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Theses of the Ph.D. dissertation entitled

**Membrane Operations in the Green Technology:
Solvent Recovery and Process Water Treatment**

submitted by

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1 INTRODUCTION

During the last decades, the need for environmentally-consciousness and the establishment of sustainable practices have become guiding principles in the milieu of chemical engineering. However, the greening of the chemical industry is a long-lasting process; and the production technologies cannot be changed dramatically in a short term, so the attention is focused on the treatment of wastes until integrated pollution prevention is not completed in wide-range of the industry.

Therefore, the application of green and clean technologies in waste treatment is playing a great role. Recently, the chemical industry is a growing field in the application of membranes as green and clean technologies, which, however often requires membrane materials with exceptional stability. Membranes have gained an important place in chemical technology and are used in a broad range of applications.

In the last few decades the use of membrane technology has grown significantly also in wastewater treatment. Nanofiltration and reverse osmosis can be also considered as the state of the art in wastewater treatment. In case of process water treatment e.g. dehydration of water containing solvents, pervaporation can offer a good solution.

When designing environmentally-conscious processes, the mass transport and separation efficiency are required to know. In engineering calculations mainly simple and experimental-based models are used. The design alternatives should be evaluated according to how they meet environmental targets, which requires the knowledge of transport models, too. To realise such design action, however, experiments are recommended to be carried out, which gives basic information to the semi-empirical models.

2 AIMS OF THE WORK

The aims of the present work can be classified into three groups:

I. Study the membrane pervaporation process as a green technology: whether it is suitable for the treatment of organic solvents. I study the applicability of pervaporation for the dehydration of isopropanol-water mixtures. The concentration of the test solutions are selected according to existing industrial needs. After the experimental work I study the modified solution-diffusion model of Rautenbach, which has been verified for the pervaporation of ethanol-water mixtures, whether it is suitable for modelling the pervaporation of isopropanol-water mixtures. The experimental results are applied for the determination of model parameters. The measured data are then compared to model values. The simulated results are also tested on industrial data.

II. The second aim of my work is to study the applicability of nanofiltration and reverse osmosis for the treatment of metal ion-containing test process waters and model the experimental results using two different models and implement the planning of experiments into the practice of membrane investigation. I study, whether nanofiltration and reverse osmosis can be modelled using the models mentioned. The objective of this aim is to determine the parameters which have influence on the fouling resistance included in the modified osmotic pressure model and to obtain the relationship between them.

III. The wide variety of industrial processes makes the arising wastewaters and process waters multifarious. Membrane separation processes can offer environmental friendly treatment methods for the arising waste- and process waters, but the question to be answered is whether the membranes are applicable for all types of waters. Therefore, I study the applicability of membranes at extremely different conditions on a bench-scale continuous flow apparatus. Beside that a case-study is performed,

aiming to design a novel hybrid treatment method for the treatment of a given wastewater from pharmaceutical industry and to prove that membranes can be applied as a part of hybrid treatment processes.

3 EXPERIMENTAL (DEVICES AND METHODS)

The pervaporation (PV), nanofiltration (NF) and reverse osmosis (RO) experiments are carried out on a laboratory-scale universal test membrane apparatus (CM-CELFA Membrantechnik AG P-28). Experiments for the applicability study are carried out on a continuous-flow test membrane apparatus (3 DTA, Uwatech Ltd.). When studying the treatment of real wastewaters with hybrid processes, bench-scale rectification column with 14 theoretical plates and conventional filtration are applied beside the universal test membrane apparatus.

The analytical methods applied are as follows: gas chromatography (Shimadzu GC-14B), Karl-Fischer titration, atomic absorption (Perkin Elmer 3100), COD measurement according to $K_2Cr_2O_7$ standard method, pH, conductivity (WTW 340i pH/conductivity meter) and viscosity (Hoeppler viscosimeter).

