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Nanofiltration Used for Desalination and Concentration in the Manufacture of Liquid Dyes Production

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1. Introduction

Reactive dye is a class of highly coloured organic substances, primarily used for tinting textiles. The dyes contain a reactive group, either a haloheterocycle or an activated double bond, which, when applied to a fibre in an alkaline dye bath, forms a chemical bond between the molecule of dye and that of the fibre. The reactive dye therefore becomes a part of the fibre and is much less likely to be removed by washing than other dyestuffs that adhere through adsorption. Reactive dyeing, the most important method for the coloration of cellulosic fibres, currently represents about 20-30% of the total market share for dyes, because they are mainly used to dye cotton which accounts for about half of the world's fibre consumption.

Generally, reactive dyes are produced by chemical synthesis. Salt, small molecular weight intermediates and residua compounds are produced in the synthesis process. These salt and residual impurities must be removed before the reactive dyes are dried for sale as powder to meet product quality requirement. Conventionally, the reactive dye is precipitated from an aqueous solution using salt. The slurry is passed through a filter press, and the reactive dye is retained by a filter press. The purity of the final reactive dye product in conventional process is low, having a salt content around 30%. Furthermore, the conventional process is carried out in various batches, which makes the entire process highly labor intensive and causes inconsistency in the production quality.

In dye manufacture, like most other processes, there is a continual search for production methods that will improve product yield and reduce manufacturing costs. Dye desalting and purification, the process by which impurities are removed to improve the quality of the product, is currently one of the biggest applications for nanofiltration (NF) technology. Dye manufacturers are now actively pursuing the desalting of the finished dye prior to spray drying because it not only improves product quality, but makes spray drying more efficient because the granulation of the dye takes place without the production dust. NF is proving to be an ideal method for this salt removal (Yu et al., 2001; He et al., 2007).

Nanofiltration is the most recently developed pressure-driven membrane separation process and has properties that lie between those of ultrafiltration (UF) and reverse osmosis (RO). The nominal molecular weight cut-off (MWCO) of NF membranes is in the range 200-1000 Da. Separation may be due to solution diffusion, sieving effects, Donnan and

dielectric effects. The rejection is low for salts with mono-valent anion and non-ionized organics with a molecular weight below 150 Da, but is high for salts with di- and multi-valent anions and organics with a molecular weight above 300 Da. Thus, NF can be used for the simultaneous removal of sodium chloride (salt) and the concentration of aqueous dye solutions (Mulder, 2000; Oatley et al., 2005).

Diafiltration is the process of washing dissolved species through the membrane, which is to improve the recovery of the material in permeate, or to enhance the purity of the retained stream. Typical applications can be found in the recovery of biochemical products from their fermentation broths. Furthermore, diafiltration can be found in removal of free hydrogel present in external solution to purify of a semi-solid liposome (SSL), purification of polymer nanoparticles, enhancing the protein lactose ratio in whey protein products, separating sugars or dye from NaCl solution (desalting), and many other fields. According to the property of the solute and the selectivity of membrane, diafiltration can be used in the process of MF, UF or NF (Al-Zoubi et al., 2007; Bowen & Mohammad, 1998; Foley, 2006; Kovács et al., 2009a; Wang et al., 2008; Weselowska et al., 2004).

The aim of this study is also devoted to the mathematical modelling of nanofiltration and description of discontinuous diafiltration by periodically adding solvent at constant pressure difference.

The proposed mathematical model connects together the design equations and model of permeation through the membrane. The transport through the membrane depends on the different approaches. Firstly the membrane is regarded to a dense layer and in this case transport is based on solution-diffusion model (Cséfalvay et al., 2009; Das et al., 2008). Second approach is regarded membrane to porous medium. Models with this approach are based mainly on extended Nernst-Planck equation. Through this approach, a system containing any number of n ions can be described using set of (3n + 2) equations. In this approach, it is assumed that the flux of every ion through the membrane is induced by pressure, concentration and electrical potentials. These models describe the transport of ions in terms of an effective pore radius r_p (m), an effective membrane thickness/porosity ratio $\Delta x/A_k$ (m) and an effective membrane charge density X_d (mol/m^{-3}). Such a model requires many experiments for determination of these structural parameters. These models are hard to solve (Bowen & Mohammad, 1998; Hussain et al., 2008; Kovács et al., 2009a; Oatley et al., 2005). The last approach is based on irreversible thermodynamics. These models assume the membrane as "black box" and have been applied in predicting transport through NF membranes for binary systems (Kedem-Katchalsky, Spiegler-Kedem models). Perry and Linder extended the Spiegler and Kedem model to describe the salt rejection in the presence of organic ion. This model describes transport of ion through membrane in terms of salt permeability P_s, reflection coefficient σ (Al-Zoubi et al., 2007; Kovács et al., 2009a; Kovács et al., 2009b; Koyuncu & Topacik, 2002; Schirg & Widmer, 1992). In our work is solution-diffusion model used. The solution-diffusion model can be replaced by more theoretical model in future.

