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Modeling of Membrane Separation and Applying Combined Operations at Biosystems

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Abstracts. The importance of the treatment of water and wastewater has been steadily increasing because of the ever greater demands to eliminate environmental pollution. Pressure-driven membrane separation processes, including ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), have been widely used in water and wastewater treatment and are applied on an industrial scale worldwide. The aim of our paper is to introduce the results of our research team on this field. The main research area within the membrane separation was the reduction of resistances. The effect of ozonation, vibration and application of dolly particles were examined in our scientific works.

Keywords: biosystems, complex membrane separation methods, resistance reduction, wastewater treatment, vibration, ozonation, dolly particles

1. Introduction

The importance of the treatment of water and wastewater has been steadily increasing because of the ever greater demands to eliminate environmental pollution. Pressure-driven membrane separation processes, including ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), have been widely used in water and wastewater treatment and are applied on an industrial scale worldwide, since these are effective methods for decreasing chemical oxygen demand (COD) caused by the presence of proteins, carbohydrates and surfactants (Balannec et al. 2002).

Many industrial water and wastewater effluents contain detergents as well in concentrations of up to 1–5 g L^{-1}, which must be largely removed prior to water recycling or discharge. In Hungary, the recent regulations relating to effluent water limit the detergent content for biological water treatment to 0.5 g L^{-1}, and that of discharge water to 0.05 g L^{-1} (Vatai 2007). Although membrane processes may differ greatly in their mode of opera-

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tion, structures and driving forces, some advantages are common to all. They are faster, more efficient and more economical, and their operation is easier to control and maintain than other conventional separation techniques (Kiss et al. 2004). Unfortunately, membrane techniques have some drawbacks too, such as high energy consumption and especially RO or the flux decline caused by membrane fouling and concentration polarization. Membrane fouling is mainly due to the accumulation of different rejected components, such as colloidal proteins. It is possible to reduce membrane fouling by optimizing the transmembrane pressure, the cross-flow velocity or other operating parameters. Concentration polarization involves time-dependent accumulation of compounds near the membrane surface.

Overview is given in this paper of these problems and solutions by the membrane transport research team of University of Szeged.

2. Theory of Membrane Separation

The membrane technology is known as a flexibly adaptable technique for varying capacity and for the diverse chemical composition of processed water (Van der Bruggen et al. 2002).

Furthermore, there is only a low need for chemicals and separation is usually performed at ambient temperature, therefore allowing temperature-sensitive solutions to be treated without constituents or chemically altered. This is important in the food industry, where temperature-sensitive products have to be processed. On the other hand, in pressure-driven membrane separation techniques, UF is becoming a viable alternative, because it can operate at lower pressures and lower energy consumption than NF or RO (Taylor et al. 1989).

2.1. Membrane filtration of food industrial wastewater

The major problem with membrane filtration is the permeate flux decline during the operation that affects directly the economy of the process. A number of technologies was used to treat wastewater, such as coagulation (Sengil and Ozacar 2006), ecological treatment system (Lansing and Martin 2006), anaerobic and aerobic reactors (Beszédes et al. 2011; Demirel et al. 2005). However, each of the used biological treatment systems, including aerobic and anaerobic processes, has its own disadvantages caused by either high energy requirement or major operational difficulty (Kaewsuk et al. 2010; Kushwaha et al. 2010). Several studies were focused on the treatment of dairy effluents and demonstrated that membrane operations were often considered as a promising method: microfiltration, ultrafiltration, nanofiltration and reverse osmosis (Vourch et al. 2008). A few works show that NF and RO are convenient operations for treating effluents at source and achieving the set targets (Balannec et al. 2002; Luo et al. 2010). The concentrated retentate of dairy wastewater can be precipitated by coagulation to obtain feed supplement for animals (Dyrset et al. 1998), or can be treated by anaerobic digestion to collect renewable energy sources, which is regarded as an economical and environment-friendly process for treatment of dairy wastewater. The significant improvements of membrane technology in reliability and cost effectiveness have increased the reuse probability and recycling of various industrial wastewaters. The recent development of newer membranes with high flux and low rejection characteristics has increased probability of water reuse and recycling. Unfortunately, membrane fouling and the resulting permeate flux decline still remain a major bottleneck in wide application. In order to solve the problem, many researchers investigated the possibility and applicability of rotating or vibrating modules in wastewater treatment (Akoum et al. 2004; Shi and Benjamin, 2011). In order to control the flux decline during the concentration of dairy effluent vibration method could be used. Only a few articles have been dedicated to the treatment of dairy wastewater by vibratory shear-enhanced processing (VSEP), but these show that nanofiltration or reverse osmosis is adequate for the concentration of milk components (Akoum et al. 2005; Luo et al. 2011).

2.1.1. Mathematical modeling: the resistance-in-series model for RO

The resistance in series model of membrane separation defines pure water flux as the quotient of the transmembrane pressure – driving force (Δp_{TM}, Pa) – and the resistance (R_M, m^{-1}, calculated by water dynamic viscosity, η_W, Pas) arising from the pore size of the membrane material feature (Cassano et al. 2007; Kiss et al. 2004).

$$J_w = \frac{\Delta p_{TM}}{R_M \cdot \eta_w} \quad (dm^3 m^{-2} h^{-1}). \tag{1}$$

The fouling resistance of the applied membranes can be determined from the water flux (J_F, ms^{-1}) – measured at a fixed temperature – after flushing the membrane with tap water and after concentration test, using the following formula:

$$R_F = \frac{\Delta p_{TM}}{J_F \cdot \eta_w} - R_M \quad (m^{-1}). \tag{2}$$

The total resistance is composed of three resistances:

$$R_T = R_M + R_F + R_P \quad (m^{-1}) \tag{3}$$

where R_P (m^{-1}) is the polarization layer resistance.

