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DESALINATION OF REACTIVE YELLOW 85
BY NANOFILTRATION

Three types (Desal 5 DK, Desal 5 DL, PES 10) of nanofiltration membranes were tested to evaluate optimal operating conditions for flux values and salt rejection in the separation of reactive dye/salt mixtures. Effects of pressure and feed composition on the separation were investigated. Experiments showed that feed composition had a significant effect on flux values. The Donnan effect was greatly responsible for salt rejection. Of the membranes tested one membrane was chosen and batch diafiltration at constant pressure and constant volume was performed through a chosen membrane. The main purpose of diafiltration experiments was to measure the dependence of the amount of the salt removed and the concentration of the salt in feed on time. This experiment was carried out in a dynamic cell.

Keywords: *nanofiltration, diafiltration, organic dye*

1. INTRODUCTION

Nanofiltration (NF) is a membrane process that can be considered to be an intermediate one between ultrafiltration (UF) and reverse osmosis (RO). NF membranes are able to reject small organic molecules of molecular weight as low as 200 Daltons. Rejection of such small molecules is possible due to combination of steric and electric (Donnan) effects. In the case of steric effect, a diameter of rejected molecules is bigger than a diameter of a membrane pore. This effect has influence on the separation of particles without charge. The Donnan effect is greatly responsible for the separation of ions. NF membranes are negatively charged, hence their surfaces repel anions. Because of the principle of electroneutrality they also repel cations in the separation of single salt solution. Due to this charged molecules whose diameters are smaller than diameters of pores in the mem-

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brane are rejected. NF membranes are used, for example, in desalination of organic dyes, in reduction of the intensity of wastewater colour, etc.

2. MATERIALS AND METHODS

2.1. MATERIALS

In the experiments, reactive yellow 85 (RY 85) was used. This dye supplied by VUOS (Pardubice, Czech Republic) is the trivalent sodium salt whose molecular weight reaches 975.67 kg/kmol. Its chemical structure is shown in figure 1. In order to characterize the membranes (compare table 1), distilled water prepared in the process of reverse osmosis was used. Sodium chloride was of p.a. purity.
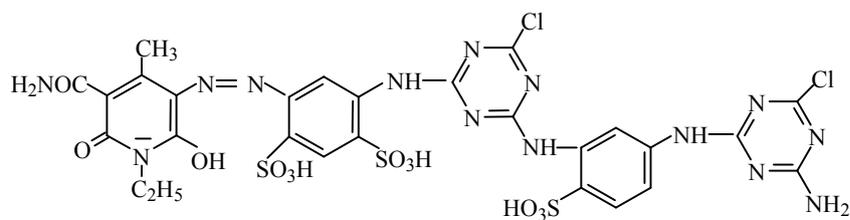

Fig. 1. Chemical structure of free acid of reactive yellow 85 (RY 85)

Table 1

NF membranes

Membrane	Producer	Area (m^2)	Material	Module
Desal 5 DK	GE Water Technologies	6.36×10^{-3}	polyamide	disk
Desal 5 DL	GE Water Technologies	6.36×10^{-3}	polyamide	disk
PES 10	Hoechst	6.36×10^{-3}	polyethersulphone	disk

2.2. EXPERIMENTAL SYSTEM

Experiments were carried out in the system depicted schematically in figure 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 recirculated to feed vessel. Pressure and temperature were measured by manometer (5) and thermometer (6), respectively. Constant temperature was maintained by cooling system (7).
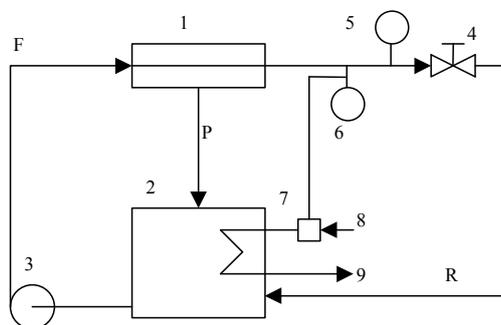
Fig. 2. Schematic diagram of experimental system:
1 – membrane module, 2 – feed vessel, 3 – high-pressure pump, 4 – back-pressure valve,
5 – manometer, 6 – temperature controller, 7 – cooling system, 8 – cooling water input,
9 – cooling water output, F – feed, P – permeate, R – concentrate flow

