UNIVERSITY OF PARDUBICE

FACULTY OF CHEMICAL TECHNOLOGY

Institute of Environmental and Chemical Engineering

Jiří Cuhorka

Diafiltration of Organic Dyes Solutions

Theses of the Doctoral Dissertation

Pardubice 2018

Study program: **Chemical and Process Engineering**

Study field: **Chemical Engineering**

Author: **Jiří Cuhorka**

Supervisor: **prof. Ing. Petr Mikulášek, CSc.**

Year of the defence: 2018

References

CUHORKA, Jiří. *Diafiltration of Organic Dyes Solutions*. Pardubice, 2018. 177 pages. Dissertation thesis (PhD.). University of Pardubice, Faculty of Chemical Technology, Institute of Environmental and Chemical Engineering. Supervisor Prof. Ing. Petr Mikulášek, CSc.

Abstract

Thesis was focused on use of nanofiltration and diafiltration during organic dyes production. In this work commercially available spiral wound modules are tested. Suitable membranes for dyes diafiltration are chosen on basis of preliminary tests. Discontinuous diafiltration is described by mathematical model. The proposed mathematical model combines the design equations and the model of permeation through the membrane. These models are based mainly on diffusion through membrane, flow in pores and models based on irreversible thermodynamics.

Abstrakt

Disertační práce byla zaměřena na uplatnění nanofiltrace a procesu diafiltrace při výrobě organických barviv. V práci je testováno několik komerečně dostupných spirálně vinutých modulů. Na základě předběžných experimentů jsou zvoleny vhodné moduly (membrány) pro vlastní diafiltraci organických barviv. Diskontinuální diafiltrace je popsána matematickým modelem. Matematický model diafiltrace spojuje materiálové bilance a rovnice popisující transport látek membránou. Jedná se hlavně o modely založené na difuzi látek membránou, na jejich toku póry membrány a/nebo se jedná o modely založené na nerovnovážné termodynamice.

Keywords:

Organic dye, nanofiltration, diafiltration, characterization, rejection, mathematical model

Klíčová slova:

Organické barvivo, nanofiltrace, diafiltrace, charakterizace, rejekce, matematický model

Table of Contents

Introduction

The dyes can be defined as soluble coloured substances that are applied to textile materials. Presently, synthetic dyes have been widely used in various industries such as textile, rubber, paper, plastic, leather tanning, etc. It is estimated that there are over 10 000 types of commercial dyes and more than $7x10^5$ tons are produced annually worldwide [1].

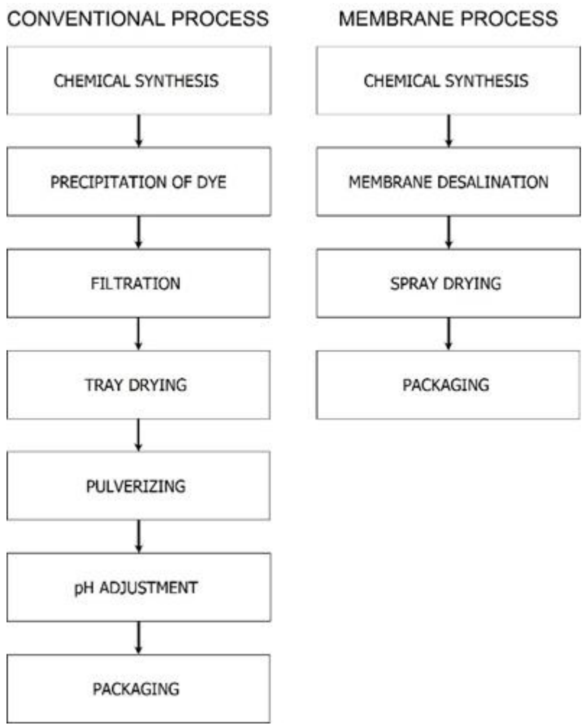

Figure 1. Conventional and alternative membrane process.

Reactive dyes are the only class of dyes amongst all the classes of dyes, which makes co-valent bond with the fibre and becomes a part of it. The development of reactive dyes has continued to be rapid, and world demand for such materials reached ca. 97000 t in 1990. Reactive dyes thus constitute the largest of the textile dye commodities on a monetary basis, accounting for ca. 17 % of the textile dye market by volume [2].

The synthesis and the use of dyes cause many environmental problems. The conventional process of production of dyes (Figure 1) includes “the salting out” step. During this step, the dye is precipitated via adding of salts. The slurry is then separated via classical filter press. However, due to the high solubility of reactive dyes, the loss can be up to 5%. Moreover, a lot of wastewater is generated from the conventional reactive dye manufacturing process. Though the composition of such wastewater varies widely, it is characterized by strong colour, high content of salts and high chemical oxygen demand (COD). Due to the polluted nature (high COD and low ratio of biochemical oxygen demand (BOD) to COD) of the wastewater, such traditional methods often fail to meet the stringent environmental discharge requirements [3]. The entire process is carried out in various batches (see Figure 1) and for this reason it is highly labour intensive and it has inconsistency in product quality. Moreover, the typical quality of final product is low. Dyes prepared by this conventional process have the salt content about 30 % [4].

The effort to cleaner production method with stable product quality brought alternative novel process, which includes membrane technology for purification of the dye. The purpose of application of membrane technology is to remove others impurities (mainly salt) from dye solution. This process must retain the dye but pass a salt. For this reason, mainly pressure driven processes, nanofiltration or ultrafiltration was used. Some attempts were performed to implement electrodialysis [5].

1. Membrane technology for dye desalination

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, but is high for salts with di- and multi-valent anions and organics with a molecular weight above 300. Thus, NF can be used for the simultaneous removal of sodium chloride (salt) and the concentration of aqueous dye solutions [6].

Membrane separation process can generally be divided into two steps: diafiltration and concentration. The diafiltration is process where permeate is discharged and new solvent is added to the feed [6]. Typical applications can be found in the recovery of biochemical products from their fermentation broths. Furthermore, diafiltration can be used for removal of free hydrogel present in external solution to purify a semi-solid liposome (SSL), purification of polymer nanoparticles, enhancement of the protein lactose ratio in whey protein products, separation of sugars or dyes from NaCl solution (desalting), and many other fields. Second step, concentration, is for the increase of dye concentration. The increase of dye concentration decreases financial costs of the following spray drying.

The great interest is also devoted to the mathematical modelling of nanofiltration and to the description of discontinuous diafiltration by periodically adding solvent at constant pressure difference. The diafiltration consists of concentration and dilution modes. In the concentration mode the retentate stream is recirculated to the feed tank and the permeate stream is collected separately. No diluant is added in this mode. A diluant is added in the second operation process. These two processes constitute one diafiltration step.

The proposed mathematical model combines the design equations and the model of permeation through the membrane. The transport through the membrane is approached in two different ways. Firstly, the membrane is considered as a dense layer and in this case the transport description is based on the solution-diffusion model [7, 8]. In the second approach the membrane is modelled as a porous medium. These models 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. It is assumed that the flux of every ion through the membrane is induced by the gradients of pressure, concentration and electrical potential. These models describe the transport of ions in terms of the effective pore radius r_p (m), the effective membrane thickness/porosity ratio $\Delta x/A_k$ (m) and the effective membrane charge density X_d ($mol.m^{-3}$). Such models require many experiments for determination of the structural parameters and are hard to solve [9, 10]. The last approach is based on irreversible thermodynamics. These models take the membrane as "black box" and have been applied in prediction of the 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 an organic ion. This model describes transport of ion through the membrane in terms of salt permeability P_s and reflection coefficient σ [11–13]. In our work Perry-Linder model is used. We can propose easy way to predict concentration in the feed for batch operations.

State of the art of use membrane technology for dye desalination

Authors [4] show the use of spiral wound nanofiltration membranes for separation of a dye from salt. They show results from NF plant with 12 spiral wound elements for 5 different dyes. Rejections of dyes are between 99.1% for most permeable dye and almost 100 % for 3 other dyes. The nanofiltration membranes are able to concentrate dye to 25.8 % and decrease NaCl content to 0.64 %. Authors [14] test cellulose acetate membrane for separation of 5 dyes from 5 different dye intermediates and salt. Membrane reached rejection over 99.9 % for 4 dyes. Only reactive Black 5 have rejection 99 %. They measured dye rejection at concentrations up to 100 $g.l^{-1}$. Authors [1] prepared nanofiltration hollow fiber membrane and tested it for dye desalination and concentration. The prepared membrane reached rejection 99.99 % for reactive brilliant blue X-BR and low to moderate salt rejection. Dye rejection decreases to 98 % at maximal concentration 6 $g.l^{-1}$. This dye concentration is below typical dye concentration for spray drying. Since for desalination it is better to have bigger permeate fluxes and smaller salt rejection, some investigation was focused on using membrane with higher permeate fluxes and smaller rejection of salt with still high rejection of dye. For this reason "loose" NF [15–17] or UF membranes [3, 18–20] were tested. Due to relatively small rejection for dyes, these types of membrane are used for treating of wastewater or generally of small concentration feeds. Authors [3] tested two UF and four NF membranes and as optimal membrane for dye desalination UF membrane ES404 has been chosen. This membrane reached high flux, small salt rejection and relatively high rejection 99.8 % of reactive brilliant blue KN-R dye, but still (particularly in comparison to the thin film composite NF membranes) permeate was colored. For this reason, they proposed and tested two stages membrane process. The permeate from diafiltration (first step) is not directly discharged but is used in the second step as feed for next UF. During this step, it is concentrated and then retentate is added to the feed in the first step. Permeate from the second step is dye free and can be discharged or recirculated as process water. The authors continued in development of the proposed two-stage process and brought it into technical and economic feasibility [20]. They showed an alternative to the NF membranes. However, it will need some extension with focus on long-term use of membranes mainly due to their potential for fouling.

