

KATARZYNA MAJEWSKA-NOWAK*

FOULING OF HYDROPHILIC ULTRAFILTRATION MEMBRANES APPLIED TO WATER RECOVERY FROM DYE AND SURFACTANT SOLUTIONS

The static sorption tests were carried out in order to evaluate the proneness of the ultrafiltration membranes to fouling by organic dyes of various molecular weights. Five dyes of anionic nature, i.e. methyl orange (MO), indigo carmine (IC), amido black (AB), titan yellow (TY) and direct black (DB), were chosen. The effect of membrane material, membrane cut-off, contact time and the presence of anionic surface-active agent (sodium dodecylsulphate (SDS)) on the fouling intensity was assessed. The Intersep Nadir, Amicon and Millipore membranes made of polyethersulfone (PES), regenerated cellulose (C), cellulose acetate (CA), and polyamide (PA) were chosen. They were characterized by different cut-off values (1, 5, 10 and 30 kDa). The permeation measurements were carried out with distilled water, aqueous solutions of different dyes, and aqueous solutions of surfactant (SDS). The sorption tests were carried out with aqueous solutions containing SDS and dye. Surfactant concentration in model solutions was below its critical micelle concentration and amounted to 100 g/m^3 . Dye concentration was equal to 100 g/m^3 . The ultrafiltration process involved a pressure of 0.05, 0.1, 0.15, and 0.2 MPa. It was found that the intensity of fouling depends on membrane material, membrane cut-off value and molecular weight of organic dyes. Membrane proneness to fouling by organic dyes could be reduced significantly when an anionic surfactant was present in the treated solution.

Keywords: *dye, ultrafiltration, fouling, hydrophilic membrane*

1. INTRODUCTION

Membrane technology offers some promising solutions to the wastewater problems arising in a textile industry. In particular, reverse osmosis (RO), nanofiltration (NF), and ultrafiltration (UF) can be successfully applied to effluent regeneration [1]–[6].

A major disadvantage of all pressure-driven membrane processes is the decline of permeate flux due to concentration polarisation and fouling phenomena. Adsorption of

* Institute of Environmental Protection Engineering, Wrocław University of Technology, pl. Grunwaldzki 9, 50-370 Wrocław, Poland.

various dissolved and suspended feed compounds on the membrane surface as well as in pore interior is the main factor affecting the fouling intensity. Generally, fouling is regarded as the “irreversible flux decline” and it increases the cost of membrane cleaning. To control a membrane fouling the following approaches can be adopted: 1) surface modification of membranes with suitable hydrophilic and charged functional groups, which are expected to retard the adsorption of hydrophobic solutes, 2) suitable feed pre-treatment, 3) periodic treatment of membranes with suitable deadsorbants [7].

Membrane fouling in the ultrafiltration of dye solutions was reported by Van der BRUGGEN et al. [8], CHAKRABORTY et al. [9], and REDDY et al. [7]. The mechanism of fouling is still unclear, although a number of factors influencing the flux have been mentioned. The extent of dye adsorption and its reversibility are determined by dye–membrane physicochemical interactions (e.g. hydrophobic and polar interactions and charge transfer), which depend on the nature of the components, dye concentration, pH and cross-flow velocity [10].

In this paper, the fouling intensity of various polymer membranes during ultrafiltration of aqueous solutions containing organic dyes and anionic surfactant was determined.

2. MATERIALS AND METHODS

2.1. MEMBRANES

Commercially available asymmetric ultrafiltration membranes were used. Of the variety of UF membranes the Intersep Nadir membranes (PES, C, CA, and PA series), Amicon Diaflo (YM series), and Millipore (PLAC series) have been chosen. The characteristics of the membranes investigated are given in tables 1 and 2. To enhance a mechanical durability of all membranes they are cast on a very porous, polymer substrate (50–250 μm thick). Polymer material, hydrophilicity and cut-off value are characteristic of each type of a membrane. In the description of a given membrane (e.g.: PES5, PA10, YM1), the number denotes its cut-off (in thousands of daltons).

