Analecta Technica Szegedinensia
Vol. 16, No. 01 ISSN 2064-7964 2022

INVESTIGATION OF ULTRAFILTRATION PARAMETERS OF DIFFERENT ORGANIC LOAD WASTEWATER TYPES

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ABSTRACT

Almost a third of Earth's freshwater resources are used by municipalities, agriculture and industries and therefore very large quantities of wastewater are generated and discharged into surface water or groundwater. If discharged inadequately and without previous treatment, wastewater can cause chemical pollution, affect aquatic life as well as human health and have a negative impact on the environment. An emerging technology for wastewater treatment is the membrane separation process due to the low cost, the use of ambient temperature, the low energy consumption compared to other traditional techniques, and the high selectivity of different separation mechanisms with compact design.
In this study, ultrafiltration (*UF*) technique was investigated to treat wastewater with different organic loads. The effects of the stirring and a three-dimensional (3D) printed spacer, integrated into the *UF* cell were analyzed on the permeate fluxes, membrane rejections of turbidity, conductivity and chemical oxygen demand (*COD*).

Keywords: ultrafiltration, food wastewater, membrane separation processes, 3D printed spacers

1. INTRODUCTION

Wastewater effluents are becoming an environmental and societal concern and can cause serious human concern because of the unknown effects on aquatic life, human health and the environment [1-2]. The use of water, especially by the food industry is much greater than other industry sectors since water is used as a raw material or for cooling, heating, cleaning, cooking, transportation and other various purposes [3]. Although food industry wastewater is difficult to characterize because its content varies according to used products, processes and the season, the main contaminants are microorganisms, biodegradable organic materials, fertilizers, pesticides, metals, nutrients, organic and inorganic materials [4]. Unlike municipal wastewater, wastewater generated by the food industry is biodegradable, nontoxic and is characterized by a high concentration of suspended solids. In Europe and the United States, the bakery industry is one of the greatest water users and more than half of the used water is later released as wastewater [5]. Bakery industry wastewater contains a substantial amount of organic materials, organic carbon, sugars, proteins, and enzymes [6]. In addition to high values of biochemical oxygen demand (*BOD)*, *COD* and a high concentration of suspended solids, bakery wastewater is also characterized by a high value of total nitrogen and a dark color [5]. The dairy industry generates large amounts of wastewater as well. Water is used in all steps of production in the dairy industry such as sanitization, heating, cooling, milk processing, packaging and cleaning of milk tankers [7]. Most of the wastewater generated by the dairy industry results from cleaning of tank trucks, milk silos, the transport lines and equipment during production. Wastewater from the dairy industry typically contains a high concentration of proteins, lipids and carbohydrates. Additionally, it has a high concentration of suspended solids, chlorides, and high *BOD* and *COD* values [3]. Some studies presented that food, bakery wastewater is an acidic wastewater rich in oil, grease and suspended solids with a high *COD* value that is generally in the range of 1-10 g/L [5, 8, 9].
Membrane separation processes are applied in a wide range of industries – food, chemical, medicine, pharmaceutical and many other fields. Membrane techniques have found their application in wastewater treatment because of their potential to remove particles, improve the aesthetic of the water and inactivate

DOI: https://doi.org/10.14232/analecta.2022.1.129-135

pathogens. On the other hand, the main disadvantage of them is the membrane fouling which causes flux decrease and a decrease in productivity. Recent studies have indicated that the changing of the hydrodynamic conditions into the membrane module can result in enhanced mixing efficiency and improved flow conditions. The use of three-dimensional (3D) printed spacers into the module can result in enhanced mixing efficiency and improved flow conditions. The use of 3D printed spacers into the module can enhance mass transfer through the *UF* membrane by reducing concentration polarization and fouling tendency. 3D printing can enable a promising new class of efficient laboratory devices for filtration processes [10-11]. On the other hand, higher mechanical stirring into the module can alleviate membrane fouling with increasing the shear rate on the surface of the membrane.
The main aim to use plastic spacers into the membrane module is the improving of the hydrodynamics of the fluid flow. They can serve as obstacles in the flow with disrupting the laminar flow profile in the boundary layer and initiate vortices. This type of mixing intensification also results in higher velocities and shear rates at the membrane surface, which can mitigate membrane fouling. The spacers can be in a form of 2D structures such as squares, triangles and circles, but the potential application of 3D printed technology has been gaining attention. Nowadays, the significant development of 3D printing has also broken into the field of wastewater treatment. The 3D printing is becoming more efficient and cheaper to design 3D printed spacers that can be integrated into membrane filter modules, which became unimaginably fine and detailed using complex geometries [12-13].
In this article, we have demonstrated the role of 3D printed spacers, promoters in performance enhancement of the ultrafiltration cell in low- and high-loaded model dairy wastewater and real bakery and dairy wastewater types. Ultrafiltration permeate fluxes, permeate flux decline, resistances and chemical oxygen demand (COD) rejections with and without spacer and stirring were studied and compared testing the different organic load wastewater types.

