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The effect of a polyelectrolyte on the efficiency of dye-surfactant solution treatment by ultrafiltration

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Abstract

The effect of a cationic polyelectrolyte (PE) on the dye and surfactant removal from aqueous mixtures by low-pressure membrane process was assessed. Flat ultrafiltration (UF) membranes made of regenerated cellulose and polyethersulfone, and characterized by different cut-off values (5, 10, and 30 kDa) were used in the experiments. The UF process involved a pressure of 0.1 and 0.2 MPa. Permeation measurements were carried out with aqueous solutions of different anionic dyes (methyl orange, indigo carmine, amido black, and direct black) and dye solutions containing an anionic surfactant – sodium dodecyl sulfate (SDS), and/or a cationic PE. Dye, surfactant, and PE concentrations in the experimental solutions amounted to 100, 100, and 0.5 g/m^3, respectively. It was found that when a cationic PE was present in the dye-surfactant mixture, this was concomitant with a decrease in membrane permeability and an increase in dye and surfactant retention. This relationship was more pronounced for polyetersulfone membranes than for membranes made of regenerated cellulose, as well as for membranes of high cut-off values.

Keywords: Ultrafiltration; Cationic polyelectrolyte; Anionic dye; Sodium dodecyl sulfate

1. Introduction

The textile industry generates large quantities of wastewaters that cannot be discharged directly to water reservoirs. Because of increasingly stringent restrictions on the organic content of industrial effluents it is necessary to eliminate organic load from wastewater before it is discharged. Due to wide range of chemicals (i.e. dyes, surfactants, mineral salts, solvents, heavy metals) used in technological processes, each textile plant should establish the most economical treatment for its effluents to eliminate especially dyes and detergents.

Wastewaters containing dyes are very difficult to treat, since the dye molecules are resistant to aerobic digestion and are stable to light, heat, and oxidizing agents [1]. During the last years

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many physical, chemical, and biological decolorization methods have been reported [2,3]. At present, the most commonly practiced treatment technology for the removal of dyestuffs from aqueous solutions is chemical coagulation followed by sedimentation [4], however in these processes massive amounts of sludge are generated. Adsorption could also be a procedure of choice, since it can be used to remove different types of dyes [3]. A literature survey shows that at the present time, there is no single process capable of adequate dye effluent treatment, mainly due to complex nature of the wastewater [5].

Membrane separation processes can be a promising alternative for the removals of a variety of dyestuffs, as well as surface active agents from aqueous solutions. Membrane pressure-driven processes are being increasingly used in the treatment of textile wastewater. Although a number of studies have been carried out involving the application of nanofiltration [6–8] and reverse osmosis [9,10] in water reuse, only a few papers deal with successful use of ultrafiltration (UF) for dyestuff removal [11–13].

The efficiency of separation of organic compound (i.e. dyes and surfactants) by UF process can be improved by applying polyelectrolytes (PEs). These polymers can act as complexing agents transforming small individual organic particles into high-molecular weight agglomerates. The complexing power depends on the properties of polymers, especially the type of charge (negative, positive, or uncharged), the charge density, and the molecular weight. The charge of dye or surfactant, which should be removed, is also of great importance. It has been found [4] that complexing agents with hydrophobic parts and positive or negative charge are able to bind the dye via hydrophobic as well as electrostatic interaction forces. The mechanism of dye incorporation into triple complexes was also intensively studied. It was shown [14] that cationic polymer tends to react with anionic textile finishing chemicals and auxiliaries, such as anionic detergents, forming intermolecular complexes. Under controlled conditions, these complexes can incorporate the dye particles. Petzold and Schwarz [4] found that PE-surfactant complexes can remove dyes due to triple complex formation. They concluded that the dyes with positive charge were effectively removed with complexes with excess of polyanion. Some experiments on interactions between organic dyes and oppositely charged surface active agents have also been studied [4]. It was observed that in the presence of linear PE, water-insoluble three component dye complexes were formed. However, no systematic investigations of dye removal in relation to the PE, dye, and surfactant charge have been done.

Therefore, the aim of the present paper was to investigate the membrane process efficiency for aqueous mixtures containing dye, surfactant, and PE. In this paper the effect of cationic PE on anionic dye and sodium dodecyl sulphate (SDS) removal from aqueous solutions by UF was reported.

