VIBRATORY MEMBRANE SEPARATION FOR WASTEWATER TREATMENT

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ABSTRACT

To meet the requirements defined by environmental protection regulations effective wastewater treatment is required to process effluents before discharging them into sewers or living waters. While membrane separation offers a quite advantageous method to reduce the organic load of wastewaters, membrane fouling is still limiting its application in wastewater treatment. In this work the possibility of increasing shear rates on the surface of the membrane is investigated in order to reduce membrane fouling. Both ultrafiltration and nanofiltration is studied, with the use of a laboratory mode Vibratory Shear Enhanced Processing (VSEP). This work mostly focuses on studying the effects of module vibration and recirculation feed flow rate on permeate flux, specific energy demand and membrane rejections. Using the same operation parameters, vibration and non-vibration mode experiments are carried out with high and low recirculation flow rate to have a more detailed understanding of the shear rate effects. Furthermore, membranes with different molecular weight cut off are tested, in order to find the one which suits the best for this purpose.

1. Introduction

The European Union is constantly making serious efforts to address environmental issues – mainly by strictening the protection regulations. The food industry – including dairy industry – uses tremendous amount of water for its processes, resulting in vast amount of effluents. Generally, these effluents can be characterized by high organic load, resulting in high chemical oxygen demand (COD) and biological oxygen demand (BOD). Regulations concerning wastewater disposal require to effectively decrease these pollutants until they meet certain criteria. In addition to the conventional wastewater treatment technologies, membrane separation is a good means to reduce both organic and inorganic load of dairy effluents (Frappart et al., 2008). An important advantage of membrane separation is the low amount of chemicals required by the process, while the technology can be run on mild operation parameters and also, it is

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easily-combinable with other technologies (Bélafiné et al.). Unfortunately, membrane separation has drawbacks. Both the efficacy and the feasibility of the technology is limited by membrane fouling caused by pore clogging or concentration polarization, leading to flux decline (Bian et al., 2000). Numerous researches are being done worldwide to address this issue, by increasing the shear rates present on the surface of the membrane. In some studies, researchers have managed to increase shear rates by using a static promoter (Koris et al., 2011). Others were experimenting with different mechanical methods, to increase shear rates for example by rotating or vibrating the membrane module. Jogdan et al. claimed that by increasing shear rates, one can reduce pore clogging, thus increase flux. In this study, the feasibility of VSEP was investigated in dairy wastewater treatment, by processing model dairy effluent with a laboratory mode VSEP equipped with ultrafiltration and nanofiltration membranes. Shear rates caused by recirculation flow rate (*RFR*) and vibration were calculated and compared. The impact of shear rates (in both low and high *RFR*), and in both vibrated and non-vibrated modes) on flux, specific energy demand and rejection values were analyzed and compared.

2. Materials and methods

2.1. Model dairy wastewater

As stated in the introduction, a model dairy wastewater was used as feed in the experiments. The model dairy wastewater was prepared from distilled water and contained skim milk powder (MilkQuick, Hungary) in a concentration of 5 g/dm^3 and CL 80 anionic detergent (HungaroChemicals, Nagycserkesz) in a concentration of 0.5 g/dm^3. Characteristics of the model dairy wastewater were measured at 50°C and is shown in Table I.

Table I.: Model dairy wastewater characteristics at 50°C

Chemical oxygen demand	Electric conductivity	pH	Turbidity	Denisity	Protein	Dry matter	Lactose	Viscosity
[mgL^{-1}]	[µScm^{-1}]	[-]	[NTU]	[kgm^{-3}]	[g/g]	[g/g]	[g/g]	[mPas]
5000	**1300**	**7.25**	**330**	**983.9**	**0.32**	**0.102**	**0.233**	**0.37**

2.2. Analythical methods

Chemical oxygen demands of the samples were determined with ET 108 digester and a PC CheckIt photometer (Lovibond, Germany). The digestion was done at 150 °C for 2 hours – as the European protocol requires. Turbidity was measured with a HACH 2100AN turbidimeter (Hach, Germany). Density measurements were done with a Mettler Toledo 30PX Densito (Mettler-Toledo, Switzerland) portable density meter. Lactose, protein and dry matter content of the samples were analyzed with a Bentley 150 infrared milk analyzer (Bentley Instruments, USA). Electric conductivity and pH were determined with a BVBA C5010 multimeter (Consort, Belgium). Viscosity was given by an A&D vibro viscosimeter SV10 (A&D, Japan). All the analytic measurements were done at least three times, and the results were averaged.

