Environment Protection Engineering

Vol. 35 2009 No. 4

KATARZYNA MAJEWSKA-NOWAK*

ULTRAFILTRATION OF DYE SOLUTIONS IN THE PRESENCE OF CATIONIC AND ANIONIC SURFACTANTS

The objective of the study was to investigate the influence of surfactant in model dye solutions on the ultrafiltration efficiency. The anionic detergent (sodium dodecyl sulphate (SDS)) and cationic detergent (hexadecyltrimethylammonium bromide (CTAB)) were added to the dye solutions. Three anionic organic dyes of molecular weights ranging from 327 to 1060 Da were applied. Intersep Nadir membranes made of polyethersulfone and regenerated cellulose were used in the experiments. The operation pressure varied from 0.1 to 0.20 MPa. The concentration of dyes in model solutions was equal to 100 g/m^3, whereas surfactant dosage amounted to 0.1, 0.6 and 1.0 CMC (critical micelle concentration). The experiments revealed dye retention by surfactant present in experimental solutions was strongly affected by the nature of detergent, membrane material and membrane cut-off value. It was also found that the presence of an anionic surfactant brought about the worsening of separation factor, whereas the cationic surfactant improved dye rejection.

1. INTRODUCTION

Wastewaters containing dyes are very difficult to treat since the dye molecules are not only resistant to aerobic digestion, but also to light, heat and oxidizing agents [1]. During the last years many physical, chemical and biological decolorization methods have been reported [2], [3]. A literature survey shows that at the present time there is no single process capable of adequately treating a dye effluent, mainly due to complex nature of wastewater [4].

Membrane separation processes can be a promising alternative for the removal of a variety of dyestuff. Although a number of studies have been carried out involving the application of nanofiltration and reverse osmosis in textile industry [5]–[7], only a few papers deal with successful use of direct ultrafiltration for dyestuff removal [8]–[10].

Micellar-enhanced ultrafiltration (MEUF) is one of the various membrane methods for removing traces of organic pollutants (including dyes) by using surfactant

* Institute of Environment Protection Engineering, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland. E-mail: katarzyna.majewska-nowak@pwr.wroc.pl

solutions [11]–[13]. The surfactants in aqueous solutions form micelles whose diameters are larger than the UF membrane pores. During the ultrafiltration process, micelles containing solubilised organic dyes are rejected by the membrane. Permeate stream is nearly free of impurities.

The objective of the experimental research was to study the effect of the nature of surfactant and its concentration as well as membrane hydrophilicity upon the retention of anionic dyes in the ultrafiltration process.

2. EXPERIMENTAL

2.1. MEMBRANES

Commercially available asymmetric ultrafiltration membranes made of polyethersulfone (PES) and regenerated cellulose (C) were used in the experiments. The membranes differed in the cut-off values (5, 10, and 30 kDa) and hydrophilicity. The characteristic of the membranes investigated is given in table 1. Intersep Nadir membranes are cast on a tough, very porous substrate of polypropylene. In the description of a given membrane (e.g., PES5, C10), the number denotes the cut-off (in kDa).

Table 1

Characteristics of Intersep Nadir membranes

Membrane type	Membrane polymer	Description	Cut-off [1] (kDa)	Contact angle [2] (deg)
PES	Polyethersulfone	Moderately hydrophilic	5, 10, 30	50.01
C	Regenerated cellulose	Definitely hydrophilic	5, 10, 30	54.76

[1] Given by producer.
[2] Determined for membranes of cut-off equal to 1 kDa.

2.2. EXPERIMENTAL SOLUTIONS

The transport and separation properties of UF membranes were determined with respect to the solutions containing dyes (table 2) as well as to the solutions containing dyes and surfactants. The surface active agents applied were of anionic type (sodium dodecyl sulphate (SDS)) or cationic type (hexadecyltrimethylammonium bromide (CTAB)). The concentration of dye in model solutions amounted to 100 g/m^3. SDS and CTAB concentration in dye solutions was equal to 0.1, 0.6, and 1.0 CMC (critical micelle concentration).