The process of desalination of aqueous dye-salt solutions by polymeric nanofiltration membranes using commercially available modules was studied. The influence of dye and salt concentration on the salt rejection and pressure applied on the flux as well as comparison of individual NF membranes for desalting purposes is presented. Extended Spiegler-Kedem model including Donnan exclusion mechanism and the term of concentration dependence of salt permeability was used for prediction of salt rejection. The great interest is also devoted to the mathematical modelling of nanofiltration and

description of discontinuous diafiltration by periodically adding solvent at constant pressure difference. This study illustrates that nanofiltration is a promising process for dye desalting and concentrating.

2.1 Mathematical modelling

Mathematical model connects together balance equations and solution-diffusion model, which is extended by dependence of salt permeability on the salt concentration in feed and Donnan equilibrium.
The balances for the concentration mode can be written as:
Solvent mass balance:

$$\frac{d\left(V_F \rho_F\right)}{d\tau} = -JA^* \rho_P \tag{1}$$

Mass balances of dye and salt:

$$\frac{d\left(V_F c_{D,F}\right)}{d\tau} = -JA^* c_{D,P} \tag{2}$$

$$\frac{d\left(V_F c_{S,F}\right)}{d\tau} = -JA^* c_{S,P} \tag{3}$$

Eq. (1) is possible to write in the form:

$$\frac{dV_F}{d\tau} = -J_V A^* \tag{4}$$

Mass balances of dye and salt are formally same and we can solve them together. Subscripts *i* represent dye and salt. Eq. (2) (or (3)), may be re-written as:

$$\frac{d\left(V_F c_{i,F}\right)}{d\tau} = -J_V A^* \left(1 - R_i\right) c_{i,F} \tag{5}$$

where R_i is real rejection.
In the concentration mode, the volume and the concentration in feed depends on the time. Expanded differential equation with using the product rule can be written as:

$$V_F \frac{dc_{i,F}}{d\tau} + c_{i,F} \frac{dV_F}{d\tau} = -J_V A^* \left(1 - R_i\right) c_{i,F} \tag{6}$$

Substituting Eq. (4) into Eq. (6) leads to:

$$V_F \frac{dc_{i,F}}{d\tau} = J_V A^* R_i c_{i,F} \tag{7}$$

Dividing Eq. (7) by Eq. (4) leads to:

$$V_F \frac{dc_{i,F}}{dV_F} = -R_i c_{i,F} \tag{8}$$

If we assume constant rejection and permeate flux (for small change of volume in feed tank, or better of yield - permeate volume divided by feed volume, it is achieved) or the average values integrations of Eq.(8) and Eq.(4) with the boundary conditions (V_{F0} to V_F) resulting in Eq.(9) and Eq.(10):

$$c_{i,F} = c_{i,F0}\left(\frac{V_{F0}}{V_F}\right)^{R_i} \tag{9}$$

$$\tau = \frac{V_{R0} - V_R}{J_V A^*} \tag{10}$$

On the base of Eq. (9) and Eq. (10) we can obtain the concentration in feed tank and the time for separation of certain permeate volume in concentration mode, respectively. Next process is diluting. Pure solvent (water) is used as diluant. Salt concentration in feed tank after this operation (c_S') is:

$$c_S' = c_{i,F0}\left(\frac{V_F}{V_{F0}}\right) \tag{11}$$

This concentration (c_S') is now equal to the salt concentration in feed tank ($c_{S,F0}$) for the next concentration mode in the second diafiltration step.
For solving of these equations we need to know dependence of rejection and permeate flux on salt concentration in feed.
The basic equations for rejection can be written as:

$$J_S = B\left(c_F - c_P\right) \tag{12}$$

$$c_P = \frac{J_S}{J_V} \tag{13}$$

This model can be extended by the dependence of salt permeability on salt concentration in the feed (Koyuncu & Topacik, 2002). To avoid some in conveniences with units, here c* is introduced and chosen to be 1 g/l.

$$B = \alpha.\left(\frac{c_{S,F}}{c^*}\right)^{\beta} \tag{14}$$

Assuming equilibrium on the membrane - solution interface we can obtain (approximating activities with concentrations) (Koyuncu & Topacik, 2002):

$$c_{S,W} = c_{S,F}.\left(1 + \frac{\nu_D.c_{D,F}.M_S}{c_{S,F}.\ M_D}\right) \tag{15}$$

In the presence of Donnan exclusion forces, induced by the impermeable organic ions, the salt transport across the membrane proceeds as if the membrane were exposed to a salt solution having concentration $c_{S,W}$ instead $c_{S,F}$. Thus the value of $c_{S,W}$ and not that of $c_{S,F}$ determines the driving force for the salt passage.

Then the expression for salt passage in the presence of retained organic ion can be written as:

$$J_S = \alpha\left(\frac{c_{S,F}}{c^*}\right)^{\beta}\left(c_{S,W} - c_{S,P}\right) \tag{16}$$

and then salt concentration in permeate can be expressed as

$$c_{S,P} = \frac{\alpha\frac{c_{S,F}^{\beta+1}}{c^{*\beta}}\left(1+\frac{\nu_D . c_{D,F} . M_S}{c_{S,F} . M_D}\right)}{J_V + \alpha c_{S,F}^{\beta} c^{*-\beta}} \tag{17}$$

