

Membrane Fouling Effect During Nanofiltration of Wastewater from Dyeing Cellulose and Polyamide Fabrics

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Abstract

The aim of research was to compare the parameters of nanofiltration of textile wastewater generated in two different dyeing processes. Tests were carried out for wastewater from dyeing cellulose fibres with direct and reactive dyes and from dyeing polyamide fibres with acid dyes. The applicability of selected nanofiltration membranes, including polysulfone, cellulose acetate and polyamide membranes, in the filtration of some wastewater streams was examined. Research was carried out to investigate the fouling of membranes during wastewater nanofiltration. During the filtration of the wastewater after reactive dyeing, a significant reduction in the process efficiency due to membrane fouling was observed. In the case of wastewater from the dyeing of polyamide fibres, a reduction in the process efficiency during the membrane operation did not occur at all or was very small.

Key words: textile wastewater treatment, membrane fouling, membrane filtration, nanofiltration.

water. They refer mainly to the dyeing of polyester fibres [7, 8]. Chidambaram *et al.* [9] carried out a series of tests with the use of different acid and alkaline dyes to analyse the impact of dye properties on membrane fouling.

Wastewater generated during dyeing processes are characterised by many parameters whose values are dependent on the dyed raw material. Depending on the type of fibres to be dyed, different chemicals and dyeing parameters are used. **Table 1** summarizes the characteristics of wastewater from dyeing cellulose and polyamide fibres.

It follows from numerous studies that in the case of wastewater from dyeing with reactive and direct dyes, the heaviest load on membrane processes is brought about by dyeing baths. They contain up to 30% of unbound dye and low-molec-

ular compounds such as inorganic salts and alkalis. Wastewater of this type is alkaline, with pH above 8. The value of COD of this wastewater ranges from 300 to 1000 mg/dm³. The streams of wastewater from rinsing and washing contain mainly surfactants and small amounts of unbound dyes. Such streams usually do not cause problems in membrane processes.

Experimental

Materials

Wastewater from the dyeing of polyamide fibres is characterised by more a uniform composition than that from dyeing with reactive and direct dyes. Dyes for synthetic fibres, acid dyes for polyamide and synten dyes for polyester are characterised by high dyeing efficiency, which causes that practically no dye remains in the wastewater after the dyeing process.

Introduction

Studies on the application of membrane filtration in textile wastewater treatment published in world literature are limited mainly to the wastewater from dyeing cellulose fibres [1 - 6]. This results primarily from the fact that the wastewater from the dyeing of cellulose products is most difficult to treat due to the presence of various compounds, including dyes, auxiliary chemicals, salts, alkalis and impurities from the raw material being processed. There are relatively few studies dedicated to another type of waste-

Table 1. Characteristics of wastewater from the dyeing of cellulose and polyamide fibres.

Parameters of dyeing wastewater	Wastewater type	
	Wastewater from the dyeing of cellulose fibres with reactive and direct dyes	Wastewater from the dyeing of polyamide fibres with acid dyes
Dye concentration in wastewater after dyeing process	up to 30% of concentration used for dyeing	trace amounts
pH of wastewater	alkaline, above 8	acidic, from 5 to 7
Chemicals used	salts (NaCl, Na ₂ CO ₃), alkalis (NaOH)	organic acids (acetic, formic)
Auxiliary substances	anionic, cationic and nonionic surfactants	anionic and nonionic surfactants, yarn preparation
Dyeing bath temperature	from 60 °C (reactive dyes) to 100 °C (direct dyes)	100 °C
COD	usually from 1000 mg O ₂ /dm ³	above 1000 mg O ₂ /dm ³
Multiplicity of rinsing and washing stages	from 3 to 5	from 1 to 3

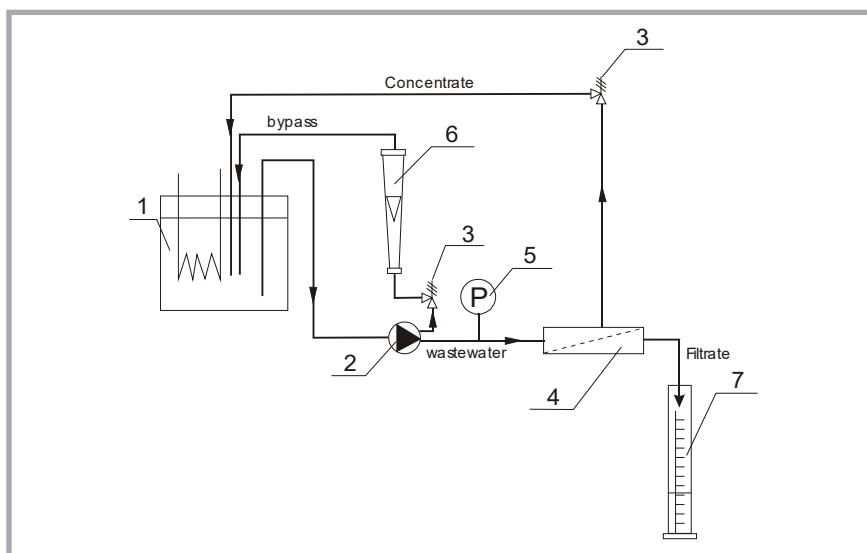


Figure 1. Schematic of the set-up for nanofiltration and reverse osmosis: 1 – thermostat, 2 – pump, 3 – control valves, 4 – pressure chamber with a membrane, 5 – manometer, 6 – rotameter, 7 – measuring cylinder.

In the dyeing of polyamide fibres, chemical auxiliary agents, mainly anionic and nonionic surfactants, are also used, which also get into the wastewater. Polyamide fibre dyeing is carried out in acidic conditions; the pH of such wastewater ranges from 5 to 7, depending on the number of rinsing and washing steps during the whole dyeing cycle. For pH adjustment mainly acetic or formic acid is used. Acetic acid contributes to an increase in COD in the dyeing wastewater, hence the value of this parameter is high.

The wastewater from polyamide fibre dyeing also includes yarn preparation, which is used in the process of hosiery knitting. These are antistatic compounds based on hydrophobic esters and mineral oils, which form an emulsion in the aqueous phase. The presence of these compounds also contributes to a significant growth in COD, which in some cases can reach even several thousand mg/dm³.

