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REMOVAL OF REACTIVE DYES FROM AQUEOUS SOLUTIONS USING ULTRAFILTRATION MEMBRANES

The removal of five reactive dyes varying in molecular weight (Reactive Orange 16, Remazol Brilliant Blue R, Reactive Orange 20, Reactive Black 5, Reactive Red 120) was evaluated by using flat ultrafiltration membranes made of polyethersulfone (PES) and regenerated cellulose (C) characterized by various cut-off values (5, 10, and 30 kDa). The ultrafiltration process was performed in a dead-end mode under the transmembrane pressure range of 0.05–0.2 MPa. Dye concentration in model solutions was equal to 100 mg/dm^3. The separation efficiency of all tested dyes was strongly dependent on the membrane type and the membrane cut-off, as well as on the applied pressure. Unexpectedly, the molecular weight of the tested reactive dyes had a minor impact on the dye removal effectiveness. The ultrafiltration membranes made of polyethersulfone and regenerated cellulose can be used in reactive dye removal on the condition that the membrane cut-off is not higher than 10 kDa. The PES and C membranes enable the separation of reactive dyes by 80–97%, and 45–89%, respectively.

1. INTRODUCTION

Organic dyes are commonly used in the textile industry for dyeing various types of fibers and fabrics such as cotton, wool, polyester fabrics, or blended fabrics made of different fibers. Reactive dyes are widely used for dyeing cotton fibers and fabrics [1, 2]. The used dye baths after dyeing processes contain unfixed reactive dyes; the range of color in dye effluents usually varies from 200 to 400 Hazen units [2, 3]. Reactive dyes are recalcitrant to biodegradation and toxic by nature. They are very harmful when they come to contact with human and aquatic life – may cause cancer, skin diseases, and allergic reactions. Reactive dyes are also responsible for aesthetic damage to water bodies, increasing water turbidity, and reducing the penetration of light through water [3–5].

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Bearing in mind that reactive dyes are complex aromatic structures resistant to degradation, the treatment of reactive dye-containing effluents is very difficult. There are several conventional methods for the removal of reactive dyes from wastewater such as coagulation and flocculation, electrocoagulation, activated carbon adsorption, and biosorption. These technologies do not always provide satisfactory results in view of effective removal of reactive dyes. Sometimes the above-mentioned methods are not economically profitable. Thus, there is an urgent need for the investigation and development of efficient methods for the removal of reactive dyes from aqueous solutions. To solve this issue, the membrane processes have been proposed by many researchers for reactive dyes separation from industrial wastewater [6–11].

Generally, attempts to treat dye solutions by membrane processes have been observed for more than 2 decades. For example, Majewska-Nowak [6] presented a study on ultrafiltration (UF) removal of acid and direct dyes from aqueous solutions in the presence of anionic surfactants and mineral salts. The dye rejection varied in the range of 60–100% depending on the dye molecular weight and solution composition. According to Majewska-Nowak's [6] suggestion other textile dyes such as reactive dyes can also be removed using the low-pressure membrane process. This assumption was supported by the mechanism of azo dyes separation involving the molecular sieve effect and adsorption of dye particles in the UF membrane pores. In turn, the results obtained by Golami et al. [7] were not so promising as the results described by Majewska-Nowak [6]. During the removal of the reactive dye from textile effluents, only reverse osmosis (RO) enabled satisfactory dye rejection (85–99.5%), whereas nanofiltration (NF) membranes were characterized by unexpectedly low dye retention (29–35%). Several years later, Rashidi et al. [8] performed a comprehensive study on the removal of reactive dyes by tight NF membranes (200 Da). The dye retention was quite satisfactory (90–97%) and was dependent on the structure, size, and electrical charge of dyes. It was also proved that for NF performed with multicomponent solutions containing 2–5 various reactive dyes, the separation efficiency of each dye was slightly higher than the dye rejection noted for the single dye solutions.

