MULTI-STAGE MEMBRANE PROCESSES FOR WASTEWATER TREATMENT

Szabolcs Kertész, Péter Bor, Sándor Beszédes, Veréb Gábor, László Zsuzsanna, Hodúr Cecilia

Department of Process Engineering, Faculty of Engineering, University of Szeged, H-6725 Szeged, Moszkvai krt. 9, Hungary
e-mail: kertesz@mk.u-szeged.hu

Abstract

In this work the feasibility of the purification of dairy wastewater was investigated by multi-stage membrane separation techniques using ultrafiltration and nanofiltration. In order to investigate the applicability of the single and multi-stage processes, first, the permeate fluxes and flux decline rates were analyzed. Secondly, membrane rejections, based on chemical oxygen demand, conductivity and turbidity were compared. Finally, the biogas production from the concentrates were measured and compared for further utilization of the membrane separation by-products.

Introduction

Before discharging into living waters or sewerage, appropriate wastewater treatment is necessary to effectively decrease the pollution, especially organic load of dairy wastewater. Effluents need to be effectively treated to meet the strickening European Union environmental regulations. Nowadays the commonly used technologies such as sedimentation or oxidation, membrane separation can offer a novel solution. Although the advantages of membrane separations are remarkable, like high flux and contaminant rejection or good mechanical strength and durability, fouling of membranes are still a critical issue which limits the application of larger scale industrial utilizations [1, 2]. Increasing the shear rate on the membrane surface by module vibration can reduce membrane fouling by altering the concentration polarization, decreasing the cake layer and to reduce the deposition of particles on the surface [3, 4]. Limited data is available from scientific articles on the application of vibratory shear enhanced processing (*VSEP*) for dairy wastewater treatment [5, 6], especially in multi-stage membrane systems [7].

Ultrafiltration (*UF*) and nanofiltration (*NF*) have been proven to be effective at dairy wastewater treatment and have many advantages: almost complete retention of proteins and clean effluent water and low energy consumption. In addition, Zhang et al. [8] have reported that the shear stress could effectively remove casein micelles and whey protein layer on the membrane surface and the cleaning temperatures of 35 and 50°C had a much greater cleaning capacity than that of 20°C. However, severe non-washable membrane fouling could form inside the pores caused by dairy particles and proteins. Recently, other studies have reported that membrane mitigation can be occurred by increasing the shear rate at the membrane surface that can scour and reduce the deposit of foulants; vibrations of the membrane can create high surface shear stresses, which can efficiently improve both the permeate flux and mass transfer [9, 10, 11].

In the present study, we investigated the efficiency of a multi-stage membrane system in terms of permeate flux, flux decline rate, membrane rejection and the concentrates biogas production performances. In the first stage a shear enhancement *UF* device was used for controlling membrane fouling in filtration dairy wastewater. In the second stage a classical cross-flow *NF* device was tested for two possible reasons: achieving more effective foulants removal and to reach a much higher volume reduction ratio in order to compare the results with only one stage test.

Experimental

Synthetic dairy wastewater was used for the separation experiments from skimmed milk powder (5 g/dm; InstantPack, Hungary) and anionic surfactant cleaning agent Chemipur CL80 (0.5 g/dm; Hungaro Chemicals, Hungary).

The electric conductivity and pH of the samples was determined with a C5010 type multimeter (Consort, Belgium). The turbidity was measured with a HACH2100AN turbidimeter (Hach, Germany). The samples were analysed with a chemical oxygen demand (*COD*) ET 108 digester and a PC CheckIt photometer (Lovibond, Germany). All of the analytical measurements were repeated three times to calculate an accurate average.

The first stage of the multi-stage membrane filtration experiments was carried out using a *VSEP* L Series membrane device equipped with a single circular membrane of 503 cm^2 with an outer radius of 13.5 cm and inner radius of 4.7 cm for *UF* (New Logic Research Inc., USA). Supporting the membrane housing there is a vertical shaft, which acts as a torsion spring and transmits the oscillations of a lower plate, and the housing containing the membrane oscillates azimuthally with displacement amplitude, which was adjusted to be 2.54 cm on the outer rim. In figure 1/a detailed schematic diagram description of *VSEP* system is given. A more detailed description of it can be found in our earlier publication [12]. The second stage of the multi-stage membrane filtration experiments was carried out with an Uwatech *3DTA* classical laboratory cross-flow membrane apparatus (Uwatech Gmbh., Germany) with the use of flat-sheet standard membranes with a filtering surface area of 156 cm^2 for both *UF* and *NF* experiments (fig. 1/b).