Analysis of membrane fouling during the filtration process and searching for methods of its reduction is a relatively new issue. The phenomenon of fouling is a complex process that requires in-depth studies. During pressure membrane filtration (MF, UF, NF and RO), fouling results mainly from the three known phenomena:

- a) formation of a gel layer on the surface due to concentration polarization,
- b) adsorption of molecules on the surface and inside the membrane pores due to the mechanism of screening, which leads to pore narrowing, and

- c) deposition of agglomerates leading to total pore blocking [10, 11].

Work carried out on a pilot scale showed that there were many factors affecting the retention of organic compounds with the use of NF/RO filtration membranes, e.g. calcification of the membrane and also the presence of other organic and inorganic compounds in the solution [12, 13]. Another problem is the precipitation of sparingly soluble salts on the membrane surface [14, 15]. While examining the effect of humic acid and CaCO₃ on the degree of retention of selected compounds, including pharmaceuticals (sulfametoxazole and carbamazepine), Vogel *et al.* [13] reported a marked decrease in the retention of tested compounds of inorganic origin caused by fouling. The deposition of inorganic particles on the membrane changed the density of the surface charge on the membrane. Hoek and Elimelech [16] suggested that the presence of a porous layer on the membrane surface inhibited the diffusion of compounds from the membrane surface back to the solution, causing concentration polarisation.

The NF filtration membrane usually consists of an ultrathin (0.1 - 0.20 µm) amorphous active polymer layer, with pores 2 - 5 nm in diameter, on the surface of a porous support membrane [17, 18]. The active layer usually has both negative and positive charge, depending on the type of monomer used for its production. The separation of substances dissolved by nanofiltration mem-

branes is primarily due to the exclusion of the size and electrostatic repulsion between the membrane surface and dissolved particles [19-21, 18]. Screening or exclusion is the most important factor in the separation of uncharged particles, while in the case of the separation of ionic substances the mechanisms of screening and electrostatic interactions are responsible for separation [18]. Electrostatic interactions between the membrane and charged particles are an important parameter which affects the process efficiency [9]. Chidambaram *et al.* [9] carried out their research on the NF 270 filtration membrane at pH 3, 7 and 10 for three dyes with negatively charged particles: Acid Red 87, Acid Black 1, Direct Blue 53, and three dyes with a positive charge: Azure A, Basic Blue 9 and Basic Green 4. The authors found that in the pH range above 7, dye particles which are negatively charged are not attracted electrostatically towards the membrane, and therefore they have no significant effect on the filtration flux reduction, while positively charged particles accumulate on the membrane surface and reduce the filtration flux. Reduction of the filtration flux increases with the growth of pH for these particles because electrostatic interaction induces the blocking of membrane pores due to concentration polarization and molecular adsorption [9]. At small pH ranges this effect is reversed, with the negatively charged particles contributing to the reduction in the filtration flux.

In our study a series of tests were carried out to compare the yield and efficiency of the nanofiltration of wastewater generated by two different processes: dyeing of cellulose fibres with reactive and direct dyes and the dyeing of polyamide fibres with acid dyes. Analysis of the results was made in relation to membrane fouling during the treatment of selected wastewater.

Methods

The process of nanofiltration was carried out by the cross-flow method at a constant flow rate, amounting to 2 dm³/min, which was adjusted by the rotameter (6). Tests were performed at a pressure of 1.5 or 0.7 MPa, at 40 °C. A nanofiltration system is shown schematically in **Figure 1**. The filtered medium is taken from thermostat (1) 5 dm³ in volume. The process is carried out so as to collect filtrate in a separate vessel (7), which causes its gradual concentration. The process is

conducted until reaching double concentration.

Several flat sheet membranes were selected for the tests. They are used in nanofiltration to determine which membrane is the best for a specific wastewater type. **Table 2** gives characteristics of membranes used in the tests.

The efficiency of the treatment processes was estimated on the basis of the efficiency of the filtration process and parameters of the wastewater treated:

- chemical oxygen demand COD in mg/dm³;
- total organic carbon TOC in mg C/dm³;
- maximum of the absorbance spectrum;
- electrolytic conductance as the salt content index.

The chemical oxygen demand and total organic carbon were analysed using HACH LANGE cuvette tests. Measurements were made on a spectrophotometer - DR 2800 (HACH LANGE, Germany). The method consists in using ready-made HACH LANGE glass cuvette tests which contain ready-made reagents. After adding an appropriate amount of wastewater, a chemical reaction takes place which results in appropriate coloration of the liquid present in the glass vial. Based on the intensity of the liquid's colour measured by the HACH LANGE spectrophotometer, which is specially adapted to tests with bar-codes identifying the sample, the device shows the values of parameters COD and TOC. The absorbance of the wastewater was measured by a UV-VIS JASCO V-630 spectrophotometer (JASCO, Japan).

The conductance and pH of the wastewater was measured by a S47-K Seven-Multi pH/conductometer (Mettler Toledo, Switzerland). The pH was measured using an InLab®RoutinePro electrode, while the electrolytic conductance was measured by an InLab®731 electrode.

The quality of dyeing and utility parameters of textile products were estimated on the basis of the following analyses:

- relative coloration intensity, determined on a Datacolor 650 spectrophotometer (Datacolor Int., USA), using a color-determining program - Datacolor Tools;
- resistance of colour to washing, according to the standard PN ISO 105-C06:1996 met. A1S;

Table 2. Comparison of membranes used for nanofiltration.

Type of membrane	Polymer	Rejection, % (MgSO ₄)	pH range	Typical flux/ Pressure dm ³ /m ² ·h/MPa	Producer
DL	TF (polysulfone)	96	2 - 11	53/0.69	GE Osmonics
DK		98		37/0.69	
HL			3 - 9	66/0.69	
CK	Acetate cellulose	92 2K-Na ₂ SO ₄	2 - 8	39/1.52	KOCH
TFC-SR3	TF (composite polyamide)		4 - 10	Not measured	
TFC-SR2	Proprietary		4 - 9		

- resistance to wet abrasion, according to the standard PN-EN ISO 105-X12:1999;
- resistance to acid and alkaline sweat, according to the standard PN-EN ISO 105-E04:1999.