The experiments were carried out with different NaCl and reactive dye concentrations. Five series of experiments were conducted with dye RY 85 and NaCl for each membrane. The dye concentrations of 0 kg/m³, 25 kg/m³, 35 kg/m³, 55 kg/m³ and 110 kg/m³ and five NaCl concentrations in the range from 2 to 65 kg/m³ were tested. Pressure from 10 to 30 bars was applied and the flow velocity was set at 0.37 m/s.

2.3. ANALYTICAL METHODS

The concentration of dye RY 85 in the feed and permeate samples was analysed with a SPECOL 11 spectrophotometer at a wavelength of 425 nm. The concentration of sodium chloride in feed and retentate was determined by their titration with silver nitrate using the Titroline Alpha potentiometric titrator. The concentration of sodium chloride in permeate was determined by measuring the conductivity of the solution. Schott's conductometer was used to measure temperature and conductivity of permeate, retentate and feed.

3. THEORETICAL BACKGROUND

Diafiltration is a process, where the retentate is diluted with solvent (water) so that the low-molecular weight solutes are washed out. Diafiltration can be carried out continuously or discontinuously. Discontinuous (batch) diafiltration is schematically shown in figure 3. Mathematically this process can be described by the following equations:

$$\frac{d(V_R \cdot \rho_R)}{d\tau} = -J \cdot A \cdot \rho_P + Q \cdot \rho_W ,$$

(1)

$$\frac{d(V_R \cdot c_{DR})}{d\tau} = -J \cdot A \cdot c_{DP}, \tag{2}$$

$$\frac{d(V_R \cdot c_{SR})}{d\tau} = -J \cdot A \cdot c_{SP}. \tag{3}$$

Equation (1) is an overall mass balance and equations (2) and (3) are the mass balances of dye and salt, respectively, V is the volume, ρ is the density, τ is the time, J is the permeate flux, A is the membrane area, c is the concentration, Q is the pure solvent flow, and the subscripts R, P, D, S and W stand for retentate, permeate, dye, salt and water, respectively.
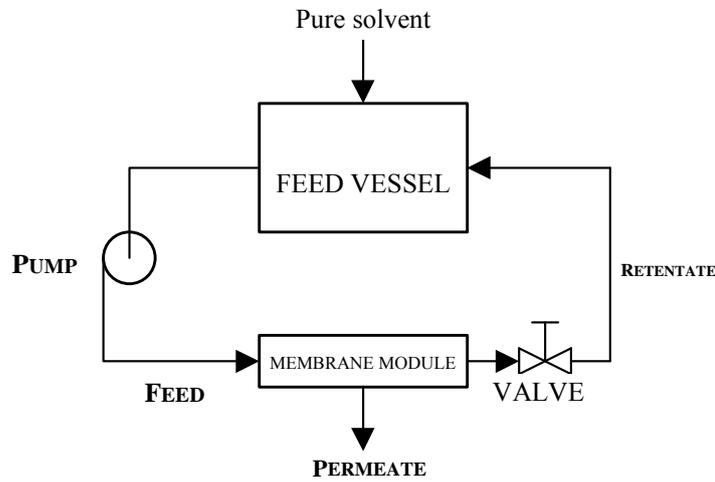

Fig. 3. Batch diafiltration experiment

Mathematical model of diafiltration is based on these first-order differential equations. Time (τ) is the independent variable. Volume of retentate (V_R), concentrations of dye (c_{DR}) and salt (c_{DR}) in retentate are dependent variables. Pure solvent flow (Q) is a function of time and is controlled variable. It is quite difficult to solve model equations and this can be done by numerical methods only.