2.1.2. Osmotic pressure model

At membrane filtration of liquid mixtures the osmotic pressure model is valid, which determines the flux (J, ms^{-1}) as the quotient of difference of the transmembrane pressure (Δp_{TM}, Pa), the osmotic pressure difference ($\Delta\pi$, Pa), and the total membrane resistance (R_T, m^{-1}). The effect of temperature is integrated into the equation, knowing permeate (practically water) viscosity (η_w, Pas):

$$J = \frac{\Delta p_{TM} - \Delta\pi}{R_T \cdot \eta_w} \quad (dm^3 m^{-2} h^{-1}). \tag{4}$$

It is possible that the glucose molecules in the boundary layer near the membrane play a role in the creation of the osmotic pressure. The glucose molecules were highlighted into the osmotic pressure model, since the glucose molecules have the biggest osmotic pressure into the fruit juice. The van't Hoff model can be applied to this phenomenon, which determines the osmotic pressure dependence on the difference of concentrate (c_r, kmol m^{-3}) and permeate (c_p, kmol m^{-3}) concentration (R = 8314.472 J kmol^{-1}K^{-1} universal gas constant, T = 298.15 K temperature of experiment):

$$\Delta\pi = \left(c_r - c_p\right) RT \quad (Pa). \tag{5}$$

The concentration of the permeate side (c_p) in all experimental runs was very low, ~ 0.1°Brix, two orders of magnitude lower than the retentate concentration. By neglecting the permeate side concentration and introducing the concentration polarization $\beta = c_m / c_r$ in the previous equation (where c_m is the concentration at the surface of the membrane), the following formula is obtained:

$$\Delta\pi = \beta \cdot c_r RT \quad (Pa). \tag{6}$$

By the combination of the above equations, the following one is obtained:

$$J = \frac{\Delta p_{TM}}{R_T \cdot \eta_w} - \frac{\beta RT}{R_T \cdot \eta_w} c_r \quad (dm^3 m^{-2} h^{-1}). \tag{7}$$

By plotting the permeate flux versus c_r, from the intercept of the fitted straight line, the average values of the total resistances during the concentration of the blackcurrant juice can be estimated.

2.1.3. Makardij's model

For determination of the rate constants characterizing the ultrafiltration process itself, the method of Makardij et al. (2002) could be followed, with the initial conditions specified as follows:

$$t = 0 \quad J = J_0, \quad \text{and} \quad k_1 c_0 J \gg k_2 Re^n. \tag{8}$$

On approaching a steady state:

$$\frac{dJ}{dt} \Rightarrow 0, \quad \text{and thus} \quad k_2 \approx k_1 \left(\frac{c_0 J}{\mathrm{Re}^n} \right)_{equilibrium}. \tag{9}$$

Equation (9) could be used to calculate the values of k_1 from the measurement of the initial flux decline.

Reynolds' number in the case of mixing was calculated as follows:

$$Re_{mix} = \frac{d^2 n \rho}{\eta} \tag{10}$$

where ρ is the retentate density (kg m^{-3}), n is the rotation rate of the stirrer (s^{-1}), η is the viscosity of the retentate (Pas), and d is the diameter of the stirrer (m).

3. Materials and Methods

3.1. Wastewater

The model wastewater was prepared from skim milk powder (3 gdm^{-3}). The feed wastewater was characterized in table I. In the experiments, Chemipur CL80 was added to the model solution as an anionic surfactant cleaning agent in the concentration of 0.01 gdm^{-3}. The skim milk powder and the cleaning agent Chemipur CL80 (used for cleaning dairy equipment) were provided by Tolnatej Rt. and Sole-Mizo Ltd. (Szeged, Hungary), respectively.

Table I. Characteristics of the feed dairy model wastewater

Ref %	Conductivity	pH	Viscosity		Turbidity	COD
[Brix°]	[μScm^{-1}]	[-]	[mPas]	T [°C]	[NTU]	[mg/l
0,4	347	8,29	1,13	23,5	347	3320

The real wastewater samples originated from a medium-sized meat processing company; the sampling point was after the grease tap. The process water originates from meat processing technology, mainly from the flushing and rinsing of equipment (slicing and packaging machines, smoking chambers). To remove grit and other large-sized solids a cloth filter was used.

3.2. Whey

Sweet whey was used for our measurement, which originated from a local dairy facility (Sole-Mizo Ltd., Szeged, Hungary), and acid whey is obtained during the production of cottage cheese and was supplied by a local dairy factory in Szeged.

3.3. Experimental setups

3.3.1. Applied classical membrane filters

Membrane filtration experiments were performed also on an Uwatech 3DTA laboratory membrane filter (Uwatech Gmbh., Germany) with a filtering surface area of 0.0156 m^2.

The transmembrane pressure (Δp_{TM}) was defined as:

$$\Delta p_{TMP} = \frac{\left(p_{in} + p_{out}\right)}{2} - p_{perm} \tag{11}$$

where p_{in} and p_{out} are the inlet and outlet pressures of the membrane module and p_{perm} was the pressure at the permeate side. In *Figure 1* a typical batch system is shown.

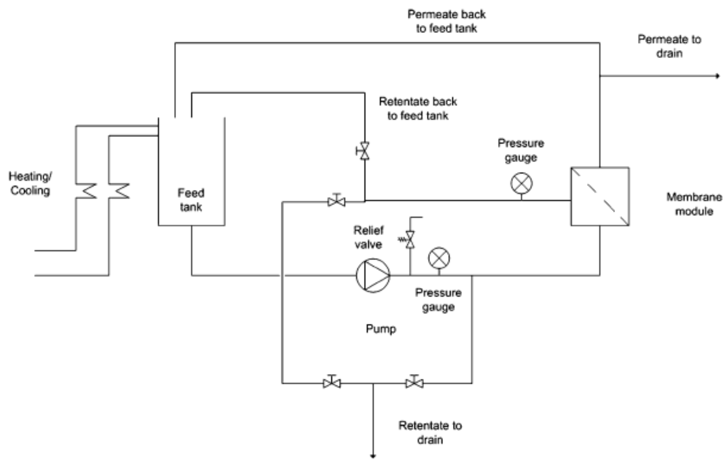


Figure 1. Schematic diagram of the total recycle and batch concentration mode operation in membrane filtration

The permeate flux was estimated with the following equation:

$$J = \frac{dV}{dt \cdot A_m} = \frac{\Delta p_{TMP}}{R_t \cdot \eta} \quad (dm^3 m^{-2} h^{-1}) \tag{12}$$