For the permeate flux these equations can be used:

$$J_V = A\left(\Delta P - \Delta\pi_s - \delta\right) \tag{18}$$

Eq. (18) is the osmotic pressure model. This model is used in similar form by many authors (Al-Zoubi et al., 2007; Cséfalvay et al., 2009; Das et al., 2008; Kovács et al., 2009a; Kovács et al., 2009b; Koyuncu & Topacik, 2002; Mulder, 2000). Parameter A (water permeability) can be concentration or viscous depended (Cséfalvay et al., 2009; Kovács et al., 2009a). For our model we assume this parameter as constant. Coefficient δ represents the effect of dye on flux. This means mainly osmotic pressure of dye. If this parameter represents only osmotic pressure of dye, then it is constant too (constant dye concentration).
The osmotic pressure gradient for salt is related to the difference of the concentration Δc by the van´t Hoff law:

$$\Delta\pi_S = \frac{\nu R^* T}{M}\Delta c_S \tag{19}$$

where
c is concentration,
*A** - membrane area,
A - water permeability,
B - salt permeability,
J - flux,
R - rejection,
*R** - universal gas constant,
M - relative molecular mass,
Δ - coefficient for dye solution,
σ - reflection coefficient
ν - valence (for NaCl is ν = 2 and for dye ν = 3).
α - coefficient for salt permeability,
B - coefficient for concentration dependence of salt permeability
subscripts
S - salt
D - dye
V - water

$_F$ - feed
$_P$ - permeate
$_R$ - retentate
$_W$ - membrane interface (wall)
$_0$ - beginning of the concentration mode

2.2 Characterization of membranes

Before diafiltration experiments characterizations of commercial membranes are carried out. For these characterizations pure water and water solutions of salt are used. From experiments with pure water model parameter A (water permeability) can be estimated. This parameter is slope of the curve (straight line) J = f (ΔP) (see Eq. (18) and Δπ = δ =0 because no salt and dye are used). In our model we assume water permeability as constant. However, an increase in concentration can cause significant changes in viscosity and a consequent modification of the water permeability. According to resistance model ($A = 1/(\mu R_M)$) the dependence of water permeability on viscosity can be expressed as:

$$A_\mu = \frac{A}{\mu_{REL}} \tag{20}$$

where A is the water permeability respect to pure water and μ_{REL} is the relative viscosity of feed solution to pure water (Kovács et al., 2009a).
In case of diafiltration fouling or gel layer effects can occur and then parameter A is depended on dye/salt concentration ratio (in resistance model is added next resistance $A=1/\mu_{REL}$ (R_M+R_F), where R_M and R_F are membrane and fouling resistance (Cséfalvay et al., 2009).
Similar experiments are made with salt solutions. Four salt concentrations (1, 5, 10 and 35 g/l) are used. From these experiments can be obtained parameter B (salt permeability) and then α and β (plotting B versus c_F). Values obtained from these experiments are not used direct but are used as first approximation values for best fit parameters (see Table 3). From results (salt rejection and flux) the suitable membranes for desalination were chosen, Desal 5DK, NF 70, NF 270 and TR 60. Membranes NF 90 and Esna 1 had higher rejection (see Fig. 3). For desalination membrane with small rejection of salt are suitable.

2.3 Comparison of membranes

For comparison of membranes, three factors were used.
The first factor is separation factor of diafiltration, ***S***:

$$S = \frac{\frac{c_D}{c_D^0}}{\frac{c_S}{c_S^0}} = \frac{c_D c_S^0}{c_D^0 c_S} \tag{21}$$

where c^0_D, c^0_S are concentrations of dye and salt at the beginning of experiment, c_D, c_S are concentrations of dye and salt in the end of experiment.
The separation factor, ***S***, represents how well the dye will be desalinated. With higher separation factor the dye desalination is better. But it is also clear that with bigger separation factor the loss of the dye will be bigger because real membranes have not 100% rejection of dye.

The dye loss factor, ***Z***, can be defined as the rates of amount of the dye in permeate to amount of the dye at the beginning of experiment:

$$Z = \frac{V.\left(c_D^0 - c_D\right)}{V.c_D^0} = 1 - \frac{c_D}{c_D^0} \tag{22}$$

The third parameter is time of diafiltration needed to reach certain separation factor, ***S***. The total time of diafiltration with n steps, τ, can be expressed (constant permeate flux in each concentration mode) as:

$$\tau_{total} = \sum_{i=1}^{n} \frac{\Delta V}{Q} = \sum_{i=1}^{n} \frac{V_{F0} - V_F}{A.J} \tag{23}$$

where *Q* is flow of permeate.

3. Methods

3.1 Membranes

Six NF membranes were chosen for this study. Properties of membranes used are given in Table 1.

Indication	Type	Producer	MWCO [Da]	Material	Module
Desal 5DK	Desal 5DK	GEW & PT	200	polyamide	spiral-wound
Esna 1	Esna 1	Hydranautics	100-300	polyamide	spiral-wound
NF 90	NF 90	Dow	90	polyamide	spiral-wound
NF 270	NF 270	Dow	270	polyamide	spiral-wound
NF 70	CSM NE 2540-70	Saehan	250	polyamide	spiral-wound
TR 60	TR 60 - 2540	Toray	400	polyamide	spiral-wound

Table 1. Properties of the membranes used

3.2 Materials

Dye was obtained from VÚOS a.s. Pardubice, Czech Republic. The commercial name is Reactive Orange 35, and a molecular weight is 748.2 Da in free acid form (three acidic groups) or 817.2 Da as the sodium salt. Fig. 1 shows structural formula of the free acid form.