Sodium dodecyl sulphate (SDS or NaDS) is also known as sodium lauryl sulphate (SLS). The molecular formula is as follows: $CH_3(CH_2)_{11}OSO_3Na$, and the molecular weight of SDS amounts to 288.38 Da. The critical micelle concentration in pure water is 2.0 g/dm^3 (8 mM) at 20 ºC [14], and the aggregation number at this concentration ranges from 54 to 64 [15]. This anionic surface active agent is used in household products such as toothpastes, shampoos, shaving foams and bubble baths for its thickening effect and its ability to create a foam. In laboratories, SDS is commonly used in gel electrophoresis, where its detergent properties help to keep the proteins being studied in a denaturated state.

Hexadecyltrimethylammonium bromide (CTAB) is also known as cetyltrimethylammonium bromide or lauroseptol. The molecular formula is the following: $C_{19}H_42BrN$ and the molecular weight of CTAB amounts to 364.45 Da. The critical micelle concentration in pure water is 0.335 g/dm^3 (0.96 mM), and the aggregation number in water amounts to 61 [11], [12]. This cationic detergent is used for solubilization of a wide variety of proteins and nucleic acids.

Retention coefficients with respect to dye particles and permeate volume fluxes were determined during the UF experiments.

Table 2

Characteristics of the experimental dyes

Dye	Molecular weight (Da)	Classsification	Dye symbol	λ_{max}^{1} (nm)	Structural formula
Methyl orange	327	Acid dye	MO	465	$C_{14}H_{14}N_9O_9SNa$
Amido black	615	Acid dye	AB	618	$C_{22}H_{19}N_5Na_2O_6S_4$
Direct black	1060	Direct dye	DB	585	$C_{34}H_{25}N_9O_7S_2Na_2$

[1] Wavelenght corresponding to the maximum absorbance of the dye solution.

2.3. ULTRAFILTRATION PROCESS

The ultrafiltration process in the presence of surface active agents was investigated in a laboratory set-up (figure 1). The membranes being tested had a diameter of 76 mm. The overall volume of the UF cell amounted to 350 cm^3. In order to maintain a constant concentration of the dye and surfactant in the feed solution, the permeate was recirculated. The UF process was run at a pressure ranging from 0.1 to 0.2 MPa.

Prior to each cycle, the membrane was treated with water at 0.20 MPa, until the constant permeate volume flux had been established. Permeate volume fluxes and retention coefficients were determined with respect to experimental dyes after the steady conditions of flow were obtained.

Permeate volume flux (J) was calculated as follows:

$$J = \frac{V}{t \cdot A} \quad (\mathrm{m^3/m^2day}),$$

where V is the permeate volume (m^3), t stands for the time (day), and A denotes the effective membrane surface area (m^2).

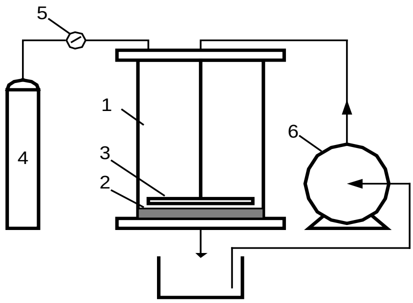

Fig. 1. Laboratory set-up: 1 – ultrafiltration cell, 2 – membrane, 3 – stirrer, 4 – gas cylinder, 5 – reducer, 6 – recirculation pump

Dye retention coefficient (R) was determined by virtue of:

$$R = \frac{c_k - c_p}{c_k} \cdot 100 \quad (\%),$$

where c_k and c_p denote the dye concentration (g/m^3) in retentate and permeate, respectively.

Dye concentration in aqueous solutions was determined spectrophotometrically at a wavelength corresponding to the maximum absorbance of the sample (table 2).

3. RESULTS AND DISCUSSION

3.1. MEMBRANE TRANSPORT PROPERTIES

The variation of the membrane permeability as a function of cationic (CTAB) and anionic (SDS) surfactant concentration has been studied. Figures 2 and 3 represent volume flux of C and PES membranes for various dye solutions containing CTAB or SDS, respectively (at ΔP = 0.1 MPa).

