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Industrial wastewater treatment by membrane filtration and pervaporation

PhD thesis

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1. INTRODUCTION

Nowadays one of the most important questions is the protection of natural water and water supplies. The water is necessary for human life, for the fauna and flora, and also needed for industrial production processes. The water requirement increases because of the population growth, the enlargement of cultural, social and hygiene demands and because of the industrial development. In the time of the appearance of humanity the amount of clean water was limitless. The requirement of quality and quantity of water was intensified parallel to civilization and the water supplies were contaminated step by step.

Foulness of natural water is generated by industries among them by the food industry. The effects of the chemicalization of agriculture are not to be despised, too. The problem of treating of domestic wastewater containing synthetic detergent gets larger. The ruination of water-quality caused by wasting of natural water supplies and by contamination of wastewater not treated.

All the fields of industry and agriculture should solve the problems of the little supply and of growing water-demand. One of the solution is the wastewater treatment and this recycle to the industrial pocess. Reusing of wastewater of food industry was furthered by acts of regulation of contaminations. It was established that the most effective and most economic way to accomplish the requirements is treating and reusing of wastewater, finally the less emissions. Spreading of application of membrane techniques plays dominant part in reusing of outlet water of food industry.

2. Purposes

The purpose of this work was to investigate membranes and membrane processes that can separate organic and inorganic substances efficiently from industrial wastewater and are suitable for environmental protection, and also can be economical. In my works I examined the applicability of membrane separation systems, the concentration of wastewater that should be suited to environmental regulations and could be led into biological sewage farm or into water of rivers. Some of separated substrates could be reused. The main objectives of my investigations were to determine the optimal operating parameters of several apparatus, to analyse costs of industrial scale unit, to minimize the investment and operation costs.

Experimental work was executed to attain the objectives as follows:

<u>In the case of model solutions</u>

- Separation of model solutions (methanol-water, ethanol-water and isopropanol-water) in laboratory scale pervaporation unit with different pervaporation membranes.
- Investigation of the effect of temperature on the factors of separation (permeate flux, separation coefficient, separation index).

- Comparison of separation properties of organophillic membranes.
- Separation of ethanol/salt-water mixture by pervaporation, investigation of effects of temperature and salt (NaCl) concentration on factors of separation (permeate flux, separation coefficient, pervaporation separation index).

<u>In case of industrial/food industrial waste water</u>

Examination of wastewater containing ethanol and salts:

- Separation of ethanol/salt from wastewater by laboratory scale pervaporation unit, investigation of effects of operation parameters.
- Comparison of parameters of separation in case of wastewater and in case of ethanol-water model solution.

Examination of wastewater containing methanol and salts:

- Application of nanofiltration for separation of methanol and salt components from wastewater and determination of retention of metal ion and the flux of filtrate.
- Application of pervaporation for methanol removal from wastewater containing methanol and salt.
- Pervaporation of model solution (~20 % methanol conc.) for comparisons.
- Application of reverse osmosis for treating wastewater containing methanol and salt.

Examination of wastewater containingsalt and a litle oil:

- Application of reverse osmosis for reducing of COD value of wastewater containing salt and a little oil.
- Application of nanofiltration for reducing of COD value of wastewater containing salt and a little oil.

Examination of wastewater containing glucose polymer:

- Direct nanofiltration and nanofiltration after ultrafiltration pre-treatment of wastewater with glucose polymer content.
- Comparison of values of COD in both cases.
- Determination of gel concentration of the investigated wastewater.

Examination of wastewater containing salts and orgamic compounds:

- Application of nanofiltration to remove of salts from fermentation wastewater and to reduce COD.
- Application of reverse osmosis to remove salts from fermentation wastewater and to reduce COD.

