extremely low mineral salt rejection (-2.12% and 14.4% for NaCl and Na$_2$SO$_4$, respectively) was beneficial for dye effluent fractionation.

Seemingly, the UF ceramic membranes have more advantages over polymeric membranes, however they need larger footprint and they are crumble (in contrast to polymeric membranes, which are flexible). UF polymeric membranes have been rarely applied in reactive dye removal. Merely, Aouni et al. (2012) evaluated the usability of UF polymeric membranes (cut-off equal to 1 and 10 kDa) in the treatment of model reactive dye (Everzol Black, Everzol Blue, and Everzol Red) solutions and real textile wastewater. High COD retentions (80–90%) were achieved, however this study was not aimed at the textile effluent fractionation. Moreover, the intensive fouling phenomenon was observed in the experiments. An integrated process UF-diafiltration with the use of UF tight polyethersulfone membrane (cut-off equal to 5 kDa) was evaluated by Lin et al. (2016). The process idea was quite similar to that described by Jiang et al. (2018a). Likewise, it was demonstrated that Reactive Blue 2 dye was removed by 99% with simultaneous passage of Na$_2$SO$_4$ salt to permeate (1% of salt rejection only).

According to the above short literature review, it can be concluded that the fractionation of reactive dye-salt mixtures by low-pressure membrane processes is still a challenge. Therefore, the presented study aimed at the evaluation of reactive dyes separation by ultrafiltration from model solutions containing mineral salts. The possibility of salt recovery from dye-salt mixtures was also evaluated. Application of low-pressure membrane process could be beneficial in view of membrane permeability and overall process efficiency.

**MATERIALS AND METHODS**

**Membranes**

UF flat membranes (Intersep Nadir) made of polyethersulfone (PES) and regenerated cellulose (C) where used in the experiments. The cut-off values of the tested membranes were equal to 10 kDa, however the mean pore radius of the C membranes was greater than the pore size of the PES membranes (4.89 and 2.04 nm, respectively) (Majewska-Nowak, 2005). The membrane active surface area was equal to 0.0045 m$^2$.

**Experimental solutions**

Model solutions of organic dyes were used in the UF tests. Five reactive dyes (anionic in nature), varied in molecular weights, were chosen for the study. The characteristics of the dyes was given in Table 1. The used dyes were purchased from Boruta Company (Poland) or from Merck Polska. The initial concentration of each dye in model solutions was equal to 100 mg/dm$^3$. All tests were performed for single dye solutions, however the solution composition varied in salt content. To simulate dye bath composition, monovalent salt (NaCl) and/or divalent salt (Na$_2$SO$_4$) were added to the dye solutions. Concentration of
Table 1. Characteristics of the reactive dyes used in the UF tests

<table>
<thead>
<tr>
<th>Dye</th>
<th>Molecular weight, Da</th>
<th>Company</th>
<th>Dye symbol</th>
<th>λ_max, nm</th>
<th>Chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactive Orange 16</td>
<td>617.53</td>
<td>Merck</td>
<td>RO16</td>
<td>486</td>
<td>C₂₆H₁₂N₂Na₂O₄S₂</td>
</tr>
<tr>
<td>Remazol Brilliant Blue R</td>
<td>626.53</td>
<td>Merck</td>
<td>RBB</td>
<td>594</td>
<td>C₃₆H₂₈N₂Na₂O₄S₃</td>
</tr>
<tr>
<td>Reactive Orange 20</td>
<td>682.18</td>
<td>Boruta</td>
<td>RO20</td>
<td>491</td>
<td>C₂₆H₁₂Cl₂Na₂O₄S₂</td>
</tr>
<tr>
<td>Reactive Black 5</td>
<td>991.8</td>
<td>Boruta</td>
<td>RB5</td>
<td>533</td>
<td>C₃₆H₂₈N₂Na₂O₄S₃</td>
</tr>
<tr>
<td>Reactive Red 120</td>
<td>1469.98</td>
<td>Merck</td>
<td>RR120</td>
<td>624</td>
<td>C₃₆H₂₈Cl₂Na₂O₄S₂</td>
</tr>
</tbody>
</table>

Note: *Wavelength corresponding to the maximum absorbance of the dye solution.

mineral salts in dye solutions was equal to 2 g/dm³ (for single salt NaCl or Na₂SO₄) and 1 g/dm³ (for each salt in a mixture of NaCl and Na₂SO₄).