To simplify this model, the following conditions should be accepted:

1. Dye rejection is 100%.
2. There is no rejection of solution and salt.
3. Dye and salt have no influence on the volume of solution.
4. Flux can be expressed by:

$$J = k \cdot \ln\left(\frac{c_{DA} - c_{DP}}{c_{DR} - c_{DP}}\right), \tag{4}$$

where c_{DA} is the concentration of dye on the membrane surface and k is the mass transfer coefficient. According to the second and the third conditions mentioned above, the following equation for permeate concentration of salt can be deduced:

$$c_{SP} = c_{SR} \frac{\rho_D}{\rho_D - c_{DR}}, \tag{5}$$

where ρ_D is the density of pure dye. Salt rejection can be expressed as follows:

$$R_S = 1 - \frac{c_{SP}}{c_{SR}} = -\frac{c_{DR}}{\rho_D - c_{DR}}. \tag{6}$$

Batch diafiltration with the solvent added periodically is carried out in two steps: (i) nanofiltration and (ii) addition of pure solvent. In the phase of nanofiltration, no pure solvent is added ($Q = 0$). Then mass balance can be replaced with the volume balance. After integration the concentration in the retentate is equal to:

$$c_{DR} = \frac{c_{DR0} \cdot V_{R0}}{V_R}, \tag{7}$$

where c_{DR0} is the concentration of dye in retentate at the beginning of nanofiltration and V_{R0} is the volume of retentate at the beginning of nanofiltration. In the process of nanofiltration, the concentration of the salt in permeate is constant ($c_{SP} = c_{SP0}$). Salt concentration in permeate can be expressed by:

$$c_{SR} = c_{SR0} \frac{\rho_D - c_{DR}}{\rho_D - c_{DR0}}. \tag{8}$$

The retentate volume and the salt concentration in retentate at the end of the nanofiltration are given by:

$$V_{R1} = \frac{c_{DR0} \cdot V_{R0}}{c_{DR1}}, \tag{9}$$

$$c_{SR1} = c_{SR0} \frac{\rho_D - c_{DR1}}{\rho_D - c_{DR0}}. \tag{10}$$

In the phase of addition of pure solvent, the concentrations of dye and salt in retentate can be defined by:

$$c_{DR2} = \frac{c_{DR1} \cdot V_{R1}}{V_{R2}}, \tag{11}$$

$$c_{SR2} = \frac{c_{SR1} \cdot V_{R1}}{V_{R2}}. \tag{12}$$

This retentate can be used as a feed for another step. A time of nanofiltration can be calculated on the basis of equations (3), (4) and (5) and the simplified conditions are as follows:

$$\tau_1 = \frac{c_{DR0} \cdot V_{R0}}{k \cdot A \cdot c_{DA}} \int\limits_{z_0}^{z_1} \frac{dz}{\ln(z)}, \quad z = \frac{c_{DA}}{c_{DR}}, \tag{13}$$

where the superscripts 0, 1 and 2 mean: before the first addition of pure solvent, after the first addition of pure solvent and after the second addition of pure solvent, respectively, the superscript A means on the membrane surface and z stands for the rate of concentration of dye on the membrane surface and in the retentate and has no physical meaning. From this model the time of one step of diafiltration and permeate concentration of salt and dye can be calculated.

4. RESULTS

4.1. EXPERIMENTS WITH DISTILLED WATER

Table 2 gives the values of distilled water flux for three types of membranes. In the case of membranes Desal 5 DK and Desal 5 DL, the fluxes and specific fluxes were almost the same. On the other hand the permeability of membrane PES 10 was twice as great as that of other membranes.

T a b l e 2

The values of distilled water flux for miscellaneous membranes

Flux [$dm^3 \cdot m^{-2} \cdot h^{-1}$]	Pressure [bar]										Specific flux [$dm^3 \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$]
	10	12	14	16	18	20	22	24	26	28	
Desal 5 DK	54.9	69.0	75.6	87.3	97.6	106.3	115.4	122.2	131.1	141.9	5.22
Desal 5 DL	58.4	70.4	81.2	89.3	101.5	109.4	120.0	129.4	137.5	147.2	5.44
PES 10	101.6	125.3	140.5	157.3	171.0	192.3	204.7	220.2	238.1	253.5	9.39

4.2. EXPERIMENTS WITH DYE/SALT MIXTURE

Feed concentration plays a significant role in nanofiltration membrane separation. In general, the higher the salt concentration, the higher the osmotic pressure and the lower the permeate flux.