2. Materials and methods

2.1. Membranes

The Nadir membranes made of regenerated cellulose (C) and polyethersulfone (PES) were used in the experiments. The membrane cut-off values varied from 5 to 30 kDa. According to producer's information, membranes made of regenerated cellulose are considered as the most hydrophilic whereas polyethersulfone membranes are characterized by moderate hydrophilicity. The characterization of investigated membranes is given in Table 1. In the description of a given membrane (e.g. PES5, C10), the number denotes the cut-off (in thousands of daltons).

2.2. Ultrafiltration process

An Amicon UF stirred cell (model 8400) with total volume of 350 cm^3 was used to determine transport and separation properties of the

Table 1
Characterization of Nadir membranes

Membrane type	Membrane polymer	Description	Cut-off[a], kDa	Hydraulic permeability, m^3/m^2 day MPa
PES	Polyethersulfone	Moderately hydrophilic	5	4.85
			10	22.5
			30	20
C	Regenerated cellulose	The most hydrophilic	5	4.75
			10	6.10
			30	70

[a]Given by producer.

membranes [15]. The effective surface area of the membrane amounted to 45.3 cm^2. Continuous passage of the permeate to UF cell enabled constant concentration of the circulating solution.

The UF process involved a transmembrane pressure of 0.1 and 0.2 MPa for all experiments. Permeate volume fluxes and retention coefficients were determined with respect to experimental surfactant and dyes after a steady conditions of flow were achieved.

2.3. Experimental solutions

The permeation measurements were carried out with distilled water, aqueous solutions of various dyes, aqueous solutions of dye and PE, aqueous solutions of SDS, aqueous mixtures of SDS and dye, and aqueous mixtures of dye, SDS, and PE. Four organic dyes of anionic nature (Table 2) have been chosen. When aqueous solution containing dye and surfactant or a mixture of dye, SDS, and PE was passed through a membrane, only one of the experimental dyes was present in the tested solution.

The concentration of SDS in model solutions amounted to 100 g/m^3, and it was below its critical micelle concentration (CMC < 2257 g/m^3) [16]. SDS or NaDS is also known as sodium lauryl sulphate (SLS). The molecular formula is as following: $CH_3(CH_2)_{11}OSO_3Na$, and the molecular weight of SDS amounts to 288.38 Da. Dye concentration in the aqueous solution was equal to 100 g/m^3. The pH and the temperature of the feed solutions were equal to 7.0°C and 25°C, respectively.

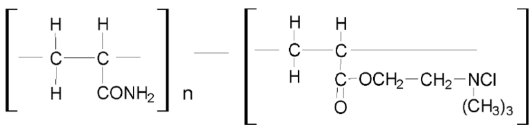
A PE Magnofloc LT 22S (Ciba Speciality Chemicals), prepared basis on the polyacrylamide (I), was used in the tests. It was a synthetic

Table 2
Characterization of the experimental dyes

Dye	Molecular weight, Da	Classsification	Dye symbol	λ_{max}[a], nm	Structural formula
Methyl orange	327.0	Acid dye	MO	465	$C_{14}H_{14}N_9O_9SNa$
Indigo carmine	466.36	Acid dye	IC	610	$C_{16}H_8N_2Na_2O_8S_6$
Amido black	615.50	Acid dye	AB	618	$C_{22}H_{19}N_5Na_2O_6S_4$
Direct black	781.20	Direct dye	DB	585	$C_{34}H_{25}N_9O_7S_2Na_2$

[a]Wavelength corresponding to the maximum absorbance of the dye solution.

flocculant of a cationic type characterized by high molecular weight. The concentration of PE in experimental solutions amounted to 0.5 g/m^3. This complexing agent has been chosen taking into account the results of our previous investigations [17].



(I)

Dye concentration in aqueous solutions was determined by spectrophotometer at a wavelength (λ_{max}) corresponding to the maximum absorbance of the sample (Table 2).

The SDS concentration in the feed and the permeate was determined by means of color reaction using the indicator Rhodamine G6 and spectrophotometric measurements of the absorbance at a wavelength of 565 nm.