The volumetric reduction factor (*VRF*) was defined as:

$$VRF = \frac{V_0}{V_R} = \frac{V_0}{V_0 - V_p} \tag{13}$$

3.3.2. Vibrated Share Enhanced Membrane Separation Process

The filtration module was a VSEP Series L (New Logic Research Inc., Emeryville, CA) *(Figure 2).* It was equipped with a single circular membrane of 503 cm^2 (13.5 cm outer radius R_2, 4.7 cm inner radius R_1). The vertical shaft supporting the membrane housing acts as a torsion spring which transmits the oscillations of a lower plate in the base, which is vibrated by an eccentric drive motor. As a result the housing containing the membrane oscillates azimuthally with displacement amplitude "*d*", which we have adjusted to be 2.54 cm (1 inch) on the outer rim at the resonant frequency of 55

Hz. A new membrane was used for each experiment to ensure the same initial membrane conditions for the entire test.

During the VSEP process, the maximum ($\gamma_{w,\max}$) and mean ($\gamma_{w,g}$) induced shear rates at the membrane surface were calculated via the following equations (Akoum et al. 2002b).

$$\gamma_{w,\max} = 2^{\frac{1}{2}} d(\pi F)^{\frac{3}{2}} \vartheta^{-\frac{1}{2}} \tag{14}$$

$$\gamma_{w,g} = \frac{2^{\frac{3}{2}}\left(R_2^3 - R_1^3\right)}{3\pi R_2\left(R_2^2 - R_1^2\right)} \gamma_{w,\max} \tag{15}$$

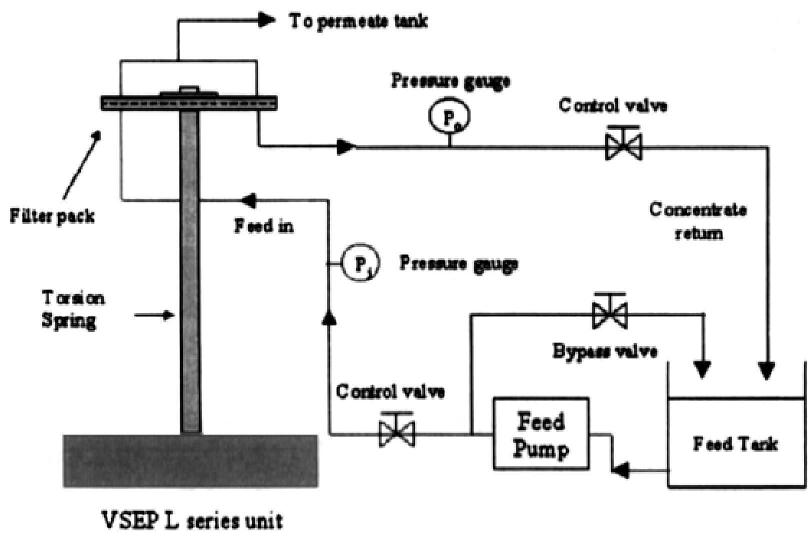


Figure 2. The vibratory shear-enhanced process L series unit

3.4. Ozonation

Ozone was produced from oxygen (Linde 3.0) with a flow-type ozone generator (Ozomatic Modular 4, Wedeco Ltd., Germany) operating via a silent electric discharge. The ozone-containing gas (flow rate 1.0 or 0.5 $dm^3\ min^{-1}$) was bubbled continuously through a 6.0 dm^3 batch reactor during the treatment. The ozone concentration in the bubbling gas was 30 $mgdm^{-3}$.

3.5. Scanning electron microscope measurements

Scanning electron microscope (SEM) pictures were performed with a Hitachi S-4700 field emission SEM (Dallas, Texas, USA) operated at an acceleration voltage of 10 kV in ultrahigh resolution mode. Different pictures were recorded and compared in order to analyze the gel layer after NF tests with the vibration and non-vibration methods.

4. Results and Discussion

4.1. Membrane separation of meat industrial wastewater

Meat industrial processing wastewater treatment technology was developed in cooperation with Department of Transport Phenomena, Oulu University, Finland. The RO concentration of meat industrial wastewater was carried out in a pilot-scale filtration unit equipped with AFC99 polyamide membranes. For the experimental design and optimization, MODDE 8.0 software was used, investigating the effects of the operation pressure, temperature and recirculation flow rate on the organic matter retention, permeate flux and the resistances calculated from the resistances in the series model.

Our results show that the investigated parameters did not significantly affect the retention but the permeate flux and the total resistance are suitable for the response parameter of modeling (Beszédes et al. 2011). Based on our results, the increasing pressure positively affects the permeate flux but at elevated pressure the total resistance increases as well. The increasing of the temperature and the recirculation flow rate could enhance the permeate flux and decrease the total resistance. The fitted quadratic model was significant at the 95% confidence interval and showed good predictive power as well as high reproducibility.

The optimal conditions for RO concentration of meat industrial wastewater were determined *(Figure 3)* at an operating pressure of 38.5 bar, recirculation flow rate of 1000 Lh^{-1} and temperature of 40°C. The TOC content and the conductivity of permeate was lower than 5 ppm and 20 μScm^{-1}, respectively, which allows for the recycling and reusing, for example, in cleaning, in the flushing process or for cooling water. The average TSS content of RO concentrate was higher than 9% with a TOC content of 2.8 gL^{-1}, protein content of 1.2 gL^{-1} and fat content of 0.35 gL^{-1}.