As can be concluded from the values of flux of the dye RY 85 and NaCl mixtures given in figure 4, the permeate flux increased with a decrease in the concentration of NaCl and dye. An increase in osmotic pressure and more efficient adsorption of the dye on the membrane surface can explain the decrease of flux. Adsorption of dye was proved by the presence of dye on the membrane surface after separation.
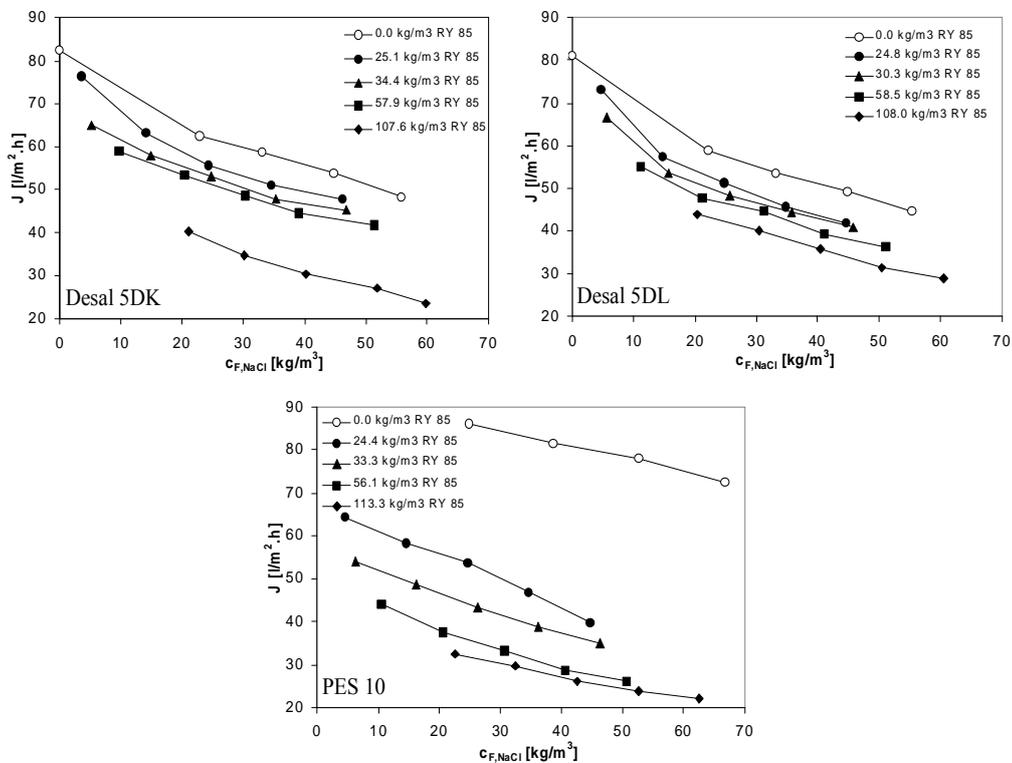

Fig. 4. Dependence of permeate flux (J) on salt concentration
in the feed ($c_{F,NaCl}$) for three membranes

Dye rejection is shown in figure 5 for the dye RY 85 and NaCl mixtures and for

miscellaneous membranes. The dye was easily rejected by all membranes. The best, i.e. almost 100%, dye rejection was found for the membrane Desal 5 DK and the least efficiency of dye rejection was found for the membrane PES 10.