3. Results and discussion

3.1. The effect of PE on membrane permeability

The effect of complexing agent on dye-surfactant UF efficiency was analyzed. Figs. 1a and b show the influence of cationic PE on membrane volume fluxes for various membrane series (5, 10, and 30 kDa, respectively). Reference data of distilled water volume fluxes for fresh membranes (H_2O) as well as permeate volume fluxes of SDS solutions (SDS + H_2O) were given.

Generally, it was found that UF of dye or surfactant containing solutions brought about an essential drop in permeate volume flux in relation to membrane permeability for distilled water. This effect was more pronounced for high-molecular weight dyes as well as for polyethersulfone membranes. However, some membranes made of regenerated cellulose (5 and 10 kDa series) exhibited an insignificant improvement of permeability during UF of SDS solutions.

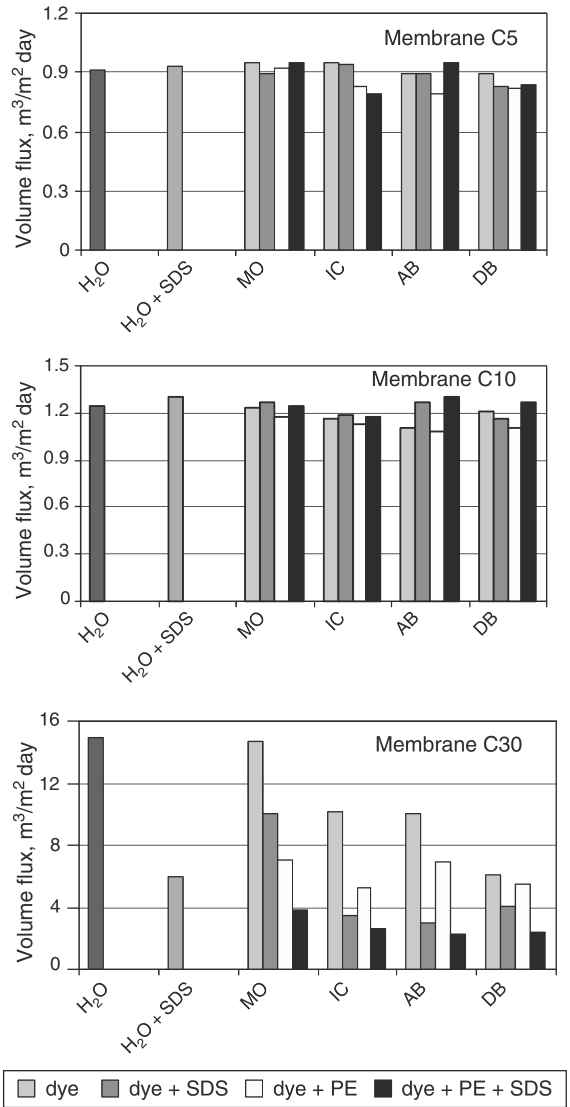


Fig. 1a. The effect of feed solution composition on permeate volume flux for membranes made of regenerated cellulose (ΔP = 0.2 MPa). MO – methyl orange, IC – indigo carmine, AB – amido black, DB – direct black.

Analyzing the effect of complexing agent it turned out that the presence of PE in dye solutions brought about an essential drop in volume fluxes for all experimental membranes and dyes applied. Dosage of PE into solutions containing