Ultrafiltration process

An Amicon UF stirred cell (model 8400) was used in the experiments. The total volume of the cell amounted to 350 cm³, whereas membranes had a diameter of 76 mm. Intermittent recirculation of the permeate to UF cell enabled constant concentration of the feed solution. The UF process involved a pressure of 0.2 MPa. The pressure was generated by nitrogen delivered from a gas cylinder. The used UF installation was described in details elsewhere (Majewska-Nowak, 2009).

Prior to the UF tests the new membranes were conditioned with distilled water at 0.2 MPa until the constant permeate flux was established. The permeate volume fluxes and retention coefficients were analyzed with respect to the solutions of experimental dyes and mineral salts after steady conditions of permeation were achieved. All measurements were made in duplicate and the average values of fluxes, dye concentrations and conductivity values were considered in the discussion of the obtained results.

The permeation measurements were carried out with distilled water, dye solutions, and dye solutions containing mineral salts (single salt Na₂SO₄ or NaCl as well as mixture of NaCl and Na₂SO₄ salts). The permeate/water volume flux was calculated according to the Eq. 1:

\[ J = \frac{V}{A \cdot t} \]  

(1)

where: \( J \) – permeate/water volume flux (m³/m²/day); \( V \) – volume of permeate/water (m³); \( t \) – time (day); \( A \) – surface area of the membrane (m²).

The relative flux was calculated according to the equation Eq. 2:

\[ RF = \frac{J_d}{J_w} \]  

(2)

where: \( RF \) – relative flux, \( J_d \) – volume flux of dye solution (m³/m²/day), \( J_w \) – volume flux of water (m³/m²/day).

The dye retention coefficient was calculated from the Eq. 3:

\[ R_d = \frac{C_id - C_{id}d}{C_id} \cdot 100\% \]  

(3)

where: \( R_d \) – dye retention coefficient (%); \( C_id \) – dye concentration in the feed/concentrate (mg/dm³); \( C_{id}d \) – dye concentration in the permeate (mg/dm³).

Dye concentration in model solutions was determined spectrophotometrically (with the use of the spectrophotometer Hitachi-1900) at a wavelength corresponding to the maximum absorbance of the sample (Table 1).

The salt rejection was evaluated indirectly by calculating the electrical conductivity (EC) retention from the Eq. 4:

\[ R_{EC} = \frac{C_{id} - C_p}{C_{id}} \cdot 100\% \]  

(4)

where: \( R_{EC} \) – EC retention coefficient (%), \( C_{id} \) – electrical conductivity of the feed/concentrate (µS/cm), \( C_p \) – electrical conductivity of the permeate (µS/cm).

Electrical conductivity of the treated solutions and permeates was measured with use of the conductometer Elmetron type CC-411.

RESULTS AND DISCUSSION

Salt effect on membrane transport properties

The study was aimed at evaluating the impact of salt content in the feed on the efficiency of ultrafiltration removal of reactive dyes. To reach this aim, generally two parameters should be rated, i.e. membrane permeability and dye rejection. Figs. 1 and 2 show the effect of salt presence in water and dye solutions, respectively.
on the permeate volume flux for tested membranes. Separation properties of UF membranes are discussed in the next chapter. Although the cut-off values of both tested membranes were the same (10 kDa), the membrane permeability was significantly diverse. The water flux for C10 membrane amounted to 1.02 m$^3$/m$^2$-day, whereas PES10 membrane exhibited lower flux (0.7 m$^3$/