In figure 6, the dependence of salt rejection on the concentration of salt in feed is shown. Rejection of the salt decreased with an increase in the concentration of salt and dye in feed at a positive value of rejection, at a negative value this relation is reversed. A negative salt rejection can be explained by the Donnan effect. The Donnan effect is less significant if the salt concentration increases.
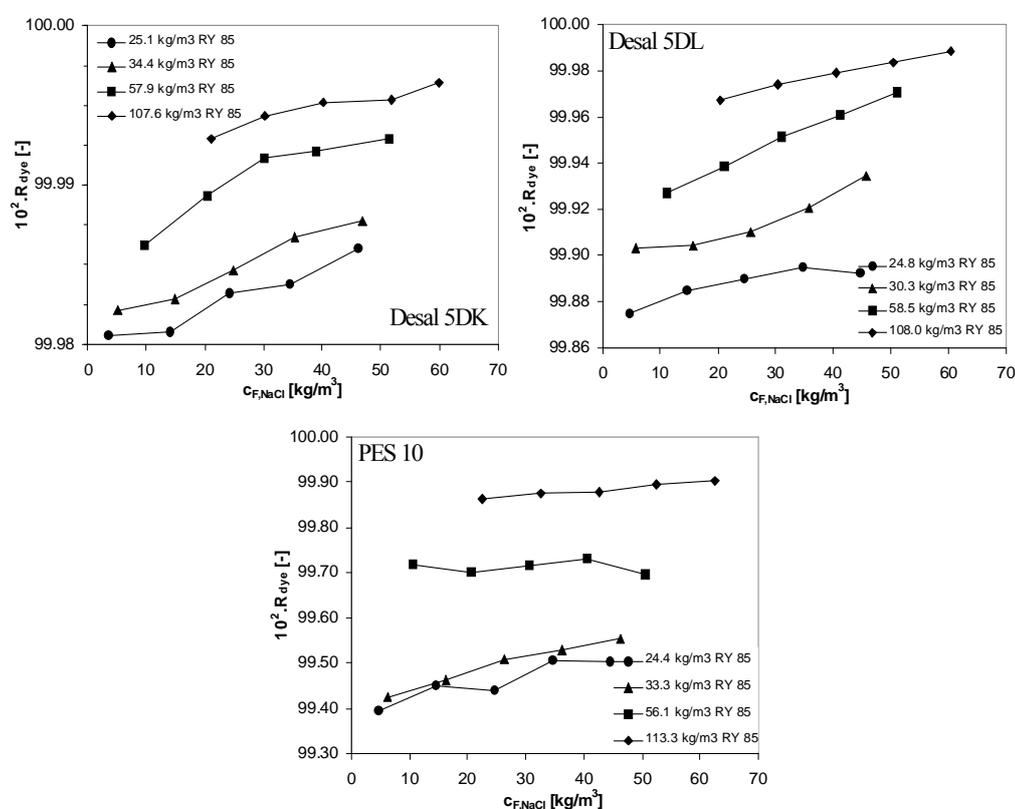

Fig. 5. Dependence of dye rejection (R_{dye}) on salt concentration
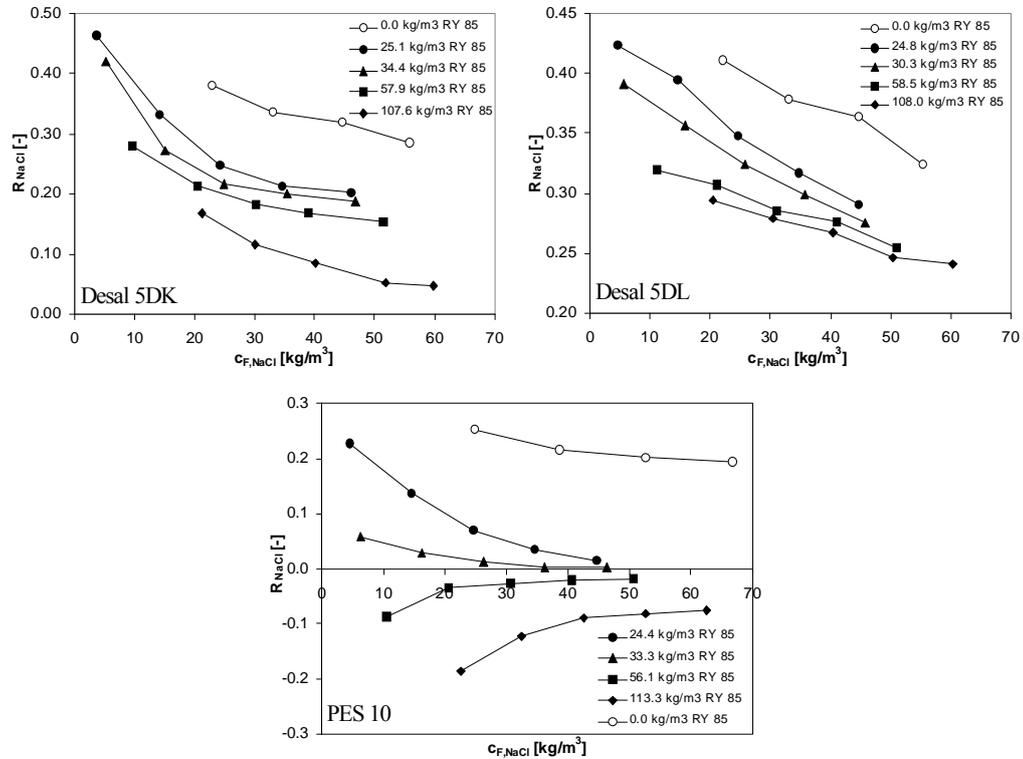in the feed ($c_{F,NaCl}$) for three membranes