2.2. ULTRAFILTRATION PROCESS

An Amicon UF stirred cell (model 8400) of a total volume of 350 cm^3 was used to determine the transport and separation properties of the membranes [12]. The effective surface area of the membrane amounted to 45.3 cm^2 . The UF cell is supplied continuously with the permeate, therefore the concentration of the circulating solution has to be constant.

The ultrafiltration process in all experiments involved a transmembrane pressure of 0.05, 0.1, 0.15, and 0.2 MPa. Permeate volume fluxes and retention coefficients of the surfactant and dyes tested were determined after the steady conditions of flow were settled.

Table 1

Characteristics of the experimental membranes

Membrane type	Membrane polymer	Description	Cut-off ¹ , kDa	Manufacturer
PES	polyethersulfone	moderately hydrophilic	5, 10, 30	Intersep Nadir
C	regenerated cellulose	the most hydrophilic	5, 10, 30	Intersep Nadir
CA	cellulose acetate	advanced hydrophilic	10	Intersep Nadir
PA	aromatic polyamide	chemically modified to be hydrophilic	5	Intersep Nadir
YM	regenerated cellulose	the most hydrophilic	1	Amicon
PLAC	regenerated cellulose	hydrophilic	1	Millipore

¹ Given by producer.

Table 2

Mean pore radius and contact angle of the membranes tested [11]

Membrane type	Mean pore radius, nm				Contact angle ¹ , deg
	Cut-off, kDa				
	1	5	10	30	
PES	–	0.62	2.04	8.38	50.01
C	–	0.82	5.01	4.89	54.76
CA	–	–	1.24	–	53.8
PA	–	2.13	–	–	66.2
YM	0.5	–	–	–	0
PLAC	0.4 ²	–	–	–	n.a. ³

¹ Determined for membranes of cut-off equal to 1 kDa.

² Approximately determined in the rejection tests.

³ Not available.

2.3. EXPERIMENTAL SOLUTIONS

The permeation measurements were carried out with distilled water, aqueous solutions of different dyes, aqueous solutions of sodium dodecylsulphate (SDS), and aqueous solutions containing SDS and dye. Five organic dyes of anionic nature (table 3)

were chosen. An aqueous solution subjected to sorption tests contained the mixture of one dye and surfactant.

In the aqueous solution, the dye concentration was equal to 100 g/m^3 . The pH and the temperature of the feed solutions were 7.0 and $25 \text{ }^\circ\text{C}$, respectively.

The concentration of SDS in model solutions amounted to 100 g/m^3 and was below its critical micelle concentration ($\text{CMC} < 2257 \text{ g/m}^3$) [13]. Sodium dodecylsulphate (SDS or NaDS) is also known as sodium lauryl sulphate (SLS). Its molecular formula is the following: $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$, and the molecular weight amounts to 288.38 Da.

Dye concentration in aqueous solutions was determined spectrophotometrically at a wavelength (λ_{max}) corresponding to the maximum absorbance of the sample (table 3).

The SDS concentration in the feed and the permeate was determined based on the colour reaction (Rhodamine G6 as indicator) and spectrophotometric measurements of the absorbance at a wavelength of 565 nm.

Table 3

Characteristics of the experimental dyes

Dye	Molecular weight, Da	Classification	Dye symbol	λ_{max} , ¹ nm	Structural formula
Methyl orange	327.0	acid dye	MO	465	$\text{C}_{14}\text{H}_{14}\text{N}_9\text{O}_9\text{SNa}$
Indigo carmine	466.36	acid dye	IC	610	$\text{C}_{16}\text{H}_8\text{N}_2\text{Na}_2\text{O}_8\text{S}_6$
Amido black	615.50	acid dye	AB	618	$\text{C}_{22}\text{H}_{19}\text{N}_5\text{Na}_2\text{O}_6\text{S}_4$
Titan yellow	695.73	direct dye	TY	399	$\text{C}_{28}\text{H}_{19}\text{N}_5\text{Na}_2\text{O}_6\text{S}_4$
Direct black	781.20	direct dye	DB	585	$\text{C}_{34}\text{H}_{25}\text{N}_9\text{O}_7\text{S}_2\text{Na}_2$

¹ Wavelength corresponding to the maximum absorbance of the dye solution.