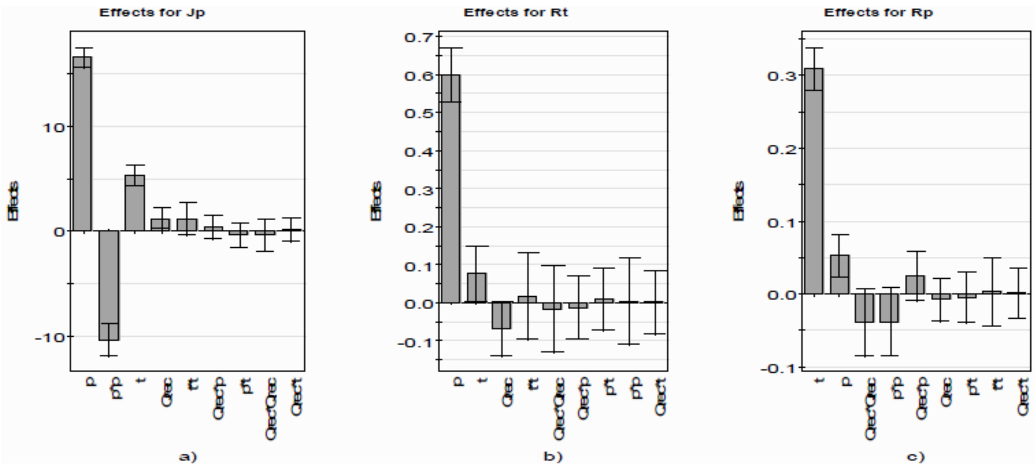


Figure 3. Effects of factors and interactions on the permeate flux (a), total resistance (b) and polarization layer resistance (c) (Beszédes et al. 2011)

The temperature was also the determinative parameter in the case of the dairy wastewater membrane separation. The retention was principally affected by the temperature, the highest retention being observed at the lowest temperature. The highest flux was measured at the highest temperature, but the pressure seemed to be more influential. Increasing pressure was associated with an increasing flux, but this phenomenon was overshadowed by influence of the changes in gel layer formation with increasing detergent concentration (Kertész et al. 2008; László et al. 2007).

The common project works of the Pannon University and Budapest Corvinus University also resulted in joint publications. One of the joint publications was on the sweet whey concentration for using its valuable components. The process modeling was based on resistance in a series model but it was completed by van't Hoff law to determine the osmotic pressure. Our presumption that the lactose is the determinative component of the whey was confirmed by our experiences and the compliance of model was also proved (Román et al. 2009).

4.2. Mitigation of resistances

4.2.1. Dolly particles

The flux is determined by the total resistance of membrane processes. We investigated the values of the different resistance forms and their mitigation methods – microparticles, enhanced share stress and vibration.

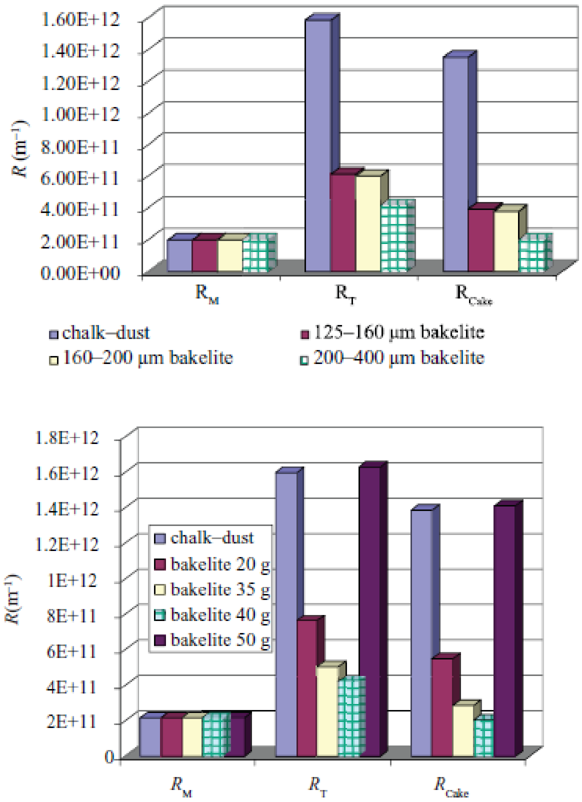


Figure 4. Effects of dolly particles on resistances (Szép et al. 2010)

When dolly particles were applied in the MF system, in some cases a 4-fold increase in flux was obtained in comparison with the cross-flow filtration conditions. A linear correlation was observed between the mass of the dolly particles and the permeate flux. The highest flux was achieved by using 40 g of 200–400 mm bakelite in the 20 liter chalk suspension. The experiments showed that increase of the dolly particle mass above 50 g per 20 liter suspension did not result in an increase in flux. The application of dolly particles increased flux, in spite of the same Reynolds number developing. This flux increasing effect of a pile of bakelite could be due to the local turbulence caused by the particles. The flow around the particle is much more turbulent on the surface of the membrane than in the bulk. This effect arises because the accelerated motion in the boundary layer makes the cake thinner, and R_{Cake} lower. R_T and R_{Cake} were significantly higher with the chalk-dust solution than with a pile of bakelite particles *(Figure 4)*. Thus, the bakelite particles decreased the resistance of the filtration. The hydrodynamic shear force reduces the fouling rate on the membrane and improves the efficiency of the cross-flow MF.

4.2.2. Vibration

Besides the dolly particles, the vibration was investigated also for resistance mitigation. The results show that the VSEP system outperforms the conventional 3DTA system in UF, in terms of both permeate flux and permeate turbidity reduction due to reduced protein transmission through the membrane. The higher permeate flux of the VSEP system results from its higher membrane shear rate, which allows increasing retention of protein and lactose with TMP. A comparison of the data measured with the two systems demonstrated a definite advantage for the VSEP system equipped with the same membrane and operated at the same pressure and temperature.

The performance of the 30 kDa ultrafiltration membrane (C30F) was investigated during the processing of whey protein concentrate solution. With the 3DTA system, the membrane suffered significant fouling and the permeate flux was reduced by up to 40%. The VSEP system underwent a milder reduction in flux: 55%, due to the higher shear rate. The permeate flux in the VSEP system is mostly controlled by the vibration frequency and not by the inlet flow-rate (Akoum et al. 2002a). Using the same laboratory LP semi-pilot VSEP device as ours, Takata et al. (1998) observed a 50% rise in permeate flux during the UF of humic substances with a 100 kDa membrane when the displacement was increased from almost 0 to 2.5 cm at 60 Hz. For the same displacement increase, our data for the UF of cheese whey revealed a 33% flux increase for a 30 kDa membrane. As the test fluids and the membranes were different, we consider that our data are coherent with those of Takata et al. (1998). The total resistance was lower with the VSEP system, and the proportions of R_G and R_F also differed. R_G was much lower than in the 3DTA system, and lower than R_F *(Figure 5)*.