Fig. 6. Dependence of salt rejection (R_{NaCl}) on salt concentration
in the feed ($c_{F,NaCl}$) for three membranes

4.3. BATCH DIAFILTRATION

Based on our previous experiments only one membrane (Desal 5 DK) was chosen for batch diafiltration.

Diafiltration was carried out at the salt concentration of 23.0 kg/m^3 and the dye RY 85 concentration of 55.5 kg/m^3. At the beginning of the process, experimental solution was concentrated and then batch diafiltration was performed with the solvent added periodically. The dependence of the salt concentration in the feed on the time of diafiltration is shown in figure 7. The concentration of salt in the feed was ten times lower.

In figure 8, an experimental dependence of the salt removed on the time of diafiltration is shown together with a simplified model of batch diafiltration (compare with equation (13)). In equation (13), the limits of integration were calculated from the concentration of dye at the beginning and end of each diafiltration step. The concentration of dye at the membrane surface was calculated from the model of concentration

polarisation [13]. The value of the diffusivity coefficient of the dye used was not available and for that reason its value for structurally similar dye was found in literature [1] ($D = 3.6 \times 10^{-10} \text{m}^2 \cdot \text{s}^{-1}$).
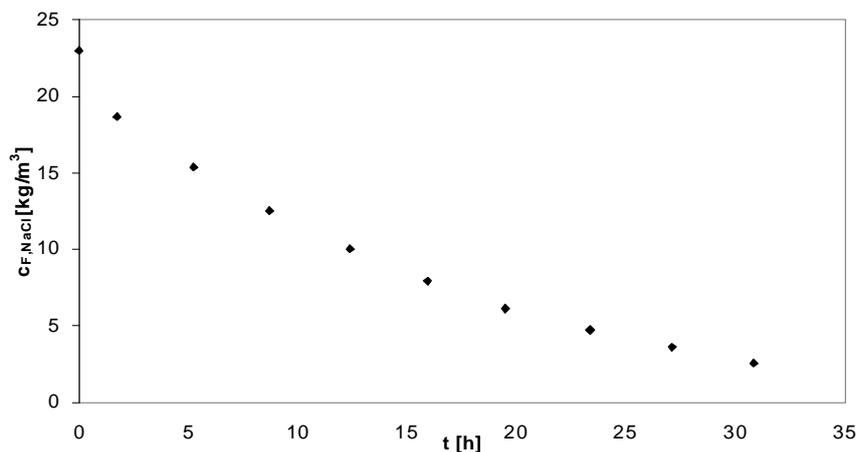