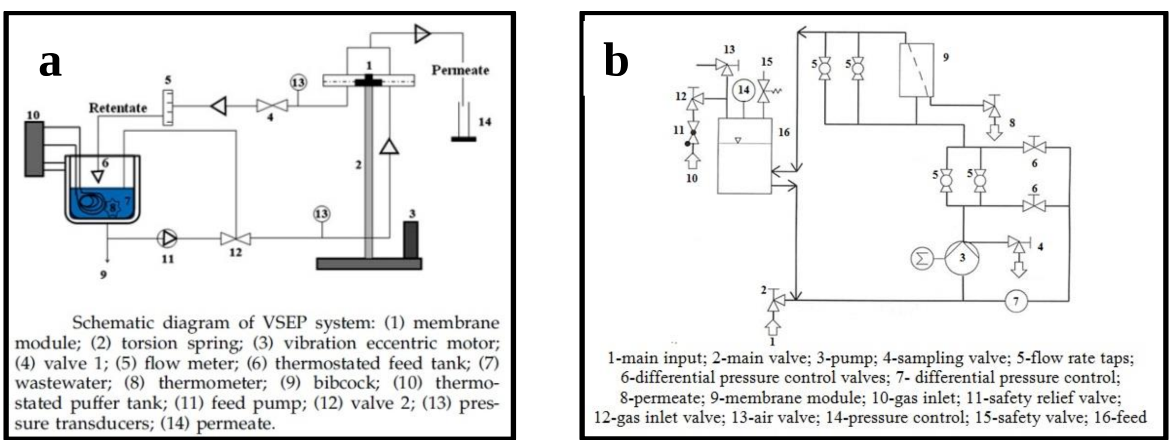

Figure 1. Diagrams of membrane separation devices (a: first stage: a vibratory shear enhanced processing [12], *VSEP* device; b: second stage: classical cross-flow membrane, *3DTA* apparatus)

All the separation experiments were carried out at 50±1°C, transmembrane pressure was set to 0.8 MPa in case of *UF*, and 3 MPa for *NF*. Three polyethersulfone 10 kDa, 7 kDa and 5 kDa *UF* membranes were tested, and a thin film composite (*TFC*) *NF* membrane with a molecular weight cut-off (*MWCO*) of 200 Da.

Batch mesophilic anaerobic digestion tests were carried out at 37°C for 30 days to determine the biogas yield from the concentrates. Biogas production was detected by pressure increase method in continuously stirred reactors with volume of 250mL equipped by OxiTop-C® measuring heads (WTW, Germany).

Results and discussion

Permeate fluxes

The single *UF* experiments were carried out three different *MWCO* in order to compare the effects of them to the second stage. The scope of the multi-stage separation experiments could be different. In one hand, when *NF* of the *UF* permeates was tested, the *UF* was practically a pre-filtration process before *NF*. By comparing the multi-stage experiments with the single filtration ones, the effect of the pre-filtration was investigated. On the other hand, when *NF* of the *UF* concentrates were carried out, the aim was to process the concentrates until a much higher volume reduction ratio (*VRR*). The volume reduction ratio, *VRR* [-], was defined as

$$\mathrm{VRR} = \frac{\mathrm{V_F}}{\mathrm{V_F - V_p}} \qquad (2)$$

where V_F is the volume of the feed [m^3] and V_P is the volume of the permeate [m^3] at any time. Since the further utilization of the membrane filtration concentrates are always an important issue, a post-treatment was also investigate. Therefore, the biogas yields of concentrates with different concentrates from different stages were tested.