2. MATERIALS AND METHODS

2.1. The tested food wastewater types
The real bakery wastewater (*Real bakery ww.*) sample was collected from a bakery in Serbia, which offers a variety of products, but specializes in the production of filled puff pastry that is frozen and stored at -18℃. This sample came from the production of pastry filled with soft white cheese. After collection, the sample was stored in sterile freezer container. The real dairy wastewater (*Real dairy ww.*) sample was collected from a dairy company in Szeged, Hungary and was frozen and stored at -18℃. Additionally, two different concentration model dairy wastewater solutions were prepared using tap water and milk powder. These solutions were prepared to represent a minimum, relatively low organic loaded dairy synthetic wastewater (*Low-loaded ww.*) and a maximum, relatively high organic loaded dairy synthetic wastewater (*High-loaded ww.*) types with *COD* value of 1000 and 10 000 mg/L respectively. The initial *COD* values were 1000, 10000, 2800 and 1400 mg/L for Low-loaded dairy, High-loaded dairy, Real bakery and Real dairy wastewater samples respectively.

2.2. The laboratory membrane separation apparatus
Ultrafiltration experiments were carried out with a *Millipore Solvent Resistant Stirred Micro- and Ultrafiltration Cell* shown on Fig. 1. (Merckmillipore, Germany). The special device is constructed from stainless steel and borosilicate glass, which offers a rapid and efficient method for concentration of smaller, laboratory samples volume up to 300 mL at low and medium pressure (max. 5 bar). In this device the solutes, molecules and particles, less than the membrane's molecular weight cut-off (*MWCO)* can pass through the membrane as filtrate while solutes bigger than the *MWCO* are retained and concentrated within the retentate side into the cell after the membrane separation process.

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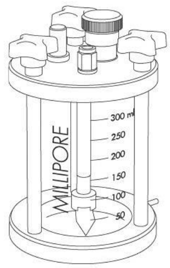

Figure 1. Millipore Solvent Resistant Stirred Cell (from device book)

2.3. The polymer membranes

Polyethersulfone (*PES*) membrane with 30 kDa *MWCO* were used for the experiments, which was chosen based on literature that indicate that it had the lowest permeate flux decline and lowest fouling degree, as well as fouling resistances using *UF* of whey model solutions compared to 5 kDa and 15 kDa [4]. The active membrane surface area was about 40 cm^2.

2.4. The laboratory *UF* experiments

Four different wastewater types were tested with the following measuring order: Firstly, distilled water was used as feed on raw, clean membrane to determine the membrane water flux before the filtration. Then, the concentration experiment was started with the *UF* of the tested wastewater at 25℃ and using *TMP* (Transmembrane Pressure) of 4 bar. Every type of wastewater was filtered with three different experiments: (1) Control *UF* experiments without stirring and the use of the 3D printed spacer;

(2) experiments with stirring at the rate of 400 rpm (it was determined earlier to be the optimal speed) without spacer; and

(3) experiments with stirring of 400 rpm and the use of a 3D printed spacer.

The membrane rejections were calculated using the measured turbidity, conductivity and *COD* values of feed and permeate samples after every type of wastewater membrane separation experiment.

2.5. The 3D printing characteristics

The spacer was designed by Cura software (Ultimaker Cure 5.0.0), printed by a Creality CR-10S Pro V2 3D printer (China). This particular design was chosen as optimal based on our Department previous results and it is shown in Fig. 02. The spacer was made from PLA (Polylactic Acid) material, printed by FDM (Fused Deposition Modelling) technique using 0.2 mm layer thickness with 100 % infill density, cubic infill pattern at 215℃ printing and 60℃ bed temperature.