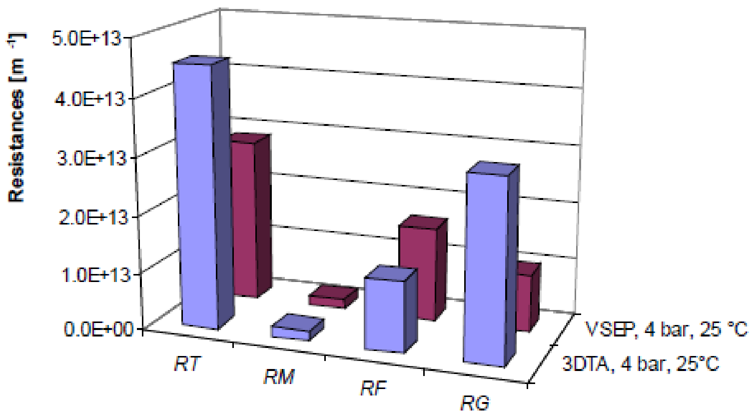
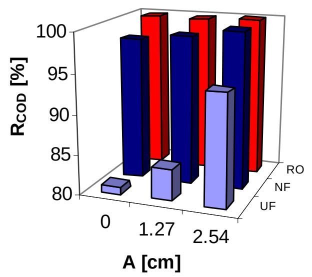


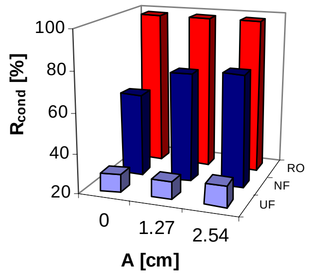
Figure 5. Resistances in VSEP and 3DTA systems during concentration of cheese whey

High concentration polarization increases the fouling, which is not reversible by modification of the process parameters. A comparison of the data measured with the two systems demonstrated a definite advantage for the VSEP system equipped with the same membrane and operated at the same pressure and temperature. The VSEP system yielded a permeate protein retention of 99.7 NTU vs. 74.5 NTU for the 3DTA system, together with a higher flux: 64 L m^{-2} h^{-1} vs. 44.2 L m^{-2} h^{-1}. The flux reduction ratio (J/J_0) was 0.60 vs. 0.42, and the total resistance 2.87×1013 m^{-1} vs. 4.54×1013 m^{-1} for the VSEP and 3DTA system, respectively (Hodúr et al. 2009a, b). The performance of a vibratory shear-enhanced processing system for ultrafiltration, nanofiltration and reverse osmosis membrane was investigated during filtration of dairy wastewater. Vibration of UF, NF and RO membranes in an L-mode VSEP system reduced the fouling at treatment of dairy wastewater. Treatment with vibration led to rejections of most ions >30.7 % for UF, >76.6 % for NF and >98 % for RO *(Figure 6)*.



	0	1.27	2.54
UF	80.86	84.00	93.85
NF	97.82	98.59	99.64
RO	99.74	99.74	99.95

(a)



	0	1.27	2.54
UF	29.01	29.11	30.71
NF	61.90	75.01	76.62
RO	97.80	98.09	97.99

(b)

Figure 6. Removal efficiency of COD (a) and of conductivity (b) with vibration amplitude at VRR = 1. (T = 50 ± 1°C; TMP = 0.8 MPa for UF, 2 MPa for NF and 3 MPa for RO; q_V = 15.14 L min^{-1})

It may be concluded from these studies that each individual, single UF, NF and RO treatment could improve a good treatability of dairy wastewater, but NF and RO could generate treated effluents that met the strict requirement of general EU COD threshold limit below 150 mg O_2 L^{-1} *(Table II)* (Kertész et al. 2010).

Table II. COD values of the permeate of single membrane filtration

COD [mg O_2 L^{-1}]	UF	NF	RO
Non-vibration	1181.9	<u>134.6</u>	<u>16.1</u>
Vibration applied	380.0	<u>22.0</u>	<u>3.0</u>

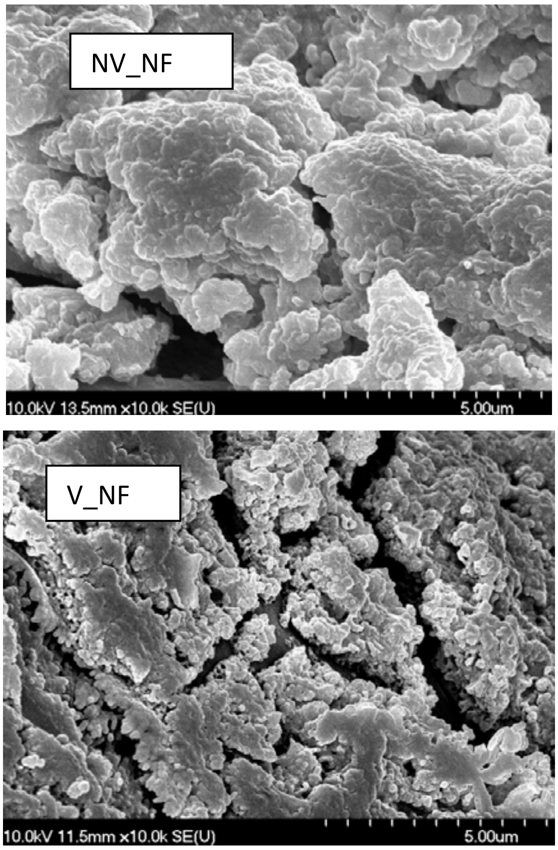


Figure 7. SEM images of a NF membrane fouled without vibration (NV_NF) and at vibration amplitude of 2.54 cm (V_NF) after long-term test of dairy wastewater treatment. All specimens are taken from a location 10 cm from the center of the membrane (Kertész et al. 2011)

For a long period of UF and NF using vibration method greatly reduced the membrane fouling mainly with the gel layer reduction. SEM images indicated that the membrane surfaces were almost uniformly covered with scale forming gel layer in the non-vibrating methods in both UF and NF system, but in the methods with vibration, the morphology of the scale layers was different. The scale in UF appeared mostly continuous compared to NF, and it became more scattered with more open space between individual clumps. A higher magnification of SEM pictures showed that the scale in NF non-vibration method formed a more aggregated and continuous, overcrowded layer, whereas the scale in the vibration method comprised of lower quantity of smaller and mainly only one layer round-like particles (*Figure 7*). Compared with the UF process, NF had a higher efficiency and less membrane fouling. The results showed that NF and RO single membrane operations allowed purified water release to the environment, but UF permeate water did not reach the COD European standard.