The volume flux of distilled water varied from 0.5 to 8.0 m^3/m^2day for the membranes made of regenerated cellulose and from 0.6 to 3.0 m^3/m^2day for the membranes made of polyethersulfone. When dye containing solutions were passing through the membranes, a considerable drop in their permeability was observed only for the membranes characterized by the highest cut-off value (C30 and PES30 membranes). This effect was especially pronounced for high-molecular-weight dyes. A slight decrease in volume flux was also observed for PES5 membrane.

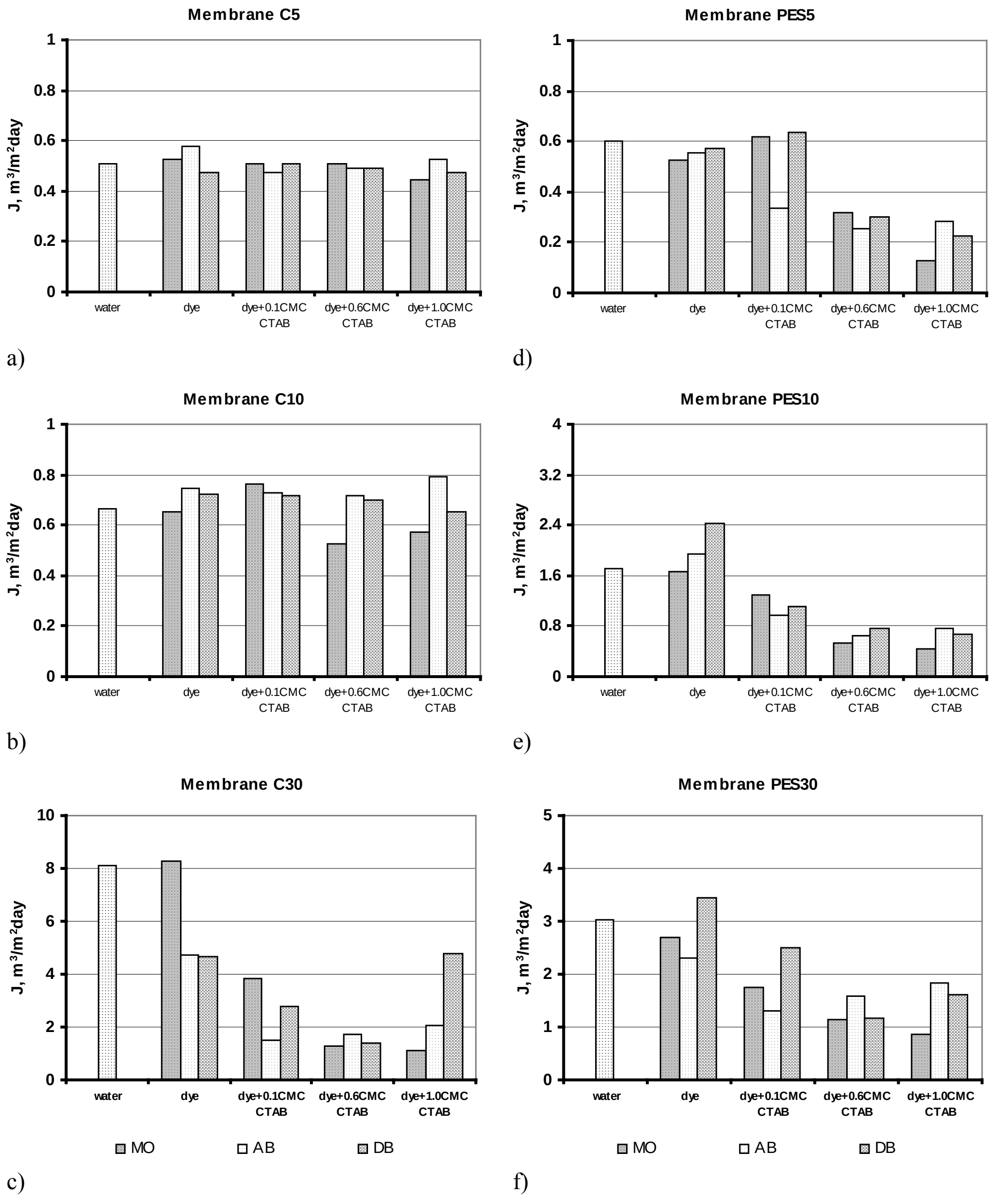

Fig. 2. Volume flux (*J*) for membranes made of regenerated cellulose (C) and polyethersulfone (PES) versus CTAB concentration in dye solution

Taking into account the presence of cationic detergent (CTAB) in dye solutions (figure 2), an essential drop in permeate volume flux was observed for all PES membranes (figure 2 d, e, f) as well as for C30 membrane (figure 2 c). Generally, an increase of CTAB concentration in dye solutions decreased the membrane permeability. When an anionic surfactant was added to dye solutions, the permeate fluxes also decreased, but to a lesser extent (figure 3). The highest drop in permeability was

