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CONCENTRATION OF DYE SOLUTIONS IN THE PRESENCE OF SURFACTANT AND MINERAL SALTS

The membrane efficiency during concentration of aqueous mixtures containing dye, surfactant, and mineral salt was evaluated. The Pellicon PLAC1 UF flat module with membrane made of regenerated cellulose (1 kDa) was used in the experiments. Five organic dyes of anionic nature (Methyl Orange (MO), Indigo Carmine (IC), Amido Black (AB), Titan Yellow (TY), and Direct Black (DB)) were chosen. The concentration of each dye was equal to 100 g/m^3. The anionic surface active agent (sodium dodecyl sulphate (SDS)) and sodium chloride (NaCl) were added to the dye solutions tested. The concentration experiments together with the evaluation of membrane transport and separation properties were conducted at the pressure range of 0.05–0.15 MPa. The effect of the concentration factor on the volume flux of dye solutions and dye rejection was studied. It was found that membrane permeability was kept almost constant during the concentration process for all experimental solutions. Dye retention was highly influenced by the solution composition. While the mixtures of dye, salt, and SDS were concentrated, the dye separation remained almost constant during the process.

1. INTRODUCTION

The textile and laundry industrial plants produce huge amounts of wastewater streams that cannot be discharged directly to water reservoirs. Used dyes and rinsing baths may contain high quantities of organic compounds (dyes, surfactants, etc.) combined with inorganic substances of very high concentrations. Purification of these complex effluents is therefore highly advisable in terms of a decrease in wastewater volume and the reuse of valuable substances.

Membrane pressure processes are being increasingly used for the treatment of laundry and textile wastewater. Although a number of studies involving the application of reverse osmosis and nanofiltration in water reuse have been carried out [1]–[7], only a few of them deal with the recovery of valuable components from exhausted dye or rinsing baths [8]–[10]. It should be stressed that membrane processes can success-

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fully be applied to the treatment of complex dye effluents, provided that they are fractionated into three streams (at least): concentrate – rich in organic compounds, permeate – rich in mineral salts, and pure water permeate. In order to adopt such a procedure, we need to investigate extensively the process efficiency, depending on the molecular interactions between components of the treated solutions. VAN DER BRUGGEN et al. [10] found that the ionic strength as well as the presence of surfactants in dye baths had only a minor influence on dye retention. TANG and CHEN [4] confirmed that dye rejection remained almost constant regardless of what the salt concentration is used. On the contrary, AKBARI et al. [11] observed a distinct decrease in dye separation factor with an increase in the concentration of mineral salts in the treated solution. KOYUNCU et al. [12] showed that various mechanisms (cake formation or adsorption) were responsible for flux decline during nanofiltration of dye and salt mixtures characterized by different ionic strengths.

Taking into consideration the inconsistency of the literature data dealing with the effect of the solution composition on dye retention, it is advisable to study membrane process efficiency in aqueous mixtures containing dye, surfactant, and mineral salt. In this paper, the results of concentration experiments on model dye solutions were reported. Salt and anionic surfactant effect on the rejection of various organic dyes was investigated.

2. MATERIALS AND METHODS

2.1. MODULE

Commercially available Millipore ultrafiltration module was used for the concentration experiments. The module was of a flat type and equipped with the membranes made of regenerated cellulose. More details of the experimental module can be found in table 1.

Table 1

Characteristics of the experimental module

Parameter	Pellicon PLAC1 module
Configuration	Flat
Membrane material	Regenerated cellulose
Cut-off	1 kDa
Effective surface area	0.1 m^2
Water flux at ΔP = 0.1 MPa	0.1 m^3/m^2day
Operational conditions: maximum temperature pH	 60 ^oC 1–12

2.2. ULTRAFILTRATION PROCESS

Cross-flow experiments were performed using ProFlux M12 ultrafiltration system (Millipore) (figure 1). The installation enabled membrane testing in various module configurations. The set-up provided liquid circulation between the feeding tank and the membrane module at a constant concentration of the circulating solution. The volume of the feeding tank amounted to 3 dm^3. The ProFlux M12 system was equipped with control panel with pressure and pump efficiency indicators. Additional sensors protected the setup against the unexpected change in pressure or variations in liquid level in the feeding tank.