At present, development is focused on the preparation of new types of membranes. This membrane should retain dye (rejection in ideal case 100 %) and salt must be easily permeable. Authors [21] improve charge of UF membrane from regenerated cellulose

(RC). For testing, they used 3 model reactive dyes (red ED-B, brilliant yellow K-G, brilliant blue KN-R). Dye rejection was 80 % but with increasing salt concentration up to 100 mmol.l^{-1}, rejection decreased to nearly zero. It was explained by electrostatic shielding and due to this reason electrostatic repulsive force between dye and membrane decrease. The hydrophilic chitosan was used to fill up the porous hydrophobic PVDF membrane modified by multi-walled carbon nanotubes (MWCNTs) [22]. This membrane reached rejection 91 % of reactive orange-16 at pH 4. Chitosan has positive charge and membrane have a negative charge at this pH and this high rejection is explained with charge interaction. Non-polyamide composite nanofiltration (NF) membranes based on N-methyl-D-glucamine-assisted polydopamine coating were prepared by simple deposition process followed by glutaraldehyde crosslinking in work [23]. Authors tested this membrane with 3 different dyes. Rejection of acid red was higher than 99 % and rejection of NaCl was below 14 %, but dye concentration in the feed was only 0.1 g.l^{-1}during testing. The sulfonated polyelectrolyte complex membranes were prepared by solution-casting and glutaraldehyde crosslinking process in work [24]. These membranes were able to retain 99.9 % of methyl blue with salt rejection only 15.8 %. Authors [25] prepared carboxyl-functionalized graphene oxide/polyamide nanofiltration membrane. They increased the hydrophilicity of membrane by incorporating carboxyl group and therefore permeability of membrane. The membrane was tested with 3 dyes. Rejection of dyes was above 94 % and for acid red 18 was above 95.1 % and rejection of NaCl was only 25 %.

All new membranes were tested at very low dye concentration (below 5 g.l^{-1}). If feed concentration is in this range, dye rejection 95-99 % is enough. For the production of dye, where dye concentration in feed is higher than 10 g.l^{-1} and usually at end of concentration step more than 100 g.l^{-1}, this value of rejection is not acceptable for desalination in one step. For example with rejection 99 % and feed concentration 100 g.l^{-1} we have in permeate 1 g.l^{-1} of dye. In this case, permeate must be „cleaned" in the second step.

2. Mathematical model

Mathematical model combines balance equations and model based on irreversible thermodynamics, Perry-Linder model.

The balances for the concentration mode can be written as:

- Solvent mass balance:

$$\frac{dV_F}{d\tau} = -JA \tag{1}$$

- Mass balances of dye and salt:

$$\frac{d(V_F c_{F,B})}{d\tau} = -JAc_{P,B} \tag{2}$$

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

If we assume constant rejection and permeate flux (for a small change of volume in the feed tank, or better a small change of yield – permeate volume divided by feed volume) mathematical operation and integrations with the boundary conditions (V_{F0} to V_F) result in Eq. (4) and Eq. (5):

$$c_{F,i} = c_{F,i}^{0} \left(\frac{V_F^0}{V_F}\right)^{R_i} \tag{4}$$

$$\tau = \frac{V_F^0 - V_F}{J_V A^*} \tag{5}$$

Based on Eq. (4) and Eq. (5) 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 a diluant. Salt concentration in the feed tank after this operation (c_S') is:

$$c_S' = c_{F,i}^{0} \left(\frac{V_F}{V_F^0}\right) \tag{6}$$

This concentration (c_S') is now equal for the next concentration mode in the second diafiltration step to the salt concentration in feed tank ($c_{S,F0}$).

For solving these equations, we need to know the dependence of rejection and permeate flux on the salt concentration in the feed.

The model based on irreversible thermodynamics is used in this work. The model derived by Spiegler and Kedem describes the salt rejection of a single electrolyte. By applying linear relationships on a local level, the solvent flux, J_v, and the solute flux, J_s, the salt rejection in the presence of retained organic ion [26] can be written as:

$$R_{real,S} = 1 - \frac{(1-\sigma_S)\left(1+\frac{z_B c_{F,B} M_S}{c_{F,S} M_B}\right)^{0.5}}{1-\sigma_S exp\left(\frac{(\sigma_S - 1)J}{\alpha_S c_{F,S}^{\beta} c^{*-\beta}}\right)} \tag{7}$$

Eq. (7) constitutes Perry-Linder model.

For the permeate flux these equations can be used:

$$J_V = A(\Delta P - \Delta\pi_s - \delta) = \frac{L_P}{R_{FOUL.}}(\Delta P - \Delta\pi_s - \delta) \tag{8}$$

Eq. (8) represents the osmotic pressure model. This model is used in a similar form by many authors. Parameter A (water permeability) can be concentration or viscous depended [8, 13]. For our model, we assume this parameter as independent on the salt concentration. It is equal to the hydraulic permeability L_P divided by the parameter R_{FOUL}. This parameter represents the fouling of the membrane and converts hydraulic permeability of a new membrane, L_P, into actual permeability of membrane. Coefficient δ represents the effect of dye on the flux, particularly through the osmotic pressure of dye. If this parameter represents only osmotic pressure of dye, then it is constant (constant dye concentration during diafiltration).

The osmotic pressure gradient for salt is related to the difference of the concentration Δc by the van´t Hoff law:

$$\Delta\pi_s = g\frac{\nu R^* T}{M}\Delta c_s \tag{9}$$

Due to non-ideality of solution at higher concentration, the osmotic coefficient is included into Eq. (9). The osmotic coefficient is concentration dependent. For solution of NaCl tabular data can be found in [27] or at NaCl concentrations ranging from 0.0001 to 0.3 M ($mol.l^{-1}$) it can be represented with the expression [28]:

Where:

A*	- membrane area,
A	- actual water permeability,
c	- concentration,
g	- osmotic coefficient,
J	- flux,
M	- relative molecular mass,
R	- rejection,
R*	- universal gas constant,
α	- coefficient for salt permeability,
β	- coefficient for concentration dependence of salt permeability,
δ	- coefficient for dye solution,
ν	- valence (for NaCl is $\nu = 2$ and for dye $\nu = 3$),
π	- osmotic pressure,
σ	- reflection coefficient,
τ	- time of diafiltration,
ω	- salt permeability.

subscripts

S	- salt,
D	- dye,
V	- water,
F	- feed,
P	- permeate,
R	- retentate,
W	- membrane interface (wall),
M	- molar,

superscript

0	- beginning of the concentration mode.

Aims of the Thesis

Seven commercially available spiral wound modules are firstly characterized by experiments with demineralized water and NaCl solutions. On basis of these results, some membranes are selected to diafiltration experiments. Desalination of three reactive dyes is the next aim of the dissertation. The influence of some operating parameters on diafiltration is tested. Effect of desalination on membrane properties, mainly focus on fouling of membrane, is evaluated. Membranes were compared, and the best membrane was chosen. Last aim of the thesis was the development of mathematical model with a precise description of batch diafiltration. In addition, the model should have low complexity and time requirement. The proposed model is experimentally validated.

Experimental

3. Experimental System

The experiments were carried out on the system depicted schematically in Figure 2.

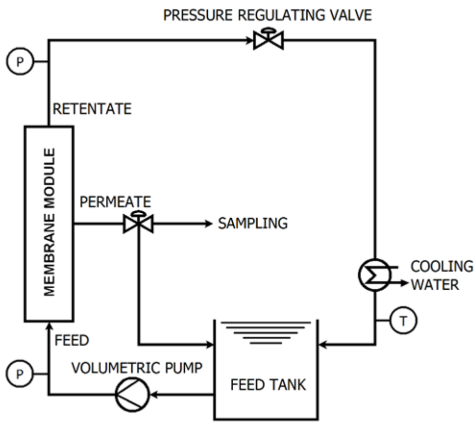

Figure 2. Schematic diagram of the experimental system.

Feed (F) was pumped by volumetric pump (Wanner Engineering, Inc., type Hydracell G13) from feed vessel to membrane module. Pressure was set by valve placed behind membrane module. Permeate (P) and retentate (R) were returned to feed vessel. A manometer measured the pressure and a thermometer measured the temperature. Stable temperature was maintained by cooling system. Temperature in all experiments was 25°C.

3.1 Materials

Dye was obtained from VÚOS a.s. Pardubice, Czech Republic. Molecular weights of C.I. Reactive orange 35, C.I. Reactive orange 12 and C.I. Reactive blue 49 are 748.1, 674.05 and 816.2 g.mol^{-1} (in free acid form), respectively.

NaCl used for all experiments was of analytical grade. The demineralized water with the conductivity between 10-20 μS.cm^{-1} was used in this study.

3.2 Membranes

Seven NF membranes were chosen for this study. All membranes are in spiral wound 2540 modules and are made from polyamide. The MWCO can be found in [29–31], except NF 70 membrane, for which data are not available. The permeabilities of membranes are specified for new membrane modules. Summarization and properties of membranes used are given in Table 1.

