Ph.D. thesis

Reduced environmental load of wastewater and liquid by-products by membrane separation processes

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1. *INTRODUCTION*

The water quality protection has got more attention within the solutions of the global environmental problems in the last decade. The pure, drinkable water is a valuable treasure all over the world. Due to the decreasing supply of water and the contamination of water resources, all forms of water have to be protected. Very often, the high amount of harmful matters (for the life or environment) or their derivatives may get into the surface water and groundwater. Since the communal and industry wastewater treatment plants try to operate in water economic mode, the recirculation of second water and water cleaning procedure gained a great importance. The collection, diversion and the treatment of the wastewater coming from different manufacturer and customer places must be ensured for protecting human health and the environment. Nowadays, the environmental awareness has been in the spotlight, which introduces new requirements in the industry and wastewater practice. There are increasing demands of wastewater treatment technologies with higher quality, including energy saver and cheaper solutions, as well as cleaner technologies. In countries European Union (also in Hungary), more stringent environmental legislations require the decreasing the contamination of the wastewater during treatment before the final release. In different industrial wastewater treatment techniques, membrane separation processes have been widely used all over the world, due to perfect separation ability with environmentally sound effects. In membrane operation processes the use of chemicals can be decreased by choosing an appropriate membrane. In many industries the pressure-driven membrane processes, especially ultrafiltration (*UF*), nanofiltration (*NF*) and reverse osmosis (*RO*) are novel techniques and they have been widely used all over the world for purification of wastewater with different origin.

In this dissertation, I propose such membrane separation processes that decrease the environmental load of wastewater and liquid by-products. Due to the stringent environmental legislations pretreatments must be utilized before the use of membrane separation techniques. In some regions of Europe and Hungary, wastewater has high organic contents, which makes it problematic for release without further treatment.

In my experiments, I examined both synthetic and real wastewater samples and industry by-products in order to gain wide scientific knowledge about membrane separation process utilization in this field. I utilized the following feeds for membrane filtrations: synthetic wastewater with heavy metal content, dairy wastewater and by-product extract obtained from red currant press residuum. Dairy wastewater purification is of great importance, because milk has the highest amount of daily processed liquid food in Hungary.

Furthermore, I examined the efficiency of combining an advanced oxidation process and membrane filtration. The effects of ozone treatment and membrane filtration on the wastewater filterability and chemical oxygen demand (*COD*) and chemical oxygen demand (*BOD*) retentions were studied. Since the biggest problem of membrane processes is the fouling phenomena, different fouling decreasing techniques were analyzed. I also had the aim of examining the vibration effects on the changes of the flux, retention and specific energy demand values during *UF*, *NF* and *RO*. My goal was to find such effective membrane filtration processes for pilot application, which permeates are clean enough for the environmental threshold limits and using them the valuable liquid by-product components could be effectively concentrated. The industrial application requires proper equipment setups for beneficial operation. I performed economical calculations to prove efficient applications of membrane processes.

During my work, I performed the following tasks:

- Critical micelle concentration (*CMC*) values of synthetic solutions as a function of concentration and temperature were examined. It is well known that micelles are formed after a certain concentration in the detergent containing solutions. These micelles can trap the contamination molecules, which micelles can be kept in the retentate by an ultrafiltration membrane.
- I performed the analysis of the effects of temperature, transmembrane pressure, solution concentrations and membrane nominal molecular weight limit (*NMWL*) on the ultrafiltration parameters' (flux, retention and resistance values) change. I also analyzed the effects of pressure, temperature and detergent concentration on the values of the flux and retention during nanofiltration of detergent synthetic solutions.
- I examined food by-product extract concentration tests by nanofiltration and reverse osmosis membrane. I determined their resistance values and their ratio in order to compare the fouling of different membranes.
- I analyzed ozone treatment and nanofiltration as a hybrid separation process for decreasing organic load of dairy wastewater. To achieve this, I examined the membrane flux and resistance changes on the effect of ozone treatment time, ozone flow rate and detergent content.

- During membrane filtration, I analyzed the vibration effects on the changes of flux and retention. I compared the specific energy demands of vibration and non-vibration membrane filtration techniques.
- I developed a mathematic model for the description of nanofiltration transport mechanisms and validated the applicability of the model.
- I made a proposal for an industrial vibratory shear-enhanced membrane processing technology. For the effective application, economical calculation formulas were introduced.