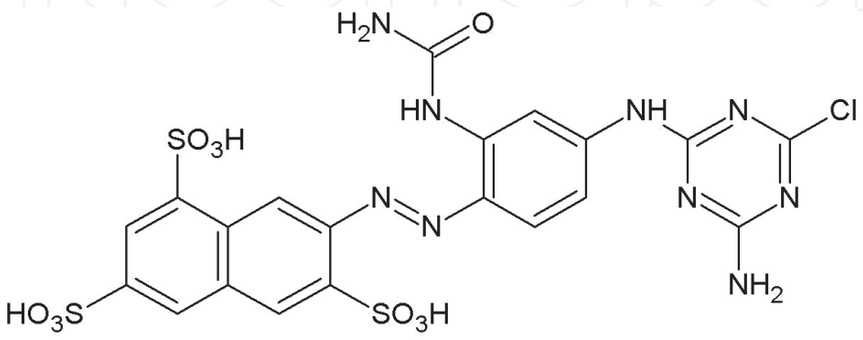


Fig. 1. Structural formula of dye (free acid)

NaCl and $MgSO_4$ used for all experiments were analytical grade. The demineralised water with the conductivity between 4-15 μS/cm was used in this study.

3.3 Experimental system

Experiments were carried out on system depicted schematically on Fig. 2. Feed (F) was pumped by pump (3) (Wanner Engineering, Inc., type Hydracell G13) from feed vessel (2) to membrane module (1). Pressure was set by valve (4) placed behind membrane module. Permeate (P) and retentate (R) were brought back to feed vessel. Pressure was measured by manometer (5). Temperature was detected by thermometer (6). Stable temperature was maintained by cooling system (7).

3.4 Analytical methods

Dye concentrations were analysed using a spectrophotometer (SPECOL 11). NaCl and $MgSO_4$ concentrations were calculated from conductivity measurements using a conductivity meter (Cond 340i). Permeate and retentate salt concentrations during diafiltration experiments were analysed using potentiometric titration.

3.5 Separation procedure

The system was operated in the full recirculation mode while both retentate and permeate were continuously recirculated to the feed tank except sampling and concentration mode of diafiltration. By changing applied pressure (from 5 to 30 bar) and concentration of salt (1, 5, 10 and 35 g/l) in characterization of membranes both the retentate and permeate were returned back to the feed tank for 0.5 h or 10 min, respectively to reach a steady state before sampling. Before first concentration mode in diafiltraton experiments and after each diluting mode the total recirculation was used 1h and minimally 5 min, respectively. The permeate flux was measured by weighing of certain permeate volume and using a stopwatch.

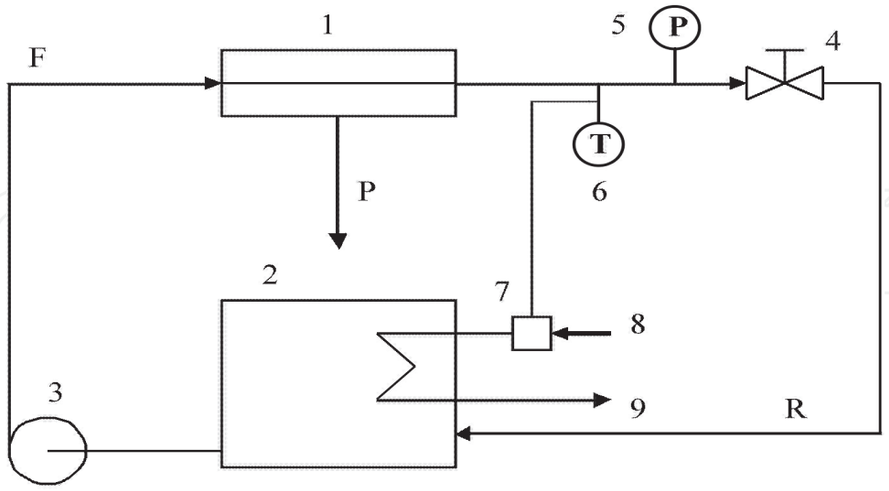


Fig. 2. Schematic diagram of the experimental set-up used: 1 membrane module, 2 feed vessel, 3 high pressure pump, 4 back pressure valve, 5 manometer, 6 temperature controller, 7 cooling system, 8 cooling water input, 9 cooling water output, F feed, P permeate, R retentate (concentrate)

4. Results and discussion

4.1 Pure water flux

Water permeability is one of the basic characteristic of NF membranes. The pure water permeability of the six membranes was determined by measuring the de-ionized water flux at different operating pressures. According to Darcy´s law, the permeate flux is directly proportional to the pressure difference across the membrane. The slope of this line corresponds to the water permeability (A).

Membrane	A [l/m².h.bar]
Desal 5DK	3.365
Esna 1	4.824
NF 90	5.845
NF 270	6.801
NF 70	2.650
TR 60	3.952

Table 2. Water permeability of membranes used

4.2 Rejection of NaCl

Basic membrane characteristics are the dependence of the permeate flux and the salt rejection on other operation parameters, i.e. the applied pressure difference and the salt concentration in feed.