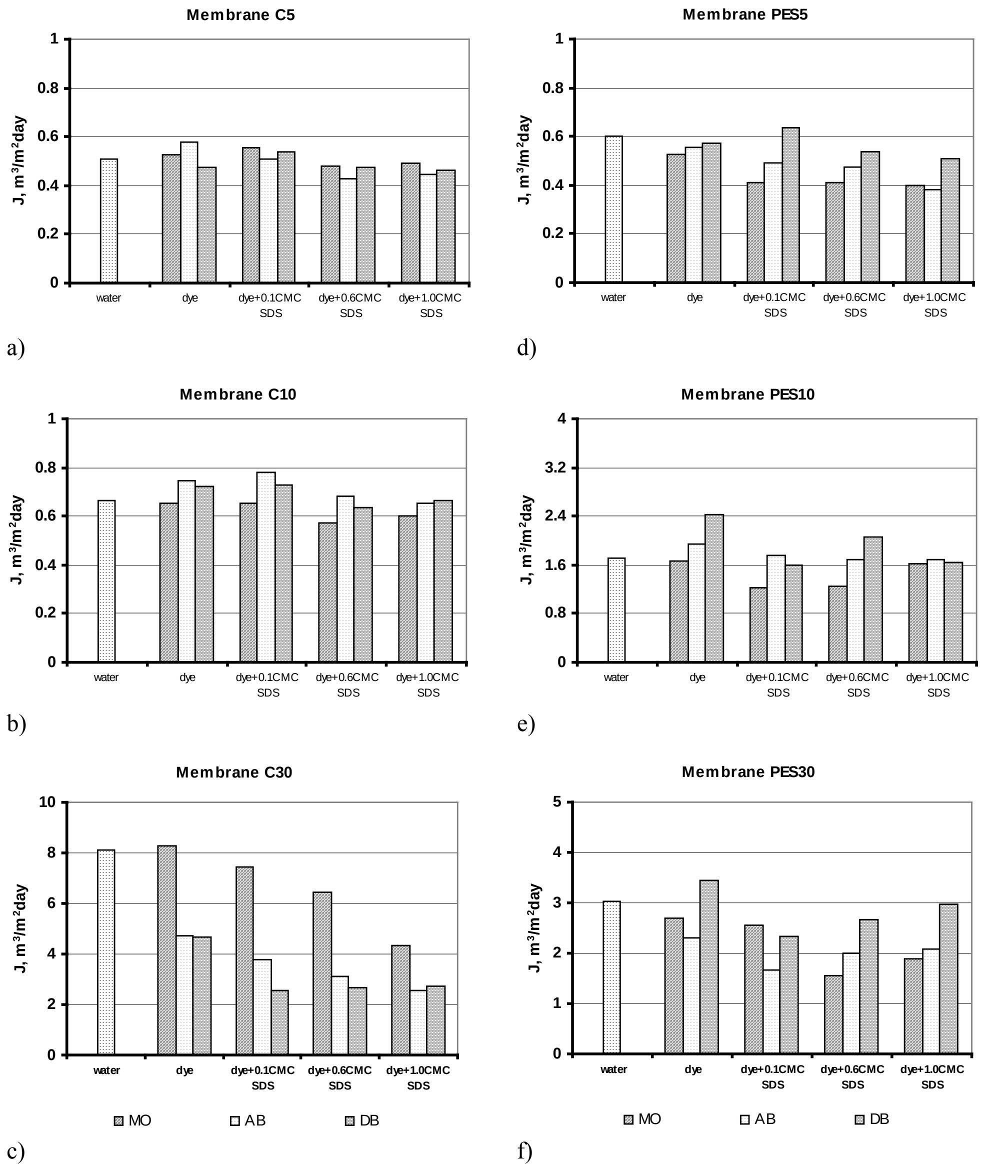

Fig. 3. Volume flux (J) for membranes made of regenerated cellulose (C) and polyethersulfone (PES) versus SDS concentration in dye solution

noticed for membranes of 30 kDa cut-off value (figure 3 c, f) which was similar to the results obtained when CTAB containing solutions were treated. Generally, regenerated cellulose membranes (5 kDa and 10 kDa series) showed less diverse values of permeability with varying composition of dye solutions, irrespective of the nature of surfactant. Even a slight increase in volume fluxes (compared to water flux) was observed for dye + SDS solutions (figure 3a, b).

In practice, the worsening of membrane permeability during ultrafiltration of model solutions containing various organic components can be attributed to adsorptive fouling. This statement can be supported by hydrophilic/hydrophobic properties of the experimental membranes and retained substances. According to manufacturer information the membranes made of regenerated cellulose are characterized by higher hydrophilicity than polyethersulfone membranes. As a consequence, the drop in permeate volume fluxes for the membranes made of regenerated cellulose is much smaller than that for polyethersulfone membranes, but this observation is valid for the membranes of the cut-off values equal to 5 and 10 kDa. For 30 kDa membrane series a dramatic drop in their permeability was found regardless of membrane material. It can be also concluded that the greater the membrane cut-off value, the more intensive its adsorptive fouling.

3.2. MEMBRANE SEPARATION PROPERTIES