Changes in the morphology and chemical composition of the membrane surface were estimated using SEM investigations performed on a VEGA3 scanning electron microscope (TESCAN, Czech Republic) equipped with the system Energy Dispersive X-ray Spectrometer EDS INCA Energy (Oxford Instruments Analytical, United Kingdom). The X-ray EDS INCA Energy microanalyser (Oxford Instruments Analytical) is equipped with a monocrystalline Si(Li) detector and used to detect elements of the composite material surfaces tested. The topography of the surface of membranes applied in experiments was tested in a high vacuum using secondary electron beams. For this purpose the surface of each preparation was sputtered with a conductive material – gold, using a vacuum sputterer (Quorum Technologies Ltd., United Kingdom). The membrane samples were observed at a magnification of 5000×, 10000× and 20000×. Microscopic images were also recorded

in a low vacuum without gold sputtering, using back-scattered electron beams, at magnification 200× and 1000× in the operating conditions of the X-ray EDS microanalyser.

Objects of the research included:

- model textile wastewater from dyeing with reactive and direct dyes prepared on the basis of a number of analyses of real textile wastewater obtained after dyeing cellulose fibres. The wastewater included two types of dyes: Reactive Red 120 (0.1 g/dm³) (Helactin Red DEBN, BORUTA-ZACHEM, Poland) and Direct Red 23 (0.04 g/dm³) (Direct Red 4BS, BORUTA-ZACHEM, Poland), NaCl [7 g/dm³], Na₂CO₃ (2 g/dm³) and cationic surfactant based on polysiloxane modified with polyamone (0.17 g/dm³);
- model wastewater after dyeing polyamide fibres with acid dye, prepared on the basis of analysis of wastewater from the real dyeing of hosiery. Wastewater denoted as K1 contained 8.33 mg/dm³ of acid dye (Acid Brown Is MPG), 250 mg/dm³ of a nonionic multicomponent leveling agent, 250 mg/dm³ of awetting and washing agent based on alkane sulfo compounds, alcohol ethers, and fatty poly-

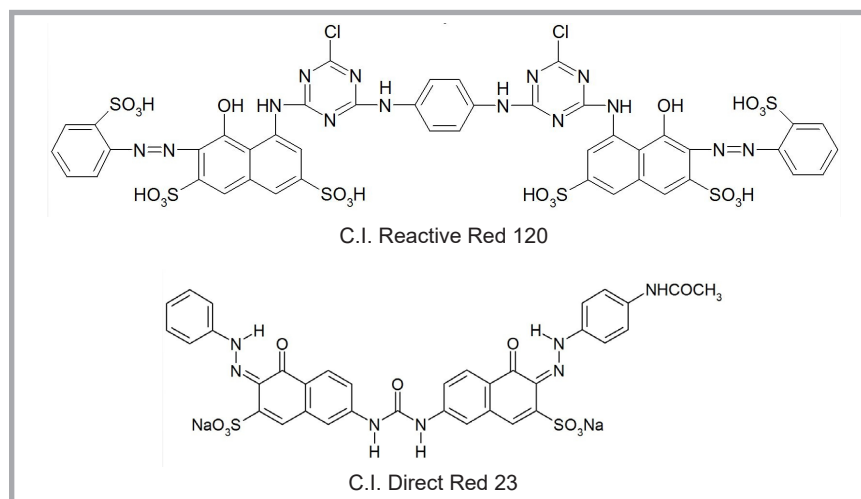


Figure 2. Formulas of test dyes used for cellulose dyeing.

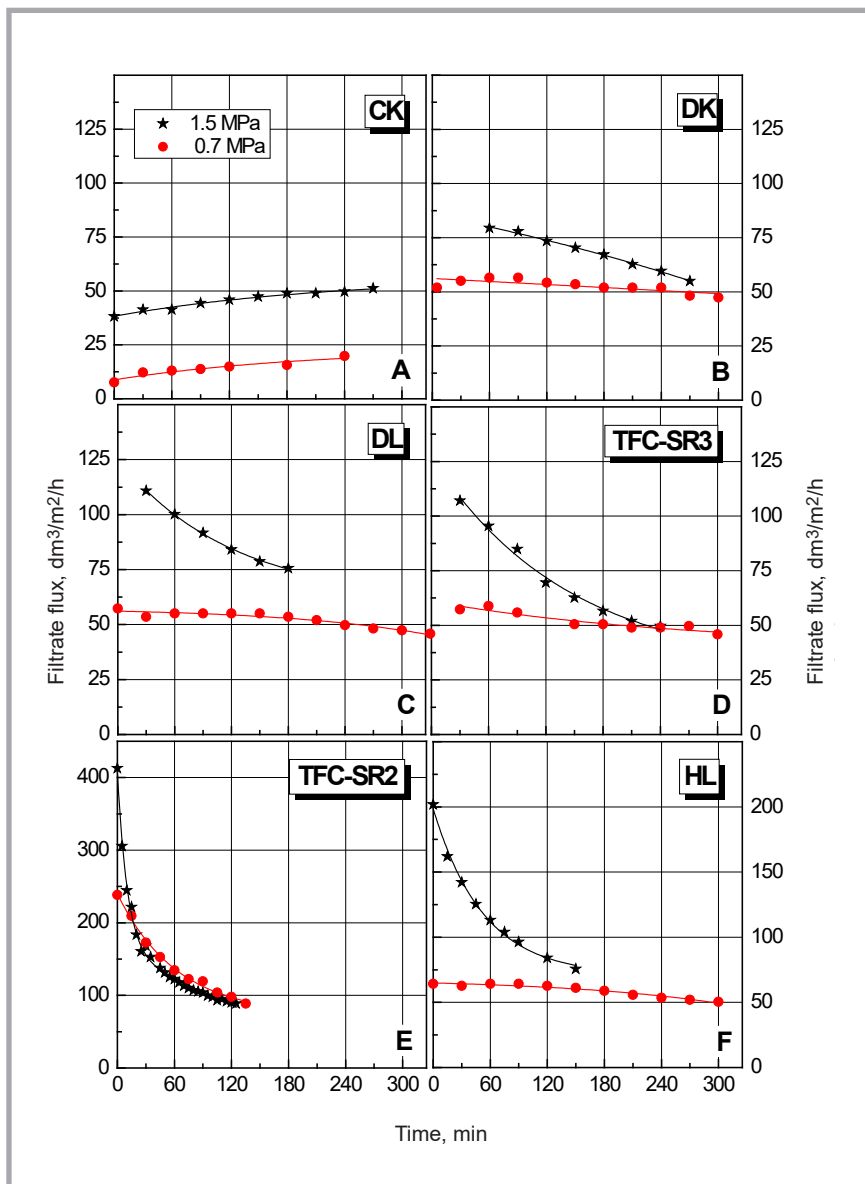


Figure 3. Changes in filtration fluxes for different membranes from the nanofiltration of wastewater after cellulose fibre dyeing.

glycols, and acetic acid CH_3COOH (used to correct pH 4.5). Wastewater denoted as K2 additionally contained

an antistatic preparation of polyamide yarn based on esters, mineral oils and antistatic emulsifiers (0.333 mg/dm^3).