Most recently, various novel membranes and integrated membrane processes have been the subject of research. In the study described by Jang et al. [9], the application of a tight ceramic UF membrane resulted in the excellent separation (>98.12%) of reactive dyes varied in molecular weight from 626 to 1025 Da. An integrated UF-diafiltration process enabled the concentration of Reactive Blue 19 to 140 g/dm^3 with a simultaneous passage of mineral salt (Na_2SO_4) to permeate. It was concluded that tight ceramic UF membranes have high potential in reactive dyes and Na_2SO_4 salt fractionation. The study performed by Homem et al. [10] provided an efficient alternative for microfiltration membranes by modifying them with graphene oxide. The obtained membranes rejected a Blue Corazol (reactive dye) with an efficiency of 97.8% (when model dye solution was used) and 96% (when the real textile wastewater was applied).

In some cases, especially when real textile effluents are treated, membrane processes are not able to reach suitable permeate quality. Thus, many integrated/hybrid technologies have been investigated. For example, Beluci et al. [11] investigated the combination of coagulation/flocculation followed by UF with polymer membranes modified by TiO_2. The proposed method was suitable for Reactive Black 5 dye removal (the rejection coefficient of this dye amounted to 100%). What is more, due to membrane modification, the permeate flux was increased by around 50% compared with the flux of the pristine membrane.

According to the above short literature review, it can be concluded that the removal of reactive dyes from aqueous solutions by membrane processes is still a challenge. Therefore, the presented study aimed at the investigation of reactive dyes separation by ultrafiltration. Application of low-pressure membrane process could be beneficial in terms of membrane permeability and overall process efficiency.

2. MATERIALS AND METHODS

Membranes. Commercially available UF membranes (Intersep Nadir) made of polyethersulfone (PES) and regenerated cellulose (C) were used in the experiments. The membranes differed in the cut-off values (5, 10, 30 kDa) and hydrophilicity. The characteristics of the investigated membranes is given in Table 1. In the description of a given membrane (e.g., PES10, C30), the number denotes the cut-off (in kDa). The Intersep Nadir membranes are cast on a tough, very porous polypropylene support. The active surface area of a membrane was equal to 0.0045 m^2.

Table 1

Characteristics of the Intersep Nadir membranes

Type	Polymer	Description	Cut-off[a] [kDa]	Mean pore radius[b] [nm]	Contact angle[c] [deg]
PES	polyethersulfone	moderately hydrophilic	5 10	0.62 2.04	50.01
C	regenerated cellulose	most hydrophilic	10 30	5.01 4.89	54.76

[a]Given by the producer.
[b]According to ref. [12].
[c]Determined for membranes of cut-off equal to 1 kDa.

Model solutions. The transport and separation properties of UF membranes were determined towards model solutions of organic dyes. Five reactive dyes, varying in molecular weights, were used in the experiments (Table 2). Reactive Black 5 and Reactive

Orange 20 were purchased from Boruta Company (Poland), whereas Remazol Brillant Blue R, Reactive Orange 16, and Reactive Red 120 were supplied by Merck Polska. All tests were performed for single dye solutions. The concentration of each dye in the model solution amounted to 100 mg/dm^3.

Table 2

Characteristics of the dyes used in the experiments

Dye	Symbol	Molecular weight [Da]	Classification	λ_{max} [nm]	Structural formula
Reactive Orange 16	RO16	617.53	reactive	486	$C_{20}H_{17}N_3Na_2O_{11}S_3$
Remazol Brilliant Blue R	RBB	626.53		594	$C_{22}H_{16}N_2Na_2O_{11}S_3$
Reactive Orange 20	RO20	682.18		491	$C_{23}H_{16}ClN_7O_{10}S_3$
Reactive Black 5	RB5	991.8		533	$C_{26}H_{21}N_5Na_4O_{19}S_6$
Reactive Red 120	RR120	1469.98		624	$C_{44}H_{24}Cl_2N_{14}Na_6O_{20}S_6$

λ_{max} is the wavelength corresponding to the maximum absorbance of the dye solution.