Figure 2. 3D printed spacer used in experiments

3. RESULTS AND DISCUSSION

3.1. Permeate flux results, as the ultrafiltration process velocity

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In Fig. 3. it can be seen that the time of the *UF* experiments of different organic load wastewater types significantly different, and the most emphasized flux decline tendencies were observed in the first part of the membrane separation processes. The initial fluxes of the control *UF* experiments were significantly lower (360 and 85 $Lm^{-2}h^{-1}$ for *Low-loaded* and *High-loaded* dairy ww. respectively) than the *UF* experiments with spacer and stirring (487 and 183 $Lm^{-2}h^{-1}$ for *Low-loaded* and *High-loaded* dairy ww. respectively). On one hand, in the model dairy wastewater ultrafiltration experiments (Fig. 3/a.), the shortest *UF* time of less than 400 s was observed with the sample of *Low-loaded* dairy ww. with spacer and 400 rpm stirring. The longest *UF* time was about 5320 s for the control *UF* of *High-loaded* dairy ww. without stirring and spacer. In general, the wastewater types with higher organic loads had lower initial and average flux values. On the other hand, in the real wastewater ultrafiltration experiments (Fig. 3/b.), the shortest *UF* time of 1000 s was observed with the sample of bakery ww. also with spacer and stirring. The longest *UF* time was about 3875 s for the control *UF* of bakery ww.. From these results it can be concluded that the module integrated 3D printed spacer together with a high stirring velocity resulted the highest flux values in all wastewater ultrafiltration experiments.

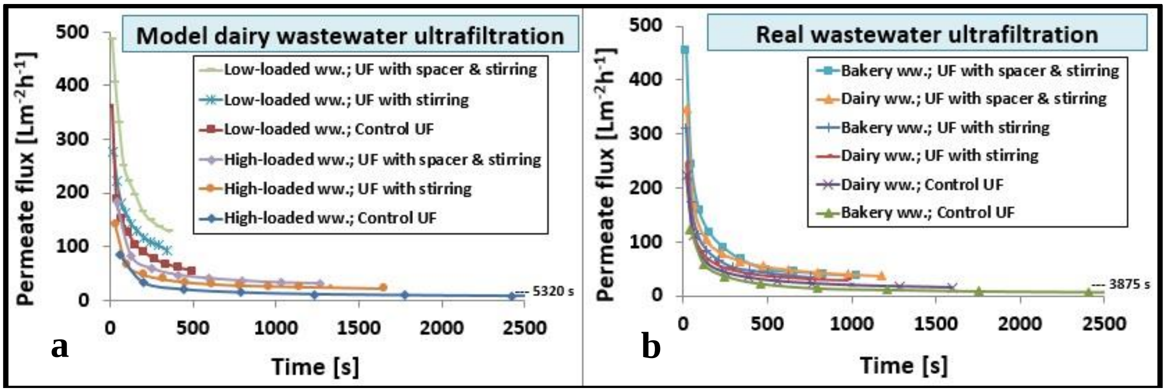

Figure 3. The permeate flux changing during ultrafiltration of model (a) and real (b) wastewater types

Next to the real permeate flux values (J), it is also important to know the permeate flux decline or the flux decreasing ratio which can be calculated from the certain flux (J) and the initial, first measured flux (J_0) value during *UF*. If we analyze this flux decline tendency (J/J_0) results of the different experiments as a function of *VRR* (Volume Reduction Ratio), it can be seen that, from the same initial flux, the flux decline was more emphasized in the control *UF* experiments. In Fig. 4. it can be also seen that the *High-loaded* model dairy wastewater types had higher permeate flux decline ratio, so the membrane fouling tendency was higher in their cases. In the case of control, where the flux decline tendency was most emphasized, it dropped to 0.15 with *Low-loaded* and 0.0575 with *High-loaded* model dairy wastewater types. It can be also observed that the *UF* experiments with spacer and stirring had lower results than the *UF* experiments with only stirring, however they had higher flux values in general.