2.3. VSEP, operating parameters and membranes used

VSEP Series LP filtration apparatus (New Logic Research Inc., USA) was used equipped with an L (Laboratory) module. Inside the module a single circular membrane was inserted, with an effective membrane area of 503 cm^2, inner radius (R_1) of 4.7 cm and outer radius (R_2) of 13.5 cm. Two polyethersulfone UF membranes were used, one with a molecular weight cut off (*MWCO*) of 10 kDa (PES-10 SYN) and one with 7 kDa (PES-5/Tyvek). Furthermore a thin film composite NF membrane with a *MWCO* of 240 Da (NF-TFC) was also tested. Membranes were kept under distilled water for at least 24 hours prior to separation experiments, which were conducted at 50°C. Transmembrane pressure (TMP) was set to 0.8 MPa during UF and 3 MPa during NF. A high, 16 dm^3/min and a low, 4 dm^3/min *RFR*s were applied in different experiments. During experiments in vibration mode, the amplitude set on 2,54 cm (1 inch) by increasing the frequency. Before starting the separation experiments flux was measured with distilled water, and after the separation experiment was finished a water flux was measured again and compared in order to determine the flux decreasing rate. 10 L of model dairy wastewater was used as feed and was processed until 2 L of retentate was left, resulting in a volume reduction ratio (VRR) of 4, though the dead volume of approximately 1,5 L of the apparatus is need to be taken into account, as well as the evaporation which is not negligible in longer experiments.

2.4. Calculated parameters

The flux decreasing rate, *FDR* [%] was calculated by Eq. 1:

$$\mathrm{FDR} = \left(1 - \frac{\mathrm{J_{WA}}}{\mathrm{J_{WB}}}\right) 100 \tag{1}$$

where J_{WA} [$m^3m^{-2}s^{-1}$] is the water flux measured – after the separation experiment - on the used, fouled membrane and J_{WB} [$m^3m^{-2}s^{-1}$] is the water flux measured – before the separation experiment – on the unused, clean membrane. The specific energy demands in non-vibration mode, e_{vn} [kWh m^{-3}] and in vibration mode, e_v [kWh m^{-3}] were defined using the following equations:

$$e_{vn} = \frac{\eta_{fp} \times P_{fp}}{J \times A_{membrane}} \quad (2), \qquad e_V = \frac{\eta_{fp} \cdot P_{fp} + \eta_V \cdot P_V}{J \times \cdot A_{membrane}} \quad (3)$$

In non-vibration mode the shear rate, γ [1s^{-1}] was determined with the following Eq. 4 (Delaunay et al., 2008). The maximal shear rate, $\gamma w max$ [1s^{-1}] and the mean shear rate γw were defined using the Eq. 5 and Eq. 6 (Al Akoum et al., 2002):

$$\gamma = \frac{4}{\frac{1}{2}h} V_{max} \quad (4)$$

$$\gamma_{w\,max} = 2^{\frac{1}{2}} A(\pi f)^{\frac{3}{2}} \nu^{-\frac{1}{2}} \quad (5) \qquad \gamma_w = \frac{2^{\frac{3}{2}}(R_2^3 - R_1^3)}{3\pi R_2\,(R_2^2 - R_1^2)}\, \gamma_{w\,max} \quad (6)$$

where *h* is the height of the fluid inside the module [m], v_{max} is the maximal flow velocity inside the module [ms^{-1}], *A* is the amplitude [m] and *f* is the frequency [Hz] of the vibration, *ν* is the dynamic viscosity of the feed [m^{2}s^{-1}]. R_2 is the outer radius of the membrane [m], R_1 is the inner radius of the membrane [m].

3. Results and discussion

3.1. Calculation of shear rates

By using Eq. 4, 5 and 6 shear rates were calculated in both non-vibration (*NV*) and vibration (*V*) mode. Also, Reynolds number (Re) was calculated in *NV* mode. Re number turned out to be 8494 if the *RFR* was set to low and 33975 if it was set to high, meaning that the flow characteristic is laminar in both cases, as the lower limit of transitional flow characteristic is Re = 30000 as far as liquid films are concerned. The shear rate we have calculated for *NV* mode was 521 with low, and 2085 with high *RFR* setting. In *V* mode, when the amplitude was set to 2,5 cm (1 inch), the mean shear rate turned out to be 121908, while the maximum shear rate was 129692.