Table 3. Degree of reduction in COD, TOC and wastewater conductance for the membranes under a pressure of 0.7 and 1.5 MPa.

	Type of membrane	Degree of parameter reduction, %			
		COD	TOC	conductance	absorbance ($\lambda = 525 \text{ nm}$)
at pressure of 1.5 MPa	CK	69.4	52.6	44.0	99.7
	DK	75.3	62.4	25.4	99.7
	DL	73.4	58.6	23.9	99.6
	TFC-SR3	81.2	76.4	35.6	99.9
	TFC-SR2	63.5	48.9	13.9	99.1
	HL	84.6	81.6	34.9	99.9
at pressure of 0.7 MPa	CK	80.4	66.0	37.2	99.6
	DK	68.2	59.2	17.2	99.7
	DL	67.0	48.0	16.5	99.6
	TFC-SR3	87.7	89.2	30.7	99.9
	TFC-SR2	60.5	50.1	10.6	99.2
	HL	85.9	81.9	26.6	100

Below formulas of the test dyes used for cellulose dyeing are presented in *Figure 2*.

The formula of Acid Brown Is MPG is not known; it is probably a mixture of various dyes.

Results and discussion

Nanofiltration of wastewater from the dyeing of cellulose fibres

Figure 3 shows the dependence of the filtration flux on the nanofiltration time for specific membranes. *Figure 4* (see page ...) presents changes in the filtrate absorbance after the nanofiltration process. Tests were performed on model textile wastewater after the dyeing process of cellulose fibres, comprising a cationic surfactant and two dyes: Reactive Red 120 and Direct Red 23. The nanofiltration process was carried out under two pressures 1.5 and 0.7 MPa, at 40 °C.

In all cases of filtration at 1.5 MPa, except for the experiment with the CK membrane made from cellulose acetate (*Figure 3.A*), there were considerable losses in process efficiency (from 31% for the DK membrane (*Figure 3.B*) to 77% for the TFC-SR2 membrane (*Figure 3.E*).

At a pressure of 0.7 MPa the initial filtration flux was similar for most membranes, reaching about $50 \text{ dm}^3/\text{m}^2 \cdot \text{h}$. The filtration at 0.7 MPa led to a small loss of process efficiency, expressed by the filtration flux (from 8 to 19%), except for the TFC-SR2 membrane. The initial filtration flux for the TFC-SR2 membrane was higher than for the other membranes tested and amounted to $240 \text{ dm}^3/\text{m}^2 \cdot \text{h}$. Its reduction during the process was as high as 63%.

When analysing the initial stage of filtration at a pressure of 1.5 MPa, the highest filtration flux was obtained for membranes in the following order: TFC-SR2 > HL > TFC-SR3 > DL > DK > CK. With an increase in the initial filtration flux, the degree of its reduction during the process increased. The highest losses of process efficiency at 1.5 MPa were reported for the membranes in the following order: TFC-SR2 > HL > TFC-SR3 > DL > DK > CK.

The biggest difference in the filtration flux depending on the membrane operating

pressure was observed for the HL membrane (*Figure 3.F*). Under a pressure of 0.7 MPa the initial process efficiency was 53 dm³/m²-h, similar to that of the other polysulfone membranes tested; however at 1.5 MPa the initial filtration flux was high term reaching 200 dm³/m²-h. At this pressure a big reduction in the process efficiency was reported. The flux reduction reached 62%.

The lowest filtration flux was obtained for the CK membrane made from cellulose acetate. The initial filtration flux at a of 1.5 MPa was 37.5 dm³/m²-h, while at 0.7 MPa it did not exceed 10 dm³/m²-h. During the process an increase in the filtration flux was observed with a simultaneous deterioration of its parameters (*Figure 4.A*), which may indicate the membrane degradation was caused by the high pH of the wastewater.

The retention coefficient of organic substances, including dyes, was the lowest for the TFC-SR2 membrane. Filtrates obtained with the use of this membrane were coloured, irrespective of the pressure at which the process of filtration was carried out (*Figure 4.E*). The initial absorbance of filtrates (measured at $\lambda_{\max} = 525$ nm) was from 0.017 to 0.023. During concentration, the absorbance increased to approximately 0.35.

In other cases, the absorbance of the wastewater during filtration ranged from approximately 0.005 to 0.02 (*Figure 4*). With respect to colour reduction in the wastewater treated, the best results were obtained for the TFC-SR3 polyamide and HL polysulfone membranes (*Figure 4.D and 4.F*). The resulting filtrates were practically colourless, particularly in the case of the HL membrane. Better results were achieved at a lower operating pressure of the membrane.

Table 3 summarises parameters of the wastewater purified in the process of nanofiltration with the use of various membranes. For the TFC-SR2 membrane the degree of COD reduction was 60 - 63%, while the decrease in TOC did not exceed 50%. Taking into account the intensive colouration of filtrates obtained on the TFC-SR2 membrane, it can be stated that they did not meet the parameters required for process water in the textile industry.

The best parameters of the filtrate were obtained for the TFC-SR3 and HL membranes. For the composite TFC-SR3 membrane made from polyamide, the