The first stage *UF* and second stage *NF* experiments were carried out in order to investigate the permeate fluxes, flux decline rates, membrane rejections and biogas production of the concentrates. First, the permeate fluxes and flux decline rates were analyzed. The permeate flux, *J* [L/m^{2}hbar] was defined using equation 1 in order to compare fluxes of the two different filtration devices:

$$\mathrm{J} = \frac{\mathrm{dV_p}}{\mathrm{dt}} \, \frac{1}{\mathrm{A_m \times TMP}} \qquad (1)$$

where V_p is the volume of permeate [L], t is the membrane filtration time [h] and A_m is the effective membrane area [m^2] and *TMP* is the transmembrane pressure [bar].

Figure 2 shows the permeate fluxes (a) and flux decline rates, J/J_0 (b) of multi-stage *UF* and *NF* membrane processes as a function of filtration time.

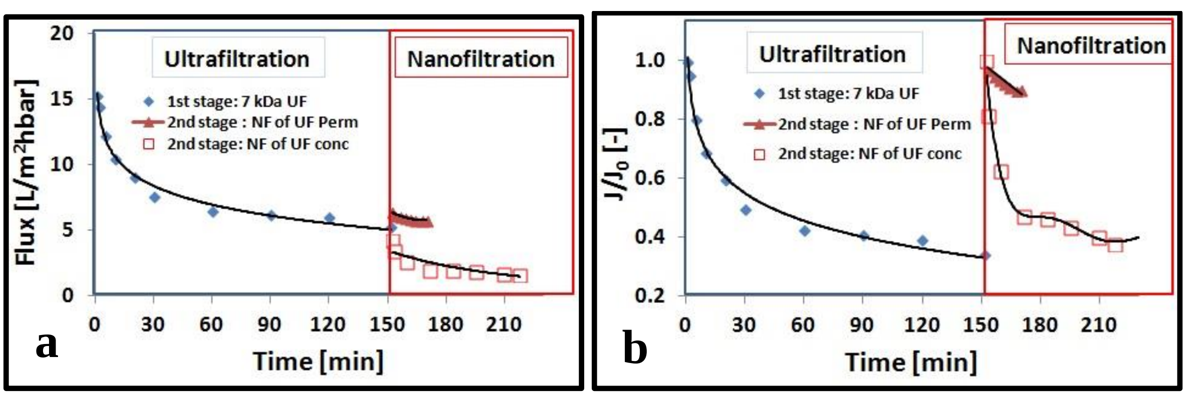

Figure 2. Fluxes of the different membrane filtration stages (a) and flux decline rates (J/J_0) with different processes (b) (first stage: *VSEP*, A_{vibr} = 2.54 cm, 7 kDa *PES* membrane; second stage: Uwatech *3DTA*, 200 Da *TFC* membrane)

Due to membrane fouling, all of the membrane fluxes decreased during the filtration procedure. As shown in right side of the figure 2/a, the *NF* of *UF* permeate fluxes were higher than the *NF* of *UF* concentrate fluxes. Furthermore the filtration time was also shorter in the case of *UF* permeate till the end of the experiments, when achieved the same final *VRR* of 8. (The *VSEP* had a dead volume of 2 L, while *3DTA* apparatus had a significantly smaller dead volume of 0.2 L.) In the first stage 10 L of feed model wastewater was ultrafiltered to a concentrate volume of 2 L to *VRR* of 5. In second stage 1.6 L of concentrate was used for the experiments and processed to a concentrate to the volume of 0.2 L (*VRR*=8). The multi-stage concentrations resulted in a total *VRR* of 40.

In figure 2/b, the average flux decline rate was higher in case of *NF* of *UF* concentrate than *NF* of *UF* permeate, revealed that a higher fouling tendency was observed in that case. Is also visible that less time is needed to achieve the same final *VRR* when permeate of *UF* was tested by *NF*. It can be also seen that by using a new nanofiltration membranes in the beginning of the second stage the extent of membrane fouling can be lessened in both *NF*, than in the first stage UF.

