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REMOVAL OF DYES BY MICELLAR ENHANCED ULTRAFILTRATION

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The aim of the present work is to compare the performance of three kinds of membranes based on the polyethersulfone: (i) neutral, (ii) anion-exchange aminated PES and (iii) cation-exchange sulfonated PES in micellar enhanced ultrafiltration in removing anionic (methyl orange and cresol red) and cationic (metylene blue and methyl violet) dyes. Hexadecylpyridinium chloride (CPC) and sodium dodecyl sulfate (SDS) have been taken as the cationic and the anionic surfactant, respectively.
For each evaluated membrane, the transport enhanced species was selected. The selection criterion was keeping the same charge on both bodies: the membrane and the surfactant. Mixtures of metylene blue or methyl violet and sodium dodecyl sulfate were filtered through PES and SPES membranes and mixtures of methyl orange or cresol red and hexadecylpyridinium chloride were filtered through PES and APES membranes.
It was found that modified membranes can better reject investigated dyes than their neutral analogue at the same critical micelle concentration (cmc). Concentrations of both surfactants on the level of 2 cmc guarantee high rejection of the investigated dyes (about 90%). The use of higher surfactant concentration results in complete rejection of the dyes.

1. Introduction

Dye containing waste stream is one of the major elements of toxic industrial waste. Various types of dyes are used in process industries like textile industry, pulp and paper manufacturing, paints industry etc. Many methods are available for the removal of colored dyes from wastewater, eg. flocculation-coagulation (Pollock, 1973), oxidation (Shu et al., 1994), adsorption on different types of activated carbon (Al-Degs et al., 2001) and membrane processes (Van deer Bruges et al., 2005).
Membrane separation processes play today an important role in the field of wastewater purification and reuse. This well consolidated technology is very interesting due to its low operational costs, conceptual simplicity, modularity, optimal quality of treated water, and being more ecological than conventional separation techniques (Mulder, 1991).
In order to separate dyes, nanofiltration (NF) is commonly used. However, the permeating flux in NF is not so high and this process requires the use of high transmembrane pressure. That operation turns them into a more expensive membrane process. Another pressure-driven process - ultrafiltration (UF) – needs smaller transmembrane pressure and its operational cost is not so high. It has been shown that ultrafiltration is efficient in the removal of larger molar substances (polymers, colloids)

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whose size ranges from 2 to 100 nm and whose molecular weight is larger than 500 Da. However, the pore size of any ultrafilter is too large to reject small molecules like dyes.
Among membrane processes, the micellar enhanced ultrafiltration (MEUF), a hybrid (non-conventional) process, has been shown to be a promising method for removing low levels of organic dyes from water (Purkait et al., 2006; Ahmed and Puasa, 2007; Bielska and Prochaska, 2007; Zaghabani et al., 2007). In MEUF, surfactant with higher concentration than the critical micelle concentration (cmc) is added to a polluted aqueous solution. The surfactant molecules form micelles, which can solubilize the organic dyes. Micelles containing the dissolved solutes are then separated by ultrafiltration using a membrane of suitable porosity, capable of retaining micelles.
Polyethersulfone (PES) is a popular thermo-resistant polymer for membrane preparation. However, its major disadvantage is its hydrophobic character that facilitates the adsorption of organic compounds on the membrane surface. This harmful phenomenon is called membrane fouling. There are many ways to protect the membrane from fouling. One of them is the introduction of ionic groups to the membrane materials by chemical treatment (Poźniak et al., 1995). Porous ion exchange membranes form a new category of filtration media. They proved to be very useful in the filtration of charge-bearing solutes (Poźniak et al., 2005, 2006, 2007, 2008).
The aim of the present work is to compare the performance of three kinds of membranes based on the polyethersulfone, sulfonated and aminated polyethersulfone in micellar enhanced ultrafiltration in removing anionic and cationic dyes from aqueous media.

2. Experimental

2.1. Modification of polyethersulfone

Sulfonation of polyethersulfone (Ultrason E2020P, from BASF) was carried out using a mixture of chlorosulfonic acid (CSA) and 1,2-dichloroethane (90 min at room temp.). The initial molar ratio of CSA to PES was 3:1.
PES was chloromethylated using a mixture of methyl chloromethyl ether with $SnCl_4$ (24 h at room temp.). The initial molar ratio of ether and $SnCl_4$ to PES was 50:5:1. The membranes were formed directly from the chloromethylated derivatives. Aminolysis of chloromethylated membranes was performed in 50 vol.-% solution of N,N-dimethylaminoethanol in a 1:1 mixture of water and methanol (7 days at room temperature).

2.2. Preparation of membranes

Porous asymmetric membranes were formed by phase-inversion method from: 13%-wt. solution of PES (neutral membrane), 30%-wt. solution of sulfonated PES (cation exchange membrane) and 19%-wt. solution of chloromethylated PES in N,N-dimethylformamide (after amination - anion exchange membrane). In all cases, water was used as a coagulation medium.
The ion exchange capacity was estimated on the basis of acid-base titration method. The porosity was determined gravimetrically and average pore diameter was calculated according to the Ferry-Faxen relationship.