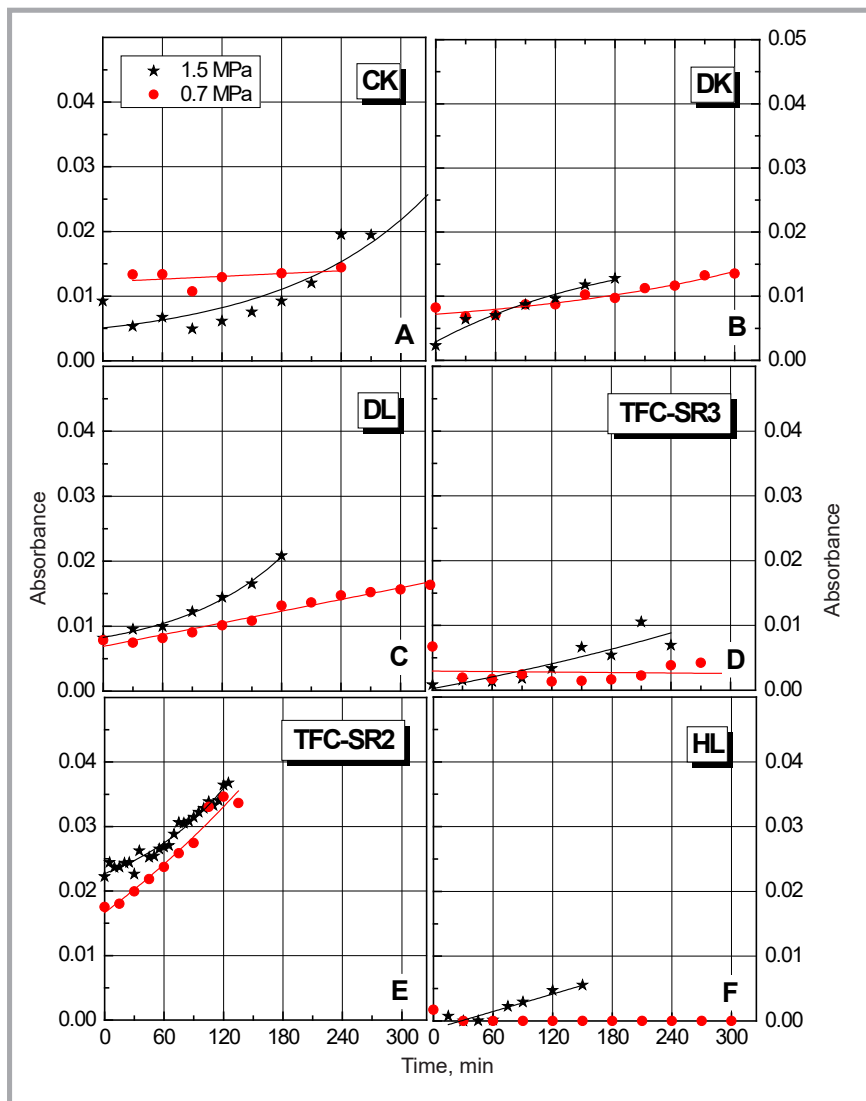


Figure 4. Changes in filtrate colour for different membranes during nanofiltration of wastewater after cellulose fibre dyeing.

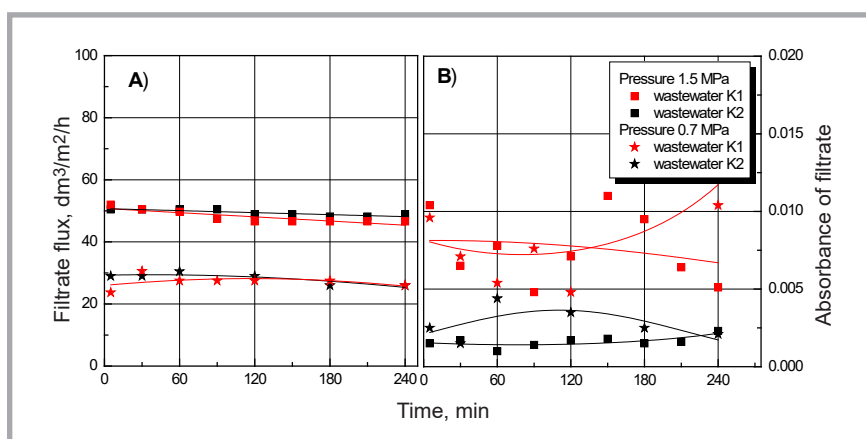


Figure 5. Filtration parameters of wastewater K1 and K2: A) dependence of filtration flux on filtration time, B) dependence of filtrate absorbance on filtration time, DK membrane.

filtrate was completely colourless and the degree of COD and TOC reduction was 81 - 88% and 76 - 89%, respectively, depending on the pressure (**Table 3**). When using the polysulfone HL mem-

brane, the filtrate was also colourless and the degree of COD reduction was 84 - 86%. TOC reduction was the highest among the filtrates tested, reaching more than 80%.

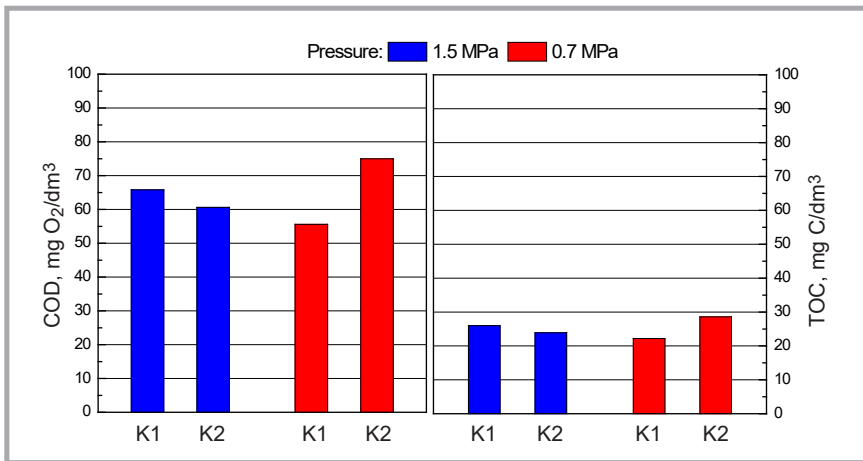


Figure 6. Comparison of COD and TOC of nano-filtered wastewater K1 and K2 under a pressure of 1.5 and 0.7 MPa and temperature 40 °C.