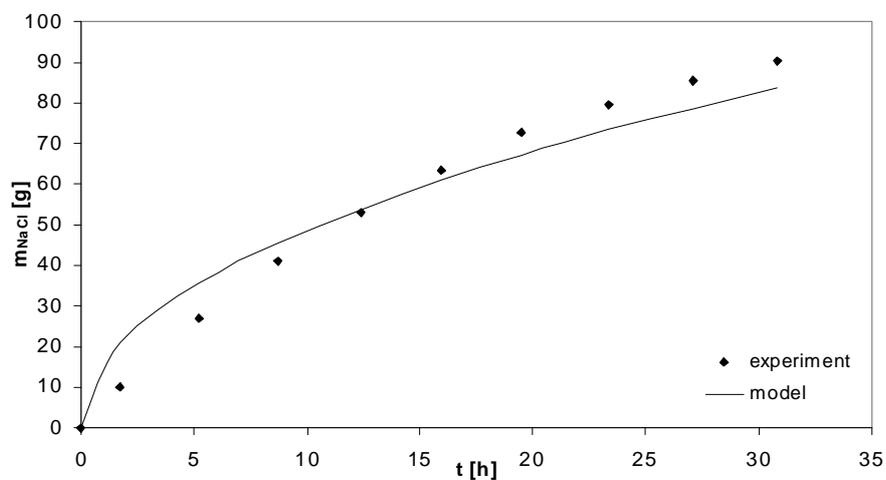Fig. 7. Dependence of salt concentration in the feed ($c_{F,NaCl}$) on time (τ) of diafiltration

Fig. 8. Dependence of the salt removed (m_{NaCl}) on time (τ) of diafiltration

From the comparison of experimental and model values (see figure 8) it can be deduced that:

a) at the time interval of 0–12.5 h experimental values of the amount of the salt removed are smaller than the values calculated from simplified model of nanofiltration,

b) at the time interval above 12.5 h experimental values of the amount of the salt
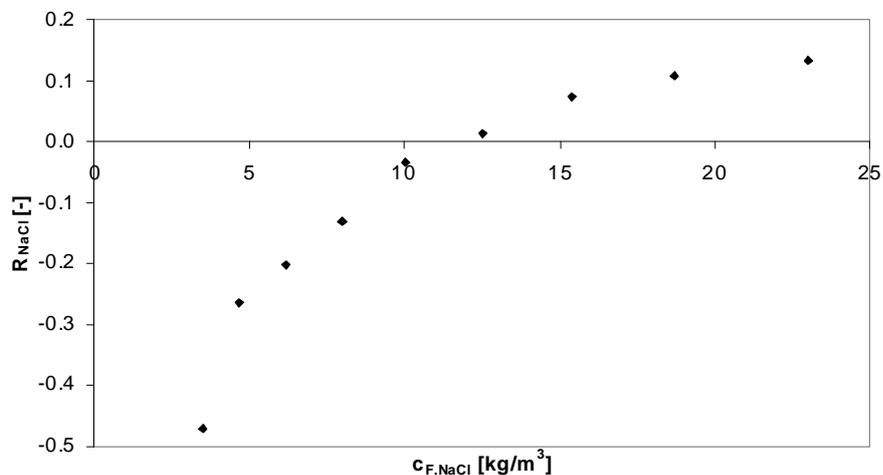
removed are bigger than model values.

Fig. 9. Dependence of salt rejection (R_{NaCl}) on salt concentration
in feed ($c_{F,NaCl}$) in diafiltration

The model assumes zero rejection of the salt independently of the time of diafiltration but, as is shown in figure 9, real rejection depends on the time of diafiltration and is not zero. This can explain the difference between the model and experiment. The comparison of figure 8 with figure 9 reveals that with a decrease in rejection of salt the quantity of the salt removed increases.

5. CONCLUSIONS

From the experiments with dye/salt mixtures is it clear that diafiltration through nanofiltration membrane is suitable for desalination of reactive yellow (RY 85). The highest the concentration of dye, the fastest the desalination of the dye solution. In this case, rejection of the salt reached minimum values. A maximum pressure results in the shortest time of diafiltration.

Diafiltration experiment has shown quite big difference between experimental and calculated values. Under conditions, described above no rejection of salt by the membrane was assumed but, as was shown, the rejection of the salt depended on the concentration of the salt in the feed. This dependence can be explained by a big influence of the Donnan effect. In order to predict better diafiltration of dye/salt mixtures by nanofiltration, the Donnan effect had to be considered in the model.

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