The effect of the nature of the surfactant as well as the membrane hydrophilicity on the dye separation efficiency was determined by comparing the filtration of dye solutions in the presence of cationic and anionic detergents. Figures 4 and 5 show, respectively, the influence of CTAB and SDS on the dye retention coefficient.

A distinct correlation between molecular weight of dye particles and retention coefficient was found for both membrane types. An increase of the molecular weight of rejected dye particles improved the membrane selectivity. This relationship was observed for all the membranes tested. It was also found that with increasing membrane cut-off values the membrane selectivity towards dye particles decreased. Membranes of the highest cut off values (30 kDa) exhibited the lowest rejection, especially for methyl orange.

It is worth noting that polyethersulfone membranes showed a slightly better separation properties than the membranes made of regenerated cellulose. High-molecular-weight dye (i.e. Direct Black) was rejected in almost 100%, irrespective of membrane series.

The influence of surfactant presence in experimental solutions on dye retention is seriously affected by the nature of detergent, membrane material and membrane cut-off value.

The results obtained proved that the retention coefficient for all the dyes tested was remarkably improved in the presence of cationic surfactant (figure 4). It has been expected that the separation efficiency of anionic dyes by cationic micelles would be high because of the opposite charge of the components. The worsening of dye retention in the presence of SDS (figure 5) supports this expectation; however, this statement is valid only for 5 kDa and 10 kDa membranes. Membranes of the highest cut-