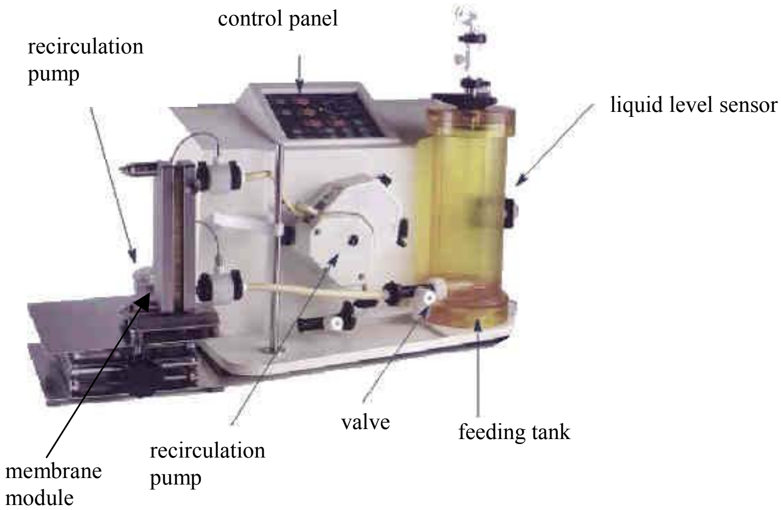


Fig. 1. The ultrafiltration ProFlux M12 (Millipore) system

The concentration experiments together with the evaluation of membrane transport and separation properties were conducted at 0.05, 0.1, and 0.15 MPa.

Permeate volume fluxes and retention coefficients were determined with respect to experimental dyes and surfactant after the steady conditions of flow were fixed.

The degree of solution concentration was established in terms of the concentration factor (*CF*) calculated by virtue of:

$$CF = \frac{V_0}{V_t},$$

where V_0 denotes the initial volume of concentrated solution (i.e., 3 dm^3) and V_t is the volume of concentrate after the time *t*. The concentration process was carried out until the volume of concentrate in the feeding tank reached 200 cm^3.

2.3. EXPERIMENTAL SOLUTIONS

The Pellion PLAC1 module properties of being able to transport distilled water, aqueous solutions of organic dyes, aqueous solution of SDS (sodium dodecyl sulphate), aqueous solutions of organic dye and SDS, and aqueous solutions containing dye, SDS and sodium salt (NaCl) were determined.

The concentration tests were carried out with aqueous solutions of different dyes, aqueous solutions containing SDS and dye, and aqueous solutions containing dye, SDS and sodium salt (NaCl).

Five organic dyes of anionic nature (table 3) were chosen. When aqueous solution containing mixture of dye and surfactant was involved, only one of the experimental dyes was present in the solution tested. In the aqueous solution, the dye concentration was equal to 100 g/m^3.

The concentration of SDS in model solutions amounted to 100 g/m^3 and was below its critical micelle concentration (CMC < 2257 g/m^3) [13]. The molecular formula of the detergent is as follows: $CH_3(CH_2)_{11}OSO_3Na$, and the molecular weight of SDS equals 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.

Salt concentration in the solutions tested was equal to 1 kg/m^3.

Table 3

Characteristics of the experimental dyes

Dye	Molecular weight, Da	Classsification	Dye symbol	λ^*_{max}, 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	$C_{22}H_{19}N_5Na_2O_6S_4$
Titan Yellow	695.73	Direct dye	TY	399	$C_{28}H_{19}N_5Na_2O_6S_4$
Direct black	781.20	Direct dye	DB	585	$C_{34}H_{25}N_9O_7S_2Na_2$

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

3. RESULTS AND DISCUSSION

3.1. TRANSPORT AND SEPARATION PROPERTIES OF THE MODULE

The study was aimed at estimating the efficiency of the concentration of dye solution by low-pressure membrane process. Salt and SDS effect on dye separation was investigated. The flat membrane module (Pellicon, Millipore) with membranes made of regenerated cellulose PLAC1 (1 kDa) was used in the experiments.

Prior to the concentration step, the module properties of being able to transport and separate various organic dyes and detergent were determined. Figure 2 shows permeate volume flux, as well as dye and SDS rejection at three values of transmembrane pressure (0.05, 0.1, and 0.15 MPa).

a)

b)

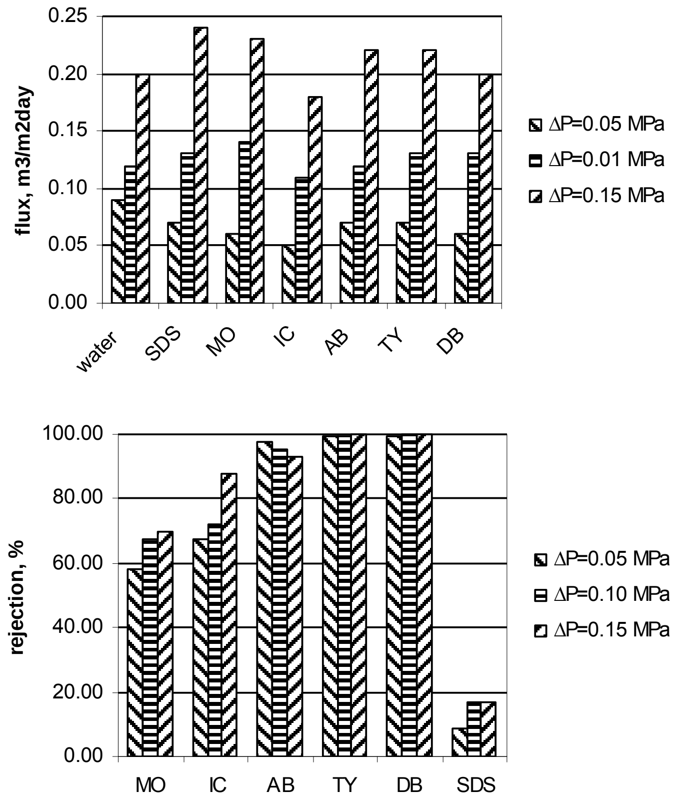


Fig. 2. Volume flux (a) and dye or SDS rejection (b) for Pellicon PLAC1 module at three various transmembrane pressures