![Fig. 1. Water volume flux (J$_w$) for membranes made of regenerated cellulose (C10) and polyethersulfone (PES10) versus composition of water salt solution (H$_2$O; H$_2$O + 2 g NaCl/dm$^3$; H$_2$O + 2 g Na$_2$SO$_4$/dm$^3$; H$_2$O + 1 g NaCl/dm$^3$ + 1 g Na$_2$SO$_4$/dm$^3$)](image1)

![Fig. 2. a) Volume flux of dye solutions (J$_d$) for membrane made of regenerated cellulose (C10) versus composition of dye solution (dye; dye + 2 g NaCl/dm$^3$; dye + 2 g Na$_2$SO$_4$/dm$^3$; dye + 1 g NaCl/dm$^3$ + 1 g Na$_2$SO$_4$/dm$^3$); b) volume flux of dye solutions (J$_d$) for membrane made of polyethersulfone (PES10) versus composition of dye solution (dye; dye + 2 g NaCl/dm$^3$; dye + 2 g Na$_2$SO$_4$/dm$^3$; dye + 1 g NaCl/dm$^3$ + 1 g Na$_2$SO$_4$/dm$^3$)](image2)
m²/day) than C10 membrane at ΔP=0.2 MPa. The obtained flux values were in accordance with the membrane pore size – the mean pore radius of the C10 membrane was equal to 4.89 nm, whereas the pore size of the PES10 membrane was lower and amounted to 2.04 nm (Majewska-Nowak, 2005).

The presence of mineral salt in water solutions generally worsens the membrane permeability. This effect was more pronounced for the C10 membrane than for the PES10 membrane and the 8% decrease in water flux was observed when NaCl salt was added individually or together with Na₂SO₄. In the case of polyethersulfone membrane the drop in water flux due to mineral salt presence was slight (4% only) irrespectively of the feed water composition. The decrease in membrane permeability observed for water salt solutions could be attributed to the rise in osmotic pressure and reduction of the driving force (Jiang et al., 2018b).

The effect of mineral salt presence in dye solutions on membrane permeability is shown in Fig.2. Similarly as for the experiments with water salt solutions, a slight decrease in membrane permeability was observed. In the case of C10 membrane the variations in permeate fluxes were more noticeable than for the PES10 membrane – the permeate flux for C10 membrane varied in the range of 0.75–0.9 m³/m²/day depending on the dye and salt type. The greatest drop in permeate flux (approximately 15% in comparison to permeate flux when no salt was added into dye solution) was observed for Remazol Brilliant Blue R (BRR) dye, when NaCl salt was present in dye solution. In turn, for Reactive Orange 16 (the dye of the lowest molecular weight) the observed permeate fluxes took the highest values (in comparison to the permeate fluxes for other dye solutions), irrespectively of the salt composition in the feed.

The impact of mineral salt in dye solutions on permeability of the PES10 membrane was rather slight – the permeate flux varied in a small range from 0.5 to 0.61 m³/m²/day. The greatest drop in volume flux due to salt presence (NaCl) was observed for Reactive Red 120 dye (the dye of the highest molecular weight). The observed worsening of membrane permeability, when dye solutions containing mineral salts are subjected to UF process, can be explained (similarly as for water salt solutions) by increasing of the osmotic pressure of the tested solutions and decreasing of driving force (i.e., the pressure difference between both membrane sides).

Besides the deterioration of permeate flux caused by mineral salts, a significant difference between pure water flux and permeate flux for dye solutions was noted. The intensity of this phenomenon, called fouling, can be evaluated by the relative flux values (RF) (Table 2). Generally, it was found that the fouling intensity was more pronounced for membrane made of polyethersulfone (PES10), than for membrane made of regenerated cellulose (C10), especially when no salt was present in the model dye solutions. In the case of the C10 membrane the relative flux amounted to 0.85–0.88, whereas for PES10 membrane the RF value was in the range of 0.75–0.84.