<u>Modelling and optimization</u>

On the base of experimental results modelling and optimization were performed:

- Mathematical modelling of mass transfer of pervaporation membrane using „resistance in series" model and Arrhenius equation.
- Mathematical modelling of reverse osmosis. Establishment of a new mathematical model for modelling of osmotic pressure on the base of equations of van't Hoff and Rautenbach.
- Optimization by dynamic programming: determination of minimal costs of the complex procedure for wastewater treatment (reverse osmosis + evaporation).

3. MATERIALS AND METHODS

Investigated materials and membranes

Model solutions containing methanol, ethanol, isopropanol and salt were investigated. Experiments were carried out with wastewater containing salt and ethanol salt and methanol, salt and organic compounds, glucose polymer, and fermentation water with salt and organics. The applied membranes were as follows: pervaporation (type of SULZER-1060, CELFA-CMG-OM-010) nanofiltration (RA55, RA75, NP45, NF-200) reverse osmosis (RO-SW30HR) and ultrafiltration (UF-FP055A) membranes. Distilled water was applied to dilute alcohols into several concentrations.

Overview of materials and methods

Type of wastewater	Investigated membranes	Applied membrane techniques	Measured and calculated parameters
Alcohol-water mixtures: (Model solutions)	CMG-OM-010, SULZER-1060	Pervaporation	Flux of permeation, membrane selectivity, separation coefficient, activation energy, conc. of alcohol. Mathematical modelling.
Alcohol-water+salt mixtures: (Model solutions)	CMG-OM-010	Pervaporation	
Industrial wastewater cont. ethanol and salt from Chinoin Inc.	CMG-OM-010	Pervaporation	
Industrial wastewater containing methanol and salt from MOL Inc.	CMG-OM-010	Pervaporation	
	RA75 RA55 NP45	Nanofiltration	Flux of filtrate, rejection of metal ions and salts, Chemical oxygen demand, conc. of alcohol.
	SW30HR	Reverse osmosis	
Food industrial wastewater with two different constitution from Hidrofilt Ltd.	NF-200	Nanofiltration	Flux of filtrate, rejection of salts, Chemical oxygen demand.
	SW30HR	Reverse osmosis	
Food industrial wastewater containing glucose polymer from Hidrofilt Ltd.	UF-FPO55A	Ultrafiltration	Flux of filtrate, rejection of salts, Chemical oxygen demand, determination of dry matter conc. and gel concentration.
	NF-200	Nanofiltration	
Fermentation wastewater containing salt and organics from Chemitechnik Pharma Ltd.	RA55 RA75 NP45	Nanofiltration	Flux of filtrate, salt conc. of filtrate, rejection of metal ions and salts, Chemical oxygen demand, dry matter conc. Mathematical modelling of osmotic pressure and optimization with dynamic programming.
	SW30HR	Reverse osmosis + Evaporation	

4. NEW SCIENTIFIC RESULTS

I. Results of pervaporation by organophillic membranes with model solutions and wastewater

1. On the base of experimental results in laboratory scale equipment I determined the order of the fluxes (J) and separation coefficients (α) of an organophillic pervaporation membrane for isopropanol (IPA), ethanol (ETHA) and methanol (METHA). The order is as follows:
$J_{IPA} > J_{ETHA} > J_{METHA}$, and $\alpha_{IPA} > \alpha_{ETHA} > \alpha_{METHA}$.
The succession is inversely proportional with the Hildebrandt dissolving parameter – polarization: $H_{IPA} < H_{ETHA} < H_{METHA}$.

2. On the base of experiments on organophillic pervaporation membranes using model solutions it was established that the separation coefficient increased with an increase in temperature, unlike in cases of hydrophilic membranes.

Temperature (°C)	Pervaporation separation coefficient (α)					
	SULZER-1060 MEMBRANE			CELFA-CMG-OM-010 MEMBRANE		
	Methanol	Ethanol	Isopropanol	Methanol	Ethanol	Isopropanol
40	2,97	2,89	5,38	2,70	6,52	7,38
50	2,73	3,41	6,75	4,19	6,61	10,71
60	3,30	3,61	7,26	4,51	6,51	10,57
70	3,37	3,73	8,01	4,53	6,92	9,84

3. Investigations of the effect of ethanol concentration assured that an increase in the concentration increased the permeate flux and the separation coefficient. The value of the separation coefficient exceeded the relative volatility (**α_{G-F}**) when the ethanol concentration was higher than 9-13 %.