3.2. Effect of vibration and RFR on flux, specific energy demand and rejections

Fluxes of nanofiltration in both *V* and *NV* mode, with the *RFR* set on both high and low are shown in Figure 1. Meeting our expectations, the highest fluxes can be achieved in vibration mode, but surprisingly, *RFR* has almost no impact on flux in *V* mode. On the other hand, the effect of *RFR* is quite remarkable in *NV* mode, the four times higher *RFR* results in two times higher fluxes. Similar experiments were conducted with ultrafiltration, and the results showed a very similar tendency.

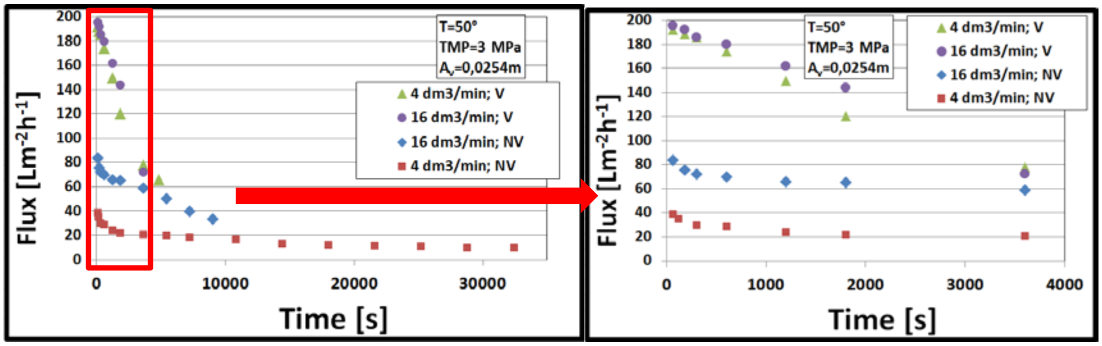

Figure 1.: The impact of vibration and recirculation flow rate on nanofiltration fluxes

Specific energy demands of the previously discussed experiments were calculated (Eq. 3 and 4) and shown in Figure 2. The conclusion we have reached concerning specific energy demand is very similar to the one we got by the comparison of fluxes. In *NV* mode the process run on low *RFR* has excessively higher specific energy demands, so we can claim that the effect of *RFR* is undoubtedly remarkable in *NV* mode. Clearly, in *V* mode, *RFR* does not seem to have an effect at all. As far as vibration is concerned, the effect is quite positive once again, we have measured the bottommost specific energy demand.

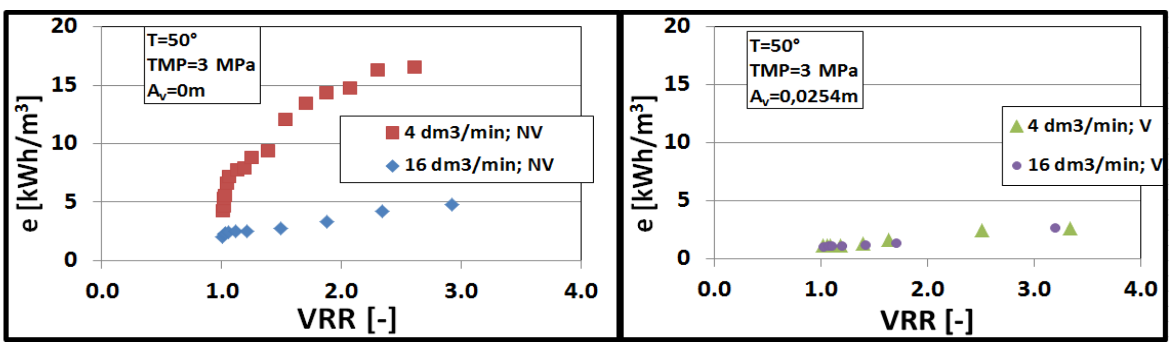

Figure 2.: Specific energy demands in low and high recirculation flow rate experiments, (a,) *NV* mode (b), *V* mode.