For the modelling of the PV experiments the modified¹ Rautenbach² model (based on the principle of solution-diffusion) is applied. The model parameters are fitted to the experimental data using the GAMS software. MS Excel is also applied for the parameter fitting. The model parameters then typed into the pervaporation module of ChemCAD simulation software, with which the experimental data and industrial pervaporation can be simulated.

¹ Mizsey, P., K. Koczka, A. Deák, and Z. Fonyó, *Simulation of Pervaporation with the "Solution-Diffusion" model*. Hungarian Chemical Journal, 2005. 7: p. 239-242.

² Rautenbach, R., C. Herion, and U. Meyer-Blumenroth, *Chapter 3. Pervaporation Membrane Separation Processes*. Membrane Science and Technology Series, ed. **R.Y.M. Huang**. Vol. 1. 1991, Amsterdam: Elsevier.

In case of modelling the NF and RO experiments two models: the solution-diffusion (SD) model³ and the resistances in series (RS) models⁴ are applied. The SD model contains the parameters of the filtration which change in the function of yield in case of batch filtration. Describing the relationship between these parameters in the function of yield, the constants of the equation are fitted to the experimental data using the STATISTICA software.

A simplification of the RS model is accomplished. For the derivation of the introduced term of “fouling resistance” dimensional analysis is applied. The other parameters of the RS model are fitted to experimental data using the STATISTICA Software. Modelling of NF and RO is accomplished in MS Excel.

4 MAJOR NEW RESULTS

1.1 Pervaporation of isopropanol-water solutions; performing the dehydration of organic solvents

The dehydration of isopropanol-water mixtures by PV is performed, and the experimental data are used in parameter fitting of the SD model. The parameter fitting is carried out using the GAMS software as well as MS Excel. The different parameters of both methods are applied for modelling. Modelled and measured data are compared. It is found that the model, which contains the parameters fitted by GAMS is in better agreement with the measured data than that of the MS Excel. Therefore the parameters fitted by GAMS are applied in ChemCAD simulation software in order to verify the applicability of the model. Since the simulated permeate fluxes are in good agreement with the measurements, the simulation of an existing industrial hybrid system (distillation followed by pervaporation) is accomplished.

³ Baker, W.R., *Membrane Technology and Applications*. 2004, Menlo Park, California: Wiley.

⁴ Schäfer, A.L., A.G. Fane, and T.D. Waite, *Principles and Applications*. 2005, Amsterdam.

Thesis 1) I determined the parameters of the improved Rautenbach model for the pervaporation of isopropanol-water mixtures. I pointed out that the permeability coefficient of the membrane is similar to that of ethanol-water mixture. Such a similarity can make the parameter estimation simpler.

I detected that for engineering considerations the parameters are valid for the modelling of the pervaporation of isopropanol-water system if the isopropanol concentration is higher than 80 wt%.

I also verified the applicability of the parameters in a professional flowsheeting software environment (ChemCAD), and the data obtained were in good agreement with industrial data. [3]

1.2 Component transport through nanofiltration and reverse osmosis membranes: modelling the transport of test solutions representing process-waters; the basics of model-are aided to design of membrane filtration

Nanofiltration and reverse osmosis of metal ion (copper, iron and nickel) containing test solutions are investigated on a bench-scale test membrane apparatus in batch mode. The experiments are carried out using a 2^p-type experimental plan. The permeate fluxes are modelled using two different models. The modelling is performed in the function of yield in both cases.

In case of the SD model the yield-dependant terms are evaluated, and the required constants of the functions are determined with the help of STATISTICA software. These are implemented into the SD model. The SD model states that since the rejection of solutes are not 100%, both the fluxes of water and solutes (ions) are needed to be taken into account. The water flux calculation needs the product of diffusion and sorption coefficient of water ($D_w \cdot K_w$), which is determined with distilled water experiments. The applicability of the assumption

of Baker3 recommending that $D_s \cdot K_s / D_w \cdot K_w = 1/10$ is studied. I derive equations to model the salt flux in another way. I determine the value of the $D_s \cdot K_s / D_w \cdot K_w$ ratio in my experiments. The measured and modelled fluxes are then compared.