2.4. SORPTION TESTS

The proneness of the membranes to fouling was established in terms of the fouling index (FI) calculated by virtue of:

$$FI = \frac{J_h}{J_0},$$

where J_h denotes the flux of distilled water after a defined time of membrane contact with the solution containing dye or SDS or both dye and SDS particles ($\text{m}^3/\text{m}^2\text{day}$), and J_0 is the flux of distilled water passing through a new (or rinsed) membrane ($\text{m}^3/\text{m}^2\text{day}$). In order to restore an initial volume flux, membranes were rinsed with 0.1 N NaOH solution for 10 minutes after each series of experiments.

The membrane was placed in a solution tested for 1, 4, 8 and 24 h in order to determine the value of *FI*. After the anticipated time had elapsed, the membrane was carefully rinsed with distilled water, and the volume flux of distilled water (at $\Delta P = 0.20$ MPa) was measured. The sorption tests with the membranes were carried out in the following water solutions: 100 g SDS/m³, 100 g dye/m³, and mixture of 100 g SDS/m³ and 100 g dye/m³.

3. RESULTS AND DISCUSSION

3.1. ULTRAFILTRATION EFFICIENCY

The study was aimed at evaluating the usability of the ultrafiltration membranes for separation of dye and SDS particles from aqueous solutions. The effect of pressure difference on the transport properties of a membrane is given in table 4.

The volume flux of distilled water varied from 0.05 m³/m²day at $\Delta P = 0.05$ MPa for PLAC1 membrane to 7.62 m³/m²day at $\Delta P = 0.20$ MPa for C30 membrane. It was found that for 10 kDa series the CA10 membrane exhibited the worst transport properties, whereas among the membranes of 5 kDa cut-off the PA5 membrane was characterized by the lowest permeability. In the case of the densest membranes (YM1 and PLAC1), the water volume flux was almost of the same order of magnitude. These findings are partly associated with a mean pore radius of the membrane (table 2). The pore size of CA10 membrane was smaller (1.24 nm) than the pore sizes of PES10 and C10 membranes (2.04 and 5.01 nm, respectively). Water volume fluxes through 5 kDa cut-off membranes are in a good agreement with pore sizes – the smallest mean pore radius was determined for PES5 membrane. The membranes of the lowest cut-off (1 kDa) were also characterized by the smallest mean pores radius (0.4–0.5 nm).

The separation properties of the membranes tested are shown in table 5. The results obtained indicate that ultrafiltration membranes show rather poor SDS rejection. This finding was also shown for low-molecular weight dye (methyl orange). It was found that with an increase in the membrane cut-off the SDS and MO rejection coefficient decreased dramatically approaching 7.1–28.3% and 4.8–9.0% for C30 and PES30 membranes, respectively. Only in the case of the densest membranes (PLAC1 and YM1), the retention of SDS and MO was higher than 70%. These results were not surprising, because sodium dodecylsulphate as well as methyl orange are characterized by very low molecular weight (288.38 and 327 kDa, respectively).

An increase in the molecular weight of rejected particles generally improved the selectivity of the UF membranes. High-molecular weight dyes (i.e. titan yellow and direct black) were rejected in 99.7–100% by almost all the membranes tested. Even

the most opened membranes (PES30 and C30) enabled very effective separation of high-molecular weight dyes (99.2–99.5 and 63–79.8%, respectively).