Chemical oxygen demand (COD) rejections of both UF and NF are shown in Figure 3. By comparing the COD rejection values calculated in both *V* and *NV* mode and also the *RFR* set both high and low we have reached to the conclusion that although slightly better rejections could be achieved in *V* mode, the difference is negligible. Practically, neither parameter has significant effect on COD rejection, especially if NF results are concerned. Though this study focuses on the effects of vibration and *RFR*, it is necessary to keep in mind that the purpose of membrane separation in wastewater treatment is to decrease the pollutants to meet certain criteria. Since the model dairy wastewater used as feed had a COD of 5000 mgl^{-1}, the UF resulted in a permeate with COD of ~2000 mgl^{-1}, while the NF produced a permeate with a COD lower than 50 mgl^{-1}.

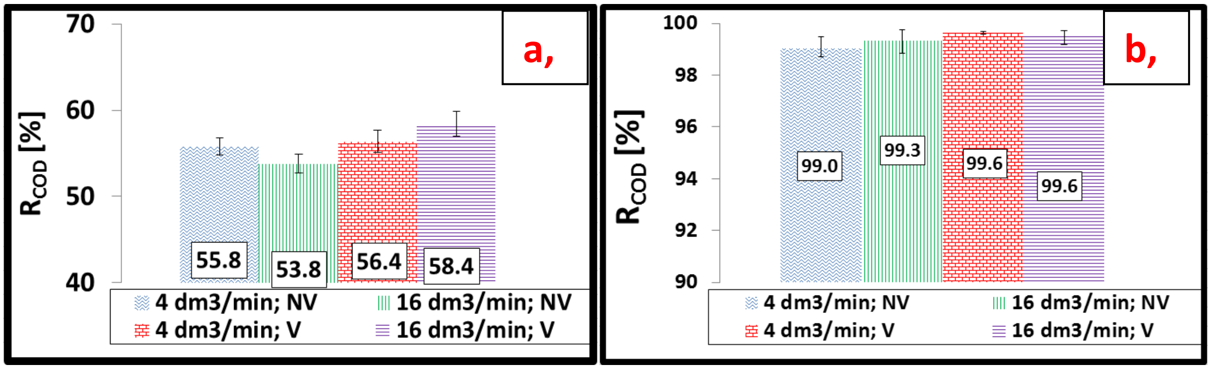

Figure 3.: Chemical oxygen demands rejections of (a,) 10 kDa UF membrane (b,) 240 Da NF membrane

Flux decreasing rates (FDR) were calculated by Eq. 2. Regarding both UF and NF, we have reached to the conclusion that increased *RFR* does not have a remarkable effect on FDR, neither in *V* mode nor in *NV* mode. On the other hand, using vibration causes a decent decrease in FDR values, especially in the case of NF.

3.3. Experiments aiming to increase rejection values

In Hungary, at present the 28/2004 KvVM regulation defines that wastewaters discharged into sewers may have a maximum of 1000 mgl^{-1} COD, and wastewaters discharged into living waters must not have a COD value higher than 50-100 mgl^{-1} (varies by region). Processing the model dairy wastewater (COD = 5000 mgl^{-1}) with UF resulted in a permeate with a COD of ~2000 mgl^{-1}, which is significantly higher than the criteria one has to meet to discharge the effluent into sewer. On the other hand, processing it with NF resulted in a permeate with a COD lower than 50 mgl^{-1}, which allows the effluent to be discharged into living waters. In order to find a way to meet the 1000 mgl^{-1} COD threshold criteria of the sewer discharging, another UF membrane with a lower, 7 kDa *MWCO* was tested. As discussed before, we have come to the conclusion that the vibration does definitely have a positive overall effect on the process, and the high *RFR* has some (minor) advantages compared to the low one, in *V* mode, thus, we have decided to run the following experiments in *V* mode, with the *RFR* set to 16 dm^3/min. Separation tests with the 7 kDa UF membrane was run by the same parameters as the 10 kDa UF tests. COD, electric conductivity and turbidity rejections of the two UF and one NF membranes were measured and shown in Figure 3./a. Comparing the 10 kDa and the 7 kDa UF rejections shows a steep increase in COD rejections. There are certain components in milk, that have molecular weight (MW) between 10 kDa and 7 kDa – for example glycomacropeptides, with a MW of 8 kDa (Berry et al., 2009) -- which means that only the 7kDa UF membrane rejects them. It explains the difference between the COD rejections of the two UF membranes. It's remarkable, that since our feed model dairy wastewater had a COD of 5000 mgl^{-1} and the COD rejection turned out to be higher than 80% with the 7 kDa UF membrane, this experiment resulted in a permeate with a COD lower than 1000 mgl^{-1} – meaning that we have managed to meet the requirements for wastewater discharging into sewers. Fig. 3./a also shows a significant, 20% increase in electric conductivity rejections, when the 10kDa and 7 kDa UF values are compared. Turbidity rejections were above 99% in every case, which was expected since the permeates were visually clear, transparent. Protein and lactose rejections of the two UF membranes are shown in Fig. 3/b. As we could assume based on the COD rejection values, the 7 kDa UF membrane had decently higher, almost 100% protein rejection values. It is also remarkable that the 7kDa UF lactose rejections are twice as high as the 10 kDa UF rejections.