Ethanol concentration of the feed (%)	Ratio of the pervaporation separation coefficient (α) and the vapour-liquid separation coefficient (α_{G-F})			
	40 °C	50 °C	60 °C	70 °C
4,26	0,23	0,42	0,50	0,47
9,45	0,67	0,88	0,98	1,01
18,86	1,32	1,38	1,29	1,45
24,17	1,44	1,73	1,78	1,49

4. On the base of pervaporation researches with wastewater it was found that the separation coefficient of wastewater was higher than the that of similar model solutions (2,5-5 %). This effect was the consequence of the presence of salt, as it was verified by experiments with ethanol-water solution + salt. The next tables compares the data of model solution and wastewater with salt in the range of 2,5-5 % of ethanol concentration.

Temperature (°C)	Flux of permeate, J ($kg/(m^2h)$)		Separation coefficient (α)	
	Ethanol-water	Wastewater	Ethanol-water	Wastewater
40	0,27	0,28	1,83	2,78
50	0,55	0,47	3,58	3,34
60	0,81	0,93	3,56	5,74
70	1,68	1,34	5,29	6,92

NaCl concentration (%)	Separation coefficient of ethanol-water (α)			
	40 °C	50 °C	60 °C	70 °C
0	2,18	3,83	4,84	4,33
0,2	8,87	7,87	8,49	9,11
2	5,38	5,73	6,44	6,77
5	5,37	7,91	7,24	11,09

II. Results of membrane filtration with wastewater of food industry

The investigated membranes and their sources shown in the table:

Source	Investigated component
Chinoin Inc.	Ethanol and salt
MOL Inc.	Methanol and salt
Hidrofilt Ltd.	Salts, organic compounds
Hidrofilt Ltd.	Glucose polymer
Chemitechnik Ltd.	Salts, organic compounds

1. On the base of the experiments using wastewater with methanol and salt content the SW30HR reverse osmosis membrane was found efficient in removing salt from wastewater, while the methanol concentration was not changed, therefore the filtrate could be recycled into the technology.

2. Measurements with wastewater of food industry with different compositions (Hydromixt A and B) assured that the filtrate stream of reverse osmosis (RO-SW30HR) could be allowed into natural water apart from the concentration of pollutants of the feed, while the filtrate of nanofiltration (NF-200) could be allowed into public sewer or into natural water in case of low concentrations.

Membrane	Constitution A COD (mg/L)	Constitution B COD (mg/L)
RO- SW30HR	41	25
NF-200	370	93

The COD value of the fermentation wastewater could be decreased efficiently by reverse osmosis membrane (SW30HR), in optimal case (P= 60 bar, T = 30 °C) the filtration could be allowed into natural waters (COD = 115 mg O_2/L).

On the base of experiments of the membrane filtration of fermentation wastewater containing salt it was determined that the nanofiltration was inefficient, none of the filtrates could leave into the sewer because of the high salt concentration.

Concentration of the filtrate of nanofiltration Salt concentration limit: 2500 mg/L			
Parameters	Membranes		
	RA 75	**RA 55**	**RP 45**
Rejection of salt (R %)	27,54	48,15	67,66
Conc. of the filtrate (mg/L)	4112	2942	1822

3. On the base of my experiments with food industrial wastewater containing glucose polymer, the complex membrane filtration process can be recommended, because of the higher yield (much less volume of the retentate) than in nanofiltration process. After treating the wastewater of food industry containing glucose polymer by the complex method (UF+NF) the final filtrate (after nanofiltration step) could be allowed to natural water or could be recycled into the technology.