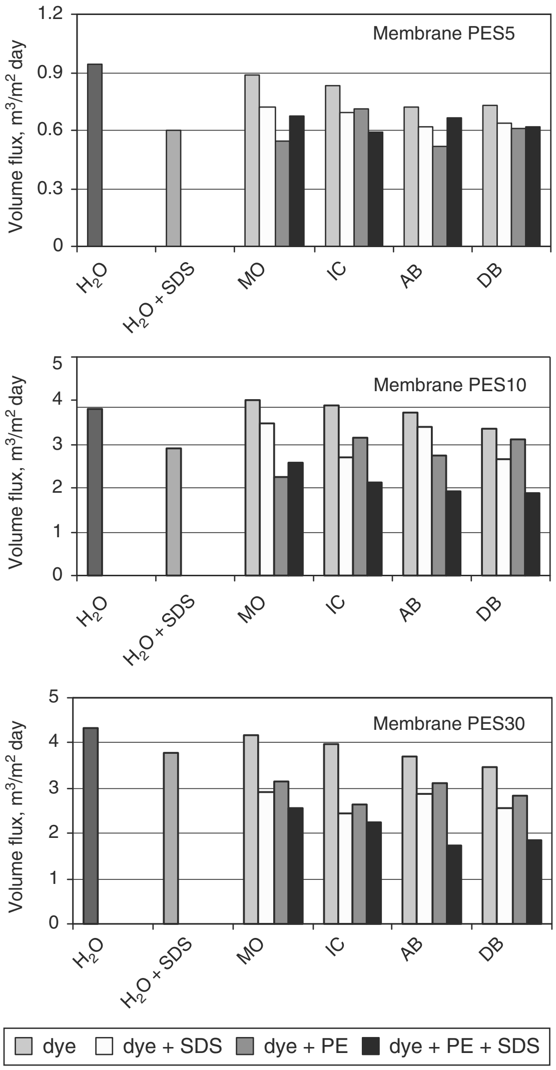


Fig. 1b. The effect of feed solution composition on permeate volume flux for polyethersulfone membranes (ΔP = 0.2 MPa). MO – methyl orange, IC – indigo carmine, AB – amido black, DB – direct black.

mixture of dye and surfactant also resulted in decreasing in membrane permeability, but this relationship was especially pronounced for membranes of high cut-off values (30 kDa) and polyethersulfone membranes. Regenerated cellulose membranes (5 and 10 kDa series) showed less diverse values of permeability with varying composition of dye solutions. Even a slight increase in volume fluxes (comparing to water flux) was observed for three-component solutions (dye + SDS + PE), especially when methyl orange and amido black were present in the testing solution.

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

It can be anticipated that the worsening of membrane transport properties was caused by adsorption of solution components (SDS, dye or PE complexes) in membrane structure. Due to rather hydrophobic nature of experimental dyes (Table 3), the adsorption of dye particles on the pore walls or on the membrane surface was facilitated in case of polyethersulfone membranes. It can be also concluded that the greater the membrane cut-off value the adsorptive fouling is more intensive.

Table 3
Hydrophobicity of the experimental dyes in terms of the octanol-water partitioning coefficient

Dye	$\log K_{ow}$[a]
Methyl orange	3.29
Indigo carmine	1.53
Amido black	3.37
Direct black	5.04

[a]Calculated with the use of VCCLAB [18].

3.2. The effect of PE on membrane separation properties

3.2.1. Dye retention

The effect of complexing agent on dye separation efficiency was determined. Fig. 2 shows the influence of PE on dye retention coefficients for polyethersulfone and regenerated cellulose membranes.

A distinct correlation between molecular weight of dye particles and retention coefficient was found for both membrane types. The increase of molecular weight of rejected dye particles improved the membrane selectivity. This relationship was