Ultrafiltration process. In the UF process of dye removal, the Amicon 8400 UF cell was used. The overall volume of the cell amounted to 350 cm^3. The membranes being tested had a diameter of 76 mm. The UF process was performed under the transmembrane pressure ranging from 0.05 to 0.2 MPa, which was generated by nitrogen coming out from a gas cylinder. The dye model solutions were continuously mixed with a magnetic stirrer. To maintain a constant concentration of the feed solution, the permeate was recirculated periodically to the filtration cell. The used installation is presented in Fig. 1.

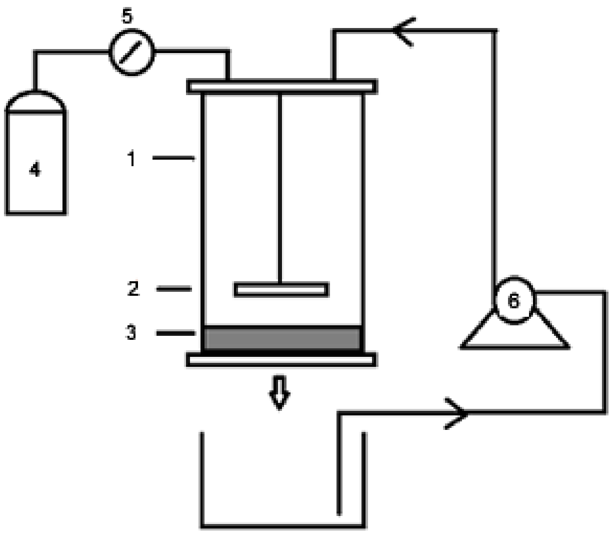

Fig. 1. Scheme of the Amicon UF cell: 1 – filtration cell, 2 – membrane, 3 – magnetic stirrer, 4 – gas (nitrogen) cylinder, 5 – pressure reducer, 6 – circulation pump

Before the experiments, the examined membranes were pre-treated with distilled water under 0.2 MPa until the constant permeate volume flux was established. Membrane conditioning lasted approximately 2–3 h. The permeate volume fluxes and retention coefficients for the experimental dyes were determined after steady conditions of flow were achieved (approximately, after 0.5–1 h of operation under a given pressure). All measurements were made in duplicate and the average values of fluxes and dye concentrations were considered in the discussion of the obtained results.

The permeate volume flux *J*, $m^3/(m^2\cdot day)$) was calculated according to the equation:

$$J = \frac{V}{At} \tag{1}$$

where: V – the volume of permeate, m^3, t – time, day, A – surface area of the membrane, m^2.

The dye retention coefficient *R*, %, was calculated from the formula:

$$R = \frac{C_i - C_p}{C_i} \times 100\% \tag{2}$$

where: C_i , C_p – initial and actual dye concentrations in the permeate, mg/dm^3.

Dye concentration in model solutions was determined spectrophotometrically (with the use of a spectrophotometer Hitachi-1900) at a wavelength corresponding to the maximum absorbance of the sample (Table 2).

3. RESULTS AND DISCUSSION

3.1. MEMBRANE SEPARATION PROPERTIES

The study was aimed at evaluating the usability of the ultrafiltration membranes for the separation of reactive dyes from aqueous solutions. The retention coefficients obtained for the tested dyes are shown in Fig. 2.

The separation efficiency of all tested dyes was strongly dependent on the membrane type and the membrane cut-off. The PES membranes exhibited higher retention coefficients towards reactive dyes than the C membranes. Analyzing the separation properties of membranes characterized by the same cut-off values it was stated that the PES10 membrane demonstrated superior dye rejection by approximately 5–10% (in comparison to the rejection for the C10 membrane). This observation was valid for all dyes irrespectively of the pressure applied and it was consistent with the membrane pore size (Table 1) – the mean pore radius of PES10 membrane amounted to 2.04 nm and was significantly smaller than the mean pore radius of C10 membrane (5.01 nm).