Membrane rejections

The original synthetic dairy wastewater had an average *COD* of 4770 mg/L, *EC* of 0.821 mS/cm and turbidity of 221.5 NTU. *COD* represents the total organic load, and *EC* shows the salts in the analyzed samples. The selectivity of the membrane, *R* [%], for a given solute was expressed by the average retention using the following equation 3:

$$R = \left(1 - \frac{c}{c_0}\right) 100 \qquad (3)$$

where c is the average concentration of the solute in the permeate phase, and c_0 is the concentration of the solute in the feed wastewater expressed by chemical oxygen demand, conductivity or turbidity.

In figure 3/a, it can be observed that the first stage resulted 75.31, 79.92 and 52.52 % *COD* rejection using 5 kDa, 7 kDa, and 10 kDa *UF* membranes, respectively. In figure 3/b, it is visible that the *COD*, *EC* and turbidity rejections could be effectively increased by the second stage. Implementation of the multi-stage clarification stages (with 7 kDa *UF* then *NF*) the *COD*, *EC* and *Turb* rejection increased by 19.08, 20.66 and 0.11 %, respectively.

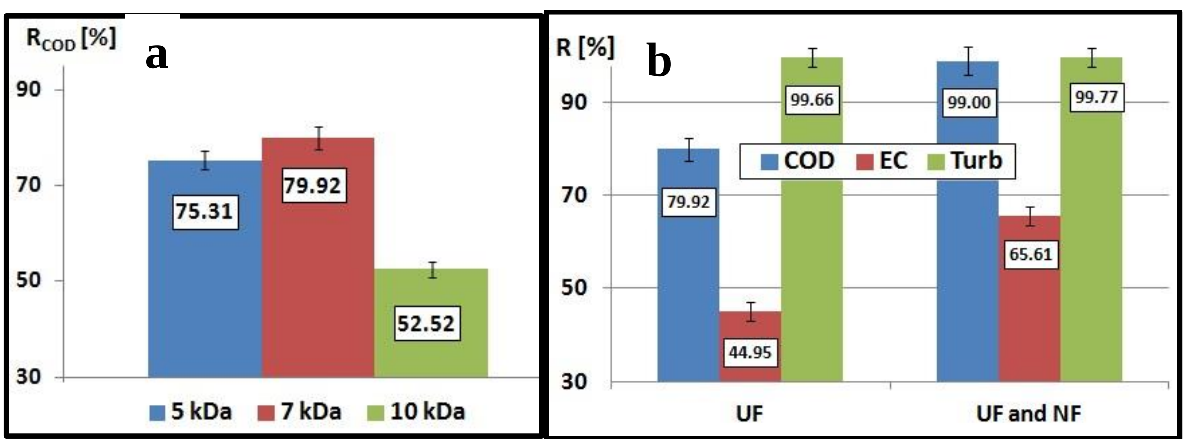

Figure 3. First stage (a) (Ultrafiltration, *UF*) and multi-stage (b) (Ultrafiltration followed by Nanofiltration, *UF* and *NF*) membrane process rejections expressed by of chemical oxygen demand (*COD*), electric conductivity (*EC*) and turbidity (*Turb*)

Figure 4 compares the biogas production of first stage of *UF* concentrates, *UF* permeate, original wastewater (fig. 4/a) and concentrates of 5 kDa *UF* followed by *NF* and 10 kDa *UF* followed by *NF* concentrates of two-stage separation tests (fig. 4/b). On the one hand, comparing the pore sizes of the *UF* membranes revealed that concentrates of the smaller pore size *UF* membrane had higher biogas production. All of the *UF* concentrates had higher, but permeate of the *UF* had lower biogas production than the original feed. On the other hand, in the multi-stage process it increased almost two times and concentrates of the 5 kDa *UF* followed by *NF* had the highest biogas production.