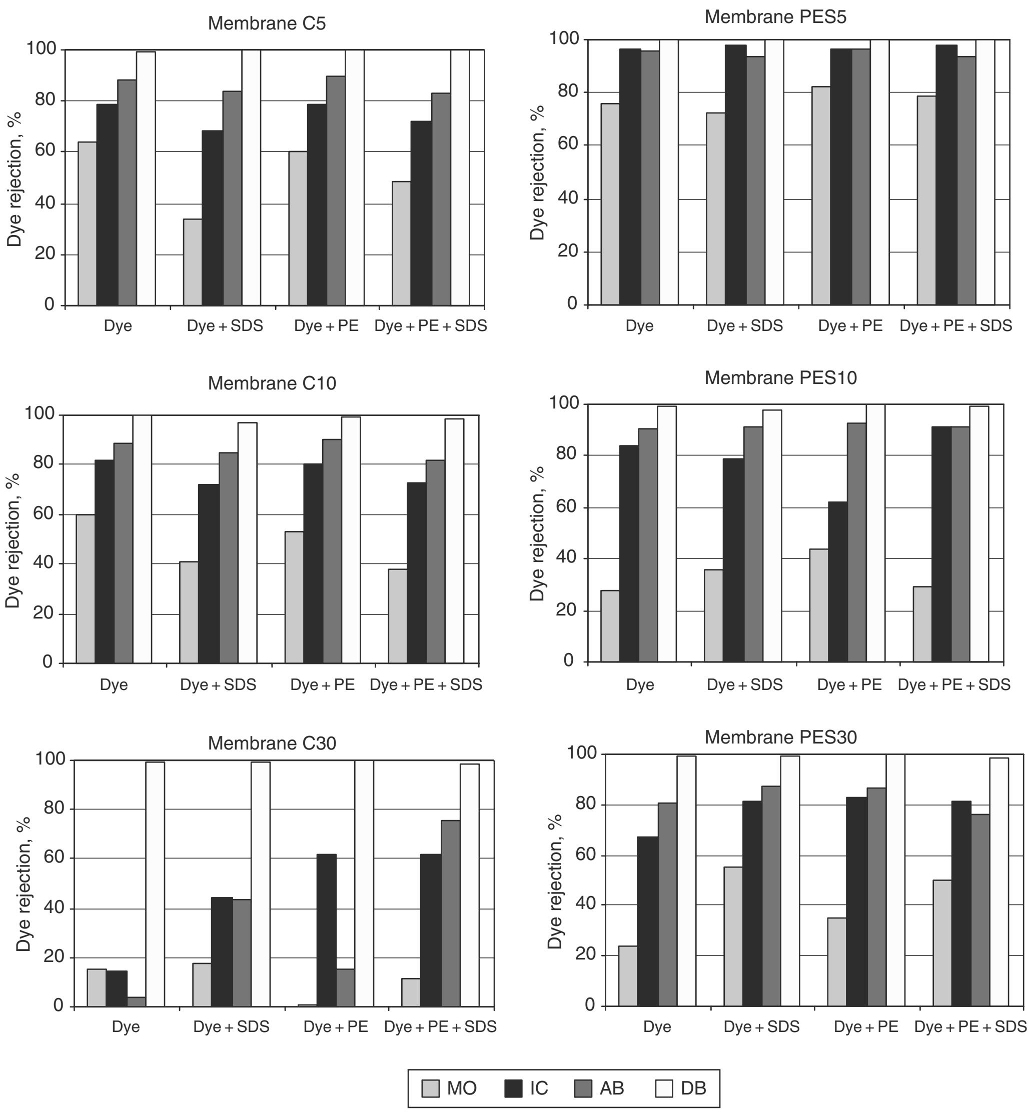


Fig. 2. The effect of feed solution composition on dye rejection for membranes made of regenerated cellulose (C series) and polyethersulfone (PES series) (ΔP = 0.2 MPa). MO – methyl orange, IC – indigo carmine, AB – amido black, DB – direct black.

observed for all tested membranes irrespectively on the solution composition, however membranes of high cut-off values (30 kDa) showed far more diverse values of rejection coefficients with increasing molecular size of dye particles. It was also observed that with increasing membrane cut-off values the membrane selectivity toward dye particles decreased. It is worth noting that polyethersulfone membranes showed a slight better separation properties, especially when low-molecular weight dyes were present in tested solution. High-molecular weight dye (i.e. direct black) was rejected in almost 100% irrespectively on membrane series and composition of the model solutions. Methyl orange, indigo carmine and amido black were rejected in various degree depending on the membrane cut-off, membrane material, and constituents of tested solutions.

The influence of surfactant presence in experimental solutions on dye retention is strongly affected by membrane material and membrane cut-off value. For polyethersulfone membranes of low cut-off values (5 and 10 kDa) no distinct difference in dye rejection coefficients was detected, whereas for polyethersulfone membrane PES30, as well as for regenerated cellulose membrane C30, the presence of SDS in the treated solutions brought about an selectivity improvement. It should be pointed out that C5 and C10 membranes behaved quite opposite – the presence of SDS in model solutions caused a serious decrease in dye rejection coefficients. Probably, an electrostatic repulsion between dye and surfactant particles resulted in converting of dye pre-aggregates into small particles, thus enabling passage of dye molecules through membrane pores or dye adsorption on membrane pores (polyethersulfone membranes).