The dye separation efficiency increased with decreasing membrane cut-off. This relationship was especially pronounced for membranes made of regenerated cellulose,

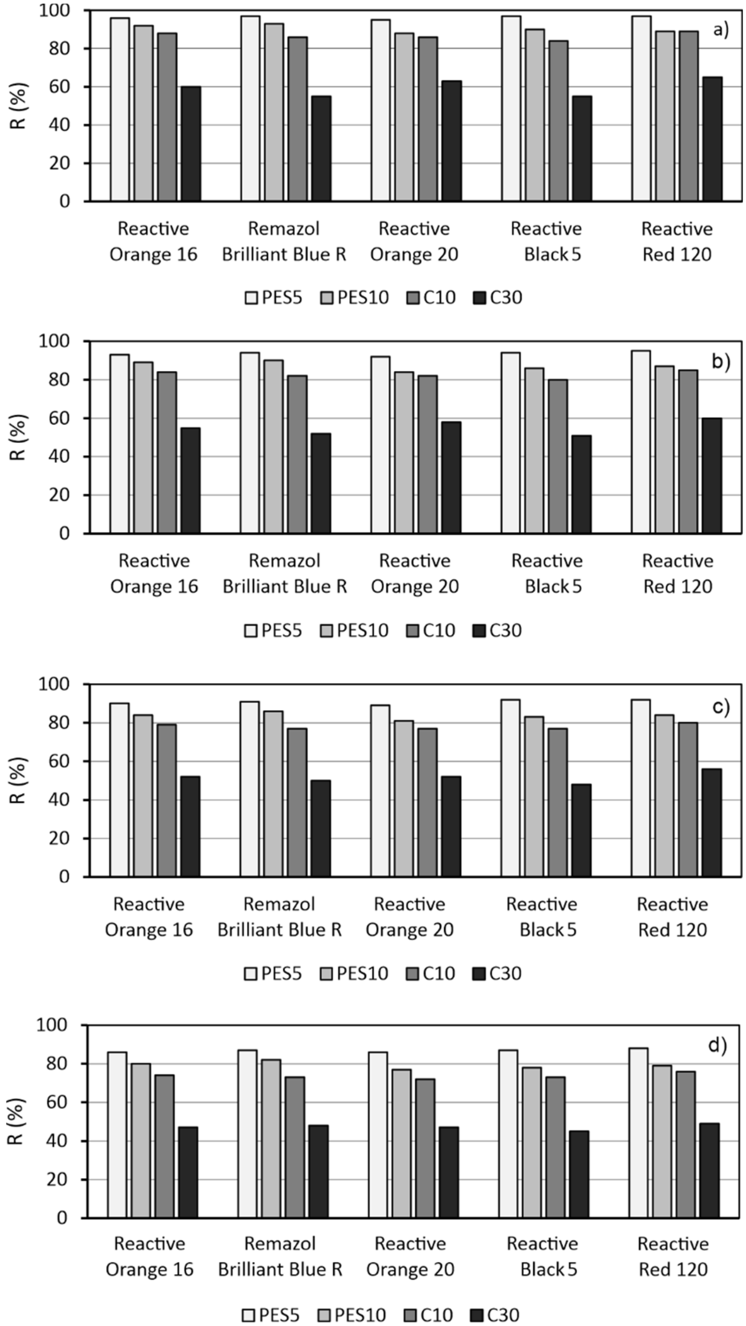

Fig. 2. Dye retention coefficient (R) for membranes made of regenerated cellulose (C) and polyethersulfone (PES) under various transmembrane pressures ΔP, MPa: a) 0.05, b) 0.10, c) 0.15, and d) 0.20

although both membranes (C10 and C30) were characterized by a similar size of pore radius (4.89 and 5.01 nm, respectively). It can be anticipated that the membrane porosity, besides the pore size, influences the transport of dye particles through UF membranes. It is worth noting that the C30 membrane exhibited significantly higher permeability than the permeability of other tested membranes (Fig. 3). Possibly, the high permeate flux caused the increased dye concentration in the near-membrane thin layer, thus facilitating the migration of a greater number of non-aggregated dye particles to the permeate (in comparison to the low permeate flux of C10 membrane).