Table 4

Water permeability of experimental membranes

Membrane type	ΔP , MPa	Water volume flux, $\text{m}^3/\text{m}^2\text{day}$			
		1 kDa	5 kDa	10 kDa	30 kDa
PES	0.05		0.22	0.64	1.22
	0.10		0.31	1.21	2.04
	0.15		0.45	1.65	3.15
	0.20		0.73	2.41	4.13
C	0.05		0.24	0.25	1.39
	0.10		0.51	0.57	3.24
	0.15		0.76	0.95	5.34
	0.20		1.02	1.27	7.62
CA	0.05			0.238	
	0.10			0.381	
	0.15			0.667	
	0.20			0.889	
PA	0.05		0.23		
	0.10		0.54		
	0.15		0.89		
	0.20		1.18		
YM	0.05	0.07			
	0.10	0.13			
	0.15	0.19			
	0.20	0.25			
PLAC	0.05	0.05			
	0.10	0.09			
	0.15	0.13			
	0.20	0.16			

There was no distinct relationship between SDS or dye retention coefficient and the pressure applied. A slight tendency to decrease the separation effect with an increase in pressure difference was observed in 10 and 30 kDa membrane series, whereas in 5 kDa membrane series the opposite result was noticed (these results are not given in this paper).

Taking into account the mean radius of pore particles (0.5–2.0 nm), the results obtained indicate that the molecular sieve-mechanism alone is insufficient to explain the separation of organic dyes by UF membranes. The electrostatic interaction between the membrane and anionic macroparticle could be regarded as a factor supporting the efficiency of ultrafiltration process.

Table 5

Separation properties of UF membranes
 ($\Delta P = 0.2$ MPa, SDS concentration – 100 g/m^3 , dye concentration – 100 g/m^3)

Membrane	Rejection coefficient, %					
	SDS	MO	IC	AB	TY	DB
PLAC1	75.5	75.5	95.6	98.3	99.9	100
YM1	77.7	73.1	95.6	97.8	99.9	100
PES5	63.2	53.5	89.3	92.8	99.8	100
C5	40.8	38.3	48.0	84.5	98.9	99.3
PA5	34.1	66.5	95.1	98.9	99.8	100
CA10	27.8	46.8	65.6	80.1	98.9	99.3
PES10	66.8	40.8	77.5	80.5	99.7	99.7
C10	26.0	31.4	58.7	76.4	98.7	99.2
C30	7.1	4.8	9.6	10.4	63.0	79.8
PES30	28.3	9.0	42.8	67.5	99.5	99.2

3.2. MEMBRANE PRONENESS TO FOULING

In order to verify the proneness of the membranes to fouling by anionic dyes (of various molecular weights), the sorption tests under the static conditions were conducted. The effect of membrane material, membrane cut-off, contact time and anionic surface-active agent (SDS) on the fouling intensity was estimated.

The values of the fouling index (FI) of the solutions containing the mixture of organic dye and surfactant are given in figures 1–8. Figures 1–4 show the effect of the contact time on FI values for four selected membranes and various organic dyes.

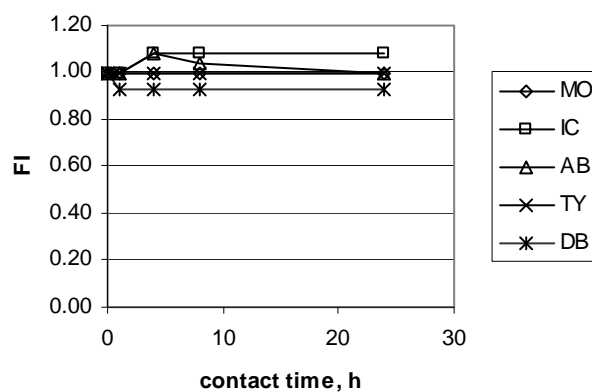


Fig. 1. Fouling index (FI) versus contact time for PLAC1 membrane in various dye solutions

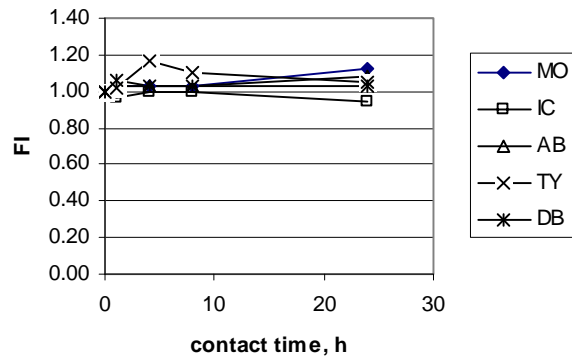


Fig. 2. Fouling index (FI) versus contact time for C30 membrane in various dye solutions