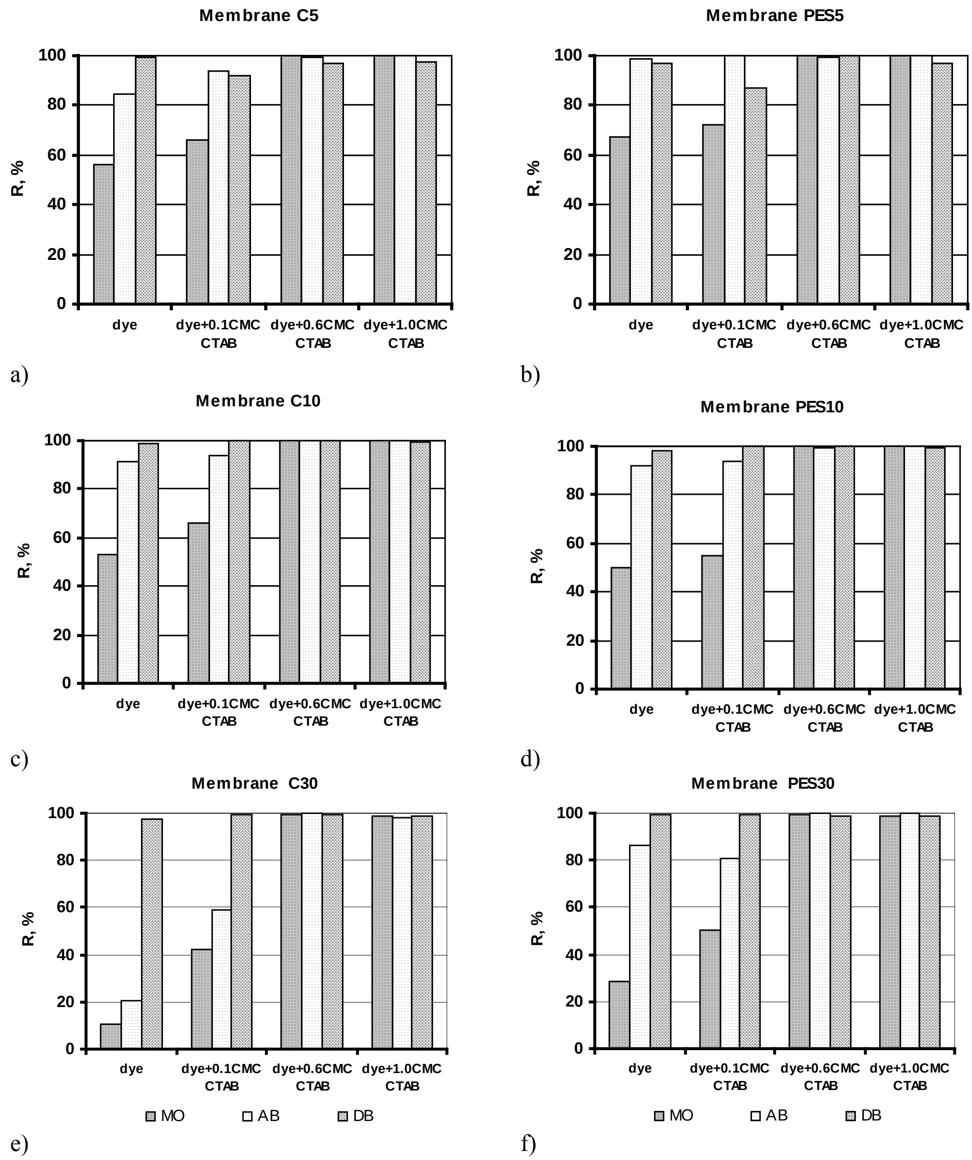

Fig. 4. Dye retention coefficient (R) for membranes made of regenerated cellulose (C) and polyethersulfone (PES) versus CTAB concentration in dye solution