The volume flux of distilled water amounted to 0.20 m^3/m^2day (at 0.15 MPa). In the case of SDS solution, the water permeability increased to 0.24 m^3/m^2day. An increase in the molecular weight of the rejected dyes generally slightly deteriorated the membrane permeability. This effect is most pronounced for the indigo carmine solution – the dye flux approached the value definitely lower than the water flux.

The results obtained indicate that the experimental module shows very good dye rejection coefficient. Even low-molecular-weight dyes (Methyl Orange, Indigo Carmine) were separated at least in 60% (depending on the pressure difference). The other dyes (Amido Black, Titan Yellow and Direct Black) were rejected in almost 98–100% (irrespective of the pressure applied).

It is worth noting that the experimental module exhibited very poor SDS rejection (less than 20%), which is in disagreement with our previous results [14] obtained for the same membrane of PLAC1 type. A possible explanation of this discrepancy could be found in different membrane configuration and testing apparatus.

3.2. SALT AND SDS EFFECT ON MODULE EFFICIENCY

The effect of salt and SDS additive on volume flux and dye rejection at the three values of applied pressure is presented in figures 3 and 4. There was no distinct impact of NaCl or surfactant in testing solutions on membrane permeability, however some generalization can be found.

As shown by the results obtained a slight decrease in volume flux was observed for solutions containing dye and salt (if we deal with the membrane permeable to dye solution). This effect was more pronounced for methyl orange and high-molecular-weight dyes (Titan Yellow and Direct Black). The decrease in membrane flux, when salt is dosed into the treated solution, could be attributed to the rise in osmotic pressure, i.e., to the reduction of driving force of the UF process. These findings seem to be quite obvious and have already been confirmed by our earlier results [15]. It is interesting to note that for dye solutions containing both salt and SDS, an unquestionable improvement of membrane permeability (in relation to dye permeate flux) was observed, especially for measurements carried out at 0.05 and 0.10 MPa. This could testify to the membrane hydrophilization due to an anionic surfactant contact with cellulose material. The results obtained also show that mineral salt additive (introduced into dye and SDS mixture) favours membrane hydrophilization much more than merely SDS presence in dye solutions.

Contrary to the membrane permeability results, the impact of mineral salt and surfactant on dye separation efficiency is much more diverse. A dramatic drop in dye rejection coefficient was observed, if only SDS was dosed to solutions containing low-molecular-weight dyes (Methyl Orange, Indigo Carmine). NaCl additive as well as NaCl with SDS additive also worsened the dye separation; however, this effect was