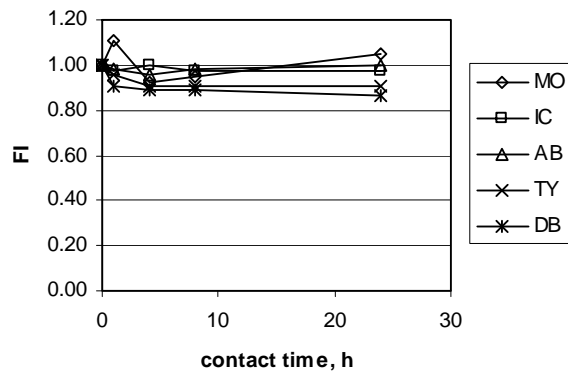


Fig. 3. Fouling index (FI) versus contact time for PA5 membrane in various dye solutions

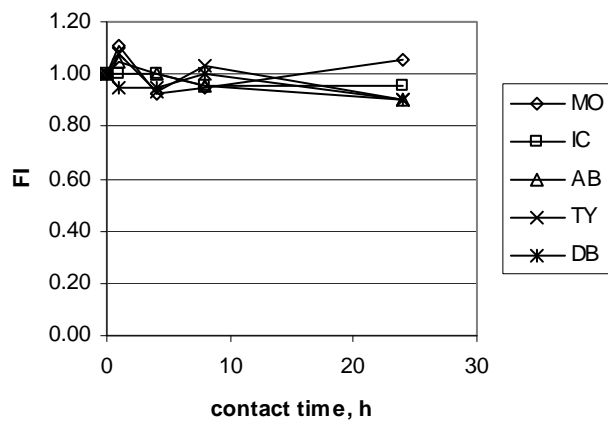


Fig. 4. Fouling index (FI) versus contact time for PES5 membrane in various dye solutions

No obvious relationship between contact time and *FI* values was found. However, the *FI* values of the membranes made of regenerated cellulose (PLAC1 and C30) were slightly higher than 1, irrespective of contact time, for almost all the dyes tested (figures 1 and 2). This is an indication that membrane permeability improved after coming into contact with solutions containing a mixture of SDS and dye particles. Our previous investigations [11] dealing with sorption of dye in aqueous solutions revealed that adsorption of dye particles in the membrane structure was responsible for membrane fouling. Comparing the former results with the present findings it can be concluded that anionic surfactant in dye solutions evidently influences the transport properties of the PLAC and C membranes. It is worth noting that these membranes are the most hydrophilic.

On the contrary, generally the *FI* values of the PA5 and PES5 membranes are slightly smaller than 1. It can be suggested that the dye is adsorbed more efficiently by moderately hydrophilic membranes. The highest the value of the fouling index, the less capable of fouling a given membrane. Among the membranes investigated, C and CA membranes have the highest fouling index, which is consistent with the values of the contact angle measured (table 1). On the other hand, the polyamide Intersep Nadir membranes, in particular PA30, are characterized by rather low fouling indexes, so they are less hydrophilic than it has been indicated by the measurements of the contact angles.

It is worth noting that fouling index values decrease with an increase in both the membrane cut-off and the molecular weight of organic dyes (figures 5–8); however the *FI* values of the membranes with high-molecular weight cut-off (PES30 and C30) were insignificantly higher than these measured in 10 kDa cut-off membrane series. This is an indication that adsorption of dye particles in pore interior governs the fouling phenomenon. It can be anticipated that the greater the molecular weight of the dye, the more intensive the membrane clogging.

The results obtained are generally in agreement with the membrane hydrophilic properties. Some inconsistency of the fouling index values with contact angle measurements could be explained by the roughness of the membrane surface.