The permeate flux increases with increasing pressure and decreases as the feed concentration of salt increases. For the lowest concentration of salt (1 g/l), the values of permeate flux were similar to the values of clean water. The lower values of permeate flux were obtained with the increasing salt concentrations in feed (increasing osmotic pressure). For membrane NF 90 fluxes were not measured at the highest salt concentration for pressure smaller than 25 bar, because the osmotic pressure was too high. Opposite problem was with membrane NF 270 at the smallest salt concentration in feed. The permeate flux was too high and pump was not able to deliver necessary volumetric flow of retentate (600 l/h) for constant conditions at all experiments.

The observed rejection increases as the pressure difference increases, and decreases with the increasing salt concentration in feed for all tested membranes. However, the minimal values were obtained during experiments with membrane NF 270. Low values of the salt rejection and higher values of the permeate flux are suitable for desalting. Fig. 3 shows the comparison of tested membranes for the lowest (1 g/l) and the highest salt concentrations in feed (35 g/l), respectively.

4.3 Diafiltration

The concentration of macrosolutes by batch NF is frequently accompanied by a diafiltration step to remove microsolutes such as salts. Batch diafiltration with periodically adding solvent at 20 bars and constant retentate flow 600 l/h was provided. Aqueous dye solutions with dye concentrations 100, 50 and 10 g/l and salt concentration between 20-23 g/l were desalted at 23°C. Volume of the pure solvent added in every dilute mode was 4l (the same volume of permeate was remove before in concentration mode). Total feed volume in tank was 52l. For every membrane and every concentration of the dye in feed fifty diafiltration steps were made. One point in Figs. 4-7 is one diafiltration step before concentration mode.

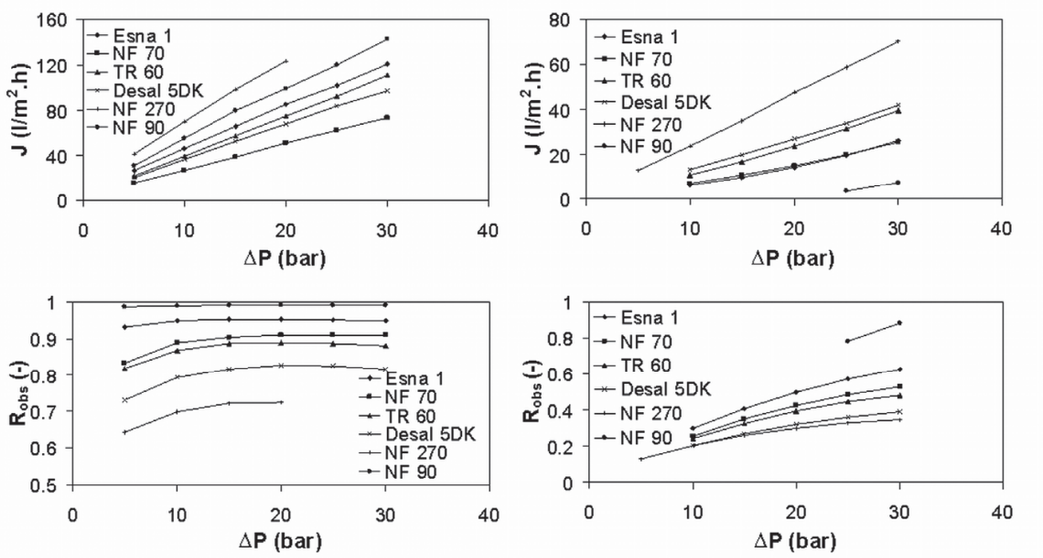


Fig. 3. Permeate flux and rejection as a function of pressure for the lowest salt concentration (1 g/l) - left figures and the highest salt concentration (35 g/l) - right figures

Four membranes only - Desal 5DK, NF 70, NF 270 and TR 60- were used for diafiltration experiments. Diafiltration with membrane NF 270 was provided only with dye concentrations 100 and 50 g/l and with membrane TR 60 only at the highest dye concentration, which is the best for desalination. For the reason of low values of permeate flux, membrane NF 90 and Esna 1 were not used for those experiments.

Dependences of rejection on salt concentration in feed are given in Fig. 4 for Desal 5DK, NF 70, NF 270 and TR 60, respectively. Membranes are compared at dye concentration 100 g/l. The lowest values of rejection (max. 0.29) were obtained for membrane Desal 5DK. The membrane NF 70 had the highest values.