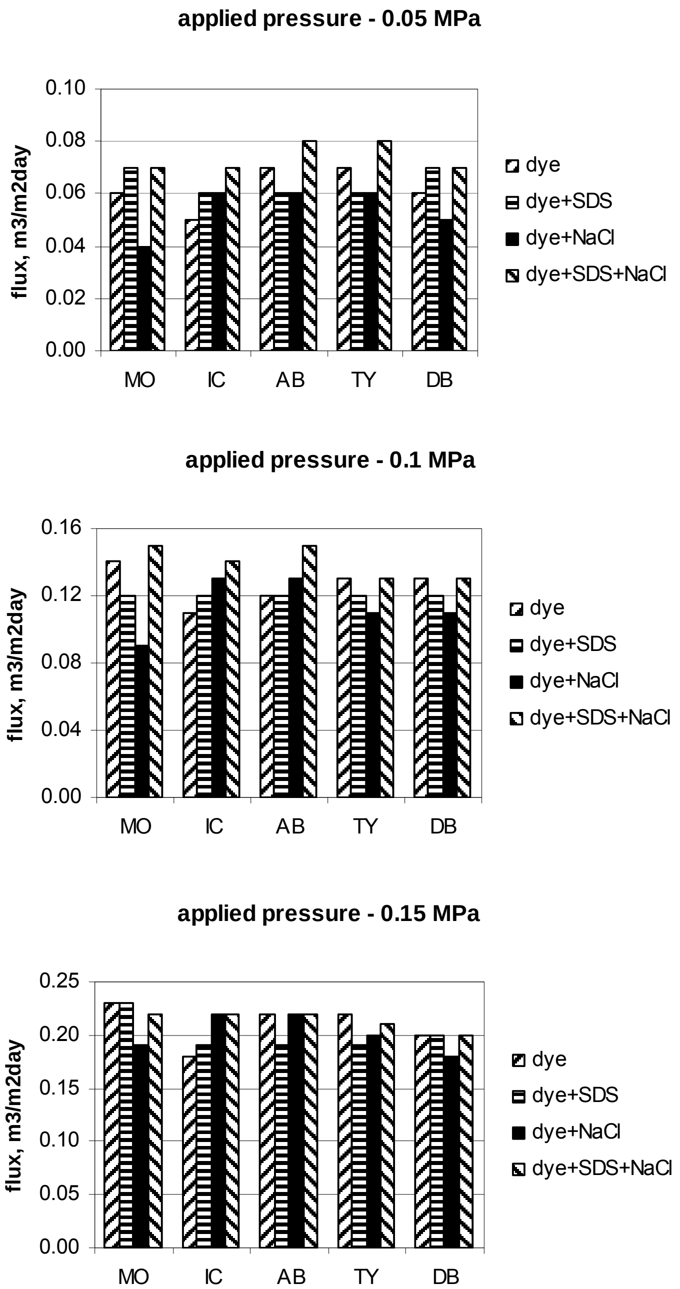


Fig. 3. The effect of SDS and NaCl on module (Pellicon PLAC1) permeability for dye-containing solutions at three transmembrane pressures

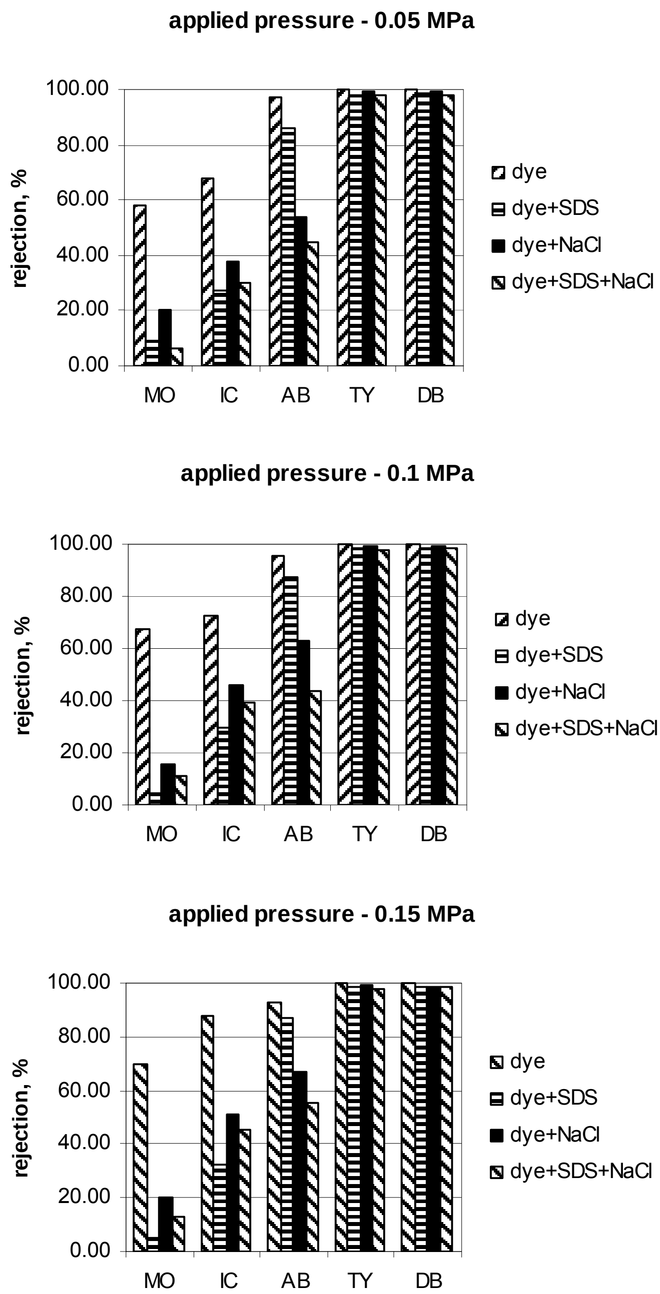


Fig. 4. The effect of SDS and NaCl on dye rejection for Pellicon PLAC1 module at three transmembrane pressures

less pronounced. In the case of high-molecular-weight dyes (Titan Yellow, Direct Black), which are rejected in 98–100%, salt and SDS additives do not affect the separation efficiency. It should be noted that for Amido Black (which is characterized by a moderate molecular weight) quite reverse effect was observed – subsequent dosing of various chemicals resulted in a decrease in rejection.

The effect of mineral salts on the separation efficiency of ionic macroparticles has been investigated by many researchers [9]–[12]; however, the results reported are rather inconsistent. One of the possible explanations is the following: when the feeds of high ionic strength are processed, the positive ions (i.e., Na^+) in solution can shield the negative groups connected with membrane surface, as well as neutralize the charges of anionic particles. Hence, the molecular sieve effect can be dominant and, as a result, the membrane selectivity markedly decreases. This explanation could be valid if the size of separated particle were comparable with mean pore radius or smaller. It can be anticipated that the particles of anionic surfactant can play a role similar to that of mineral salts, as in aqueous solutions they weaken the membrane negative charge, but to a lesser extent due to their low ionic strength.