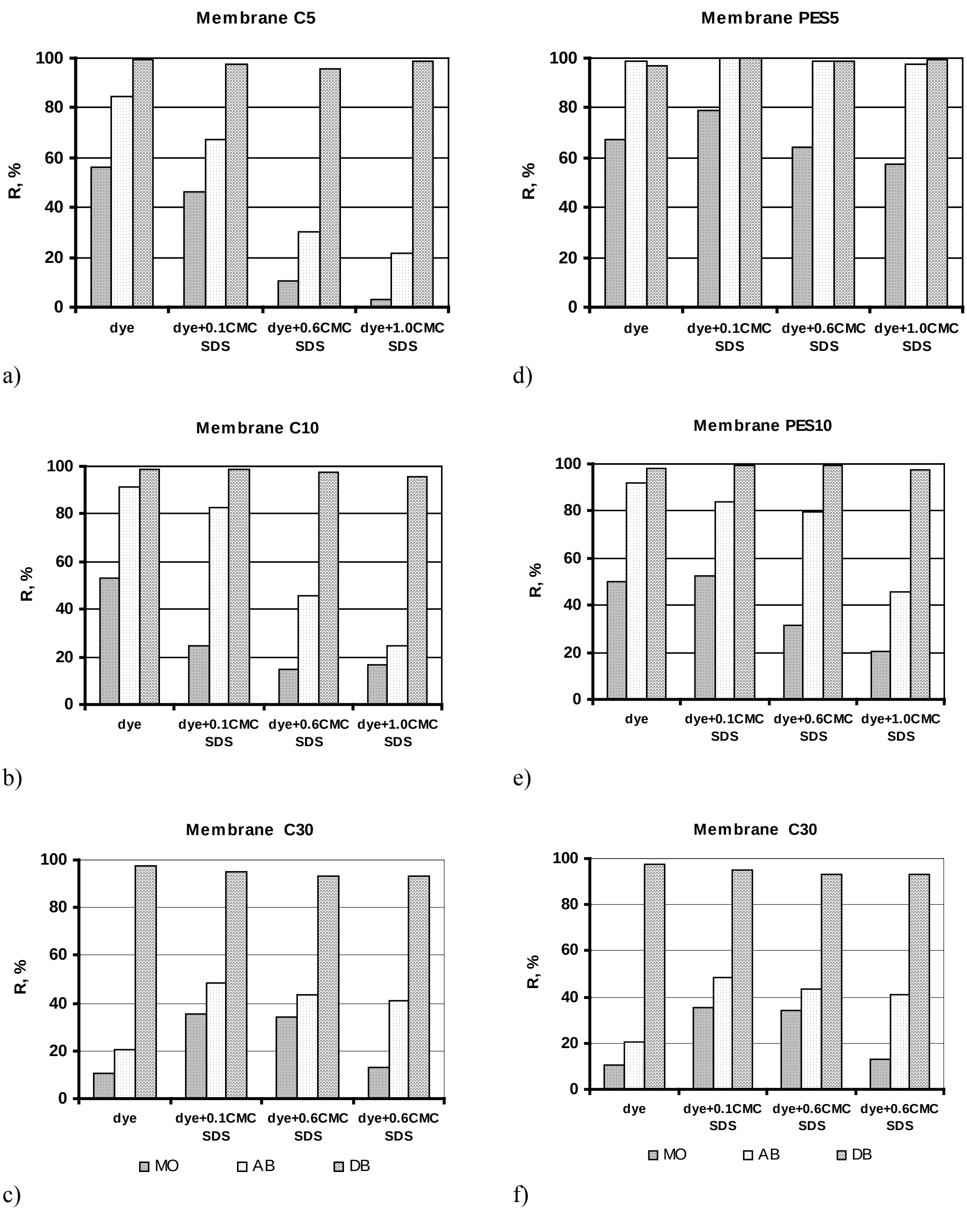

Fig. 5. Dye retention coefficient (*R*) for membranes made of regenerated cellulose (C) and polyethersulfone (PES) versus SDS concentration in dye solution

-off values (30 kDa) exhibited a slight improvement of the retention of low-molecular-weight dyes when SDS was present in the treated solution (figure 5c, f). Taking into account the hydrophilic properties of membranes, it turned out that dye rejection deterioration in the presence of SDS was more pronounced for more hydrophilic membranes made of regenerated cellulose.