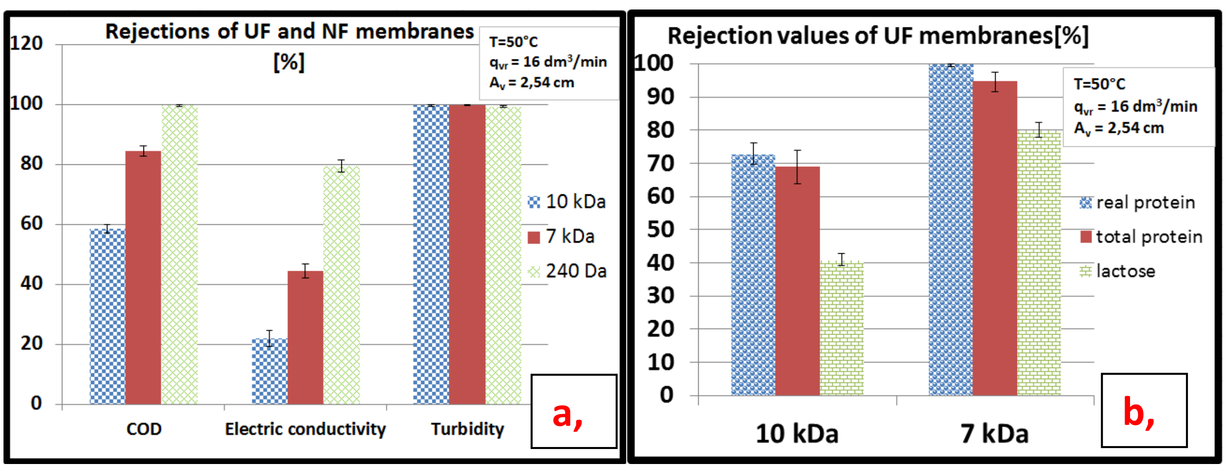

Figure 3.: Rejection values measured calculated for different UF and NF membranes

As previously stated, experiments with both UF membranes were carried out by the same parameters. The fluxes turned out to be practically equal, but the specific energy demands showed a noteworthy difference: during the experiment with the 10 kDa UF membrane specific energy demand measured at the 30-minute mark was 1,66 kWh/m^3, while this value at the same

30-minute mark turned out to be 2,21 1,66 kWh/m^3 when the 7 kDa UF membrane was used, so for the better rejection values we have to invest more energy.

4. Conclusion

In this study, UF and NF of the tested dairy model wastewater were investigated. We can conclude that higher shear rate definitely has positive effect on the process in almost every regards. Increased shear rate resulted in higher flux, overall rejection values, as well as a drastically decreased specific energy demand. Furthermore, flux decreasing rates became lower. By calculating and comparing the shear rates in experiments with different operating parameters (both vibration and non-vibration mode, both low and high recirculation flow rate) we have reached the conclusion that vibration causes a tremendously higher shear rate increasing than setting the *RFR* high does. This explains another observation we have made, namely, that in non-vibration mode the *RFR* played a quite important role, the higher *RFR* resulted in a remarkable positive change in every regard. Unexpectedly, in vibration mode, the *RFR* had negligible impact on most investigated aspects, the results were practically the same whether the *RFR* was set high or low. Also, regarding that the requirements defined by the regulations have to be met, we have compared permeate COD values with the limits set by the law and concluded that permeate quality of the NF and 7 kDa UF could reach the threshold COD limit, while 10 kDa could not.

Acknowledgements:

SUPPORTED BY THE ÚNKP-16-1 NEW NATIONAL EXCELLENCE PROGRAM OF THE MINISTRY OF HUMAN CAPACITIES

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