It seemed that complexing agent should have a positive effect on dye separation. This finding was confirmed for 5 and 10 kDa membrane series, while for more open membranes (30 kDa) ambiguous results were obtained. It was also observed that favorable influence of PE was more visible for low-molecular weight dyes (i.e. methyl orange, indigo carmine). For high-molecular weight dye (i.e. direct black) rejected in high degree, the presence of PE in the model solution was of less importance.

The results obtained again confirmed that hydrophobic/hydrophilic properties of membranes as well as solute hydrophobicity play an essential role in UF separation. Generally, polyethersulfone membranes showed better retention toward dye particles than membranes made of regenerated cellulose. This phenomenon can be attributed to more intensive adsorption of hydrophobic dyes on pore walls for less hydrophilic polyethersulfone membranes. This finding is especially pronounced for membranes of high cut-off values (30 kDa). It is also worth noting that the most positive effect of PE on dye rejection was obtained for the dye characterized by the lowest hydrophobicity (indigo carmine).

3.2.2. SDS retention

Fig. 3 shows the effect of a cationic PE on SDS retention coefficient for various membrane series (5, 10, and 30 kDa, respectively). Reference data of SDS separation efficiency obtained for detergent model solutions containing only SDS as well as for SDS and dye solutions were given.

The experimental results indicated that the presence of anionic dye in the feed solution generally worsen the SDS retention coefficient. However, this relationship was strongly affected not only by the kind of organic dye but also by membrane material. For PES membranes of low cut-off values (5 kDa) the presence of organic dyes in separated solutions caused only a slight deterioration of SDS separation coefficients, whereas for the C5 membranes the decrease in detergent separation efficiency was more distinct. In the case of 10 kDa membrane series the drop in SDS retention was evident irrespective of membrane material. This deterioration in membrane separation properties was especially detected