The modelling of the permeate fluxes of the same NF and RO experiments of metal ion-containing solutions is accomplished using the simplified RS model as well. The simplification of the RS model is that I introduce the so called fouling resistance characterising the different resistances arising during operation in one term. The equation of fouling resistance is derived by dimensional analysis. It is verified that among others the hydrated ionic diameter influences the value of the fouling resistance. The constants of yield-dependant parameters in the RS model are fitted to the experimental data with the STATISTICA software. The measured and modelled fluxes are compared. The comparison of the two modelled fluxes is also done, and it is concluded that the simplified RS model is in better agreement with the measured fluxes than that of the SD model.

Thesis 2) I successfully extended the application of the solution-diffusion model recommended by Baker for the modelling of nanofiltration and reverse osmosis of different metal (copper, iron, nickel) salt solutions in batch operation. I determined the necessary constants and coefficients of the model on experimental basis. I carried out my experiments according to 2^p -type experimental plans. I derived the ratio of product of diffusion and sorption coefficients of salt and water. I determined that for dilute solutions (equal to or less than 2 kg/m^3) its value is 45-50. (See Eq.1.)

$$\frac{D_w K_w}{D_s K_s} = \frac{\rho_p - c_{s,0} \cdot (1 - R)}{c_{w,0} \cdot (1 - R)} \cdot \frac{1 - \exp\left(\frac{-v_s \cdot \Delta p}{R T}\right)}{1 - \exp\left(\frac{-v_w \cdot (\Delta p - \Delta \pi)}{R T}\right)} \cong 45 - 50 \quad (\text{Eq.1.})$$

where D is the diffusion coefficient in the membrane [m^2/s], K is the sorption coefficient [-], ρ is the density [kg/m^3], c is concentration [kg/m^3], R is rejection [-], v is molar volume [m^3/mol], Δp is the transmembrane pressure [Pa], \mathfrak{R} is the universal gas constant [=8.314 J/(K·mol)], T is temperature [K], $\Delta\pi$ is the osmotic pressure difference between the feed and permeate side of the membrane [Pa], index w stands for water, s for salt, p for permeate, and 0 for initial state.

However, since this ratio depends on the salt concentration the ratio of 10 recommended by Baker can be applied in a wide, higher concentration range. My measurements and calculation proves that this assumption can be also well applied for dilute solution [1, 2] but the exact value I derived is more accurate.

Thesis 3) I simplified and then successfully applied the resistances in series model for the same membrane filtration problems, described in point 2. I introduced the fouling resistance what I derived on dimensional analysis basis. I proved that the hydrated ionic diameter affects the fouling resistance. I determined that the resistances in series model is more accurate for the modelling of membrane filtration than the solution-diffusion model. [1, 2]

The simplified resistances in series model is as follows (Eq.2.):

$$J_p = \frac{\Delta p - \Delta \pi}{\eta \cdot (R_m + R_f)} \quad (\text{Eq.2.})$$

where J_p is volumetric permeate flux [$\text{m}^3/(\text{m}^2\cdot\text{s})$], Δp is the transmembrane pressure [Pa], $\Delta\pi$ is the osmotic pressure difference between the feed and permeate side of the membrane, η is the dynamic viscosity of permeate [Pa·s], R_m is the membrane resistance [1/m], R_f is the fouling resistance [1/m].

The equation of R_f , that I derived by dimensional analysis is as follows (Eq.3.):

$$R_f = \left(\frac{V_P}{V_F} \right)^a \left(\frac{c_0 \cdot \mathfrak{R} \cdot T}{p} \right)^e \cdot \frac{1}{d_h} \cdot \left(\frac{v \cdot d_h}{v_f} \right)^i \cdot \left(\frac{g \cdot d_h^3}{v_f^2} \right)^j \quad (\text{Eq.3.})$$

where V_P is the volume of permeate [m³], V_F is the volume of feed [m³], c_0 is the initial concentration [mol/m³], \mathfrak{R} is the universal gas constant [=8.314 J/(K·mol)], T is temperature [K], p is the transmembrane pressure [Pa], d_h is the hydrated ionic diameter [m], v is the flow velocity above the membrane surface [m/s], v_f is the kinematic viscosity [m²/s], g is gravity [m/s²], powers a , e , i and j are empirical constants.