The worsening of membrane permeability during ultrafiltration of solutions containing various organic components is a well-known phenomenon, which can be attributed to adsorptive fouling. Membrane fouling is strictly related to hydrophilic/hydrophobic properties of the experimental membranes and retained substances.

Table 2. The relative flux values for ultrafiltration of reactive dye solutions

<table>
<thead>
<tr>
<th>Dye solution (no salt)</th>
<th>Membrane</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PES10</td>
<td>C10</td>
</tr>
<tr>
<td>Reactive Orange 16</td>
<td>0.77</td>
<td>0.88</td>
</tr>
<tr>
<td>Remazol Brilliant Blue R</td>
<td>0.80</td>
<td>0.85</td>
</tr>
<tr>
<td>Reactive Orange 20</td>
<td>0.84</td>
<td>0.88</td>
</tr>
<tr>
<td>Reactive Black 5</td>
<td>0.79</td>
<td>0.88</td>
</tr>
<tr>
<td>Reactive Red 120</td>
<td>0.75</td>
<td>0.88</td>
</tr>
<tr>
<td>Dye solution + 2 g NaCl/dm³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactive Orange 16</td>
<td>0.74</td>
<td>0.88</td>
</tr>
<tr>
<td>Remazol Brilliant Blue R</td>
<td>0.81</td>
<td>0.74</td>
</tr>
<tr>
<td>Reactive Orange 20</td>
<td>0.82</td>
<td>0.77</td>
</tr>
<tr>
<td>Reactive Black 5</td>
<td>0.79</td>
<td>0.77</td>
</tr>
<tr>
<td>Reactive Red 120</td>
<td>0.71</td>
<td>0.77</td>
</tr>
<tr>
<td>Dye solution + 2 g Na₂SO₄/dm³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactive Orange 16</td>
<td>0.74</td>
<td>0.83</td>
</tr>
<tr>
<td>Remazol Brilliant Blue R</td>
<td>0.78</td>
<td>0.83</td>
</tr>
<tr>
<td>Reactive Orange 20</td>
<td>0.80</td>
<td>0.83</td>
</tr>
<tr>
<td>Reactive Black 5</td>
<td>0.76</td>
<td>0.85</td>
</tr>
<tr>
<td>Reactive Red 120</td>
<td>0.73</td>
<td>0.83</td>
</tr>
<tr>
<td>Dye solution + 1 g NaCl/dm³ + 1 g Na₂SO₄/dm³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactive Orange 16</td>
<td>0.77</td>
<td>0.85</td>
</tr>
<tr>
<td>Remazol Brilliant Blue R</td>
<td>0.87</td>
<td>0.88</td>
</tr>
<tr>
<td>Reactive Orange 20</td>
<td>0.83</td>
<td>0.88</td>
</tr>
<tr>
<td>Reactive Black 5</td>
<td>0.78</td>
<td>0.88</td>
</tr>
<tr>
<td>Reactive Red 120</td>
<td>0.77</td>
<td>0.85</td>
</tr>
</tbody>
</table>
According to the manufacturer information, the membranes made of regenerated cellulose are characterized by higher hydrophilicity than polyethersulfone membranes, thus the RF values noted for C10 membrane were higher than the RF values calculated for PES membrane (when no salt was added in dye solutions). For UF experiments with dye-salt solutions more intensive fouling was still observed for the PES10 membrane than for the C10 membrane (with the exception of RBB dye solution), however the differences between RF values for C10 and PES10 membrane were much smaller. On the other hand, the presence of single salt (NaCl or Na$_2$SO$_4$) in the dye solutions brought about a slightly higher fouling intensity in comparison to fouling intensity observed when there was no salt in the dye solutions. It seems that the increased fouling intensity due to salt presence was caused by the shielding effect of salt ions and thus facilitated adsorption of dye particles on the membrane surface or inside the membrane matrix. When high ionic strength feeds are processed, the positive ions (Na$^+$) in solution can shield the negative groups (Cl$^-$ or OH$^-$) connected with the membrane surface. Thus, the electrostatic repulsion between the membrane and anionic dye particles is diminished and dye adsorption on/in membrane will be possible (Lin et al., 2015). On the other hand, due to presence of mineral salts in high concentration in the feed, the membrane swelling can occur – some solutes can interact with membrane material creating additional free volumes and more open pores in membrane matrix, and thus increasing the permeate flux (Luo et al., 2013). In this case, the rather small spherical particles of RBB dye (see also next chapter) can enter the enlarged membrane pores causing fouling or they can even occur in the permeate.