Table 1. General description of the membranes used

Indication	Type	Producer	Area (m^2)	Permeability L_P ($l.h^{-1}.m^{-2}$)
Desal 5DK	Desal 5 DK1072	GEW & PT	2.6	2.96
Esna 1	Esna 1 LP2	Hydranautics	2.4	5.13
NF 90	NF 90	Dow	2.6	5.91
NF 270	NF 270	Dow	2.6	6.64
NF 70	CSM NE 2540- 70	Saehan	2.5	3.42
TR 60	TR 60- 2540	Toray	2.5	8.08
XN 45	XN 45 2540	TriSep	2.4	5.51

Results

4. Binary System of NaCl

Firstly, membranes were characterized in binary system of NaCl in water. Basic membrane characteristics are the dependence of the permeate flux and the salt rejection on other operating parameters such as 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 $g.l^{-1}$), the values of permeate flux were similar to the values of pure water. The lower values of permeate flux were obtained with the increasing salt concentrations in feed (increasing osmotic pressure). Membranes NF 270, TR 60 and XN 45 were not measured at the smallest salt concentration in the feed at 30 bar. The permeate flux was too high and pump was not able to deliver necessary volumetric flow of retentate (600 $l.h^{-1}$) for constant conditions at all experiments. Opposite problem was encountered at the highest salt concentrations in feed (35 $g.l^{-1}$). During this experiment, fluxes at pressure of 5 bar were negligible and it was measured from 10 bar (except NF 270) and only from 25 bar for membrane NF 90 due high osmotic pressure. Figure 3 shows the comparison of tested membranes for the lowest (1 $g.l^{-1}$) and for the highest salt concentrations in feed (35 $g.l^{-1}$).

The observed rejection increases as the pressure difference increases and decreases with the increasing salt concentration in the 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. Figure 4 shows the comparison of tested membranes for the lowest (1 g.l^{-1}) and for the highest salt concentrations in feed (35 g.l^{-1}). Due to higher rejection membranes NF 90 and Esna 1 were not used for diafiltration. Both membranes had rejection over 90 % at the smallest salt concentration. Membrane NF 90 was used for preparation of demi water.

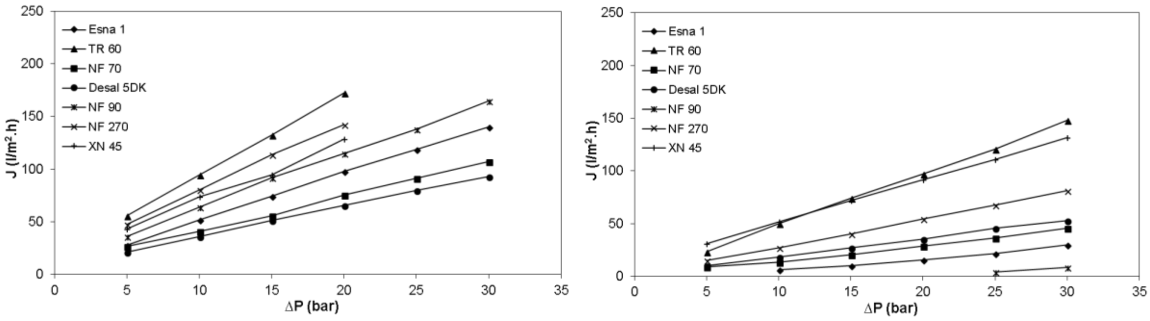

Figure 3. Permeate flux as a function of pressure difference for the lowest salt concentration (left, 1 g.l^{-1}) and for the highest salt concentration (right, 35 g.l^{-1}).

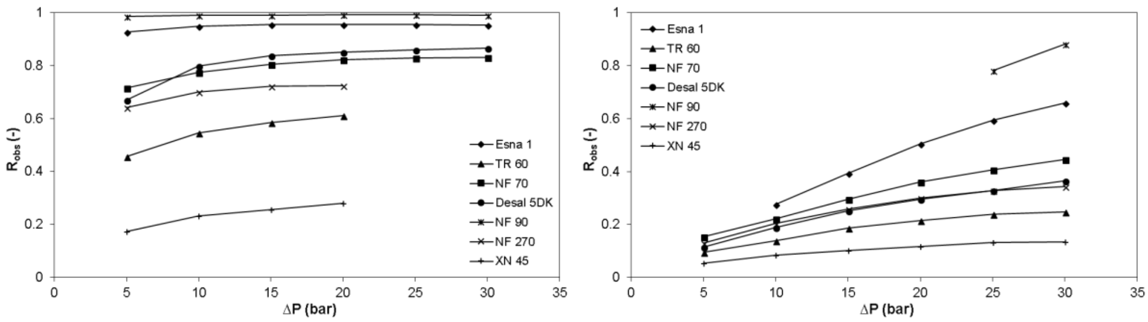

Figure 4. Rejection as a function of pressure difference for the lowest salt concentration (left, 1 g.l^{-1}) and for the highest salt concentration (right, 35 g.l^{-1}).

5. Diafiltration of dyes

5.1 ORANGE 35

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^{-1} was carried on. The volume of the pure solvent added in every dilute mode was 4 l (The same volume of permeate was removed before in concentration mode). Total feed volume in tank was 52 l. For every membrane and every concentration of the dye in feed sixty diafiltration steps were realized. Aqueous dye solutions with dye (C.I. Reactive orange 35, ORANGE 35) concentrations 180, 125 and 75 g.l^{-1} and salt concentration in the range

55–60 g.l^{-1} were desalted at 25°C. One point in Figures 5-15 represents one diafiltration step.

The permeate flux decreased while the 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. Membrane TR 60 reached the highest flux (up to 60 l.m^{-2}.h^{-1}).

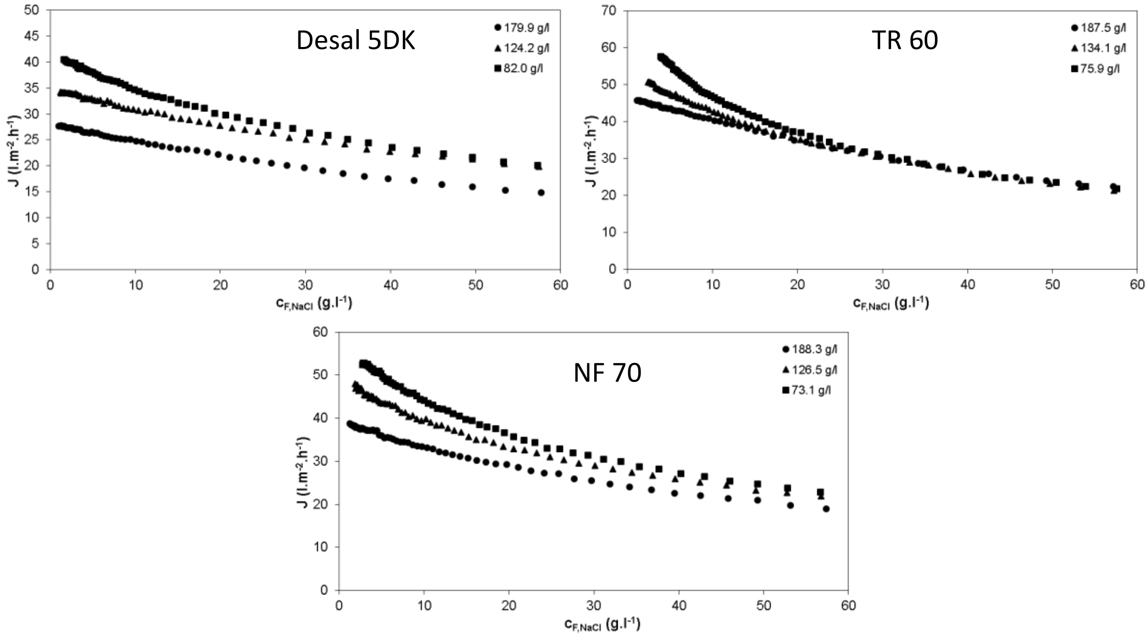

Figure 5. Permeate flux as a function of salt concentration in feed during diafiltration.

The dependences of rejection on salt concentration in feed are given in Figure 6 for all membranes tested. It can be seen that rejection decreases with increasing dye concentration in the feed, which can be explained by Donnan potential which strengthens the flow of salt through the membrane. Membrane Desal 5DK reached the smallest salt rejection below 16 % for the highest dye concentration.