Taking into consideration, that the hydrated ionic diameter expressed in SI is in 10⁻¹² order of magnitude, that is taken to the power of three results in a very small number. In spite of the division by the kinetic viscosity, which in the range of 10⁻⁶, the result is at the highest in the range of 10⁻¹⁵. Therefore it is obvious to merge the fourth and fifth terms of Eq.3. into a constant. The equation of R_f derived is simplified as follows:

$$R_f = B \cdot \left(\frac{V_P}{V_F} \right)^a \left(\frac{c_0 \cdot \mathfrak{R} \cdot T}{\Delta p} \right)^e \cdot \frac{1}{d_h} \quad (\text{Eq.4.})$$

where B [-] is a constant. The powers a and e , and B have to be determined by experiments.

1.3 Applicability study of membranes as a part of a process water treating novel hybrid method and at extremely different conditions

Since the treatment of test mixtures and solutions are performed with success, the question to be answered is whether the membranes can actually be applied for the treatment of real waste and/or process waters. Therefore an applicability study is carried out using wastewaters of different origins and of different compositions. The exact compositions of the waters are not known, so the chemical oxygen demand (COD) is applied instead. One-step filtration (NF or RO) experiments pointed out that the required emission limits can not be reached, so two-step filtration (NF followed by RO) are carried out. In case of the dumpsite leachate treatment the two-step filtration is appropriate, but in case of the wastewater from pharmaceutical industry it isn't enough.

It is also studied whether membrane filtration can be combined with other treatment methods. In case of a given pharmaceutical wastewater a hybrid process (containing membrane filtration) is designed and applied with success.

Thesis 4) I determined the wide-range-applicability of membrane filtration for the wastewater treatment to reduce the chemical oxygen demand. I recommended a two-step-filtration process (nanofiltration followed by reverse osmosis) for the dumpsite leachate treatment. Such a process proved to be successful for the necessary treatment. [4]

On the other hand, in case of a real pharmaceutical wastewater such a two-step-procedure could reduce the chemical oxygen demand to the 6% of the initial value but this reduction was still not enough for possible emission. Therefore I recommended a three-step-membrane filtration.

I developed a novel hybrid separation process for the treatment of process water of pharmaceutical origin. The process consists of conventional filtration, rectification and membrane filtration. [6, 14]

5 APPLICABILITY OF THE RESULTS

In spite that my thesis work belongs mainly to the field of fundamental research; my results can help engineers to orient on the emerging field of environmental conscious process engineering.

The laboratory-scale experimental data with modelling are crucial part of industrial-scale plan design. In chemical engineering, the transport models are usually based on empirical equations, so bench-scale experiments are the elementary steps to determine the parameters of the transport models. These parameters could be applied then in novel separation processes.

My studies on pervaporation of isopropanol-water mixtures are taken into consideration in the pervaporation of ternary mixtures, including also isopropanol. That scientific paper is under review now. Moreover, my results prove that the parameters obtained describe the industrial pervaporation separation process of iso-propanol-water. On the other hand, the pervaporation module applied on the ChemCAD environment enables design engineers to make rigorous separations of such separation systems.

Simplification of transport models makes the modelling easier, and simpler. It is important, however, that a simple model should contain well-defined terms. The dimensional analysis, which I used for the derivation of fouling resistance in the simplified model, verifies that the simplified model of resistances in series model is adequate. This simplified model gives a help to engineers for the design of separation process based on membrane filtration.

The applicability study points out, that membranes can be applied in a large-scale of wastewater treatment. These research results may assist stakeholders to choose membrane separation processes as clean technology, or membranes technology as a part of hybrid separation process in waste and process water treatment.

6 PUBLICATIONS

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