2. *MATERIALS AND METHODS*

In the first part of my experiments, for the ultrafiltration of the synthetic solutions I used the *MEUF* (Micelle enhanced ultrafiltration) type (Model 8400, Millipore, Sweden, 0,0040 m^2) laboratory device, and to evaluate these results I used the *MODDE* 8,0 (Umetrics AB, Umeá, Sweden) statistic program. The membranes of *MEUF* (Millipore, Amicon *PL* series, Sweden) were made of regenerated cellulose with 3, 5 és 10 kDa of *NMWL*. I carried out nanofiltration of detergent solutions with *3DTA* device (Uwatech Gmbh., Germany, 0,0156 m^2), and I used the Statistica release 8. program for the data estimation. The concentration of red currant extracts were done with an *RO* polyamide membrane of *DDS* device (*DDS* Minilab 20, Denmark, 0,18m^2), a *NF* polyamide membrane of Millipore equipment (Millipore, France, 0,3m^2) and an *NF* and *RO* composite membrane of *3DTA* device.

The ozone gas was produced from oxygen bottle (Linde 3.0, Hungary) with an ozone generator (Ozomatic Modular 4, Wedeco, Germany). The concentration of the ozone was measured with an UV spectrophotometer (WPA Lightwave S2000, Germany) at 254nm.

Vibration during membrane filtrations (New Logic International, Emeryville, USA) were carried out with an L-mode vibratory shear-enhanced processing (VSEP) device. For this equipment the following membranes were tested: *UF* polyethersulfone (*NMWL*: 7000 Da), *NF* composite (240 Da), and *RO* polyamid membrane (50 Da).

During my experiments synthetic (sodium dodecyl sulfate, zinc chloride, sodium chloride and butanol containing) solutions, food wastewater (dairy synthetic and real wastewater), detergent solutions (sodium dodecyl sulfate and *CL80* anionic detergent) and red currant liquid extract were filtered and concentrated by membrane separation processes.

To determine the conductivity of samples, I used a multimeter (Model 20, Denver Instruments and Consort C535, Belgium). I analyzed the chemical oxygen demand of the samples with a digester and a photometer (ET 108 digester and Lovibond PC CheckIt photometer, Germany) with DIN ISO 15705: 2003-01 method. Normal butanol was determined by a gas chromatograph (Agilent, 6890N) method. The amount of the detergent phosphore-molibdenat-blue color reaction UV spectrophotometer method (WPA Lightvawe S2000, Germany) was determined after calibration at 654nm. For the determination of zinc, atom absorption spectroscopy (Perkin Elmer 4100 with flame atomization methods) was used.

3. *SUMMARY AND NEW SCIENTIFIC RESULTS*

I. New scientific results related to the examination of critical micelle concentration

1. I proved that the critical micelle concentration (*CMC*) of sodium dodecyl sulfate (*SDS*) solutions are significantly decreased by the presence of electrolyte, and the presence of normal butanol only cause this effect slightly [1].
2. I diagnosed that the counter ion binding (*E*) of electrolyte content *SDS* solutions is much higher than in electrolyte free *SDS* solutions. With increasing of *SDS* concentration at *CMC* value (and above) the conductivity significantly changes [1].

II. New scientific results related to the analysis of synthetic solutions and wastewater

3. I proved that during the ultrafiltration of synthetic wastewater having more components, higher *SDS* concentration results lower porous membrane fouling.

   I demonstrated that the regenerated cellulose membranes have lower membrane fouling after membrane filtration of higher *SDS* concentration, and have higher membrane fouling after membrane filtration of synthetic wastewater having lower *SDS* concentration.
4. I showed that during the nanofiltration of detergent content solutions the fouling index (*k*) values were most affected by temperature, and by increasing it the *k* values decrease. There is a significant difference between fouling index values at 20 and 30 or 40°C, but at the same time, there is no real difference at 30 and 40°C [2].

III. New scientific results related to decreasing the volume of liquid by-products by NF and RO concentration

5. I proved that during concentration tests of red currant liquid extract, porous fouling resistance (R_F) has the highest ratio in the total resistance (R_T) using polyamide membranes. Using composite nanofiltration flat-sheet membrane (*NF2*), the polarization layer resistance (R_P) has the highest effect on the flux decreasing, which is in accordance with its lower retention values [3].

Regarding my measurements, the optimal running pressure for both *NF* and *RO* systems was 3.0 MPa. The maximum total solid content was 6.8 and 8.9°Brix for *RO* and *NF*, respectively.

I showed that the lowest ratio of porous fouling resistance and polarization layer resistance (R_F/R_P) was in the case of *NF2,* and the highest in the case of *NF1* (using polyamide nanofiltration spiral wound membrane).