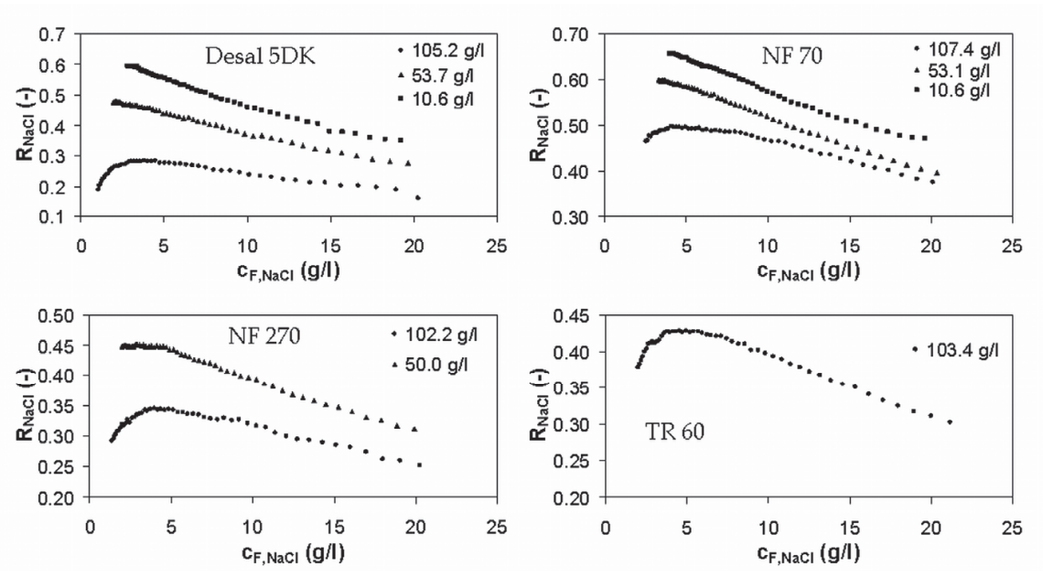


Fig. 4. Salt rejection as a function of salt concentration in feed

Dependences of flux on salt concentrations are shown in Fig. 5. The highest values of flux (70.3 l/m².h) were obtained in experiments with membrane NF 270. The permeate flux decreased while salt concentration increased. This is due to the effect of osmotic pressure along with the concentration polarization. Due to the concentration polarization phenomenon, the osmotic pressure of the aqueous solution adjacent to the membrane active layer is higher than the corresponding value of the feed solution. As a result, the osmotic pressure would increase dramatically while the salt concentration increased.
In Fig. 6 dependences of salt concentrations on time of diafiltration are shown.

Membrane	A [l/m².h.bar]	α [l/m².h]	β [-]	δ [bar]
Desal 5DK	3.365	5.758	0.620	7.503
NF 70	2.650	4.839	0.381	4.664
NF 270	6.801	10.350	0.529	8.561
TR 60	3.952	6.693	0.474	5.888

Table 3. Model parameters.

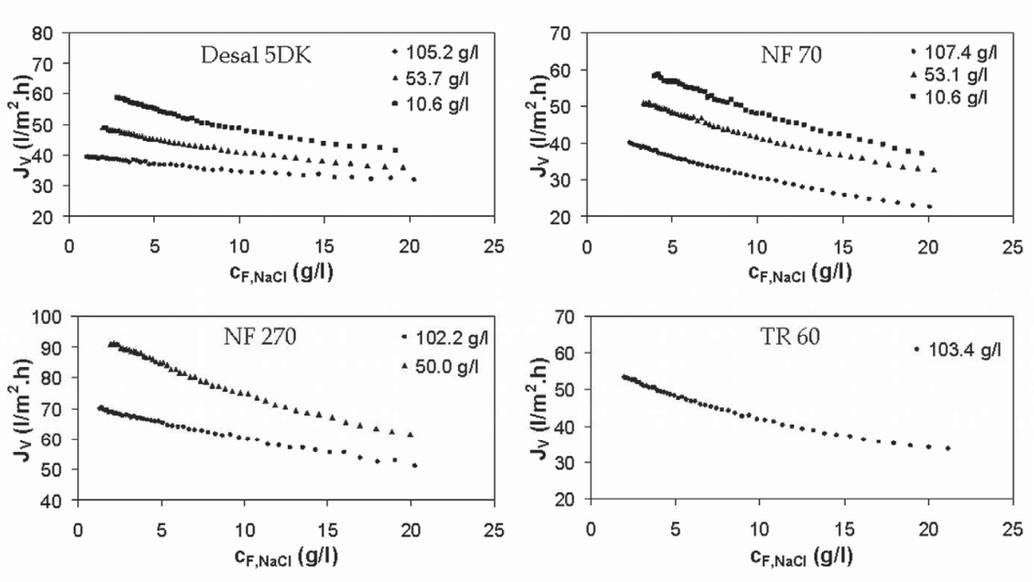


Fig. 5. Permeate flux as a function of salt concentration in feed

The comparisons of experimental and model data for the highest dye concentration (100 g/l) are shown in Fig. 7. Salt concentrations are calculated using Eq. (9) and Eq. (11). Rejection needed for these equations is calculated on basis of Eq. (17). Best fit parameters for proposed model are given in Table 3.
From Table 3 can be shown that δ is not only osmotic pressure (if we assume water permeability as constant), because the values of δ are different. From these results we can assume, the highest effect of dye on flux is for membrane NF 270. This membrane is the most fouled from these membranes. It is appropriate assumed the change in water permeability (A) in case of desalination of dyes.

In our experiments, the decrease of permeate flux was mainly caused by the effect of concentration polarization and the increase of the viscosity of dye solution. The dye formed a boundary layer over the membrane surface (concentration polarization) and consequently, increased the resistance against the water flux through the membrane. At the same time, the viscosity of solution increased with higher concentration.