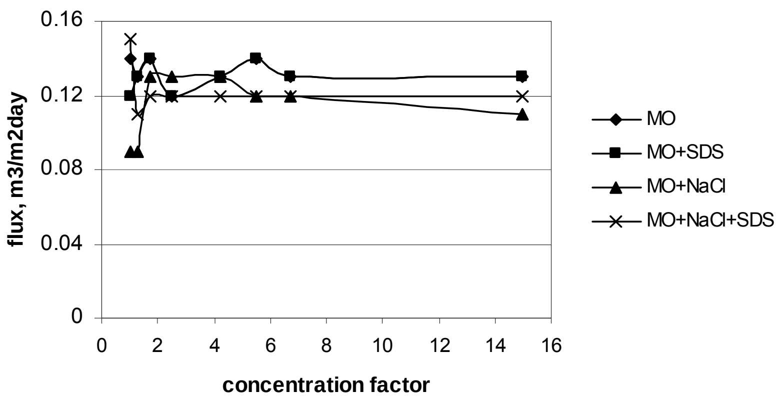
3.3. CONCENTRATION EXPERIMENTS

Transport and separation properties of Pellicon module were evaluated at constant composition of treated dye solutions, i.e., the permeate was recirculated to the feeding tank. In order to verify the efficiency of the concentration process, various dye solutions differing in the type of additive were subjected to ultrafiltration, which was performed without permeate recirculation. The concentration process was carried out until the volume of concentrate in the feeding tank reached 200 cm^3, i.e., the concentration factor (*CF*) took the maximum value of 15.

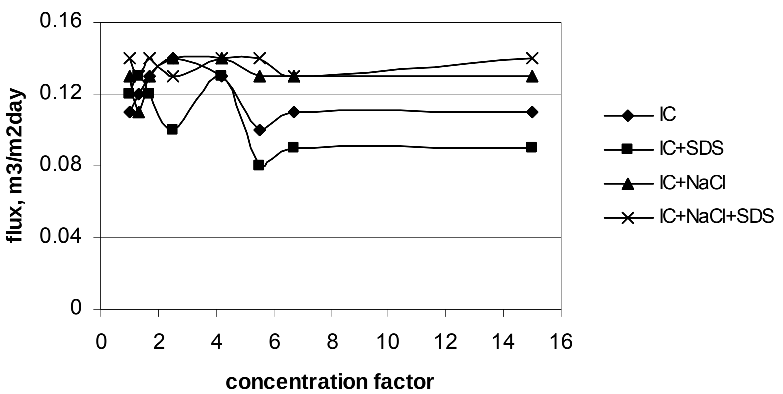
The effect of concentration factor on the volume flux of dye solution and dye rejection coefficient in the concentration process is presented in figures 5 and 6. To make the results more clear, each sub-graph is drawn for one type of dye only.

No obvious relationships were found between concentration factor, volume fluxes and composition of treated solution. However, it is very promising to note that the membrane permeability was kept almost constant during the concentration process. Some unimportant fluctuations in fluxes were observed in the initial stage of the process for all dye solutions, but later membrane permeability became stable. The greatest diversity in flux values, depending on the solution composition, was observed for Indigo Carmine, Amido Black, and Titan Yellow. In aqueous solutions containing these dyes, the lowest flux values measured at the end of the concentration process were characteristic of an aqueous mixture of dye and SDS.

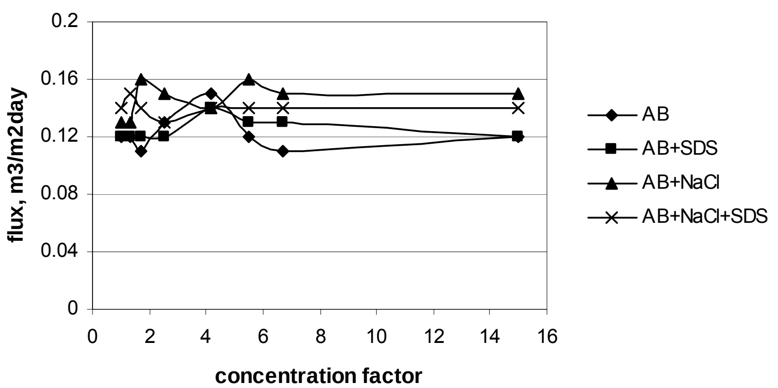
applied pressure - 0.1 MPa, dye - Methyl Orange