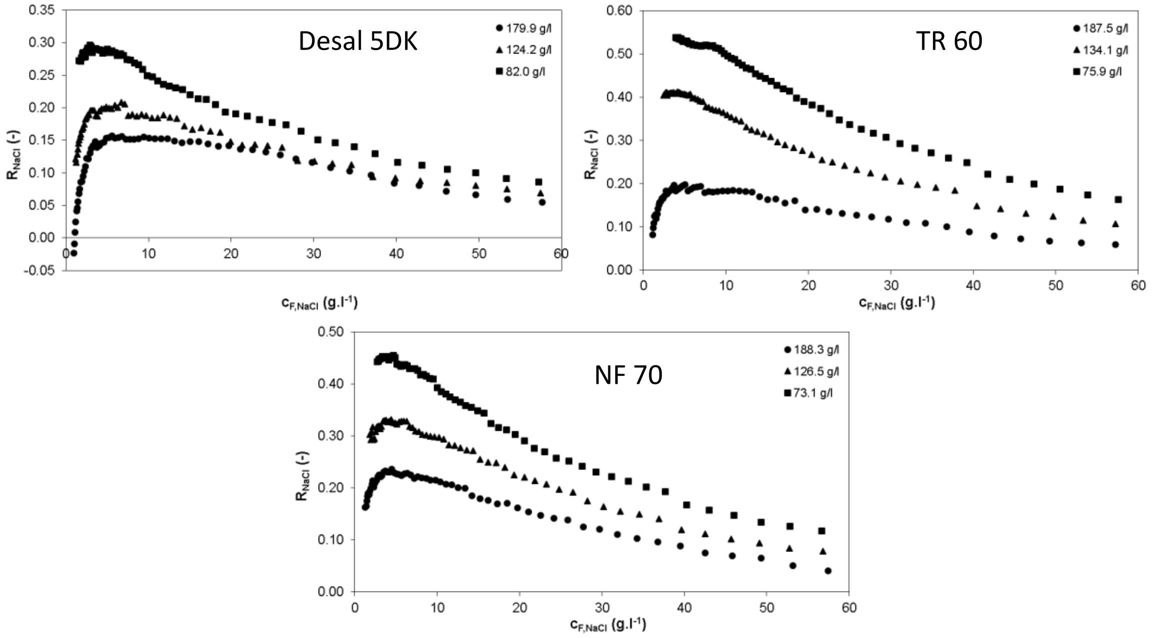

Figure 6. Salt rejection as a function of salt concentration in feed during diafiltration.

The progress of desalination with tested membranes is in Figure 7. Membranes are compared at the smallest (left picture) and the highest (right picture) dye concentration. It is clearly seen that the fastest desalination is with membrane TR 60. Membrane Desal 5DK reached the longest time for sixty steps of diafiltration.

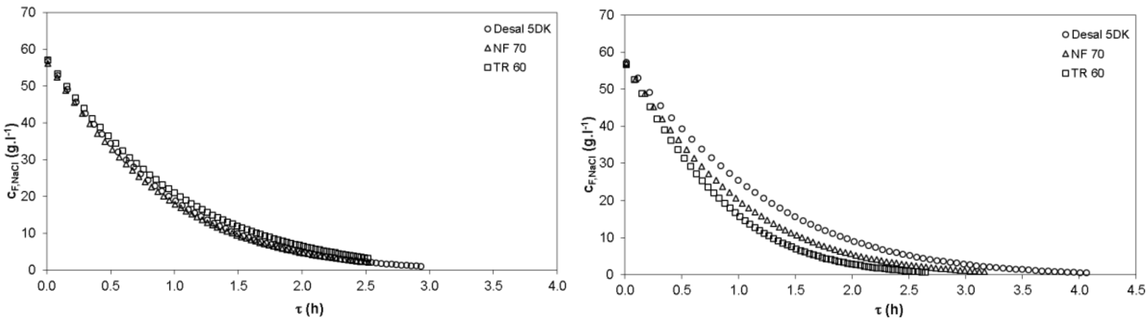

Figure 7. Salt concentration in feed as a function of diafiltration time for the lowest dye concentration (left, 75 g.l^{-1}) and for the highest dye concentration (right, 180 g.l^{-1}).

Table 2. Total time of diafiltration, τ, separation factor, S, and loss of dye, Z, during diafiltration (ORANGE 35)

Desal 5DK				
$c^0_{F,NaCl}$	(g.l^{-1})	57.65	57.41	57.24
$c_{F,NaCl}$	(g.l^{-1})	0.77	0.98	1.39
$c^0_{F,dye,S}$	(g.l^{-1})	179.90	124.20	82.00
$c_{F,dye,E}$	(g.l^{-1})	179.86	124.18	81.99
τ	(hr)	4.05	3.22	2.92
S	(-)	74.86	58.74	41.11
Z	(%)	0.02	0.01	0.01

TR 60				
$c^0_{F,NaCl}$	(g.l^{-1})	57.14	57.16	57.52
$c_{F,NaCl}$	(g.l^{-1})	0.92	2.18	3.65
$c^0_{F,dye,S}$	(g.l^{-1})	187.50	134.10	75.90
$c_{F,dye,E}$	(g.l^{-1})	186.71	133.52	75.60
τ	(hr)	2.64	2.59	2.51
S	(-)	61.94	26.07	15.68
Z	(%)	0.42	0.43	0.40
NF 70				
$c^0_{F,NaCl}$	(g.l^{-1})	57.33	56.70	56.61
$c_{F,NaCl}$	(g.l^{-1})	1.08	1.62	2.49
$c^0_{F,dye,S}$	(g.l^{-1})	188.30	126.50	73.10
$c_{F,dye,E}$	(g.l^{-1})	188.26	126.48	73.08
τ	(hr)	3.15	2.69	2.51
S	(-)	53.04	34.97	22.77
Z	(%)	0.02	0.02	0.02

From Table 2 it is clearly shown that the total time of diafiltration τ decreases with decreasing dye concentration. The time for the highest dye concentration is less than twice that for the lowest dye concentration for all tested membranes (the time/amount of dye desalted ratio is smaller for higher concentration of dye). The 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 shortest time was obtained for membrane TR 60. The best separation factor was obtained for membrane Desal 5DK. The loss of dye is almost the same for membrane Desal 5DK and NF 70 at all concentrations of dye. Only for membrane TR 60 higher loss of dye was found.

5.2 ORANGE 12

Aqueous dye solutions with dye (C.I. Reactive blue 12, ORANGE 12) concentrations 100, 50 and 10 g.l^{-1} and salt concentration in the range 20–23 g.l^{-1} were desalted at 25°C. Due lower salt concentration in feet at start of experiment only fifty diafiltration steps were realized. Others operating parameters were as in diafiltration of dye Orange 35.

Four membranes only – Desal 5DK, NF 270, TR 60 and NF 70 – were used for diafiltration experiments. For the reason of low values of permeate flux, membrane NF 90 and Esna 1 were not used for those experiments. Membrane XN 45 was obtained only for experiments with dye C.I. Reactive blue 49. The dependences of the flux on salt concentration are shown in Figure 8. The highest values of flux (70.3 l.m^{-2}.h^{-1}) were obtained in experiments with membrane NF 270.

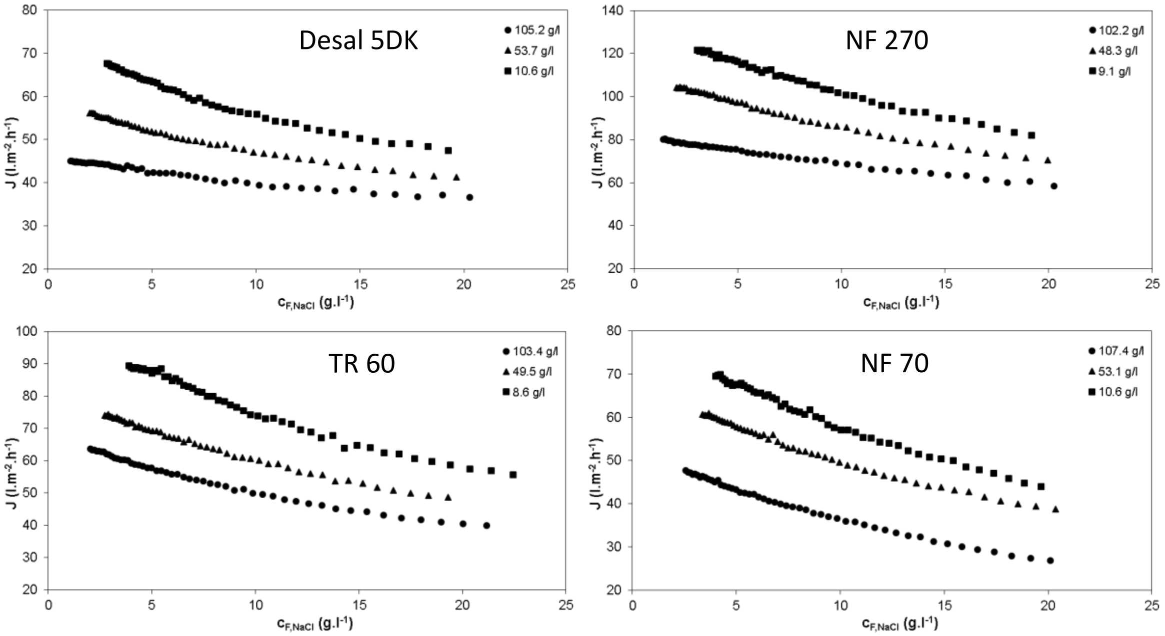

Figure 8. Permeate flux as a function of salt concentration in feed during diafiltration.

The lowest values of rejection (max. 0.29) were obtained for membrane Desal 5DK. The membrane NF 70 had the highest values. Membranes are compared at the highest dye concentration (100 g.l^{-1}) in Figure 10.

The shortest time was obtained for membrane NF 270. The best separation factor was obtained for membrane Desal 5DK (very similar values, except for the highest dye concentration, were obtained for membrane NF 270). The loss of dye is almost the same for membrane Desal 5DK, NF 70 and NF 270 at all concentrations of dye. Only for membrane TR 60 higher loss of dye was found.