Another important parameter that significantly influences the dye separation is the applied transmembrane pressure. It was found that with the increasing pressure, the dye retention coefficients decreased irrespectively of the membrane type and tested dye. For example, the dye retention coefficient under the pressure of 0.05 MPa was in the range of 55–97%, whereas under 0.2 MPa, the dye rejection amounted to 45–87%. The worsening of the membrane separation properties with increasing transmembrane pressure can be attributed to the elevated dye concentration in the membrane boundary layer and the increased dye passage through the membrane pores.

Based on the results given in Fig. 2, it can be concluded that the dye molecular weight has a minor impact on the retention coefficients. The removal efficiency was quite similar for all dyes tested. Merely, in the case of Reactive Red 120 and Reactive Black 5, the retention coefficients were slightly higher than those for other dyes tested. Reactive Red 120 and Reactive Black 5 are characterized by the highest molecular weights (991.8 and 1469.98 Da, respectively), thus it seems that the rejection of these dyes should be the best.

Unexpectedly, the differences in the percentage removal of reactive dyes depending on their molecular weight seem to be too small. This is an indication that not only the molecular sieve effect governs the dye transport through the UF membranes, but other phenomena such as dye adsorption in the membrane pores as well as interactions between dye particles and membrane surface charge are also possible. It can be assumed that the electrostatic repulsion between the anionic dye particles and the negative surface charges of the UF membranes is primarily responsible for dye separation. This explanation is reasonable as the molecular weight of all dyes (<1.5 kDa) is much lower than the cut-off of the applied membranes (5, 10, 30 kDa). On the other hand, adsorptive fouling can also occur, contributing to the dye removal from the feed solution. The particle size exclusion phenomenon seems to be less important in the reactive dye retention by UF membranes unless the aggregation of dye particles takes place in the membrane boundary layer.

Summing up, it can be concluded that the UF membranes made of polyethersulfone and regenerated cellulose can be used in reactive dye removal on the condition that the membrane cut-off is not higher than 10 kDa. The PES and C membranes enable reactive dye separation by 80–97%, and 45–89%, respectively.

3.2. MEMBRANE TRANSPORT PROPERTIES

The water volume flux for the experimental membranes depending on the applied pressure is shown in Fig. 3. Due to various cut-off values, the membrane permeability was significantly diverse. The flux of water varied from 0.21 to 0.61 $m^3/(m^2 \cdot day)$ for polyethersulfone membranes and from 0.44 to 10.24 m^3/m^2day for membranes made of regenerated cellulose. The obtained values were following the membrane characteristics (Table 1), however, the unexpected high flux of C30 membrane implied that the porosity of this membrane was greater than the porosity of other membranes tested. On the other hand, the permeability of all membranes increased proportionally to the increasing transmembrane pressure.

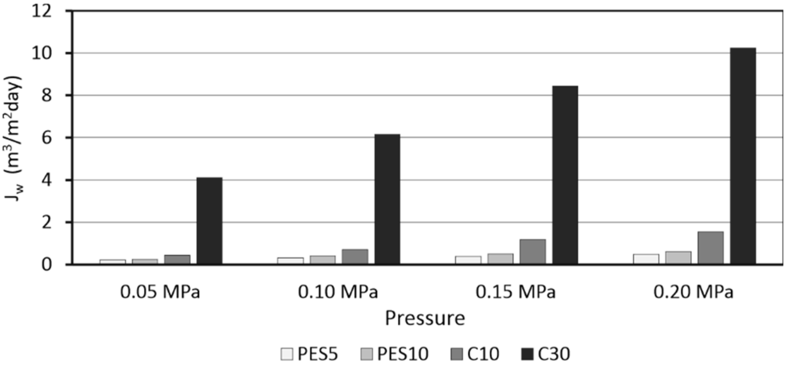

Fig. 3. Water volume flux (J_w) for membranes made of regenerated cellulose (C) and polyethersulfone (PES) versus transmembrane pressure