The effect of vibration on the nanofiltration and reverse osmosis was investigated also in the case of concentration of pig manure. In this case the result was the same, i.e. total resistance was decreased, gel layer resistance was decreased, flux value was increased. The concentrated pig manure up to 10, 14 °Brix could be used effectively for biogas production (Kertész et al. 2010).

4.3. Combined membrane processes

Model dairy wastewaters (prepared from milk powder by dilution) were treated with ozone, and the effects of the ozonation time and the surfactant concentration on the flux, the membrane resistances, membrane fouling and gel formation were measured. Analysis of the effects of the ozonation time, detergent content and the bubbling gas flow rate during ozonation on various membrane filtration parameters demonstrated that both affected the flux and the membrane fouling by flocculation. The results indicated that the microflocculation effect of ozone can play a significant role at a higher gas flow rate, with a decrease in membrane fouling and an increase in gel formation; at a lower flow rate, the effect of the degradation of large molecules is more pronounced, causing a higher flux, and decreasing membrane resistances. The detergent content may increase the extent of fouling and gel formation, but it did not change the flux (László et al. 2007).

The data was analyzed by three-way analysis of variance (ANOVA): the effect of ozonation time, the flow rate of bubbling gas and the detergent concentration were analyzed in *Table III*. The Shapiro-Wilk test was shown and used to control data to a Gaussian distribution.

Table III. The results of Shapiro-Wilk test for data (László et al. 2009)

	p-Level							
	Time				Flow rate of bubbling gas		Detergent content	
	0 min	5 min	10 min	20 min	0.5 Lmin^{-1}	1 Lmin^{-1}	0.0 g L^{-1}	0.01 g L^{-1}
J/J_W	0.123	0.231	0.213	0.850	0.747	0.523	0.575	0.432
R_F	0.073	0.664	0.176	0.235	0.365	0.580	0.695	0.075
R_G	0.085	0.373	0.844	0.312	0.507	0.471	0.547	0.088
$R\%$	0.124	0.235	0.742	0.564	0.321	0.742	0.167	0.070

The effect of combined cleaning techniques, i.e. ozonation for 2, 5 or 10 min before ultrafiltration with a PES membrane with a cut-off of 5 kDa was studied on meat industrial wastewater. The results prove that the ozonation pretreatment for at least 10 min degrades large organic molecules into smaller fragments. This size reduction results in a higher relative flux and a smaller fouling index. These values predict longer operating-management options. The findings demonstrated in *Figure 8* show that ultrafiltration with a cut-off of 5 kDa following ozonation for 2 or 5 min is a satisfactory purification method for such wastewater, since the COD of the permeate met the requirements of the Regulations of the Hungarian Ministry of Environmental Protection (150 mg dm^{-3}). Longer ozonation led to a slightly higher COD, but also a higher permeate flux.

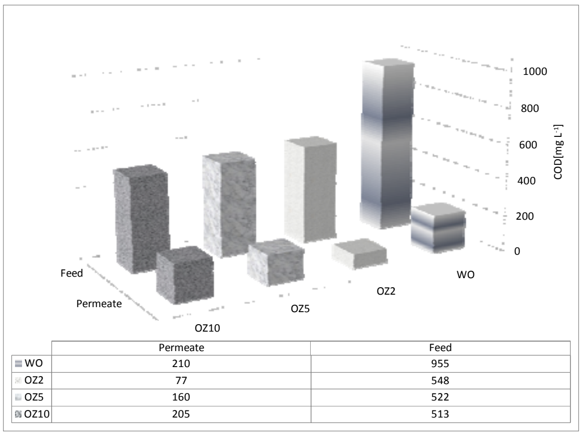


Figure 8. The COD data of non-ozonated or pre-ozonated and ultrafiltered samples (Non-OZ (WO) – without ozonation, OZ2 – ozonation for 2 min, OZ5 – ozonation for 5 min, OZ10 – ozonation 10 min)

Makardij et al. (2002) developed a new modeling method with which to characterize fouling in cases of microfiltration and ultrafiltration. This modeling system generates two rate constants characterizing the membrane process itself: k_1 – the rate constant for the flux decline ($m^3kg^{-1}s^{-1}$) and k_2 – the rate constant for the removal of the deposit from the membrane. The determined values are presented in *Table IV*.

Table IV. Rate constants of flux decline (k_1) and removal of the deposit (k_2)

	Non-OZ3	**OZ2**	**OZ5**	**OZ10**
k_1	2.67E-05	3.61E-05	4.46E-05	1.55E-04
k_2	1.02E-11	6.56E-12	7.95E-12	2.68E-11

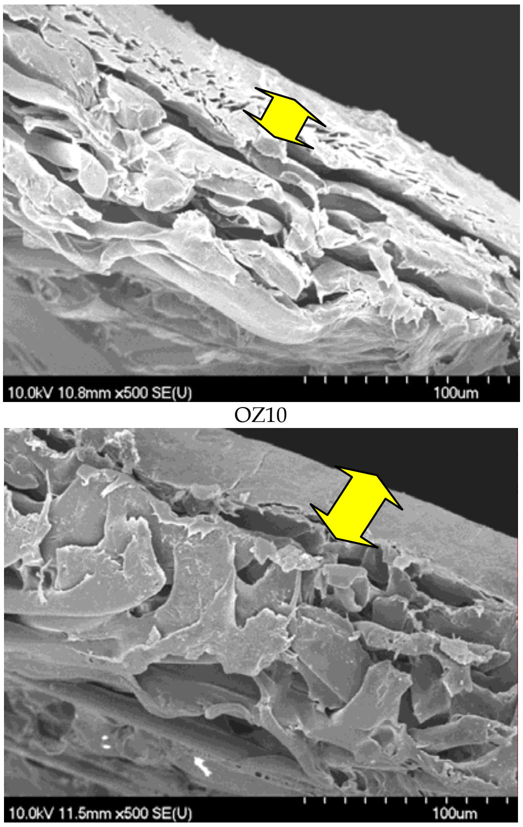


Figure 9. SEM photos of the cross-section of the ultrafiltration membrane after separation of the non-ozonated samples (Non-OZ) and the samples ozonated for 10 min (OZ10)