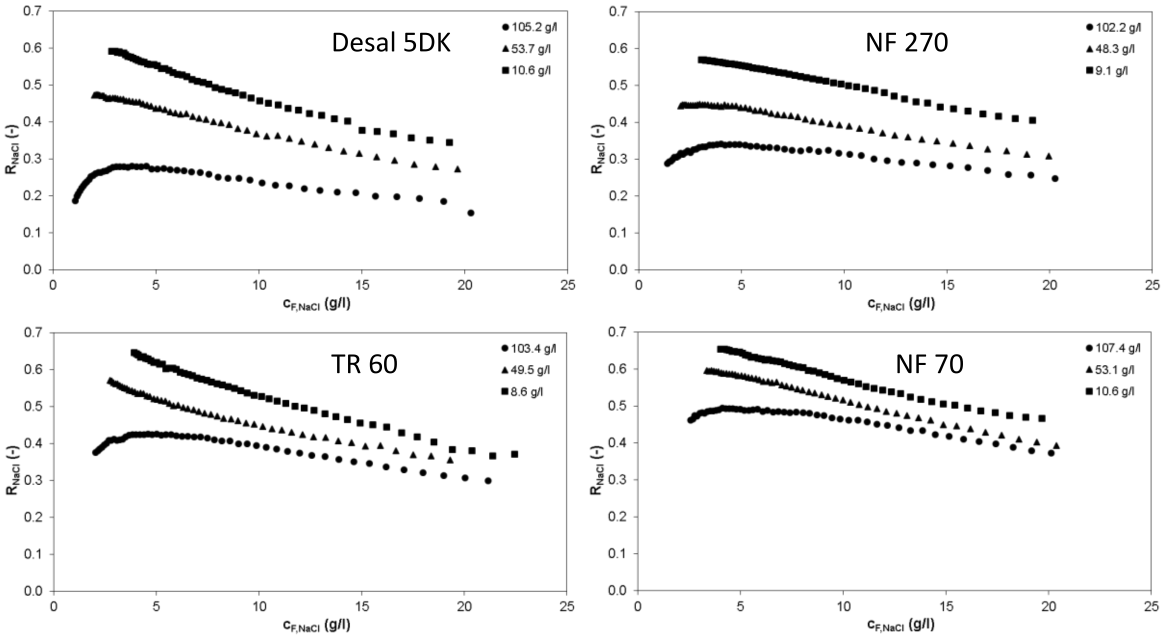

Figure 9. Salt rejection as a function of salt concentration in feed during diafiltration.

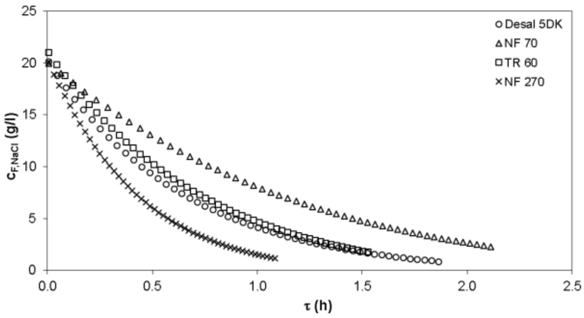

Figure 10. Salt concentration in feed as a function of diafiltration time (c_D=100 g.l^{-1}).

Table 3. Total time of diafiltration, τ, separation factor, S, and loss of dye, Z, during diafiltration (ORANGE 12)

Desal 5DK				
$c^0_{F,NaCl}$	(g.l^{-1})	22.00	19.59	19.18
$c_{F,NaCl}$	(g.l^{-1})	0.97	1.88	2.70
$c^0_{F,dye,S}$	(g.l^{-1})	105.17	53.75	10.61
$c_{F,dye,E}$	(g.l^{-1})	105.15	53.74	10.60
τ	(hr)	1.86	1.55	1.32
S	(-)	22.71	10.42	7.09
Z	(%)	0.02	0.01	0.07
NF 270				
$c^0_{F,NaCl}$	(g.l^{-1})	22.00	19.90	19.13
$c_{F,NaCl}$	(g.l^{-1})	1.28	1.90	2.90
$c^0_{F,dye,S}$	(g.l^{-1})	102.15	48.30	9.10
$c_{F,dye,E}$	(g.l^{-1})	102.12	48.28	9.10
τ	(hr)	1.08	0.86	0.74
S	(-)	17.19	10.49	6.59
Z	(%)	0.03	0.04	0.05
TR 60				
$c^0_{F,NaCl}$	(g.l^{-1})	21.11	19.24	22.38
$c_{F,NaCl}$	(g.l^{-1})	1.88	2.58	3.75
$c^0_{F,dye,S}$	(g.l^{-1})	103.41	49.50	8.60
$c_{F,dye,E}$	(g.l^{-1})	102.74	49.31	8.56
τ	(hr)	1.52	1.28	1.08
S	(-)	11.16	7.43	5.94
Z	(%)	0.64	0.39	0.42
NF 70				
$c^0_{F,NaCl}$	(g.l^{-1})	20.06	20.30	19.61
$c_{F,NaCl}$	(g.l^{-1})	2.40	3.21	3.86
$c^0_{F,dye,S}$	(g.l^{-1})	107.42	53.05	10.56
$c_{F,dye,E}$	(g.l^{-1})	107.38	53.04	10.56
τ	(hr)	2.11	1.57	1.37
S	(-)	8.35	6.33	5.08
Z	(%)	0.03	0.03	0.05

5.3 Blue 49

Aqueous dye solutions with dye (C.I. Reactive blue 49, BLUE 49) concentration 100 $g.l^{-1}$ and salt concentration in the range 20–23 $g.l^{-1}$ were desalted at 25°C. Others operating parameters were like diafiltration of ORANGE 12 dye.

Membranes – Desal 5DK, NF 270, TR 60, NF 70 and XN 45 – were used for diafiltration experiments. New membrane modules Desal 5DK and TR 60 were used. Diafiltration processes with tested membranes are compared in Figure 11. Membrane XN 45 reached the lowest salt concentration after fifty diafiltration steps. Membrane NF 270 had the shortest time of diafiltration. Due high molecular weight of this dye, all membranes had relatively small loss of dye.

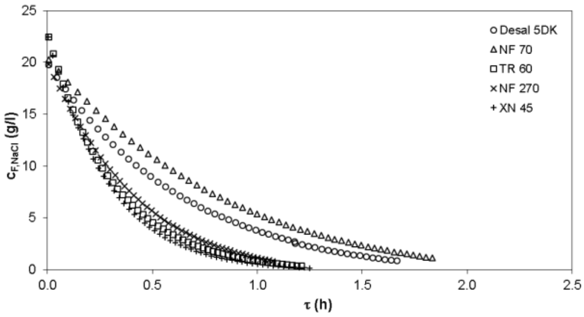

Figure 11. Salt concentration in feed as a function of diafiltration time.

6. Mathematical modelling

The comparison of experimental (points) and model data (lines) for the highest dye concentration (100 $g.l^{-1}$, ORANGE 12) are shown in Figure 12–14. The salt concentrations are calculated using Eq. (4) and Eq. (6). Rejection and flux needed for these equations are calculated on basis of Eq. (7) and (8), respectively. Best-fit parameters for proposed model are given in Table 4. From Table 4 it can be shown that parameter δ which mainly represents osmotic pressure of dye is relatively constant. This parameter is between 5.08–5.71 bar. From parameter R_{FOUL}, which represents additional resistance caused by dye, it is clearly shown that membrane TR 60 has the biggest fouling potential. For membrane Desal 5DK this parameter was less than 1 (no physical meaning) which can be explained by some experimental error during measurements of permeability.

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 the solution increased with higher concentration.

Table 4. Model best fit parameters

Parameter		Desal 5DK	NF 270	TR 60	NF 70
α	$(g.m^{-2}.h^{-1})$	3.75	7.98	3.28	2.80
β	(-)	0.77	0.62	0.72	0.60
σ	(-)	0.88	0.90	0.86	0.89
δ	(bar)	5.08	5.21	5.57	5.71
R_{FOUL}	(-)	0.97	1.17	1.84	1.02

From Figures 12 and 13 it can be shown that the model fits the experimental results very well. Due to considerably lower salt concentrations in permeate the concentration polarization was minimized. The diafiltration process benefits to obtain pure salt-free product and this can be predicted by the mathematic model based on description of discontinuous diafiltration by periodically adding solvent at constant pressure difference.

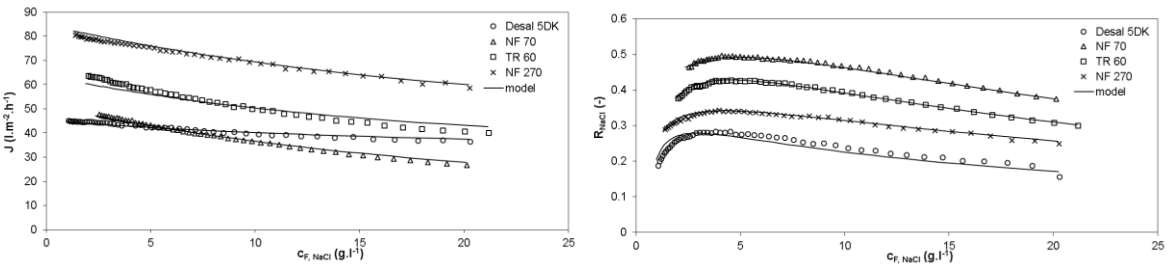

Figure 12. Comparison of experimental and model data of permeate flux and salt rejection on salt concentration in feed during diafiltration.