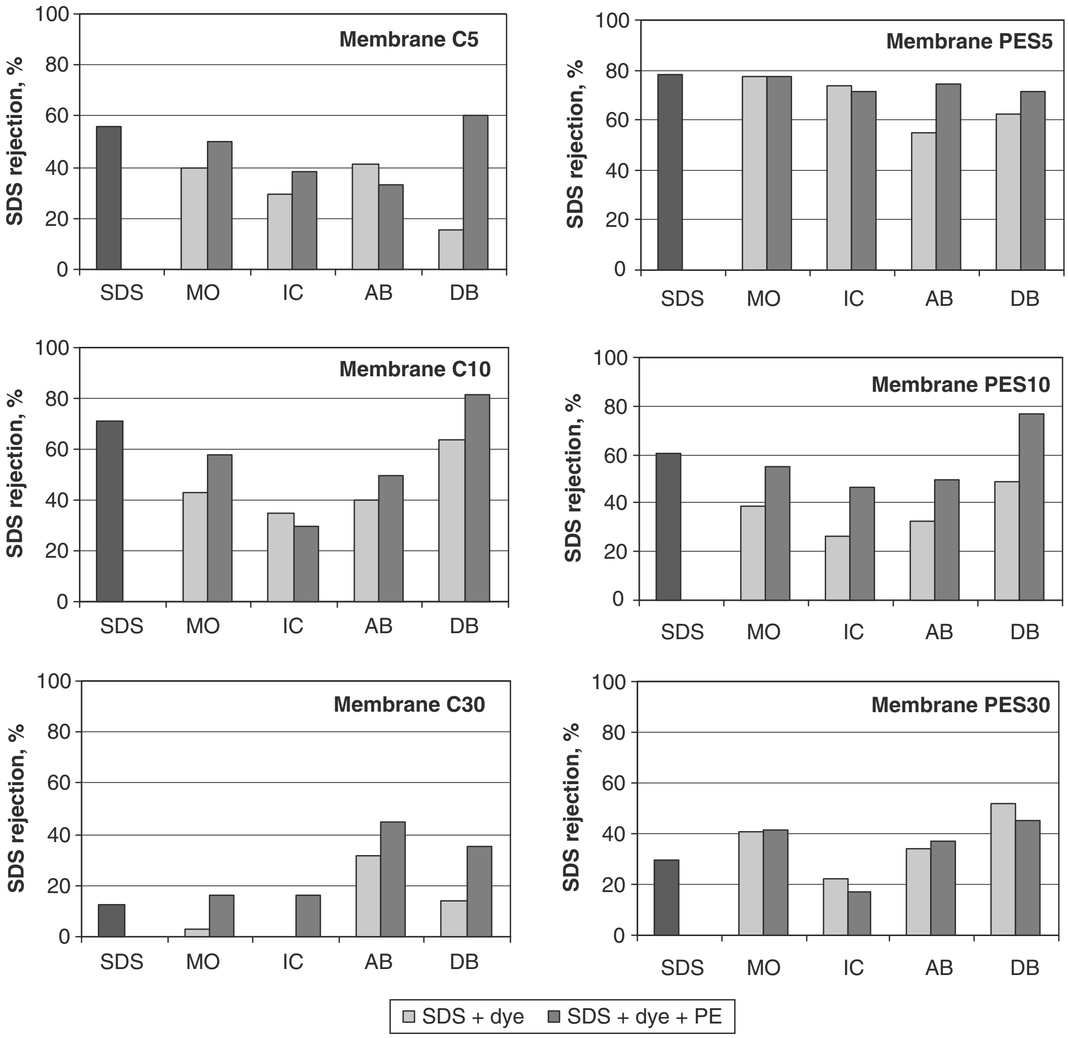


Fig. 3. The effect of feed solution composition on SDS rejection for membranes made of regenerated cellulose (C series) and polyethersulfone (PES series) (ΔP = 0.2 MPa). MO – methyl orange, IC – indigo carmine, AB – amido black, DB – direct black.

for low-molecular weight dyes (i.e. methyl orange and indigo carmine).

It should be pointed out that for more open membranes of cut-off values equal to 30 kDa the opposite phenomenon was observed, i.e. the increase in SDS retention was detected, but only when high-molecular weight dyes were present in the feed solutions.

It seems that the mechanism governing the surfactant separation from a solution containing anionic dyes can be explained by adsorption of surfactant monomers in membrane pore interior, thus reducing the pore size or by converting of SDS pre-micells to small particles as a result of electrostatic repulsion between surfactant and dye particles.

Analyzing the effect of cationic PE on SDS rejection coefficient in the presence of anionic dyes it was found that the addition of complexing agent into feed solution in principle brought about moderate improvement of surfactant retention in comparison with SDS retentions obtained for dye-detergent solutions. However, it should be pointed out that for 5 and 10 kDa membranes a distinct increase in SDS rejection coefficients in the case of SDS-dye-PE mixtures has arisen only when high-molecular weight dye (direct black) was present. In the event of the other dyes, the detected SDS retentions, even taking into consideration the positive effect of PE, were still much lower than SDS retentions obtained for model solutions containing only surface active agent. On the other hand, a significant profitable effect of cationic PE on SDS retention was observed for opened membranes (cut-off values equal to 30 kDa), especially for C30 membrane series.

The results obtained were much worser than expected. In our previous experiments [17] on the effect of various PEs on SDS retention a quite good improvement of the process efficiency was found. The increase in SDS separation in the presence of PE was connected with creation of specific agglomerates, which could be retained by the membrane. Bremmell et al. [19] stated that in the case of a cationic PE and an anionic surfactant two mechanism of complexation should be taken into account: at first, the anionic surfactant is attracted to the cationic PE due to electrostatic forces, and after neutralization, the surfactant particles are adsorbed as a result of hydrophobic interaction between the hydrocarbon chains. However, according to Biekturow et al. [20] it is possible that polymer chain changes its confirmation from a linear to more compact (spherical) form. It is supposed that under the anionic dye presence in SDS-cationic PE solution the access of ionic solutes to active centers of PEs is restricted. As a consequence, more small dye and surfactant particles are present in the separated solution.

4. Conclusions

(1) An improvement of the membrane separation properties toward anionic dyes and SDS in the presence of a cationic PE was observed. Polyethersulfone membranes exhibited a slight better separation properties than membranes made of regenerated cellulose.

(2) An essential drop in membrane permeability occurred when a cationic polyelectrolyte was added to the dye-surfactant aqueous mixture.

(3) The adsorptive fouling tendency was more pronounced for polyethersulfone membranes than for regenerated cellulose membranes, as well as for more hydrophobic dyes and more open membranes.

Acknowledgments

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