It was surprising to observe that in some cases the *FI* value was higher than 1. This effect was more pronounced for the membranes made of cellulose derivatives whose molecular weight cut-off was high. Van de BRUGGEN et al. [8] arrived at similar conclusions. A relative flux in nanofiltration experiments of rinsing textile wastewater containing detergents reached 110–115%. Hydrophilic membrane Desal DL (0.3 kDa cut-off) was used. Surfactants are known to adsorb in the membrane pores, thereby causing flux decline [14]. Especially nonionic surfactants are adsorbed on hydrophobic membranes causing a more pronounced flux decline than ionic surfactants [15]. Van de BRUGGEN et al. [8] observed a different behaviour of the Desal DL5 membrane. During static adsorption experiments surfactants were adsorbed on the membrane surface. This can render the membrane surface more hydrophilic.

Probably, the contact of cellulose material with surfactant solutions is responsible for modification of membrane structure and increase in membrane permeability. It can be anticipated that hydrophobic tail of the surfactant interacts with a membrane, while the hydrophilic head remains available, so the water flux is higher than an initial pure water flux. However, further research is required to elucidate the mechanism of fouling. It is advisable to measure the contact angles of pure water on a fresh and surfactant-“polluted” membranes to support the above statements.

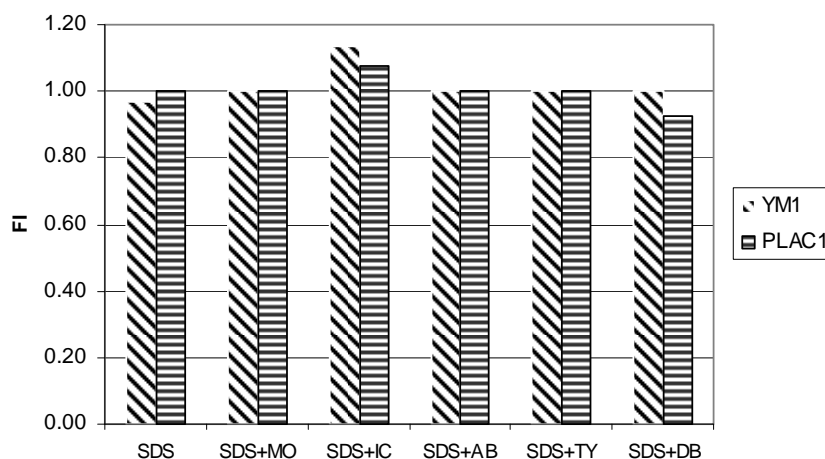


Fig. 5. Fouling index (*FI*) determined after 24 h contact of YM1 and PLAC1 membranes with SDS solution and SDS-dye solutions

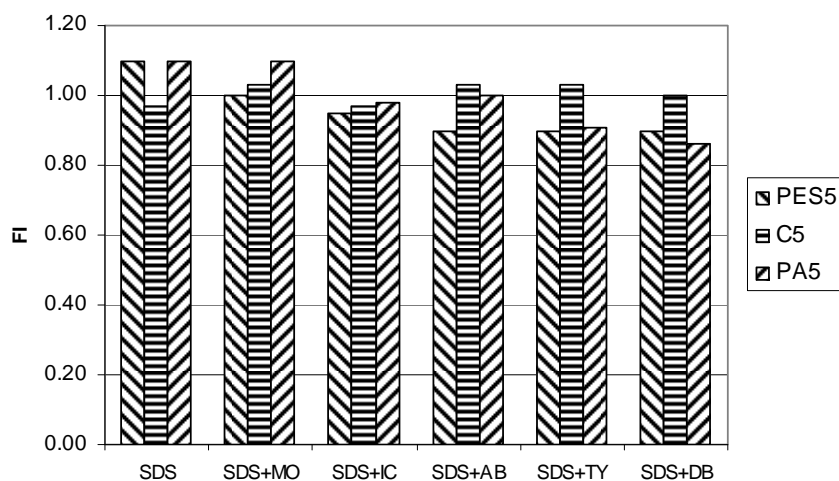


Fig. 6. Fouling index (*FI*) determined after 24 h contact of PES5, C5, and PA5 membranes with SDS solution and SDS-dye solutions