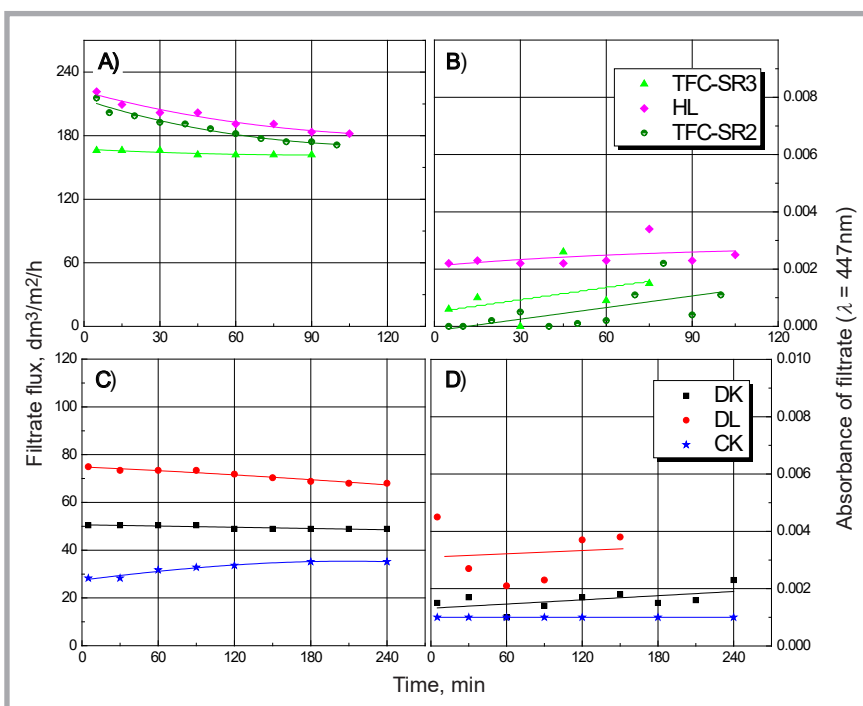


Figure 7. Dependence of filtration flux on time for different nanofiltration membranes; model wastewater K2 from dyeing polyamide fibres (pressure 1.5 MPa, temperature 40 °C).

Large losses of process efficiency are caused by many factors. Wastewater after the dyeing of cellulose fibres contained a cationic surfactant which could interact with the surface of the membrane in the alkaline medium. Additionally

the presence of inorganic salts in the bath can significantly deteriorate filtration parameters because of strong concentration polarisation and an increase in osmotic pressure. Reactive dyes contain reactive groups which react with OH⁻ groups of

Table 4. Degree of reduction in COD, TOC and colour of wastewater K2 from the dyeing of polyamide fibres for membranes tested at a pressure of 1.5 MPa.

Membrane type	Degree of parameter reduction, %		
	COD	TOC	Absorbance (λ = 447 nm)
CK	93.2	75.2	99.9
DK	96.7	86.2	99.8
DL	95.3	77.8	99.7
TFC-SR3	97.3	86.5	99.8
TFC-SR2	95.8	83.3	99.9
HL	97.5	89.5	99.8

cellulose in the alkaline medium. Their solubility depends on sulfone groups which in an aqueous medium dissociate into the ion of dye B-SO₃⁻ and sodium ion Na⁺. These properties of the dyes may promote their adsorption on the membrane surface and pores, thus contributing to a reduction in the process efficiency.

Nanofiltration of wastewater from the dyeing of polyamide fibres

Like for wastewater from the dyeing of cellulose products, a series of tests were performed on the use of nanofiltration in the treatment of model wastewater from dyeing polyamide fibres with acid dyes.

Figures 5 show the effect of the presence of yarn preparation on nanofiltration efficiency. Tests were carried out on model wastewater K1 and K2 on the DK membrane under a pressure of 0.7 and 1.5 MPa. Results confirmed that the presence of yarn preparations had no effect on the process efficiency and membrane fouling (**Figure 5.A**). It was observed that the presence of the hydrophobic oil fraction in wastewater K2 contributed to a better reduction in the filtrate colour (**Figure 5.B**).

Figure 6 shows the values of COD and TOC of filtrates obtained from the nanofiltration of wastewater K1 and K2. The initial values of COD and TOC for wastewater K1 and K2 were as follows:

- Wastewater without yarn preparation (K1) COD = 876 mg O₂/dm³; TOC = 123 mg C/dm³
- Wastewater with yarn preparation (K2) COD = 1793 mg O₂/dm³; TOC = 173 mg C/dm³

It follows from **Figure 6** that the parameters for both types of wastewater tested are similar, which indicates that the presence of yarn preparation in the initial wastewater has no effect on the degree of reduction in COD and TOC during the nanofiltration process.

Figure 7 shows the dependence of the filtration flux on the filtration time of wastewater K2 (containing yarn preparation) using various types of membranes. The tests were carried out under a pressure of 1.5 MPa at temperature 40 °C.

Tests for wastewater from polyamide fibre dyeing showed that the filtration flux was reduced only slightly during the process. For most of the membranes tested the effect of fouling did not exceed 10%. The initial filtration flux ranged from 35