applied pressure - 0.1 MPa, dye - Indygo Carmine



applied pressure - 0.1 MPa, dye - Amido Black



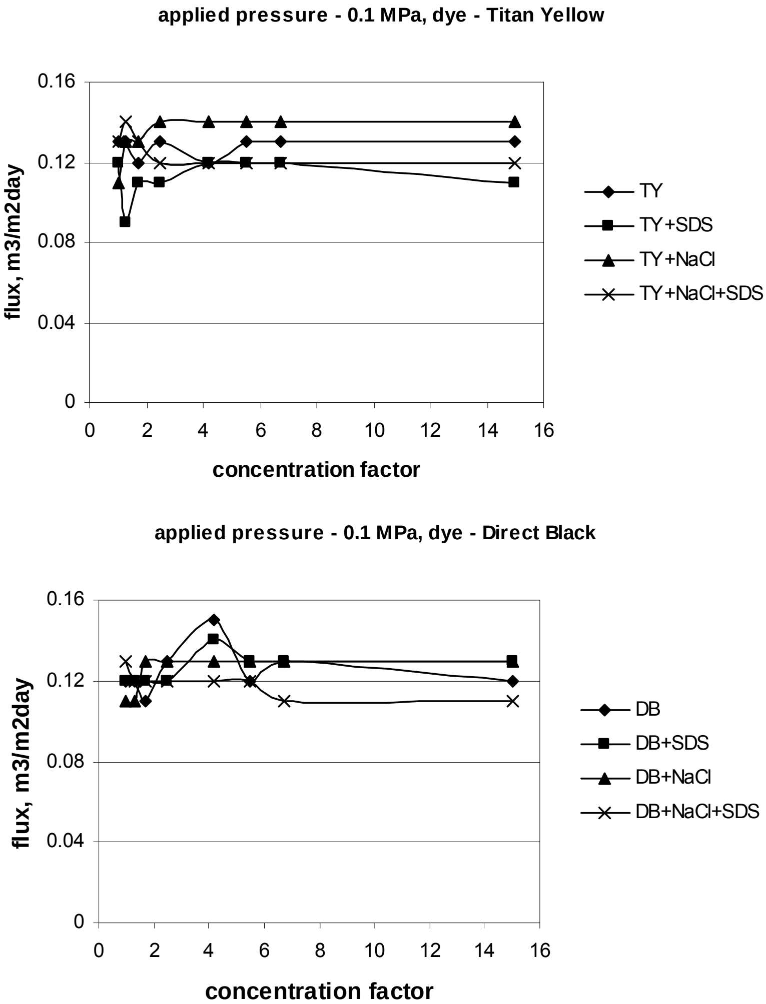
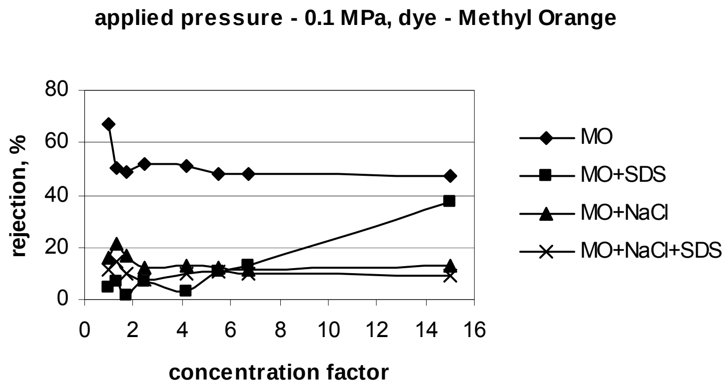
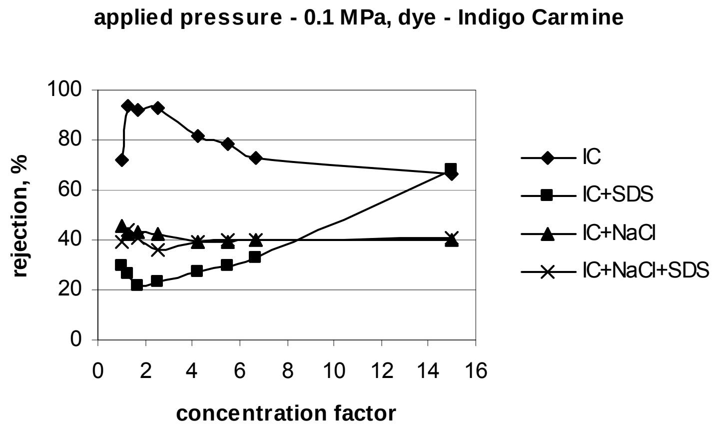
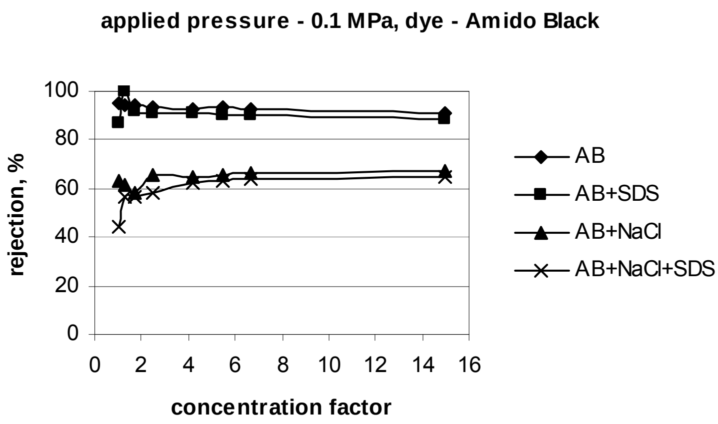