The permeate flux of dye solutions for PES and C membranes is given in Fig. 4. When dye-containing solutions were passing through the membranes a decrease in their permeability was observed. To evaluate the magnitude of fouling intensity, the relative flux was calculated as a ratio of J/J_w (where J denotes the permeate flux of dye solutions and J_w – the water flux for a given membrane under a given pressure). The calculated values of the relative flux are shown in Table 3. It was found that the fouling intensity was more pronounced for membranes made of regenerated cellulose than for membranes made of polyethersulfone. In the case of the C10 membrane, the relative flux decreased below 0.8 at ΔP = 0.15 and 0.2 MPa. Similarly, for the C30 membrane, the relative flux decreased to 0.75 (ΔP = 0.05 MPa). A slight tendency of the increasing fouling intensity with the increasing molecular weight of tested dyes was also observed.

In practice, the worsening of membrane permeability during ultrafiltration of model solutions containing various organic components can be attributed to adsorptive fouling. This statement is generally supported by the hydrophilic/hydrophobic properties of the experimental membranes and retained substances. According to manufacturer information, the membranes made of regenerated cellulose are characterized by higher hy-

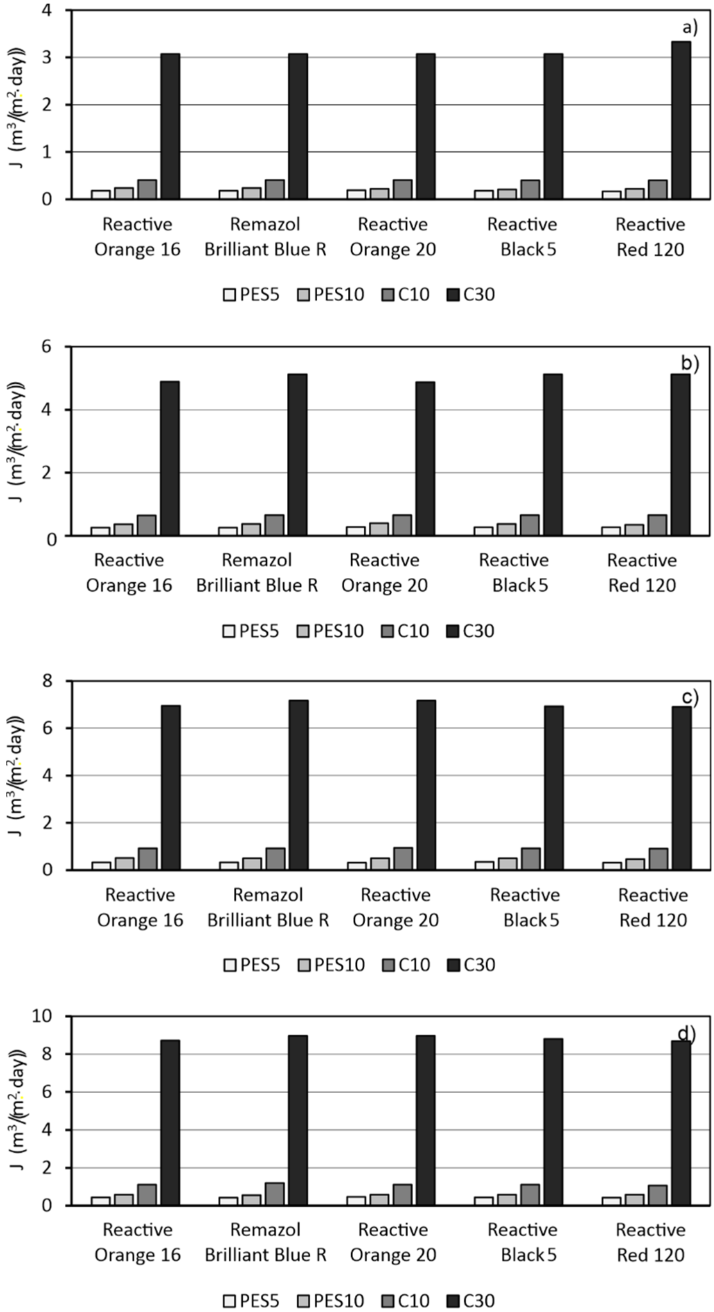

Fig. 4. Permeate flux of dye solution (J) for membranes made of regenerated cellulose (C) and polyethersulfone (PES) under various transmembrane pressures ΔP, MPa: a) 0.05, b) 0.10, c) 0.15, and d) 0.20