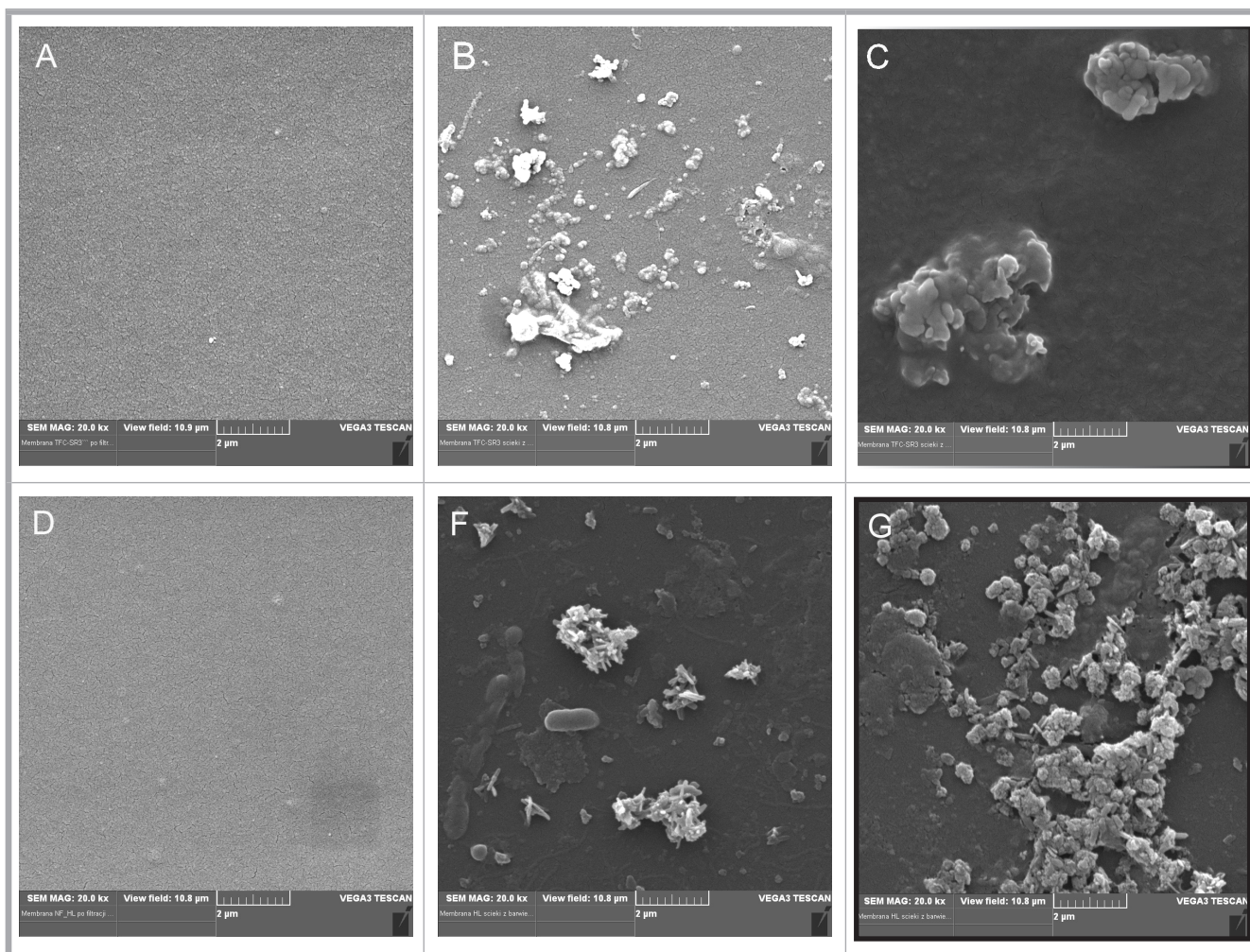


Figure 8. Microscopic picture of the TFC-SR3 membrane: *A*) after filtration of deionized water (time 2 h), *B*) after filtration of wastewater from cellulose fibre dyeing (time 2 h), *C*) after filtration of wastewater from polyamide fibre dyeing (time 2 h), and the HL membrane: *D*) after filtration of deionized water (time 2 h), *F*) after filtration of wastewater from cellulose fibre dyeing (time 2 h), *G*) after filtration of wastewater from polyamide fibre dyeing (time 2 h).

(for the CK membrane, **Figure 6.C**) to $222 \text{ dm}^3/\text{m}^2 \cdot \text{h}$ (for the TFC-SR2 membrane, **Figure 6.A**).

The best process efficiency was achieved for the TFC-SR2 and HL membranes (**Figure 7.A**). The initial filtration fluxes through these membranes were 215 and $222 \text{ dm}^3/\text{m}^2 \cdot \text{h}$. A slight fouling effect was observed. The decrease in efficiency was relatively small, amounting to 18 – 20%.

The TFC-SR3 membrane showed lower process efficiency than the TFC-SR2 and HL membranes. The filtration flux was $166 \text{ dm}^3/\text{m}^2 \cdot \text{h}$, but no fouling was reported, which was indicated by a horizontal curve representing the dependence of the filtration flux on time (**Figure 7.A**).

The polysulfone DK and DL membranes were characterised by lower efficiency, although no distinct fouling effect was reported (**Figure 7.C**). Despite similar properties, the DL membrane was much better than the DK membrane. The fil-

tration flux for the DL membrane was $75 \text{ dm}^3/\text{m}^2 \cdot \text{h}$, while for the DK membrane it was $50 \text{ dm}^3/\text{m}^2 \cdot \text{h}$. The reduction in the filtration flux for these membranes was 3 to 9%, respectively.

In all cases completely decolourised filtrates were obtained, whose absorbance did not exceed 0.004. **Table 4** summarises the reduction in COD and TOC in model wastewater K2 obtained by nanofiltration with the use of different membranes. The highest reduction was achieved for the DK, HL and TFC-SR3 membranes, while the worst effects were obtained for the CK membrane. However, in all cases the degree of COD reduction was above 90%, and TOC – usually above 80% (except for the DL and CK membranes). The best membrane appeared to be the TFC-SR3 membrane (made of composite polyamide), which was characterised by a high filtration flux and resistance to fouling.

Scanning electron microscopy (SEM) and microanalysis EDS

Tests were performed using a scanning electron microscope for selected HL and TFC-SR3 membranes which had previously been applied for the filtration of wastewater from dyeing cellulose fibres (**Figures 8.B** and **8.F**) and polyamide fibres (**Figures 8.C** and **8.G**). Filtration was carried out for 2 hours at a pressure of 1.5 MPa and temperature of $40 \text{ }^\circ\text{C}$. For comparison, microscopic pictures were taken of membranes which had previously been used for the filtration of clean deionized water (**Figures 8.A** and **8.D**). The agglomerates of contaminant particles ($0.4 \text{ }\mu\text{m}$) observed on the membrane surface in the case of wastewater from the dyeing of cellulose fibres were much smaller than in the wastewater from dyeing polyamide fibres (**Figure 8.B** and **8.F**).

For membranes used in filtering wastewater from dyeing polyamide fibres,

Table 5. Percentage of elements on the surface of HL membrane in mol %.

Filtered medium	Type of element detected, molar percentage						
	C	O	Na	Si	S	Cl	Fe
deionized water	76.92	17.70	-	-	5.38	-	-
wastewater from dyeing of cellulose fibres – sample 1	75.39	19.48	0.03	0.15	4.88	0.03	0.04
wastewater from dyeing of cellulose fibres – sample 2	71.45	23.20	0.07	0.47	4.48	0.05	0.28
wastewater from dyeing of cellulose fibres – sample 3	75.07	19.72	0.03	0.51	4.61	0.04	0.02
wastewater from dyeing of polyamide fibres	75.64	19.77	-	-	4.52	-	0.05

Table 6. Percentage of elements on the surface of TFC-SR3 membrane in mol %.