Fig. 5. The effect of the concentration factor on volume flux
of Pellicon PLAC1 module for various dye solutions

The results obtained are to some extent inconsistent with our former investigation on dye bath concentration [16]. We confirmed insignificant, but regular drop in membrane permeability with an increase in the concentration factor. However, this finding was proved for dye solutions with no surfactant additive. In the light of our former and current results, it can be concluded that membrane hydrophilization caused by SDS plays an essential role in the process efficiency. Even at increasing dye concentration the surfactant interaction with a membrane is strong enough to remain a hydrophilic head of surfactant available to water particles.


applied pressure - 0.1 MPa, dye - Methyl Orange
rejection, %
concentration factor
MO
MO+SDS
MO+NaCl
MO+NaCl+SDS


applied pressure - 0.1 MPa, dye - Indigo Carmine
rejection, %
concentration factor
IC
IC+SDS
IC+NaCl
IC+NaCl+SDS


applied pressure - 0.1 MPa, dye - Amido Black
rejection, %
concentration factor
AB
AB+SDS
AB+NaCl
AB+NaCl+SDS

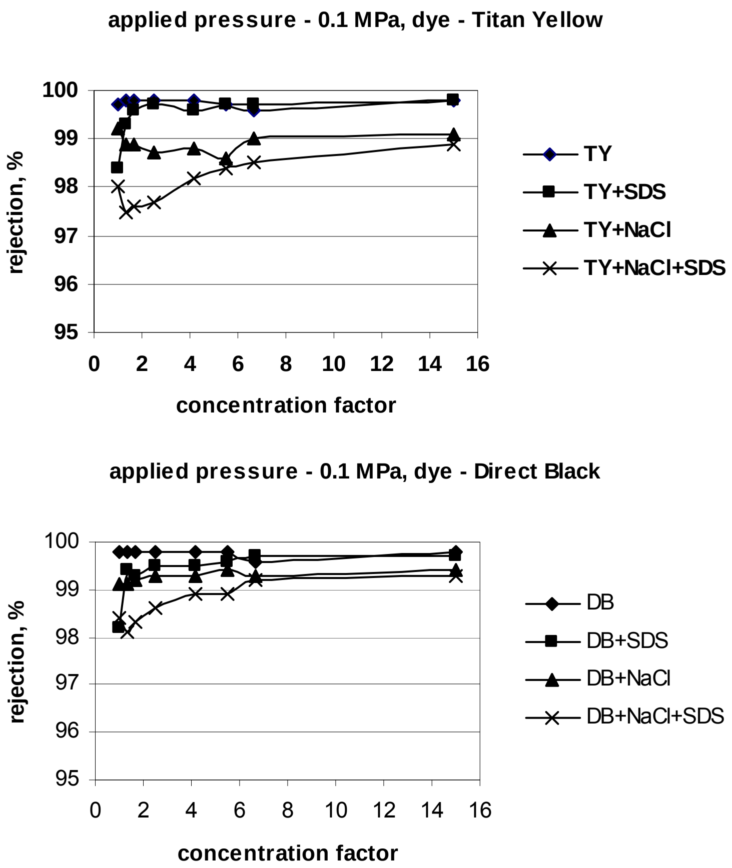


Fig. 6. The effect of the concentration factor on dye rejection
of Pellicon PLAC1 module for various dye solutions

Based on the dye rejection coefficients obtained in the concentration process it is also difficult to draw general conclusions. However some relationships are worth mentioning. As shown by the curves in figure 6, the smaller the molecular weight of the dye, the more pronounced the decrease in rejection coefficient with an increase in the concentration factor. This statement is valid only for dye solution with no additives. While mixtures of dye and salt (without or with SDS) were concentrated, the dye separation remained almost constant during concentration process. It was surprising to note nearly a two fold increase in dye rejection coefficient values when the mixtures of low-molecular-weight dyes and surfactant were subjected to the concentration procedure.

Summing up, the presence of various chemical compounds in dye solutions is of great importance when ultrafiltration efficiency is taken into account. Probable membrane hydrophilization resulting from the surfactant (SDS) contact with a membrane has an advantageous effect on permeability and dye rejection during the dye solution concentration by ultrafiltration. It can also be expected that in the case of solutions containing high-molecular-weight dyes (whose rejection by UF membranes approaches 98–100%) and surfactant of the same charge, the concentration process can lead to two valuable streams – dye concentrate and permeate rich in surface active agent.

4. CONCLUSIONS

1. The UF Pellicon PLAC1 flat module (1 kDa) yields 60–100% retention of organic dyes, provided that there is no surfactant or mineral salt in the treated solution. Dye separation coefficient depends on the dye molecular weight.