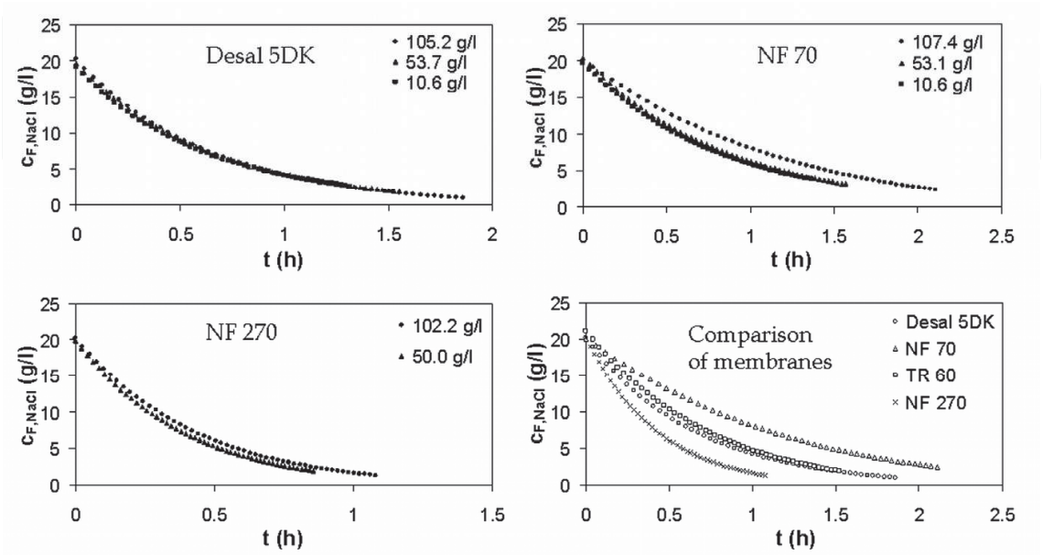


Fig. 6. Salt concentration as a function of diafiltration time for membranes Desal 5DK, NF 70, NF 270 and comparison of tested membranes at dye concentration 100 g/l

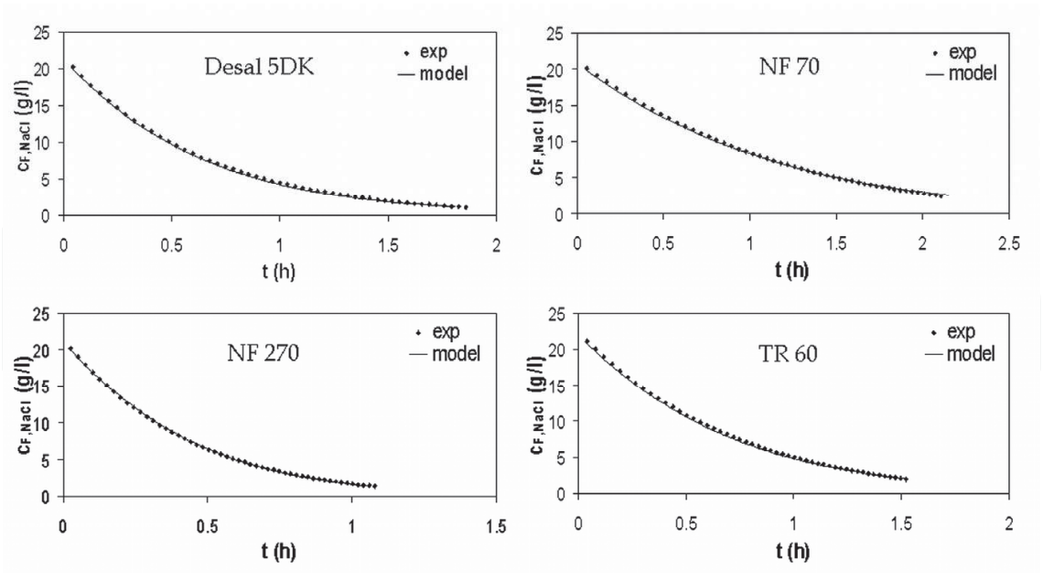


Fig. 7. Comparison of experimental and model data for the highest dye concentration

From Fig. 7 can be shown that the experimental results in permeate fit the model very well. Due to considerably low salt concentrations in permeate, concentration polarization was minimized. The diafiltration process benefits to obtain pure salt product and this can be

predicted by a mathematic model on the basis of description of discontinuous diafiltration by periodically adding solvent at constant pressure difference.

DESAL 5DK				
$c_{F,NaCl,Z}$	(g/l)	22.00	19.62	19.21
$c_{F,NaCl,K}$	(g/l)	0.97	1.88	2.70
$c_{F,dye,Z}$	(g/l)	105.17	53.75	10.61
$c_{F,\ dye,K}$	(g/l)	105.15	53.74	10.60
τ_{total}	(hod)	1.86	1.55	1.32
S	(-)	22.71	10.44	7.10
Z	(%)	0.02	0.01	0.07
NF 70				
$c_{F,NaCl,Z}$	(g/l)	20.08	20.33	19.64
$c_{F,NaCl,K}$	(g/l)	2.40	3.21	3.86
$c_{F,\ dye,Z}$	(g/l)	107.42	53.05	10.56
$c_{F,\ dye,K}$	(g/l)	107.38	53.04	10.56
τ_{total}	(hod)	2.11	1.57	1.37
S	(-)	8.37	6.34	5.09
Z	(%)	0.03	0.03	0.05
TR 60				
$c_{F,NaCl,Z}$	(g/l)	21.14	20.56	19.72
$c_{F,NaCl,K}$	(g/l)	1.88	2.22	3.16
$c_{F,\ dye,Z}$	(g/l)	103.41	53.65	10.71
$c_{F,\ dye,K}$	(g/l)	102.74	53.16	10.52
τ_{total}	(hod)	1.52	1.25	0.98
S	(-)	11.17	8.98	6.25
Z	(%)	0.65	0.48	0.18
NF 270				
$c_{F,NaCl,Z}$	(g/l)	22.00	19.92	20.64
$c_{F,NaCl,K}$	(g/l)	1.28	1.90	2.68
$c_{F,\ dye,Z}$	(g/l)	102.15	49.98	10.52
$c_{F,\ dye,K}$	(g/l)	102.12	49.97	10.53
τ_{total}	(hod)	1.08	0.86	0.67
S	(-)	17.19	10.50	6.89
Z	(%)	0.03	0.04	0.04