The data show that the k_1 values are larger than the k_2 values, which demonstrates that the fouling mechanisms have a stronger effect on the membrane separation than that of deposit removal. However, there are differences between the samples. The constants k_2 reveal that the ability to remove the deposit layer is one order of magnitude higher, than in the case of the samples ozonated for 10 min, than for those ozonated for 2 min or 5 min. The k_1 values increase fairly linearly with the duration of ozonation.

The developed gel layer and the cross section of the separation and supported layer of the membrane are presented in *Figure 9*. The arrows show the thickness of the deposited gel layer at 10 min long ozonated samples and untreated samples as well.

5. Conclusion

Based on the previously detailed results, the following can be concluded:

- The hydrodynamic shear force caused by bakelite dolly particles reduces the fouling rate on the membrane and improves the efficiency of the cross-flow MF. This effect arises because the accelerated motion in the boundary layer makes the cake thinner, and R_{Cake} lower.
- The total resistance was lower with vibrated membrane separation and the proportions of gel resistance and fouling resistance also differed; gel layer resistance was much lower than in the non-vibrated separation.
- The scale of the non-vibrated nanofiltration formed a more aggregated and continuous, overcrowded layer, whereas the scale in the vibration method comprised a lower number of smaller and mainly only one layer round-like particles.
- The vibration had a bigger effect in the case of ultra- and nanofiltration than at reverse osmosis.
- The microflocculation effect of ozone can play a significant role at a higher gas flow rate, with a decrease in membrane fouling and an increase in gel formation.
- The effect of degradation of large molecules is more pronounced at a higher gas flow rate, causing a higher flux and decreasing membrane resistances.

- During the ultrafiltration of the ozonated wastewater samples, the rate constant for the flux decline is larger than the rate constant for the removal of the deposit from the membrane, i.e. fouling mechanisms have a stronger effect on the membrane separation than that of deposit removal.

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Nomenclature

A	active membrane filtration area (m^2)
BD_5	biodegradability during 5 days (%)
BOD_5	biochemical oxygen demand (5 days) (gm^{-3}, mg g^{-1})
COD	chemical oxygen demand (gm^{-3}, mg g^{-1})
c_r	concentrate (retentate) concentration (kmol m^{-3})
c_p	permeate concentration (kmol m^{-3})
c_m	concentration at the membrane surface (kmol m^{-3})
d	peak-to-peak vibration amplitude at the periphery of the membrane (m),
F	vibration frequency (Hz)
J	permeate flux (Lm^{-2} h^{-1} or ms^{-1})
J_0	initial permeate flux ($Lm^{-2}h^{-1}$)
J_F	fouled membrane water flux ($Lm^{-2}h^{-1}$ or ms^{-1})
J_w	clean water flux (Lm^{-2} h^{-1} or ms-1)
$m_{methane}$	mass of the produced methane [kg]
MF	microfiltration
NF	nanofiltration
NEP	net energy product (J)
PCI	Paterson Candy International
Q	recirculation flow rate (Lh^{-1})
R	universal gas constant ($Jkmol^{-1}K^{-1}$)
R_1 and R_2	inner and outer radius of the membrane (m)
R_{cake}	cake resistance (m^{-1})
R_F	fouling resistance (m^{-1})
R_G	gel layer resistance (m^{-1})
R_M	membrane resistance (m^{-1})

R_P	polarization layer resistance (m^{-1})
R_T	total resistance (m^{-1})
Re	Reynolds number
RO	reverse osmosis
VRR	volume reduction ratio
t	time (h)
T	temperature (K)
TMP	transmembrane pressure (Pa)
TOC	total organic carbon (gL^{-1})
TSS	total soluble solids (°Brix)
UF	ultrafiltration
V_0	volume of the feed (L)
V_R	volume of the retentate (L)
V_P	volume of the permeate (L)
V	volume of the permeate (dm^3)
β	concentration polarization
$\gamma_{w,max}$	maximum shear rates at the membrane surface (m^{-1})
$\gamma_{w,g}$	mean shear rates at the membrane surface (m^{-1})
$\Delta\pi$	osmotic pressure difference (Pa)
Δp_{TM}	pressure difference between the two sides of the membrane (Pa)
η	viscosity (Pas)
$\eta_{w,g}$	viscosity of water (Pas)
ρ	density (kgm^{-3})
τ	time of treatment (h)

References

Akoum, O., Ding, L.H., Chotard-Ghodsnia, R., Jaffrin, M. Y., Gésan-Guiziou G. (2002a) Casein micelles separation from skimmed milk using a VSEP dynamic filtration module. *Desalination* 144: 325–330.

Akoum, O., Jaffrin, M.J., Ding, L.H., Paullier, P., Vanhoutte, C. (2002b) An hydrodynamic investigation of microfiltration and ultrafiltration in a vibrating membrane module. *Journal of Membrane Science* 197(1–2): 37–52.

Akoum, O., Jaffrin, M.J., Ding, L.H., Frappart, M. (2004) Treatment of dairy process waters using a vibrating filtration system and NF and RO membranes. *Journal of Membrane Science* 235: 111–122.

Akoum, O., Jaffrin, M.J., Ding, L.H. (2005) Concentration of total milk proteins by high shear ultrafiltration in a vibrating membrane module. *Journal of Membrane Science* 247: 211–220.