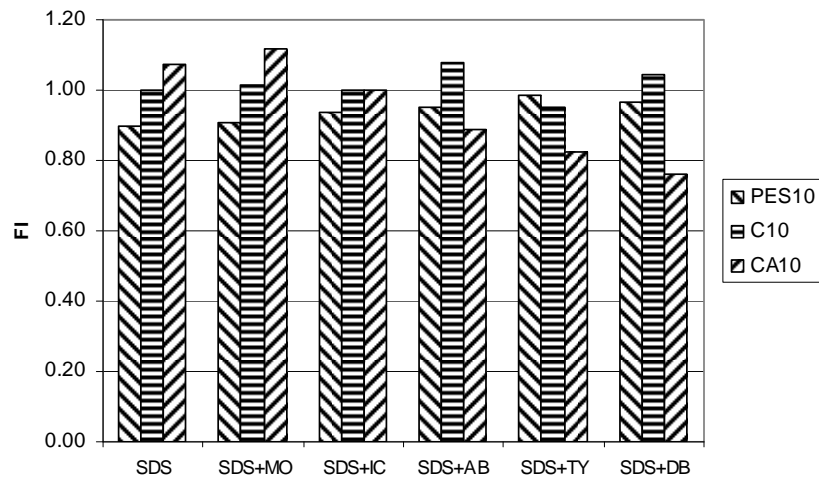


Fig. 7. Fouling index (FI) determined after 24 h contact of PES10, C10, and CA10 membranes with SDS solution and SDS-dye solutions

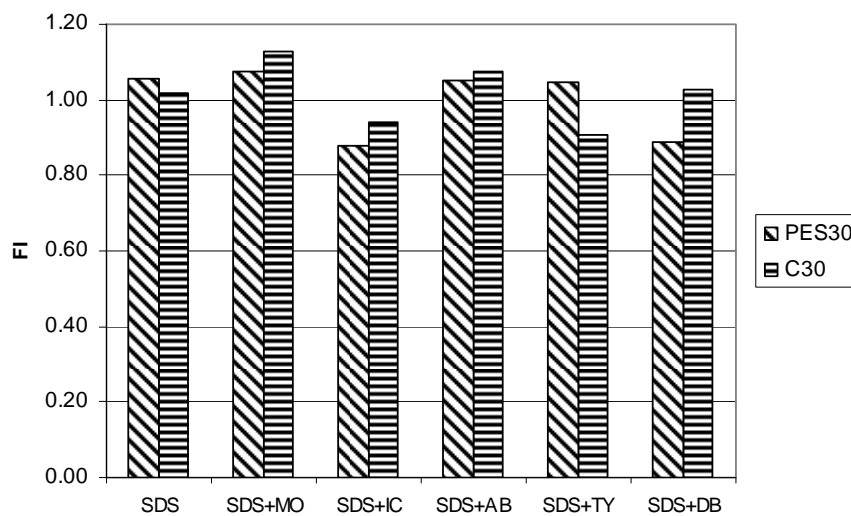


Fig. 8. Fouling index (FI) determined after 24 h contact of PES30 and C30 membranes with SDS solution and SDS-dye solutions

4. CONCLUSIONS

1. Membrane fouling during ultrafiltration of dye solutions is caused by adsorption of organic particles on the membrane surface and in pore interior. The intensity of

fouling depends on membrane material, membrane cut-off value and molecular weight of organic dyes.

2. Fouling index value decreases with an increase in the membrane cut-off and molecular weight of organic dyes when the solutions containing a mixture of dye and surfactant are involved.

3. Membrane proneness to fouling can be reduced significantly when an anionic surfactant is present in the treated solution. This effect becomes more pronounced when the membrane hydrophilicity increases leading even to a flux increase (in relation to a pure water flux before ultrafiltration).