Chemical oxygen demand, COD (mg O_2/L)			
Sample	**Direct NF**	**Pre-filtration by UF**	**Treatment of UF-filtrate by NF**
		(complex treatment)	
Mean filtrate	136	1630	115
Retentate	11700	7510	12800
Original waste water	4490	5510	1630*

*filtrate of ultrafiltration

4. Gel concentration was determined in the case of the highest solidification of food industrial wastewater with glucose polymer content: 7,02 %.

III. Results of mathematical modelling and optimization

1. Modelling of pervaporation by the resistance in series model

Applying the resistance in series model it was realized that the mass transfer was determined by the membrane resistance in all cases of alcohol-water mixtures, while the hydrodynamic conditions have practically no effect in the investigated range (Re = 7000-14000). The order of the membrane resistances (the invert of the mass transfer coefficients) was as follows: $\frac{1}{Q_{MEM}^{IPA}} < \frac{1}{Q_{MEM}^{ETHA}} < \frac{1}{Q_{MEM}^{METHA}}$

Mass transfer coefficients of the SULZER-1060 membrane

Q_{MEM} [mol/(m^2 Pa·s)] 10^{-5}	**Methanol-water**	**Ethanol-water**	**Isopropanol-water**
	0,02	0,10	0,23

2. Activation energy of pervaporation

On the base of my experiments the activation energy of the investigated organophillic pervaporation membranes was determined applying the Arrhenius equation. It was found that the value of the activation energy depends on type of membranes, the chemical properties of mixtures and the concentration of the organic solvent.

	Activation energy of pervaporation membranes applying for separation of alcohols: E (kJ/mol)			
	in the range of 13-20% conc.		in the range of 2,5-5% concentration	
Alcohols	**SULZER-1060**	**CELFA CMG-OM-010**	**SULZER-1060**	**CELFA CMG-OM-010**
Methanol	54,75	52,62	58,37	63,96
Ethanol	37,76	39,92	55,11	58,48
Isopropanol	43,86	40,72	72,65	62,30

3. Effect of salt concentration on the activation energy

The activation energy of ethanol-water mixture with 5 % conc. of ethanol was determined with changing of salt concentration. In the case of low salt concentration the value of activation energy was lower than without salt, and then increased with an increase in salt concentration.

Salt concentration (%)	**Activation energy, E (kJ/mol)**
0	58,48
0,2	43,21
2	47,98
5	53,70

4. Modelling of membrane filtration with respect of osmotic pressure

A new model was established for membrane filtration of wastewater containing salt and quantified in case of fermentation waste water.

The recommended new osmotic pressure model is:

$\Delta\pi = 0{,}087 \cdot c_R^{0,24} \cdot T$, which was named H-R model.

where C_R [m/m %], T [K]

The mathematical model integrated the van't Hoff principle, expressing the linear correlation of the osmotic pressure and the temperature ($\Delta\pi \sim T$); and the Rautenbach equation, which shows a non-linear correlation between osmotic pressure and concentration ($\Delta\pi \sim c_R^n$).

Results of NaCl solution fitted to the van't Hoff model, the exponent of the new H-R model was less than 1 in the case of fermentation wastewater and fitted well to the measured values. With the value of $\Delta\pi$ the flux of wastewater could be calculated, so the new model is appropriate for design.

5. Optimization with dynamic programming

Two-step equipment was investigated for fermentation wastewater cleaning: first the wastewater was concentrated by reverse osmosis membrane (the cleaned water can be removed), than the retentate phase was concentrated further by evaporation to minimize the volume of wastes.

The optimum of the two-step system was studied by the method of dynamic programming to determine the final concentration of the reverse osmosis' product that ensures the minimal costs. Up-to-date economic data and correlations based on experiments were applied for calculations. For optimal operation of reverse osmosis 40 °C of temperature, 50 bar of pressure and the concentration until C_R = 6,60 m/m % assures the minimal total costs.