Balannec, B., Gésan-Guiziou, G., Chaufer, B., Rabiller-Baudry, M., Daufin, G. (2002) Treatment of dairy process waters by membrane operations for water reuse and milk constituents concentration. *Desalination* 147: 89–94.

Beszédes, S., Papp, N., Pongrácz É., Keiskki R., Hodúr C. (2011) Development of membrane wastewater purification process for meat industry SME's. *Annals of Faculty Engineering Hunedoara* 9(1): 133–139.

Cassano, A., Donato, L., Drioli, E. (2007) Ultrafiltration of kiwifruit juice: operation parameters, juice quality and membrane fouling. *Journal of Food Engineering* 79: 613–621.

Demirel, B., Yenigun, O., Onay, T.T. (2005) Anaerobic treatment of dairy wastewaters: a review. *Process Biochemistry* 40: 2583–2595.

Dyrset, N., Selmer-Olsen, E., Havrevoll, O., Ratnaweera, H., Storro, I., Birkeland, S.E. (1998) Feed supplement recovered from dairy wastewater by biological and chemical pretreatment. *Journal of Chemical Technology and Biotechnology* 73: 175–182.

Hodúr, C., Kertész, Sz., Csanádi, J., Szabó, G. (2009a) Comparison of 3DTA and VSEP systems during the ultrafiltration of sweet whey. *Desalination and Water Treatment* 10: 265–271.

Hodúr, C., Kertész, Sz., Csanádi, J., Szabó, G., László, Zs. (2009b) Investigation of vibratory shear-enhanced processing system. *Progress in Agricultural Engineering Sciences* 5(1): 97–110.

Kaewsuk, J., Thorasampan, W., Thanuttamavong, M., Seo, G.T. (2010) Kinetic development and evaluation of membrane sequencing batch reactor (MSBR) with mixed cultures photosynthetic bacteria for dairy wastewater treatment. *Journal of Environmental Management* 91: 1161–1168.

Kertész, Sz., László, Zs., Horváth, Zs., Hodúr, C. (2008) Analysis of nanofiltration parameters on removal of an anionic detergent. *Desalination* 221: 303–311.

Kertész, Sz., Beszédes, S., László, Zs., Szabó, G., Hodúr, C. (2010) Nanofiltration and reverse osmosis of pig manure: Comparison of results from vibratory and classical modules. *Desalination and Water Treatment* 14(1–3): 233–238.

Kertész, Sz., László, Zs., Forgács, E., Szabó, G., Hodúr, C. (2011) Dairy wastewater purification by vibratory shear enhanced processing. *Desalination and Water Treatment* 35(1–3): 195–201.

Kiss, I., Vatai, Gy, Bekassy-Molnar, E. (2004) Must concentrate using membrane technology. *Desalination* 162(1–3): 295–300.

Kushwaha, J.P., Srivastava, V.C., Mall, I.D. (2010) Treatment of dairy wastewater by commercial activated carbon and bagasse fly ash: parametric, kinetic and equilibrium modelling, disposal studies. *Bioresource Technology* 101: 3474–3483.

Lansing, S.L., Martin, J.F. (2006) Use of an ecological treatment system (ETS) for removal of nutrients from dairy wastewater. *Ecologycal Engineering* 28: 235–245.

László, Zs., Kertész, Sz., Mlinkovics, E., Hodúr, C. (2007) Dairy waste water treatment by combining ozonation and nanofiltration. *Separation and Science Technology* 42(7): 1627–1637.

László, Zs., Kertész, Sz., Beszédes, S., Hovorka H.Zs., Szabó, G., Hodúr, C. (2009) Effect of preozonation on the filterability of model dairy waste water in nanofiltration. *Desalination* 240: 170–177.

Luo, J., Ding, L., Wan, J., Paullier, P., Jaffrin, M.J. (2010) Application of NF-RDM (nanofiltration rotating disk membrane) module under extreme hydraulic conditions for the treatment of dairy wastewater. *Chemical Engineering* 163: 307–316.

Luo, J., Ding, L.H. (2011) Influence of pH on treatment of dairy wastewater by nanofiltration using shear-enhanced filtration system. *Desalination* 278: 150–156.

Makardij, A., Farid, M., Chen, X.D. (2002) A simple and effective model for cross flow microfiltration and ultrafiltration. *The Canadian Journal of Chemical Engineering* 80: 28–36.

Román, A., Wang, J., Csanádi, J., Hodúr, C., Vatai, Gy. (2009) Partial demineralization and concentration of acid whey by nanofiltration combined with diafiltration. *Desalination* 241: 288–295.

Sengil, I.A., Ozacar, M. (2006) Treatment of dairy wastewaters by electrocoagulation using mild steel electrodes. *Journal of Hazardous Materials* 137: 1197–1205.

Shi, W., Benjamin, M.M. (2011) Effect of shear rate on fouling in a Vibratory Shear Enhanced Processing (VSEP) RO system. *Journal of Membrane Science* 366: 148–157.

Szép, A., Kertész, Sz,, László, Zs., Hodúr, C. (2010) The hydrodynamic effect of microparticles on membrane resistance. *Desalination and Water Treatment* 14(1–3): 227–232.

Takata, K., Yamamoto, K., Brian, R., Watanabe, Y. (1998) Removal of humic substances with vibratory shear-enhanced processing membranes filtration. *Desalination* 117: 273–282.

Taylor, J.S., Mulford, S.J., Duranceau, S.J., Barrett, W.M. (1989) Cost and performance of membrane processes. *Journal American Water Works Association* 81(11): 52–60.

Van der Bruggen, B., Vandecasteele, C. (2002) Distillation vs. membrane filtration: overview of process evolutions in seawater desalination, *Desalination* 143: 207–218.

Vatai Gy. (2007) Mezőgazdasági alapanyagok és élelmiszerek kíméletes feldolgozása komplex membránműveletekkel. MTA dissertation.

Vourch, M., Balannec, B., Chaufer, B., Dorange, G. (2008) Treatment of dairy industry wastewater by reverse osmosis for water reuse. *Desalination* 219: 190–202.