Table 4. Total time of diafiltration, τ_{total}, the separation factor, **S**, and the loss of dye, **Z**. (subscript $_{Z,\ K}$ are start and end of diafiltration, respectively)

From Table 4 is clearly shown, the total time of diafiltration τ_{total} decrease with decreasing dye concentration. The shortest time had membrane NF 270. Time for the highest dye concentration is not two times higher than with medium dye concentration for all tested membranes (the time/amount of dye desalted ratio is the smaller for higher concentration of dye). Separation factor decreases with decreasing concentration of dye and it is the second reason why the highest dye concentration was used as the best mode for desalination. The best separation factor had membrane Desal 5DK (very similar values, except the highest dye concentration, had membrane NF 270). The loss of dye is almost same for membrane Desal 5DK, NF 70 and NF 270 at all concentrations of dye. Only for membrane TR 60 are obtained higher loss of dye.

5. Conclusion

The separation performance of dye, salt and dye solution with six different nanofiltration membranes were investigated, followed by the study of the optimum of diafiltration and concentration process of dye solution.

Asymmetric and negatively charged polyamide thin-film composite membranes of near similar molecular weight cut-off were characterized for key physical and surface properties, and employed to perform the laboratory-scale experiments to investigate the impacts of membranes properties on reactive dye removal from dye/salt mixtures through NF process. It was found that properties of the NF membrane play an important role in dye removal rate, stable permeate flux and their change behaviour with operational conditions.

The electrostatic repulsive interaction between dye and membrane surface promotes the dye removal and decreases concentration polarization and dye adsorption on the membrane surface. But, the action will be weakened as the dye concentration or salt concentration increased.

It was seen that salt concentration decreases the dye retention of the membrane. The domination of the steric (size exclusion) effect over the Donnan (charge) effect is the main reason for this. At very high salt concentration, the surface charge of the membrane is neutralized, whereby the separation mechanism depends only on the molecular size of the dye. However, as there is a loss of membrane selectivity due to neutralization of charge the separation, there is a diffusion of dye in to the permeate side of the membrane due to accumulation of the dye layer over the surface.

From the results presented above it is clear that the best concentration of the dye in feed for desalination of reactive dye by batch diafiltration is 100 g/l. In this case the salt rejection reaches minimal value due to Donnan potential which strengthens the flow of salt through the membrane.

The best membrane for desalination is NF 270 which has smaller dye loss factor and the shortest time of diafiltration. Very suitable membrane is also Desal 5DK, which has the best separation factor and dye loss factor, but this membrane has longer time of diafiltration (see Table 4). For desalination qualitative description it is convenient to use the proposed model.

Reactive dye desalination and purification processes generate a large volume of effluent but with low quantities of pollutants. The process is one of the high water-consumption processes in the dye production industry that results in high wastage of water which becomes discharge effluent. Membrane processes can be applied to treat the wastewater and recycle it back into the manufacturing process. The cleaner process can not only improve the

rejection efficiencies and flux recovery, but can also recycle permeate from the desalting and purification process.

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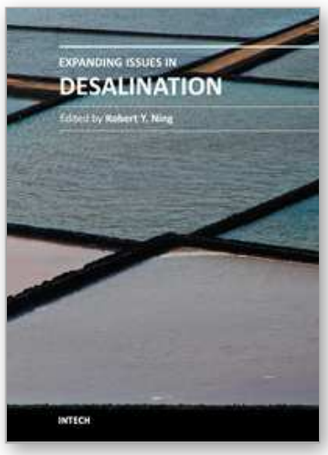
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Expanding Issues in Desalination

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For this book, the term â€œdesalinationâ€ is used in the broadest sense of the removal of dissolved, suspended, visible and invisible impurities in seawater, brackish water and wastewater, to make them drinkable, or pure enough for industrial applications like in the processes for the production of steam, power, pharmaceuticals and microelectronics, or simply for discharge back into the environment. This book is a companion volume to â€œDesalination, Trends and Technologiesâ€, INTECH, 2011, expanding on the extension of seawater desalination to brackish and wastewater desalination applications, and associated technical issues. For students and workers in the field of desalination, this book provides a summary of key concepts and keywords with which detailed information may be gathered through internet search engines. Papers and reviews collected in this volume covers the spectrum of topics on the desalination of water, too broad to delve into in depth. The literature citations in these papers serve to fill in gaps in the coverage of this book. Contributions to the knowledge-base of desalination is expected to continue to grow exponentially in the coming years.

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