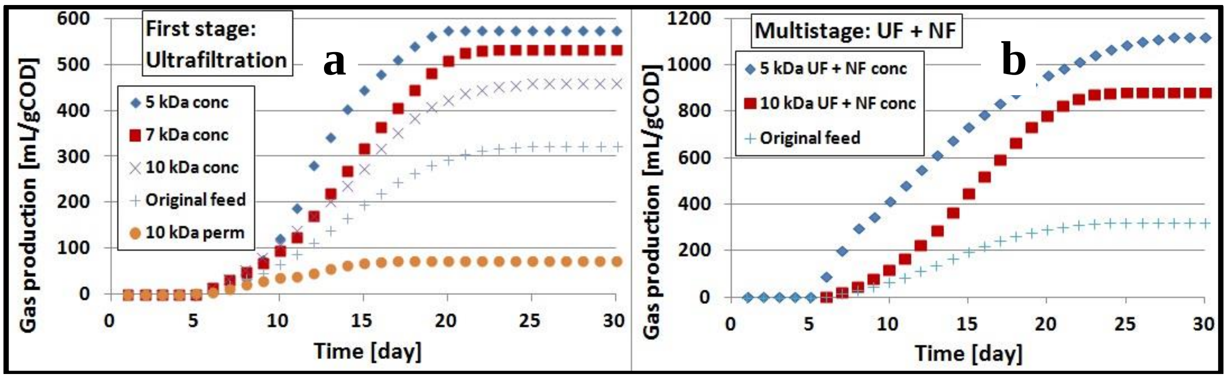

Figure 4. First stage (a) (Ultrafiltration, *UF*) and multi-stage (b) (Ultrafiltration followed by Nanofiltration, *UF* and *NF*) membrane process biogas productions from different concentrates

Conclusion

In this study the purification of dairy wastewater was investigated by multi-stage membrane separation techniques by ultrafiltration and nanofiltration. In order to investigate the effects of the second stage of the processes, the influences of permeate fluxes, flux decline rates, membrane rejections and biogas production were measured and compared. The nanofiltration of ultrafiltration permeate fluxes were higher than the nanofiltration of ultrafiltration concentrate fluxes. It was observed that the chemical oxygen demand, conductivity and turbidity membrane rejections significantly increased by the second nanofiltration stage. Comparing the pore sizes of the ultrafiltration membranes revealed that concentrates of the smaller pore size ultrafiltration membrane had higher biogas production. All of the ultrafiltration concentrates had higher, but it's permeate had lower biogas production than the feed. Furthermore, in the multi-stage process, it increased almost two times and concentrates of the 5 kDa ultrafiltration followed by nanofiltration had the highest biogas production.

Acknowledgements

Supported by the UNKP-17-4 New National Excellence Program of the Ministry of Human Capacities. The authors are also grateful for the János Bolyai Research Scholarship of the Hungarian Academy of Sciences and the project Hungarian Science and Research Foundation (OTKA contract number K 115691).

References

[1] K. Wang, A.A. Abdalla, M.A. Khaleel, N. Hilal, M.K. Khraisheh, Desalination 411 (2017) 190.
[2] B. Wu, R. Wang, A.G. Fane, Water Res. 110 (2017) 120.
[3] L.H. Ding, M.J. Jaffrin, Sep. Sci. Technol. 49 (2014) 1953.
[4] J. Luo, W. Cao, L.H. Ding, Z. Zhu, Y. Wan, M.Y. Jaffrin, Sep. Sci. Technol. 96 (2012) 194.

[5] M.Y. Jaffrin, J. Membr. Sci. 324(1-2) (2008) 7.
[6] O. Akoum, M.Y. Jaffrin, L.H. Ding, M. Frappart, J. Membr. Sci. 235 (2004) 111.
[7] B. Farizoglu, S. Uzuner, Biochem. Eng. J. 57 (2011) 46.
[8] W. Zhang, L. Ding, M.Y. Jaffrin, B. Tang, Chem. Eng. J. 325 (2017) 457.
[9] T. Li, A.W.K. Law, M. Cetin, A.G. Fane, J. Membr. Sci. 427 (2013) 230.
[10] F. Zhao, H. Chu, Y. Zhang, S. Jiang, Z. Yu, X. Zhou, J. Zhao, J. Membr. Sci. 529 (2017) 215.
[11] M. Pourbozorg, T. Li, A.W.K. Law, Water Res. 99 (2016) 101.
[12] Sz. Kertész, Á. Veszprémi, Zs. László, J. Csanádi, G. Keszthelyi-Szabó, C. Hodúr, Desal. Water Treat. 55 (2015) 2836.