The results obtained indicate that the electrostatic interactions between ionic dyes and surfactants play an important role in the separation efficiency. The interaction of anionic dyes with oppositely charged CTAB is mainly coulombic in nature. This interaction results in dye solubilization in CTAB micells. The micells containing dissolved organic dyes are easily rejected by UF membranes. It is worth noting that the dye retention improvement was observed at CTAB concentrations below CMC, i.e. at 0.1 and 0.6 CMC. On the contrary, the presence of SDS in model solutions caused a serious decrease in dye rejection coefficients (for 5 kDa and 10 kDa membranes). Probably, an electrostatic repulsion between dye and surfactant particles resulted in the converting of dye pre-aggregates into small particles, thus enabling passage of dye molecules through membrane pores or dye adsorption in membrane pores.

4. CONCLUSIONS

1. The transport properties of polymeric membranes are significantly influenced by the composition of the treated solution. In general, the presence of surfactants in dye solutions decreases a membrane permeability.

2. The influence of surfactant present in experimental solutions on dye retention is greatly affected by the nature of detergent, membrane material and membrane cut-off value.

3. The presence of an anionic surfactant in model solutions accounts for the worsening of the dye separation factor, whereas the cationic surfactant improves dye rejection.

ACKNOWLEDGEMENT

This work was supported by grant for statutory activity of the Department of Environmental Engineering, Wrocław University of Technology.

REFERENCES

[1] SUN O., YANG L., *The adsorption of basic dyes from aqueous solutions on modified pre-resin particles*, Water Research, 2003, 37, 1535–1544.

[2] MARMARA O., POSTE C., *Colour removal from textile plant effluents*, American Dyestuff Report, 1996, 15–21.

[3] CRINI G., *Non-conventional low-cost adsorbents for dye removal: A review*, Bioresources Technology, 2006, 97, 1061–1085.

[4] PETZOLD G., SCHWARZ S., *Dye removal from solutions and sludges by using polyelectrolytes and polyelectrolyte–surfactant complex*, Separation and Purification Technology, 2003, 31, 318–324.
[5] YOUNG KU, PEI-LIU LEE, WEN-YU WANG, *Removal of acidic dyestuffs in aqueous solution by nanofiltration*, Journal of Membrane Science, 2005, 250, 159–165.
[6] ALLÉGRE C., MOULIN P., MAISSEU M., CHARBIT F., *Savings and reuse of salts and water present in dye house effluents*, Desalination, 2004, 162, 13–22.
[7] KOPECKÝ V., MIKULÁŠEK P., *Desalination of reactive yellow 85 by nanofiltration*, Environment Protection Engineering, 2005, 31, 187–198.
[8] PORTER J., GOMEZ A.C., *The rejection of anionic dyes and salts from water solution using a polypropylene microfilter*, 2000, 128, 81–90.
[9] PETROV S.P., STOYCHEV P.A., *Ultrafiltration purification of waters contaminated with bifunctional reactive dyes*, Desalination, 2003, 154, 247–252.
[10] MARCUCCI M., NOSENZO G., CAPANELLI G., CIABATTI I., CORRIERI D., GIARDELLI G., *Treatment and reuse of textile effluents based on new ultrafiltration and other membrane technologies*, Desalination, 2001, 138, 75–82.
[11] ZAGHBANI N., HAFIANE A., DHAHBI M., *Separation of methyl blue from aqueous solution by micellar enhanced ultrafiltration*, Separation and Purification Technology, 2007, 55, 117–124.
[12] BIELSKA M., PROCHASKA K., *Dyes separation by means of cross-flow ultrafiltration of micellar solutions*, Dyes and Pigments, 2007, 74, 410–415.
[13] ZAGHBANI N., HAFIANE A., DHAHBI M., *Removal of Safranin T from wastewater using micellar enhanced ultrafiltration*, Desalination, 2008, 222, 348–356.
[14] CHAKRABORTY S., PURKAIT M.K., DAS GUPTA S., DE S., BASU J.K., *Nanofiltration of textile plants effluents for colour removal and reduction in COD*, Separation and Purification Technology, 2003, 31, 141–151.
[15] TANG C., CHEN V., *Nanofiltration of textile wastewater for water reuse*, Desalination, 2002, 143, 11–20.