Taking into account the obtained results, the more general conclusion can be formulated that besides the membrane hydrophilic/hydrophobic properties, the difference between the pore size and the size of dye particles is also important in adsorptive fouling.

**Salt effect on membrane separation properties**

Besides the membrane permeability, the separation efficiency towards selected pollutants is also important in the UF process evaluation. The retention coefficients obtained for the tested dyes depending on the salt content in the feed are shown in Fig. 3.

Generally, the separation efficiency of all tested dyes was dependent on the salt presence in the treated solution. The effect of mineral salt on dye retention was more pronounced for the C10 membrane than for the PES10 membrane. In the case of the C10 membrane the dye retention coefficients varied in the wide range – from 55 to 83%, whereas for PES10 membrane the degree of dye separation was less diverse and amounted to 81–96%. Basically, for both membranes worsening of dye separation efficiency due to salt presence was observed. For the C10 membrane the drop in the dye retention coefficient due to mineral salt presence (in comparison to dye retention with no salt in the dye solution) predominantly amounted to 12–17%, whereas this drop for the PES10 membrane was approximately equal to 3–5% (with the exception of RBB dye, for which even 16% drop in dye retention was noted).

The membrane made of polyethersulfone (PES10) exhibited higher retention coefficients towards reactive dyes than the membrane made of regenerated cellulose (C10). This observation was valid for all dyes irrespectively of the solution composition and it was consistent with the membrane pore size – the mean pore radius of the PES10 membrane amounted to 2.04 nm and was significantly smaller than the mean pore radius of the C10 membrane (5.01 nm) (Majewska-Nowak, 2005). As it was already demonstrated in the previous chapter, the C10 membrane exhibited higher permeability than the PES10 membrane. Possible, the high permeate flux caused the increased dye concentration in the near-membrane boundary layer, thus facilitating migration of a greater number of non-aggregated dye particles to the permeate.

Based on the results given in Fig. 3 it can be concluded that the dye molecular weight has minor impact on the retention coefficients, irrespectively of the membrane type, excluding Remazol Brilliant Blue dye. The rejection of RBB dye was rather low (C10 membrane) or unexpectedly high (PES10 membrane) in comparison to the rejection rates observed for RO16 dye. Both dyes are characterized by a similar molecular weight (Table 1), however they differ in chemical structure and particle shape – RO16 dye is a mono-azo dye and it’s particle is elongated (Jiang et al., 2018b), whereas RBB dye belongs to antraquinone dyes and it’s particle has a shape close to a sphere (Jiang et al.,
Therefore, the particles of RBB dye can easily enter and pass large pores of the C10 membrane, whereas the PES10 membrane with small pores is a sufficient barrier to retain particles of this dye in the concentrate (similarly as the particles of RO16 dye are retained).