ACKNOWLEDGEMENTS

The financial support of the State Committee for Scientific Research, Grant #3 T09D 025 26, is greatly appreciated.

REFERENCES

- [1] PURKAIT M.K., DAS GUPTA S., DE S., *Removal of dye from wastewater using micellar-enhanced ultrafiltration and recovery of surfactant*, Separation and Purification Technology, 2004, 37, pp. 81–92.
- [2] RIBEIRO M.R., BERGAMASCO R., GIMENES M.L., *Membranes synthesis study for colour removal of a textile effluent*, Desalination, 2002, 145, pp. 61–63.
- [3] YOUNG KU, PEI-LIU LEE, WEN-YU WANG, *Removal of acidic dyestuffs in aqueous solution by nanofiltration*, Journal of Membrane Science, 2005, 250, pp. 159–165.
- [4] CHAKRABORTY S., PURKAIT M.K., DAS GUPTA S., DE S., BASU J.K., *Nanofiltration of textile plant effluents for colour removal and reduction in COD*, Separation and Purification Technology, 2003, 31, pp. 141–151.
- [5] TANG C., CHEN V., *Nanofiltration of textile wastewater for water reuse*, Desalination, 2002, 143, pp. 11–20.
- [6] AKBARI A., REMIGY J.C., APTEL P., *Treatment of textile dye effluent using a polyamide-based nanofiltration membrane*, Chemical Engineering and Processing, 2002, 41, pp. 601–609.
- [7] REDDY A.V.R., TRIVEDI J.J., DEVMURARI C.V., MOHAN D.J., SINGH P., RAO A.P., JOSHI S.V., GHOSH P.K., *Fouling resistant membranes in desalination and water recovery*, Desalination, 2005, 183, pp. 301–306.
- [8] Van der BRUGGEN B., CORNELIS G., VANDECASTEELE C., DEVREESE I., *Fouling of nanofiltration and ultrafiltration membranes applied for wastewater regeneration in the textile industry*, Desalination, 2005, 175, pp. 111–119.
- [9] CHAKRABORTY S., BAG B.C., DAS GUPTA S., BASU J.K., DE S., *Prediction of permeate flux and permeate concentration in nanofiltration of dye solution*, Separation and Purification Technology, 2004, 35(2), pp. 141–152.
- [10] GOMES A.C., GONCALVES I.C., De PINHO M.N., *The role of adsorption in nanofiltration of azo dyes*, Journal of Membrane Science, 2005, 255, pp. 157–165.
- [11] MAJEWSKA-NOWAK K., KABSCH-KORBUTOWICZ M., BRYJAK M., WINNICKI T., *Separation of organic dyes by hydrophilic ultrafiltration membranes*, 7th World Filtration Congress, Budapest, Hungary, 1996, Vol. 2, pp. 885–889.
- [12] KOWALSKA I., KABSCH-KORBUTOWICZ M., MAJEWSKA-NOWAK K., BOR F.L., *An assessment of ultrafiltration membrane materials in sodium dodecyl sulphate removal from water solutions*, Envi-

- ronment Protection Engineering, 2001, 27(3–4), pp. 19–25.
- [13] BENITO I., GARCIA M.A., MONGE C., SAZ J.M., MARINA M.L., *Spectrophotometric and conductometric determination of the critical micellar concentration of sodium dodecyl sulfate and cetyltrimethylammonium bromide micellar systems modified by alcohols and salts*, Colloids and Surfaces, A: Physicochemical and Engineering Aspects, 1997, 125, pp. 221–4.
- [14] JÖNSSON A.S., JÖNSSON B., *The influence of non-ionic and ionic surfactants on hydrophobic and hydrophilic ultrafiltration membranes*, Journal of Membrane Science, 1991, 56, pp. 49–76.
- [15] MIETTON-PEUCHOT M., RANISIO O., PEUCHOT C., *Study of behaviour of membranes in the presence of anionic or non-ionic surfactants*, Filtration and Separation, 1997, 34(8), pp. 883–886.