Filtered medium	Type of element detected, molar percentage						
	C	O	Na	Si	S	Cl	Fe
deionized water	83.67	13.72	-	-	2.56	-	-
wastewater from dyeing of cellulose fibres – sample 1	78.95	17.89	0.04	0.65	2.37	0.05	0.06
wastewater from dyeing of cellulose fibres – sample 2	83.04	13.94	0.02	0.14	2.77	0.06	0.02
wastewater from dyeing of polyamide fibres	83.18	14.02	-	-	2.72	-	0.03

large agglomerates of particles (5 μm) were observed. The HL membrane (**Figure 8.G**) was far more contaminated than the TFC-SR3 membrane (**Figure 7.C**). The wastewater from polyamide dyeing contained trace amounts of acid dyes. The wastewater contained a nonionic surfactant which was neutral for the charge on the membrane surface. In addition to acid dyes, the wastewater from polyamide fibre dyeing contained yarn preparations which constituted the fraction of mineral oils, esters and antistatic emulsifiers. The micelles (big agglomerates) visible in the pictures formed groups which constituted a fraction of the above-mentioned oils. Comparing the filtration flux for the wastewater without yarn preparation K1 and with it K2 (**Figure 5**), no differences were observed, which suggests that these were big neutral particles not interacting with the membrane surface. However, the presence of these high-molecular mineral oils facilitated the retention of other compounds present in the solution (**Figure 7.B** and **7.D**).

A qualitative analysis of elements present on the surface of HL and TFC-SR3 membranes was made after the process of nanofiltration using a monocrystalline silicon lithium detector Si(Li). Analyses were performed for the wastewater

after dyeing cellulose and polyamide fibres. **Table 5** summarises the results of analyses obtained for the HL membrane, and **Table 6** gives those for the TFC-SR3 membrane.

The HL membrane is a typical polysulfone membrane in which the aryl-SO₂-aryl bond occurs. Analysis of the membrane surface made it possible to detect elements with a molecular weight higher than lithium, i.e. carbon, oxygen and sulfur. In the case of wastewater after dyeing cellulose fibres, in addition to carbon, oxygen and sulfur, silicon atoms were also detected. Silicon came mainly from the polysiloxane-based cationic surfactant. Trace amounts of Na and Cl, at concentrations from 0.03 to 0.07% mol, were also observed, which is understandable, since in dyeing processes NaCl and Na₂CO₃ are used. Their low concentration observed on the membrane surface is due to the fact that they are monovalent ions, which are not retained on the membrane surface and can pass freely into the filtrate. There were also trace amounts of iron atoms. In dyeing processes iron salt is not applied, but it could come from commercial products used for dyeing [22].

Similar results were obtained for the TFC-SR3 membrane (**Table 6**). Irrespective of the filtered medium used in the tests, similar concentrations of elements contained in the membrane such as carbon, oxygen and sulfur were observed.

Use of filtrates in dyeing processes

The resulting filtrates were re-used as water in dyeing processes. The quality of the dyeing was assessed based on the difference in colour in the CIE L*a*b* system and on the basis of colour fastness.

Samples of knitted cotton fabric were dyed in a medium obtained after the processing of model textile wastewater and in clean water with reactive dye Remazol Brilliant Yellow 3GL or direct dye Helion Orange 3 RL. Based on the results of colour difference evaluation and colour fastness obtained with the use of filtrates from model textile wastewater containing a cationic surfactant, it was found that they could be used for cotton fibre dyeing with the use of direct dyes. For all samples, good dyeing quality was obtained. A problem is the use of the filtrate in the processes of rinsing and washing at higher temperatures. Salt present in the filtrate at a high temperature causes further bonding of the dye with the fibre, causing darker coloration. It is necessary to correct the doses of salts and alkalis in the dyeing before starting the process and to perform rinsing and washing at lower temperatures.

In the case of reactive dyes the permissible value of DE*Lab = 1.5 was significantly exceeded. Only the filtrate obtained on the TFC-SR3 membrane met the criteria for process water quality. The colour difference indicator was 1.07.

Table 7. Colour difference (DE*Lab) of polyamide fabrics dyed in treated wastewater compared to samples dyed in water.

Membrane type/pressure, MPa	DE*Lab	
	Colour intensity 0.1%	Colour intensity 0.5%
DL/1.5	1.10	1.34
HL/1.5	0.91	0.81
DK/1.5	0.86	1.42
TFC-SR3/1.5	0.46	1.01
TFC-SR2/1.5	0.59	0.90

Colour fastness obtained in dyeing in water recovered from the purified wastewater and in clean water was at a similar level; the difference was not bigger than 1 degree regardless of the type of membrane and dye used. In most cases the resistance of the dyeings to washing, sweat and abrasion in cotton fabric was estimated to be 4 - 5 or 5 on a grey scale from 1 to 5, where 1 denoted the biggest change and 5 indicated no change.

Table 7 gives results of the evaluation of the colour difference DE*Lab and colour fastness of polyamide fabric samples dyed with a selected acid dye - Isonyl Brun MPG in two intensities, in clean water and in water recovered after nanofiltration of the model wastewater. There was a slight discrepancy in the colour difference DE*Lab of fabrics dyed in the purified model wastewater. The colour difference DE*Lab ranged from 0.81 to 1.42 depending on the membrane used for nanofiltration.

Results of colour resistance at intensities of 0.1 and 0.5% obtained in dyeing with Isonyl Brun MPG to washing, sweat and abrasion showed that the dyeing quality was good irrespective of the source of water used for this.

Conclusions

The research allowed us to observe differences in the dynamics of membrane fouling for various types of textile wastewater. The research showed that the composition of wastewater contributed significantly to the reduction in the filtration efficiency of membranes due to fouling. This was observed particularly for the wastewater after the dyeing of cellulose fibres. Wastewater after dyeing with reactive and direct dyes used for cellulose fibres contained low-molecular compounds, salts, alkalis and high-molecular organic compounds.

In the case of wastewater after the dyeing of polyamide fibres the filtration fluxes were close to or lower than those in the wastewater after the dyeing of cellulose fibres. However, the reduction in filtration efficiency of the membrane for wastewater after the dyeing of polyamide fibres did not occur or was very small.

Microscopic pictures confirmed that on the membrane surface after filtration of the wastewater from the dyeing of polyamide fibres there were large agglomerates of organic compounds which could induce increased filtration resistance by blocking the membrane surface but did

not cause changes in the membrane structure. Large agglomerates were micelles formed from yarn preparations coming from the dyed knitted fabrics.

It was found that the HL and TFC-SR3 membranes had the best filtration parameters. At a high degree of retention of organic substances the highest filtration flux among all tested membranes was achieved.

It was reported that filtrates obtained during the filtration of wastewater after cellulose fibre dyeing can be re-used as process water in dyeing with direct dyes. Filtrates obtained from the filtration of wastewater after the dyeing of polyamide fibres can be used in re-dyeing with acid dyes. The quality of dyeing was good and the parameters tested were within the range of values acceptable from the point of view of functional properties.

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