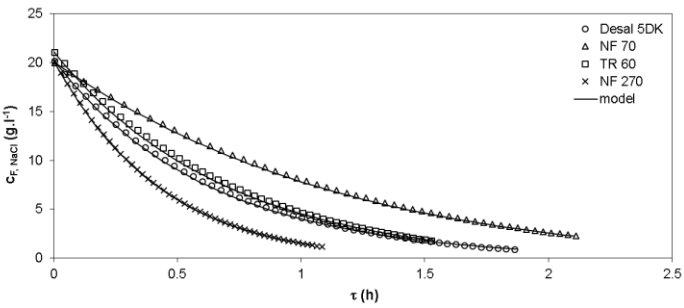

Figure 13. Comparison of experimental and model data of salt concentration in feed on time of diafiltration.

7. Fouling

In this part is shown how membrane is changed after desalination of dyes due to fouling. Different states of membrane modules Desal 5DK and TR 60 are compared in Figure 14. It is clearly shown that characteristic (permeability) of membrane Desal 5DK are for different states (after cleaning with demi water) similar. But for membrane TR 60 another trend can be found. The decreased permeability (slope decrease) with increasing number of desalting experiments. It is due to fouling. It confirms result from a mathematical model. This membrane reached the highest R_{FOUL}. Results from two different modules of the same membrane (new membranes are for EXP 3) are shown in

Figure 14. Differences between two modules are relatively high, but still in declared difference from the producer.

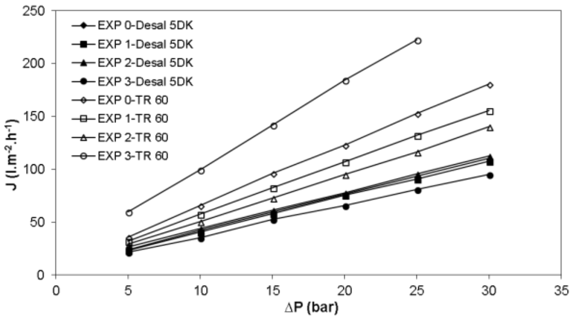

Figure 14. Permeate flux as a function of pressure difference for the different states of module and two module of membrane Desal 5DK (left) and TR 60 (right).

Conclusion

The separation performance of dye, salt and dye solution with seven 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 similar molecular weight cut-off were characterized for key physical and surface properties. These membranes were 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 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. However, this effect is weakened as the dye concentration or salt concentration is increased.

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 $g.l^{-1}$. In this case, the salt rejection reaches minimal value due to Donnan potential that strengthens the flow of salt through the membrane and no problem was with a solubility of dye.

The best membrane for desalination is NF 270, which has smaller dye loss factor and the shortest time of diafiltration. The very suitable membrane is also Desal 5DK, which has high separation factor and dye loss factor, but this membrane has a longer time of diafiltration (see Table 3). Membrane XN 45 had the highest separation factor, but no long experiment was done. This membrane must be characterized with focus on fouling. For desalination qualitative description, it is convenient to use the proposed model.

List of references

[1] WEI, X., KONG, X., SUN, Ch., CHEN, J. Characterization and application of a thin-film composite nanofiltration hollow fiber membrane for dye desalination and concentration. *Chemical Engineering Journal*, 2013, 223, 172–182.

[2] CHINTA, S.K., VIJAYKUMAR, S. Technical facts and figures of reactive dyes used in textiles. *Int. J. Sci. Technol. Res.*, 2013, 4, 308–312.

[3] HE, Y., LI, G., JIANG, Z., WANG, H., JIANG, Z., ZHAO, J., SU, H., HUANG, Q. Diafiltration and water recovery of Reactive Brilliant Blue KN-R solution by two-stage membrane separation process. *Chemical Engineering and Processing: Process Intensification*, 2010, 49, 476–483.

[4] YU, S., GAO, C., SU, H., LIU, M. Nanofiltration used for desalination and concentration in dye production. *Desalination*, 2001, 140, 97–100.

[5] XUE, Ch., CHEN, Q., LIU, Y.-Y., YANG, Y.-L., XU, D., XUE, L., ZHANG, W.-M. Acid blue 9 desalting using electrodialysis. *Journal of Membrane Science*, 2015, 493, 28–36.

[6] MULDER, Marcel. *Basic Principles of Membrane Technology*. Dordrecht: Springer Netherlands, 1996. ISBN 9789400917668.

[7] DAS, Ch., DASGUPTA, S., DE, S. Steady-state modelling for membrane separation of pretreated soaking effluent under cross flow mode. *Environmental Progress*, 2008, 27, 346–352.

[8] CSÉFALVAY, E., PAUER, V., MIZSEY, P. Recovery of copper from process waters by nanofiltration and reverse osmosis. *Desalination*, 2009, 240, 132–146.

[9] BOWEN, W. R., MOHAMMAD, A.W. Diafiltration by Nanofiltration: Prediction and Optimization. *AIChE J.*, 1998, 44, 1799–1812.

[10] HUSSAIN, A.A., NATARAJ, S.K., ABASHAR, M.E.E., AL-MUTAZ, I.S., AMINABHAVI, T.M. Prediction of physical properties of nanofiltration membranes using experiment and theoretical models. *Journal of Membrane Science*, 2008, 310, 321–336.

[11] KOYUNCU, I. Reactive dye removal in dye/salt mixtures by nanofiltration membranes containing vinylsulphone dyes: effects of feed concentration and cross flow velocity. *Desalination*, 2002, 143, 243–253.

[12] MANDALE, S., JONES, M. Membrane transport theory and the interactions between electrolytes and non-electrolytes. *Desalination*, 2010, 252, 17–26.

[13] KOVÁCS, Z., DISCACCIATI, M., SAMHABER, W. Modelling of amino acid nanofiltration by irreversible thermodynamics. *Journal of Membrane Science*, 2009, 332, 38–49.

[14] HE, Y., LI, G.-M., WANG, H., JIANG, Z.-W., ZHAO, J.-F., SU, H.-X., HUANG, Q.-Y. Experimental study on the rejection of salt and dye with cellulose acetate nanofiltration membrane. *Journal of the Taiwan Institute of Chemical Engineers*, 2009, 40, 289–295.

[15] LIN, J., YE, W., ZENG, H., YANG, H., SHEN, J., DARVISHMANESH, S., LUIS, P., SOTTO, A., VAN DER BRUGGEN, B. Fractionation of direct dyes and salts in aqueous solution using loose nanofiltration membranes. *Journal of Membrane Science*, 2015, 477, 183–193.

[16] LIN, J., TANG, Ch. Y., YE, W., SUN, S.-P., HAMDAN, S. H., VOLODIN, A., VAN HAESENDONCK, Ch., SOTTO, A., LUIS, P., VAN DER BRUGGEN, B., Unravelling flux behavior of superhydrophilic loose nanofiltration membranes during textile wastewater treatment. *Journal of Membrane Science*, 2015, 493, 690–702.

[17] CHEN, P., MA, X., ZHONG, Z., ZHANG, F., XING, W., FAN, Y. Performance of ceramic nanofiltration membrane for desalination of dye solutions containing NaCl and Na2SO4. *Desalination*, 2017, 404, 102–111.

[18] LIN, J., YE, W., BALTARU, M.-C., TANG, Y. P., BERNSTEIN, N.J., GAO, P., BALTA, S., VLAD, M., VOLODIN, A., SOTTO, A., LUIS, P., ZYDNEY, A.L., VAN DER BRUGGEN, B. Tight ultrafiltration membranes for enhanced separation of dyes and Na2SO4 during textile wastewater treatment. *Journal of Membrane Science*, 2016, 514, 217–228.

[19] AOUNI, A., FERSI, C., CUARTAS-URIBE, B., BES-PÍA, A., ALCAINA-MIRANDA, M.I., DHAHBI, M. Reactive dyes rejection and textile effluent treatment study using ultrafiltration and nanofiltration processes. *Desalination*, 2012, 297, 87–96.

[20] HE, Y., LI, G., JIANG, Z., WANG, H., ZHAO, J., SU, H., HUANG, Q. Diafiltration and concentration of Reactive Brilliant Blue KN-R solution by two-stage ultrafiltration process at pilot scale: Technical and economic feasibility. *Desalination*, 2011, 279, 235–242.

[21] CHEN, X., ZHAO, Y., MOUTINHO, J., SHAO, J., ZYDNEY, A. L., HE, Y. Recovery of small dye molecules from aqueous solutions using charged ultrafiltration membranes. *Journal of Hazardous Materials*, 2015, 284, 58–64.

[22] WASIM, M., SAGAR, S., SABIR, A., SHAFIQ, M., JAMIL, T. Decoration of open pore network in Polyvinylidene fluoride/MWCNTs with chitosan for the removal of reactive orange 16 dye. *Carbohydrate Polymers*, 2017, 174, 474–483.

[23] CHEN, Y., HE, CH. High salt permeation nanofiltration membranes based on NMG-assisted polydopamine coating for dye/salt fractionation. *Desalination*, 2017, 413, 29–39.