6. I proved with my experiments that the composite reverse osmosis flat-sheet membrane (*RO2*) is the most effective for the liquid red currant extract concentration.

   In the case of *RO2*, the total resistance is lower (about half of the *RO1* – polyamide reverse osmosis flat-sheet membrane), the average flux values are high and the retention is also high. Its membrane resistance is high, but the sum of the R_F and R_P is only 30% of the total resistance.

IV. New scientific results related to hybrid (ozone treatment and nanofiltration) process

7. I proved that before membrane filtration the ozone pretreatment increases the retentions of chemical oxygen demand (*COD*) and biochemical oxygen demand (*BOD*), which is caused by the ozone microflocculation effect. The retentions of *COD* increase with a low extant by lower gas flow rate, because more ozone can dissolve into the sample. In this way, a looser structure with a more compact polarization layer is formed on the surface of the membrane, which increases retention values. On the contrary, using a detergent cause destabilized micelles, which decreases the retention values [4].

   I showed that using ozone pretreatment with lower ozone gas flow rate before membrane filtration of dairy wastewater, the microflocculation effect is more significant, resulting in higher fluxes and lower retention values. Using higher ozone gas flow rate, since the flocculated molecules are sensitive and fragile, they can go into the membrane porous easier resulting higher porous membrane fouling [5].

8. I showed that at the feed side of the nanofiltration, the presence of the detergent destabilized the microflocculated particles. The nanofiltration of detergent content solutions had lower fluxes, than the detergent free

solutions. The smaller size destabilized particles can go into the porous easier, which increases the R_F value.

V. *New scientific results related to vibration membrane filtrations*

9. I introduced a new formula to express and emphasize the vibration effect. The vibration flux increasing rate (*VFN*) tells the flux increasing rate by applying vibration.

$$VFN = \frac{J_V \cdot 100}{J_{VN}} \quad [\%], \text{ where}$$

J_V fluxes with vibration $[lm^{-2}h^{-1}]$ and

J_{VN} fluxes without vibration $[lm^{-2}h^{-1}]$.

I showed that using vibration with the same parameters, results in a two times higher flux (a $VFN \approx 200\%$) by the end of the filtrations (*VRR*: volume reduction ratio = 5), in all cases (*UF, NF and RO)*.

10. I analyzed the pressure-normalized fluxes as a function of increasing shear rate on the surface of the membrane. I proved that higher fluxes can be achieved by using higher shear rates [6]. In cases of *UF* and *NF* the flux differences are both significantly high, but in case of *RO* there is only a little difference in fluxes of vibration and non-vibration techniques.

11. I proved that the vibration significantly decreases the polarization layer formation on the surface of the membrane, and consequently the total resistance is also decreased.

I experimentally confirmed that the main effect of vibration is the decreasing of the polarization layer, however the vibration also decreases the porous fouling [7].

12. I showed that during vibratory membrane filtrations the membrane retentions were improved. This effect is more significant with higher pore size membranes, than with smaller pore size membranes.

13. I introduced new formulas for the economic comparison of vibration and non-vibration techniques using specific energy demands (e_V, e_{VN}):

$$e_v = \frac{P_{VM} \cdot \eta_{VM} + P_{SZ} \cdot \eta_{SZ}}{A' \cdot J} \quad [kWhm^{-3}]$$

$$e_{VN} = \frac{P_{SZ} \cdot \eta_{SZ}}{A' \cdot J} \quad [\text{kWhm}^{-3}]$$, where

e_V	vibration specific energy demand	[$kWhm^{-3}$],
e_{NV}	non-vibration specific energy demand	[$kWhm^{-3}$],
P_{VM}	vibration motor power consumption	[kW],
η_{VM}	vibration motor efficiency	[-]
P_{SZ}	feed pump power consumption	[kW],
η_{SZ}	feed pump efficiency	[-]
A'	membrane area	[m^2] and
J	flux	[$m^3 m^{-2} h^{-1}$].

14. I proved that in cases of *UF* and *NF,* after a certain critical pressure value the vibration membrane filtration is more economical than the non-vibration mode. In the case of *RO*, the vibration specific energy demands are higher, than non-vibration specific energy demands at each pressure.

Almost in all cases, the non-vibration specific energy demands were increased and the vibration specific energy demands were decreased with pressure increasing.

I proved that in the concentration tests the vibration specific energy demand converge to a lower value compared to the non-vibration case. From *UF* to *RO* this tendency is more remarkable.

4. SCIENTIFIC PUBLICATIONS, PAPERS RELATED TO THE THESIS

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