T (°C)	**ΔP_{TM} (bar)**	**X_1 (%)**	**C_{RO} (M Ft/year)**	**$C_{Evap.}$ (M Ft/year)**	**Total cost (M Ft/year)**
30	40	6,52	0,51	3,70	4,21
30	50	6,07	0,49	3,98	4,47
30	60	5,61	0,48	4,29	4,77
40	40	6,51	0,50	3,70	4,20
40	**50**	**6,60**	**0,46**	**3,56**	**4,02**
40	60	5,98	0,48	4,02	4,50
50	40	6,50	0,50	3,71	4,21
50	50	6,43	0,48	3,74	4,22
50	60	6,35	0,47	3,84	4,31

Calculations reflect the fact that although the investment cost of the reverse osmosis membrane unit amounts big part of total cost, the operating cost of evaporation is much higher than the reverse osmosis unit's. Applying reverse osmosis for concentration the highest possible value is recommended for lower costs of evaporation.

5. CONCLUSIONS AND PROPOSITIONS

I. Investigation of pervaporation of model solutions and industrial wastewater

The two investigated pervaporation membranes are suitable for removing alcohols for model solutions and industrial wastewater. The type of CELFA-CMG-OM-10 membrane is advisable for industrial application because of the high flux of permeate and high separation coefficient in the studied range. The established mathematical model based on experimental results gives chances:

- to design industrial scale equipment for treating the investigated wastewater (wastewater containing methanol, ethanol and salts),
- for cost estimation of the treatment of mixtures and wastewater containing the studied alcohols (isopropanol, ethanol, methanol),
- for optimizing the wastewater treatment by pervaporation and other processes (membrane filtration and evaporation)

The cleaned wastewater after pervaporation can be recycled into the technology or can be led into natural water. The pervaporation process makes an offer of direct recovering of organic compounds for reusing. The process is closed, continuous, has low investment costs and makes a decreasing in energy costs comparing with conventional possibilities.

II. Cleaning of industrial wastewater by membrane filtration

One-step or complex cleaning processes for wastewater treatment can be planned on the base of experiments with industrial and food industrial wastewater.

- Connection of reverse osmosis and evaporation is advisable for treating fermentation wastewater (wastewater containing salts and organic compounds). The complex method decreses the volume of the wastewater to 5 % of the feed (in case of optimal conditions). The cleaned water (approximately 95 % of the feed) can be recycled into the technology.

- The two-step cleaning process is advisable to treating of wastewater containing glucose polymer (wastewater with containing glucose polímer):
  - the first step can remove the suspended matter and macromolecules by ultrafiltration,
  - the following second step can carry on the cleaning of the wastewater by nanofiltration until high yield (90-95 %),
  - reusing of the concentrate in the technology and recycling or releasing the cleaned water (90 % of the amount of original wastewater) is feasible by the two-step cleaning process,
  - as a part of the industrial design optimization of the complex two-step process is advisable by dynamic programming.

- The investigated wastewater of food industry with different compositions (wastewater with containing salts and a little oil) can be concentrated by reverse osmosis and can be recycled or released (93-97 % of amount) into natural water depending on its concentration. Application of reverse osmosis is advisable.

- Pervaporation is effective for recovering of alcohols from wastewater (wastewater with containing methanol, ethanol and salts) containing beside the organic substrates (alcohols), salt and non-volatile organic components. The retentate of pervaporation contains salt non-volatile organic components and can be concentrated by membrane filtration (RO, NF). The cleaned water is recyclable. Cost analysis and cost comparison with the costs of biological cleaning is recommended before applying the technology.

6. PUBLICATIONS RELATED TO THE DISSERTATION

Articles published in international and national papers
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15. **Mora Molina J.,** Vatai Gy., Békássy-Molnár E. (2001): Cleaning of industrial waste water containing alcohol and salt by nanofiltration and pervaporation (In Hungarian: Alkohol- és sótartalmú ipari szennyvíz tisztítása nanoszűréssel és pervaporációval), *Annual Meeting on Technical Chemistry'01,* Proccedings p. 181.Veszprém, Hungary.

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