2. Anionic surfactant (SDS) and mineral salt (NaCl) in dye solutions strongly influence the process efficiency. NaCl and SDS doses result in an essential worsening of the rejection coefficient of low-molecular-weight dyes. In the case of organic dyes rejected in 98–100%, salt and SDS additives do not affect the separation efficiency.

3. The membrane permeability is kept almost constant during the concentration process irrespective of the solution composition. While mixtures of dye, salt, and SDS were concentrated, the dye separation remained almost constant during the process.

4. Taking into account poor SDS rejection it can be anticipated that ultrafiltration of solutions containing high-molecular-weight dyes (rejected in almost 100%) can lead to two valuable streams – dye concentrate and permeate rich in surface active agent.

ACKNOWLEDGEMENTS

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REFERENCES

[1] RIBEIRO M.R., BERGAMASCO R., GIMENES M.L., *Membranes synthesis study for colour removal of a textile effluent*, Desalination, 2002, 145, pp. 61–63.

[2] 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.

[3] 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.

[4] TANG C., CHEN V., *Nanofiltration of textile wastewater for water reuse*, Desalination, 2002, 143, pp. 11–20.

[5] 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.

[6] SIMONIC M., PETRINIC I., SOSTAR-TURK S., *Treatment of the laundary wastewater by using the membrane technology*, Textiles, 2004, 47, pp. 167–174.
[7] ARCHER A.C., MENDES A.M., BOAVENTURA R.A.R., *Separation of an anionic surfactant by nanofiltration*, Environmental Science and Technology, 1999, 33, pp. 2758–2764.
[8] 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.
[9] SHU L., WAITE T.D., BLISS P.J., FANE A., JEGATHEESAN V., *Nanofiltration for the possible reuse of water and recovery of sodium chloride salt from textile effluent*, Desalination, 2005, 172, pp. 235–243.
[10] VAN DER BRUGGEN B., DAEMS B., WILMS D., VANDECASTEELE C., *Mechanism of retention and flux decline for the nanofiltration of dye bath from the textile industry*, Separation and Purification Technology, 2001, 22–23, pp. 519–528.
[11] AKBARI A., DESLAUX S., REMIGY J.C., APTEL P., *Treatment of textile dye effluents using a new photografted nanofiltration membrane*, Desalination, 2002, 149, pp. 101–107.
[12] KOYUNCU I., TOPACIK D., WIESNER M.R., *Factors inluencing flux decline during nanofiltration of solutions containing dye and salts*, Water Research, 2004, 38, pp. 432–440.
[13] 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, pp. 141–152.
[14] MAJEWSKA-NOWAK K., *Fouling of hydrophilic ultrafiltration membranes applied to water recovery from dye and surfactant solutions*, Environment Protection Engineering, 2005, 31, pp. 230–241.
[15] MAJEWSKA-NOWAK K., KABSCH-KORBUTOWICZ M., WINNICKI T., *Salt effect on the dye separation by hydrophilic membranes*, Desalination, 1996, 108, pp. 221–229.
[16] MAJEWSKA-NOWAK K., KABSCH-KORBUTOWICZ M., *Application of low-pressure membrane process to dye effluent treatment*, Environment Protection Engineering, 1999, 25, pp. 139–144.

ZATĘŻANIE ROZTWORÓW BARWNIKÓW W OBECNOŚCI SUBSTANCJI POWIERZCHNIOWO CZYNNEJ I SOLI MINERALNYCH

Zbadano efektywność ultrafiltracyjnego zatężania wodnych roztworów barwników organicznych z dodatkiem substancji powierzchniowo czynnej i soli mineralnych. W badaniach wykorzystano ultrafiltracyjny moduł Pellicon z płaskimi membranami wykonanymi z regenerowanej celulozy (1 kDa). Właściwości transportowe i separacyjne modułu określono w stosunku do pięciu anionowych barwników organicznych (oranż metylowy, czerwień indygo, czerń amidowa, żółcień tytanowa, czerń bezpośrednia). Stężenie barwników w roztworach modelowych wynosiło 100 g/m^3. Do roztworów barwników dodawano anionową substancję powierzchniowo czynną (dodecylosiarczan sodu (SDS)) oraz chlorek sodu. Wstępne badania właściwości membran oraz proces zatężania prowadzono przy ciśnieniach od 0,05 do 0,15 MPa. Określono wpływ współczynnika zatężania na wielkość strumienia objętościowego i stopień zatrzymania barwników przez membrany. Stwierdzono, że przepuszczalność membran utrzymywała się praktycznie na stałym poziomie dla wszystkich testowanych roztworów. Współczynnik separacji barwników zależał przede wszystkim od składu roztworu poddawanego procesowi ultrafiltracji. W przypadku roztworu zawierającego barwnik, sól mineralną i SDS stopień zatrzymania barwnika utrzymywał się w zasadzie na stałym poziomie w czasie procesu zatężania.