Although there was no distinct impact of dye molecular weight on dye separation efficiency, in the case of the C10 membrane the retention coefficients for RB5 and RR120 dyes were slightly higher than the retention coefficients noted for other dyes tested (especially for experimental series with no salt addition) (Fig. 3a). Reactive Black 5 and Reactive Red 120 are characterized by the highest molecular weight (991.8 and 1469.98 Da, respectively), thus it seems that the rejection of these dyes should be the best. However, the differences in the percentage removal of reactive dyes varying in molecular weight seems to be too small. This is an indication that not only the molecular sieve effect governs the dye transport through the tested membranes, but other phenomena such as dye adsorption in the membrane pores, dye ability to create aggregates as well as interactions between dye particles, mineral salts and membrane matrix. This explanation is reasonable as the molecular weight of all dyes (< 1.5 kDa) is much lower that the cut-off of the applied membranes (10 kDa).

Salt passage through UF membranes

The cut-off of UF membranes is high enough to let permeation of low-molecular weight substances as mineral salts. In view of the used dye baths valorization, it is important to evaluate the degree of salt recovery in the permeate. The salt removal efficiency was evaluated indirectly by determining the variation in electrical conductivity (EC) in the feed solution and in the permeate. The initial EC values of single dye solutions (with no salt addition) were very low (88–91 µS/cm) in comparison to the initial EC values of water salt solutions (2.8–4.5 mS/cm), thus such approach enabled the evaluation of salt retention with rather
good approximation. The rejection coefficients for electrical conductivity are shown in Figure 4.

Generally, the obtained results indicated that the salt removal from dye-salt solutions was very low, especially for the C10 membrane. The EC rejection coefficients for monovalent salt were below 15%, whereas salt rejection for Na$_2$SO$_4$ or salt mixture did not exceed 23%. The obtained results are in accordance with the expectation and are promising in view of salt separation from dye-salt mixtures. It can be assumed that the salt separation efficiency can be enhanced with the use of diafiltration. However, the results obtained for the PES10 membrane were less promising in view of dye-bath valorisation. Unexpectedly, the retention of divalent salt (Na$_2$SO$_4$) was rather high and reached even 55% when Reactive Red 120 dye was present in the solution. Consequently, the salt mixture was also retained much better than for the C10 membranes. Merely, the NaCl retention was below 20%. As it was already indicated, the PES10 membrane has smaller pores than the C10 membrane, thus the salt rejection could be slightly better for the PES10 membrane than for the C10 membrane. However, taking into account the size of salt molecules, this is insufficient explanation for salt rejection by UF membranes. Possible, some other phenomena take part in the salt transport across UF membranes (interactions of salt molecules with dye particles or with membranes, precipitation of divalent salt present in high concentration, especially in the membrane boundary layer).

CONCLUSIONS

The presence of mineral salt in the dye solutions treated by ultrafiltration generally worsen the membrane permeability. This effect was more pronounced for membrane made of regenerated
cellulose than for polyethersulfone membrane and even the 15% decrease in permeate flux was observed when NaCl salt was added into dye solutions. The decrease in membrane permeability observed for dye-salt mixtures could be attributed to the rise in osmotic pressure and reduction of the driving force, as well as to the adsorptive fouling of dye particles on the membrane surface or in the membrane pores.

The separation efficiency of all tested dyes was dependent on the salt presence in the treated solution. The negative effect of mineral salt on dye retention was more pronounced for membrane made of regenerated cellulose (C) than for polyethersulfone membrane (PES) – the dye rejection coefficients varied from 55 to 83% and from 81 to 96%, respectively. The drop in the dye retention coefficient due to mineral salt presence amounted to 12–17% and 3–5% for C and PES membranes, respectively. The reactive dye transport through the UF membranes is governed not only by the molecular sieve effect, but other phenomena should be also involved (dye adsorption in the membrane pores, dye ability to create aggregates, interactions between dye particles, mineral salts and membrane material).

In the course of dye-salt mixtures treatment by UF, the salt rejection coefficients for monovalent salt were below 15%, whereas salt rejection for Na2SO4 or salt mixture did not exceed 23%, but only for the membrane made of regenerated cellulose. The obtained results are promising in view of salt separation from dye-salt mixtures. It can be assumed that the salt separation efficiency can be enhanced with the use of diafiltration.

REFERENCES