[24] YE, CH.-CH., ZHAO, F.-Y., WU, J.-K., WENG, X.-D., ZHENG, P.-Y., MI, Y.-F., AN Q.-F., GAO C.-J. Sulfated polyelectrolyte complex nanoparticles structured nanoflitration membrane for dye desalination. *Chem. Eng. J.*, 2017, 307, 526–536.

[25] ZHANG, H., LI, B., PAN, J., QI, Y., SHEN, J., GAO, C. Carboxyl-functionalized graphene oxide polyamide nanofiltration membrane for desalination of dye solutions containing monovalent salt. *J. Membr. Sci.*, 2017, 569, 128–137.

[26] KOYUNCU, I., TOPACIK, D. Effect of organic ion on the separation of salts by nanofiltration membranes. *Journal of Membrane Science*, 2002, 195, 247–263.

[27] HAMER, W.J., WU, Y.-CH. Osmotic Coefficients and Mean Activity Coeffitients of Uni-univalent Electrolytes in Water at 25°C. *Journal of Physical Chemistry*, 1972, 1, 1047–1100.

[28] URAMA, R.I., MARINAS, B.J. Mechanistic interpretation of solute permeation hrough a fully, aromatic polyamide reverse osmosis membrane. *Journal of Membrane Science*, 1997, 123, 267–280.

[29] PARK, N., KWON, B., SUN, M., AHN, H., KIM, Ch., KWOAK, Ch., LEE, D., CHAE, S., HYUNG, H., CHO, J. Application of various membranes to remove NOM typically occurring in Korea with respect to DBP, AOC and transport. *Desalination*, 2005, 178, 161–169.

[30] TAHAIKT, M., AIT HADDOU, A., EL HABBANI, R., AMOR, Z., ELHANNOUNI, F., TAKY, M., Kharif, M., Boughriba, A., Hafsi, M., Elmidaoui, A. Comparison of the performances of three commercial membranes in fluoride removal by nanofiltration. Continuous operations. *Desalination*, 2008, 225, 209–219.

[31] BARGEMAN, G., VOLLENBROEK, J.M., STRAATSMA, J., SCHROËN, C.G.P.H., BOOM, R.M. Nanofiltration of multi-component feeds. Interactions between neutral and charged components and their effect on retention. *Journal of Membrane Science*, 2005, 247, 11–20.

List of Students' Published works

Publications in journals with IF

CUHORKA, Jiří, MIKULÁŠEK, Petr. Performance evaluation of nanofiltration membranes for diafiltration of dyes solutions: Experimental observations and model evaluation. *Desalination and Water Treatment*, 2010, vol. 16, no. 1-3, s. 110–119. ISSN 1944-3994.

MIKULÁŠEK, Petr, CUHORKA, Jiří. Nanofiltration in the manufacture of liquid dyes production. *Water Science and Technology*, 2010, vol. 61, no. 7, s. 1865–1873. ISSN 0273-1223.

GHERASIM, Cristina-Veronica, CUHORKA, Jiří, MIKULÁŠEK, Petr. Analysis of lead(II) retention from single salt and binary aqueous solutions by a polyamide nanofiltration membrane: Experimental results and modelling. *Journal of Membrane Science*, 2013, Vol. 436, s. 132–144. ISSN 0376-7388.

MIKULÁŠEK, Petr, CUHORKA, Jiří. Desalination and concentration of liquid dyes by nanofiltration. *Desalination and Water Treatment*, 2015, vol. 55, no. 10, s. 2711–2720. ISSN 1944-3994.

MIKULÁŠEK, Petr, CUHORKA, Jiří. Removal of Heavy Metal Ions from Aqueous Solutions by Nanofiltration. *Chemical Engineering Transactions*, 2016, Vol. 47, s. 379–384. ISSN 2283-9216

KOČANOVÁ, Veronika, CUHORKA, Jiří, DUŠEK, Libor, MIKULÁŠEK, Petr Application of nanofiltration for removal of zinc from industrial wastewater. *Desalination and Water Treatment*, 2017, vol. 75, s. 342–347. ISSN 1944-3994.

Publications in other scientific reviewed journals

CUHORKA, Jiří, MIKULÁŠEK, Petr, CHÝLKOVÁ, Jaromíra, ŠKORVAN, Ondřej. Application of Membrane Processes for the Separation of Hydrocarbons from Wastewater. *Scientific Papers of the University of Pardubice*, Series A, Faculty of Chemical Technology, 2012, vol. 18, pp. 141–155. ISSN 1211-5541.

ŠPINOVÁ, Michaela, CHÝLKOVÁ, Jaromíra, CUHORKA, Jiří. Evaluation of Functional Efficiency of Plant for Biological Treatment of Wastewater from University Hospital. In *Recent Advances in Environmental Science*. WSEAS Press, 2013, pp. 98–103. ISBN 978-1-61804-167-8.

CHÝLKOVÁ, Jaromíra, CUHORKA, Jiří, MIKULÁŠEK, Petr. Spectrophotometric Monitoring of Petroleum Products Removal from Wastewater by Using Pressure Driven Membrane Processes. In *Recent Advances in Environmental Science*. WSEAS Press, 2013, pp. 93–97. ISBN 978-1-61804-167-8.

MIKULÁŠEK, Petr, CUHORKA, Jiří, PALATÝ, Zdeněk, CHÝLKOVÁ, Jaromíra, ŠKORVAN, Ondřej. Zpracování odpadní vody z myček automobilů tlakovými membránovými procesy. *CHEMagazin*, 2013, vol. 2, pp. 30–33. ISSN 1210-7409.

CHÝLKOVÁ, Jaromíra, CUHORKA, Jiří, MIKULÁŠEK, Petr. The effect of surfactants upon spectrophotometric monitoring of the efficiency of removal of crude petroleum products from waste water by means of pressure-driven membrane processes. *WSEAS Transactions on Environment and Development*, 2014, vol. 10, no. 2014, pp. 60–70. ISSN 1790-5079.

WALLACE, Edvin, CUHORKA, Jiří, MIKULÁŠEK, Petr. Investigation of the Structural and Charge Properties of a Polyamide Nanofiltration Membrane. *Scientific Papers of the University of Pardubice*, Series A, Faculty of Chemical Technology, 2017, vol. 23, pp. 225–243. ISSN 1211-5541.

CUHORKA, Jiří, KAŠPAROVÁ, Markéta, MIKULÁŠEK, Petr. Odstraňování reziduí léčiv z vodných roztoků pomocí nanofiltrace. *Waste Forum*, České ekologické manažerské centrum, 2018, vol. 2, pp. 225–234. ISSN 1804-0195.

Monographs and selected chapters

MIKULÁŠEK, Petr, CUHORKA, Jiří. Chapter 19. Nanofiltration Used for Desalination and Concentration in the Manufacture of Liquid Dyes Production. In *Expanding Issues in Desalination*. 1. vyd. Rijeka: InTech, 2011, pp. 379–394. ISBN 978-953-307-624-9.

MIKULÁŠEK, Petr, CUHORKA, Jiří. Chapter 7. Nanofiltration Process Efficiency in Liquid Dyes Desalination. In *Advancing Desalination*. 1. vyd. Rijeka: InTech, 2012, pp. 137–162. ISBN 978-953-51-0704-0.

MIKULÁŠEK, Petr, CUHORKA, Jiří. Chapter 12. Application of nanofibrous membranes and their suitability for membrane bioreactor processes in wastewater treatment. *Fibrous Filter Media* (The Textile Institute Book Series), Edited by Philip J. Brown and Christopher L. Cox, Elsevier Ltd., Kidlington, UK, 2017, pp. 275–290. ISBN 978-0-08-100573-6.

MIKULÁŠEK, Petr, CUHORKA, Jiří, DOLEČEK, Petr. Chapter 2. Nanofiltration Used for Desalination in the Liquid Dye Production. *Nanofiltration: Applications, Advancements and Research*, Edited by Donald E. Hamilton, Nova Science Publishers, Inc., New York, USA, 2017, pp. 21–49. ISBN 978-1-53611-952-7.

Contributions presented at international scientific conferences

CUHORKA, Jiří, MIKULÁŠEK, Petr. Desalination of dyes solutions by nanofiltration. Proceedings of *36th International Conference of Slovak Society of Chemical Engineering*, Tatranské Matliare, Slovakia 2009.

CUHORKA, Jiří, MIKULÁŠEK, Petr. Evaluation of nanofiltration for diafiltration of dyes solutions: Experimental observations and model verification. *Membrane Science and Technology Conference of Visegrad Countries, PERMEA 2009*, Prague, Czech Republic 2009.

MIKULÁŠEK, Petr, CUHORKA, Jiří. Performance evaluation of nanofiltration membranes for diafiltration of dye/salt mixtures: Experimental observations and model verification. *EUROMEMBRANE 2009 Conference*, Montpellier, France 2009.

CUHORKA, Jiří, MIKULÁŠEK, Petr. Semi-batch diafiltration of reactive dyes solutions. In *Proceedings of the 5th Membrane Science and Technology Conference PERMEA 2010*. Bratislava: Slovenská spoločnosť chemického inžinierstva, 2010, pp. 323–335. ISBN 978-80-227-3339-7.

CUHORKA, Jiří, MIKULÁŠEK, Petr. Comparison of NF membranes for desalination purpose and modelling of semi-batch diafiltration. In *Proceedings of the 19th International Congress of Chemical and Process Engineering*. Praha: Česká společnost chemického inženýrství, 2010, pp. 1–13. ISBN 978-80-02-02250-3.