drophilicity than polyethersulfone membranes (Table 1). However, the decrease in permeate volume fluxes for the membranes made of regenerated cellulose was greater than the flux decrease for polyethersulfone membranes. It seems that the increased fouling intensity of the C membranes was caused by the greater pore size (in comparison to the pore size of the PES membranes), and thus facilitated adsorption of dye particles inside the membrane matrix. Based on 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.

Table 3

Relative flux values for ultrafiltration of reactive dye solutions

Dye	Membrane			
	PES5	PES10	C10	C30
ΔP = 0.05 MPa				
Reactive Orange 16	0.85	1.0	0.93	0.75
Remazol Brilliant Blue R	0.85	1.0	0.93	0.75
Reactive Orange 20	0.90	0.92	0.93	0.75
Reactive Black 5	0.85	0.88	0.91	0.75
Reactive Red 120	0.80	0.92	0.91	0.81
ΔP = 0.1 MPa				
Reactive Orange 16	0.81	0.90	0.93	0.80
Remazol Brilliant Blue R	0.81	0.93	0.94	0.83
Reactive Orange 20	0.88	0.98	0.94	0.79
Reactive Black 5	0.84	0.93	0.94	0.83
Reactive Red 120	0.84	0.85	0.94	0.83
ΔP = 0.15 MPa				
Reactive Orange 16	0.85	1.02	0.77	0.82
Remazol Brilliant Blue R	0.85	1.0	0.77	0.85
Reactive Orange 20	0.82	1.0	0.79	0.85
Reactive Black 5	0.89	1.0	0.77	0.82
Reactive Red 120	0.82	0.92	0.76	0.82
ΔP = 0.2 MPa				
Reactive Orange 16	0.92	0.95	0.72	0.85
Remazol Brilliant Blue R	0.88	0.90	0.77	0.88
Reactive Orange 20	0.96	0.97	0.72	0.88
Reactive Black 5	0.90	0.95	0.72	0.86
Reactive Red 120	0.92	0.95	0.69	0.85

4. CONCLUSIONS

- The ultrafiltration (UF) membranes made of polyethersulfone (PES) and regenerated cellulose (C) can be used in reactive dye removal on the condition that the membrane cut-off is not higher than 10 kDa. Under the pressure range of 0.05–0.2 MPa, the

PES and C membranes enable reactive dye separation by 80–97% and 45–89%, respectively.

• The separation efficiency of reactive dyes in the course of the ultrafiltration process depends on the membrane material and membrane cut-off, as well as on the applied pressure. Polyethersulfone membranes exhibit better separation properties than membranes made of regenerated cellulose, which can be attributed to the greater pore size of the C membranes than the pore size of the PES membranes. The increasing transmembrane pressure brings about the worsening of the dye retention coefficients, irrespectively of the membrane type and tested dye.

• The molecular weight of reactive dyes has a minor impact on the dye retention coefficients. It can be assumed that the reactive dye separation by ultrafiltration membranes occurs due to 1) the electrostatic repulsion between the anionic dye particles and the negative surface charges of the UF membranes, 2) the adsorptive fouling of reactive dye particles in membrane pores; 3) size exclusion effect, especially when the dye particles are present in an aggregation state in the membrane boundary layer.

• In the course of the ultrafiltration, the drop in permeate volume flux for the membranes made of regenerated cellulose is greater than the flux decrease for polyethersulfone membranes. The membrane hydrophilic/hydrophobic properties as well as the difference between the pore size and the size of dye particles are important in adsorptive fouling intensity.

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