2.3. Micellar enhanced ultrafiltation

The Amicon 8200 dead-end cell with a filtration surface area of 19.6 cm^2 was used. The transmembrane pressure was equal to 0.1 MPa. Mixtures of metylene blue (M=320 Da) or methyl violet (M=394 Da), c=1 $mmol/dm^3$, and sodium dodecyl sulfate, SDS, (8.1, 16.2 and 40.5 $mmol/dm^3$, equivalent to 1, 2 and 5 cmc) were filtered through PES and

SPES membranes. Mixtures of methyl orange (M=327 Da) or cresol red (M=404 Da), c=1 mmol/dm^3 and hexadecylpyridinium chloride, CPC, (0.88, 1.76 and 4.40 mmol/dm^3, equivalent to 1, 2 and 5 cmc) were filtered through PES and APES membranes. In the permeate CPC, MB, MV, MO and CR concentrations were determined using spectrophotometer UV/VIS (SPECORD M40) at 259, 660, 590, 462 and 436 nm, respectively. SDS concentration was determined by the two-phase titration method.
To evaluate the filtration efficiency in removing dyes, the rejection coefficient (R) was calculated:

$$R = [1 - (c_p/c_f)] \times 100 \quad (1)$$

c_p and c_f - the concentration of dye in the permeate and feed, respectively.

3. Results

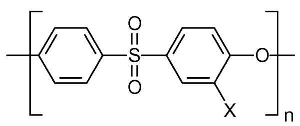
For the purpose of this study three kinds of membranes have been obtained; they are similar in their physical structure but differ in chemical composition (Tab. 1).

Table 1. Properties of ultrafiltration membranes

Membrane	Ion exchange capacity mmol/g	Average pore diameter nm	Membrane porosity %	Rejection of surfactant* %
PES	0.00	13	72	75
SPES	0.75	17	79	87
APES	1.68	12	76	89

* SDS for SPES membrane and CPC for APES membrane (c=2 cmc)

Porous membranes can be used for MEUF process only when the micelle diameter is greater than the pore size of the porous membrane. This condition seems to be fulfilled for PES, APES and SPES membranes as the rejection parameter for both tested surfactants reached high values (Tab. 1).
It is known that amination of a polymer results in the introduction of positive charges on the membrane surface while sulfonation results in the introduction of negative ones.



X = $-H$, $-SO_3^-$, or $-CH_2N^+(CH_3)_2C_2H_4OH$

To reduce the tendency of surfactant deposition on the membrane surface, for each evaluated membrane, the transport enhanced species was selected. The selection criterion was keeping the same charge on both bodies: the membrane and the surfactant. That is why SPES membrane was selected for SDS and APES membrane for CPC.
It can be seen that dyes are better rejected at sulfonated and aminated membranes than at their neutral analogue at the same critical micelle concentration (Figs. 1 and 2). From these data one might conclude that some repulsion forces between the micelle and the charged membrane play a critical role in that phenomenon.

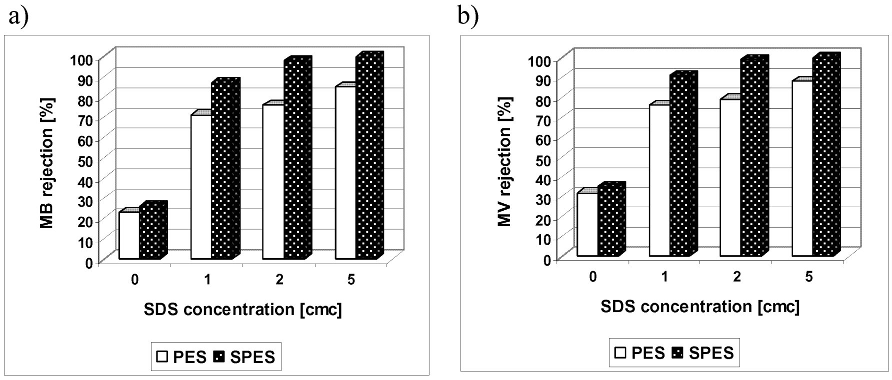


Fig. 1. Rejection of cationic dyes as a function of SDS concentration:
a) methylene blue, b) methyl violet

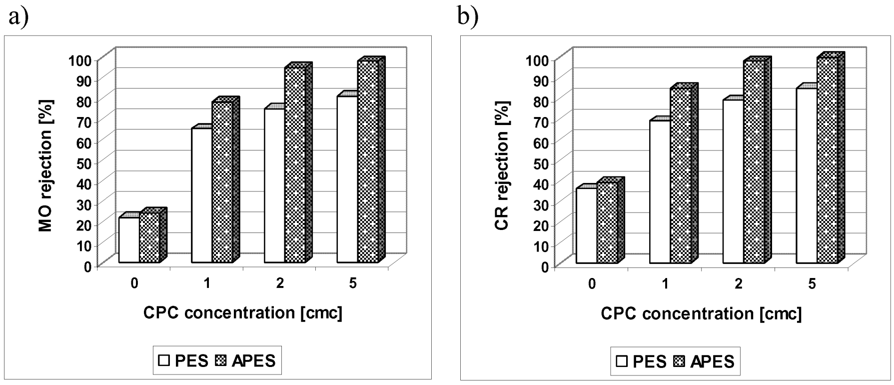


Fig. 2. Rejection of anionic dyes as a function of CPC concentration:
a) methyl orange, b) cresol red

Concentrations of both surfactants on the level of 2 cmc (1.76 and 16.2 mmol/dm^3 for CPC and SDS, respectively) guarantee high rejection of the investigated dyes. The use of higher surfactant concentration results in almost complete rejection of the dyes.

4. Conclusions

Polyethersulfone membranes and mostly their aminated and sulfonated derivatives can be applied for the separation of dyes by means of MEUF process. It is suggested that 2 cmc concentrations of surfactants should be used to reach the satisfactory level of dye rejection when modified polyethersulfone membranes are used.

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