MIKULÁŠEK, Petr, CUHORKA, Jiří, CHÝLKOVÁ, Jaromíra, ŠKORVAN, Ondřej. The use of crossflow ultrafiltration in the separation of hydrocarbons wastewater. *1st International Conference on Desalination using Membrane Technology* (MEMDES 2013), Sitges, Španělsko 2013.

MIKULÁŠEK, Petr, CUHORKA, Jiří, CHÝLKOVÁ, Jaromíra, PALATÝ, Zdeněk, ŠKORVAN, Ondřej. Investigation of pressure driven membrane processes for treatment of emulsified oily wastewater from car washes. Proceedings book of "*The 6th Membrane Conference of Visegrad Countries – PERMEA 2013*", Warsaw, Poland 2013, pp. 190–198. ISBN 978-83-7789-227-5.

MIKULÁŠEK, Petr, CUHORKA, Jiří. Desalination and concentration of liquid dyes by nanofiltration. International Conference „*Desalination for the Environment, Clean Water and Energy*“, 11. – 15. May 2014, Limassol, Cyprus.

KOČANOVÁ, Veronika, CUHORKA, Jiří, DUŠEK, Libor, MIKULÁŠEK, Petr. Removal of zinc from aqueous solutions by nanofiltration. In *XXXII. European membrane society summer school 2015 "Integrated and Electromembrane Processes"*. September 6–10, Česká Lípa: Česká membránová platforma (CZEMP), 2015, pp. 18. ISBN 978-80-904517-3-5.

MIKULÁŠEK, Petr, CUHORKA, Jiří. Partial desalination and concentration of liquid dyes by nanofiltration combined with diafiltration. *International Conference „EUROMEMBRANE 2015“,* Aachen, 2015.

KOČANOVÁ, Veronika, CUHORKA, Jiří, DUŠEK, Libor, MIKULÁŠEK, Petr. Application of nanofiltration for removal of zinc from industrial wastewater. Proceedings of *International Conference on Membrane Processes,* PERMEA/MELPRO 2016, 15–19 May 2016, Prague, Czech Republic, pp. 173/1–173/14. ISBN 978-80-904517-6-6.

WALLACE, Edwin, CUHORKA, Jiří, MIKULÁŠEK, Petr. Influence of operating parameters on the rejection of zinc ions from aqueous solution by a nanofiltration polyamide membrane. In *44th International Conference of the Slovak Society of Chemical Engineering*, Demänovská dolina, 2017, pp. 6–15. ISBN 978-80-89597-58-1.

CUHORKA, Jiří, MIKULÁŠEK, Petr. The comparison of commercial spiral wound nanofiltration membranes for desalination and concentration of liquid dye. International Conference *Desalination Using Membrane Technology*, Las Palmas, 2017.

KOČANOVÁ, Veronika, CUHORKA, Jiří, DUŠEK, Libor, MIKULÁŠEK, Petr, NOVOTNÝ, Ladislav. Combined electrodeposition and nanofiltration for removal of zinc from model industrial wastewater. 34th EMS Summer School 2017, *Membranes in Biorefineries,* June 26–30, 2017, Lund, Sweden, book of abstracts, pp. 73–74.

WALLACE, Edwin, CUHORKA, Jiří, MIKULÁŠEK, Petr. Interpretation of Structure and Electrical Properties of a Polyamide Nanofiltration Membrane. NANOCON 2017: *9th International Conference on Nanomaterials - research & application,* October 18th-20th 2017, Hotel Voroněž I, Brno, Czech Republic. Proceedings of abstracts. Ostrava: Tanger, 2017, pp. 157. ISBN 978-80-87294-78-9.

KOČANOVÁ, Veronika, CUHORKA, Jiří, DUŠEK, Libor, MIKULÁŠEK, Petr, NOVOTNÝ, Ladislav. Combined electrodeposition and nanofiltration for removal of zinc from industrial wastewater. *International Conference on Membrane Processes „MELPRO 2018“*, Prague, Czech Republic, 2018, pp. 179. ISBN 978-80-906831-2-9.

WALLACE, Edwin, CUHORKA, Jiří, MIKULÁŠEK, Petr. Characterization of nanofiltration membrane and its application for the separation of heavy metals from wastewater. *International Conference on Membrane Processes „MELPRO 2018“*, Prague, Czech Republic, 2018, pp. 128. ISBN 978-80-906831-2-9.

WALLACE, Edwin, CUHORKA, Jiří, MIKULÁŠEK, Petr. Characterization of nanofiltration membrane and its application practical use for the separation of zinc from wastewater. In *45th International Conference of the Slovak Society of Chemical Engineering*, Tatranské Matliare, 2018, pp. 146. ISBN 978-80-89597-89-5.

MIKULÁŠEK, Petr, CUHORKA, Jiří. Removal of heavy metal ions from aqueous solutions by nanofiltration. *International Conference „EUROMEMBRANE 2018“,* Valencia, 2018.

Contributions presented at national scientific conferences

KOČANOVÁ, Veronika, CUHORKA, Jiří, DUŠEK, Libor, MIKULÁŠEK, Petr. Use of nanofiltration to remove zinc from wastewater. In *Membranes and Membrane Processes*. Česká Lípa: Česká membránová platforma (CZEMP), 2015, pp. 31. ISBN 978-80-904517-4-2.

WALLACE, Edwin, CUHORKA, Jiří, MIKULÁŠEK, Petr. Investigation of the structural properties of polyamide nanofiltration membrane. Proceedings of Workshop of Students‘ Presentations 2016 „*Membranes and Membrane Processes*“, 12th October 2016, Straz pod Ralskem, Czech Republic, pp. 26/1–26/13. ISBN 978-80-904517-8-0.

KOČANOVÁ, Veronika, CUHORKA, Jiří, DUŠEK, Libor, MIKULÁŠEK, Petr. Využití membránových procesů k odstraňování těžkých kovů z průmyslových odpadních vod. 44. ročník konference *Průmyslová toxikologie a ekotoxikologie 2017,* Kouty nad Desnou, 3. – 5. 5. 2017, sborník, pp. 26–27. ISBN 978-80-7560-046-2.

CUHORKA, Jiří, MIKULÁŠEK, Petr. Porovnání nanofiltračních spirálově vinutých modulů pro odsolování organických barviv. Konference “*Membránové procesy pro udržitelný rozvoj – MEMPUR 2017*”, 29. 5. – 1. 6. 2017, Pardubice, sborník abstraktů, pp. 44. ISBN 978-80-904517-9-7.

KOČANOVÁ, Veronika, CUHORKA, Jiří, DUŠEK, Libor, MIKULÁŠEK, Petr. Využití nanofiltrace pro odstraňování zinku z průmyslových odpadních vod. Konference „*Membránové procesy pro udržitelný rozvoj – MEMPUR 2017*", 29. 5. – 1. 6. 2017, Pardubice, sborník abstraktů, pp. 45. ISBN 978-80-904517-9-7.

WALLACE, Edwin, CUHORKA, Jiří, MIKULÁŠEK, Petr. Investigation of Zinc (II) retention from aqueous solution by a polyamide nanofiltration membrane: Experimental results and modelling. Konference „*Membránové procesy pro udržitelný rozvoj – MEMPUR 2017*", 29. 5. – 1. 6. 2017, Pardubice, sborník abstraktů, pp. 83. ISBN 978-80-904517-9-7.

KOČANOVÁ, Veronika, CUHORKA, Jiří, DUŠEK, Libor, MIKULÁŠEK, Petr. Removal of Zinc from Industrial Wastewater by a Polyamide Nanofiltration Membrane. Proceedings of Workshop of Students‘ Presentations 2017 „*Membranes and Membrane Processes*“, 18th October 2017, Straz pod Ralskem, Czech Republic, pp. 48/1–48/6. ISBN 978-80-906831-0-5.

WALLACE, Edwin, CUHORKA, Jiří, MIKULÁŠEK, Petr. Characterization of a Polyamide Nanofiltration Membrane. Proceedings of Workshop of Students‘ Presentations 2017 „*Membranes and Membrane Processes*“, 18th October 2017, Straz pod Ralskem, Czech Republic, pp. 47/1–47/11. ISBN 978-80-906831-0-5.

Projects

Research team member, project TA01020730 „*Separace uhlovodíků z vod a sledování jejich kvality*“ (main solver: prof. Ing. Petr Mikulášek, CSc., Univerzita Pardubice, co-solver: ASIO, spol. s r.o.), 2011–2013.

Contract research

CUHORKA, Jiří, MIKULÁŠEK, Petr. Provedení testů RO dělení směsi triethylenglykolu a vody. ATEKO Hradec Králové, 2012.

MIKULÁŠEK, Petr, CUHORKA, Jiří. Diafiltrace a frakcionace polymerních disperzí. SYNPO, a.s. Pardubice, 20 pp., 2013.

MIKULÁŠEK, Petr, CUHORKA, Jiří. Provedení testů separačních vlastností nanovlákenných membrán. NAFIGATE Corporation, a.s., Praha, 2014–2015.

SLEZÁK, Miloslav, KREJČOVÁ, Anna, CUHORKA, Jiří. Zjištění příčin snížení účinnosti absorbéru. KYB Manufacturing Czech s.r.o., Staré Čívice, 61 pp., 2016.