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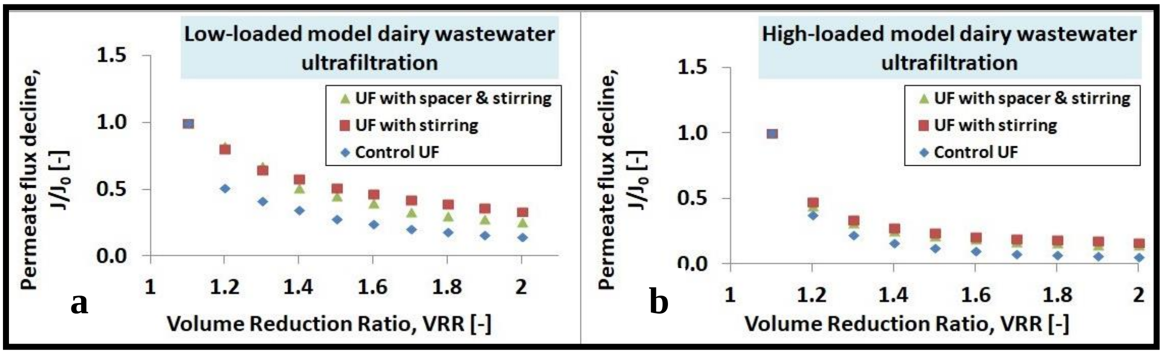

Figure 4. The permeate flux declines during ultrafiltration of low-loaded (a) and high-loaded (b) model dairy wastewater types

3.2. Resistance results, as the membrane fouling tendency
In Fig. 5. it can be seen that the different resistance values of the *UF* experiments of different wastewater types significantly different. The clean membrane own resistances were negligible and the reversible resistances were the most emphasized ones in all cases. The control *UF* experiments had the highest and the *UF* experiments with spacer and stirring resulted the lowest total resistance values. On one hand, in the model dairy wastewater ultrafiltration experiments (Fig. 5/a.), the *High-loaded* dairy ww. had much higher resistance values than the *Low-loaded* dairy ww.. On the other hand, in the real wastewater ultrafiltration experiments (Fig. 5/b.), the Control *UF* with bakery ww. resulted higher total resistance than dairy ww.. However, the reversible resistances were higher in dairy ww. *UF* experiments. From these results, it can be concluded that the module integrated 3D printed spacer together with a high stirring velocity resulted the lowest resistance values in all wastewater ultrafiltration experiments.

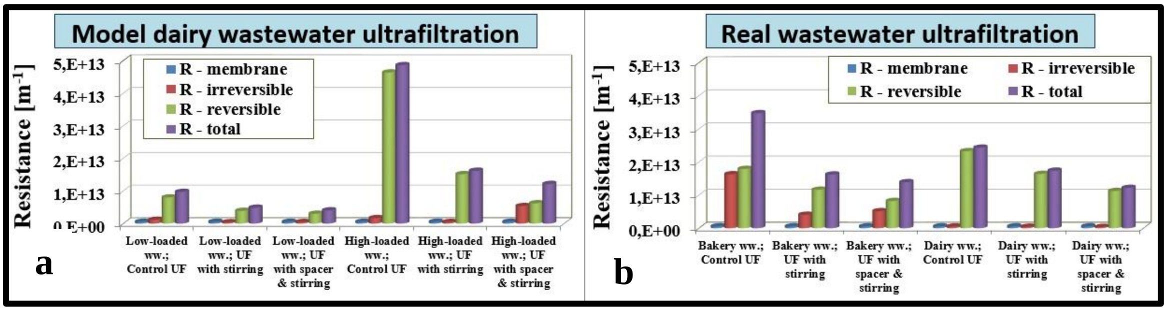

Figure 5. The resistance values of ultrafiltration of model (a) and real (b) wastewater types

3.3. The ultrafiltration membrane rejection results, as the process quality
The membrane percentage removal of *COD* is shown in Fig. 05. It can be seen that the rejection varied in a wide range from 13 to 74 %. On one hand, in the model dairy wastewater ultrafiltration experiments (Fig. 5/a.), the lowest rejection of 13 % was observed with the control *UF* experiment of *Low-loaded* dairy ww. without spacer and stirring, while the highest rejection of 32 % for the *High-loaded* dairy ww. *UF* with stirring. On the other hand, in the real wastewater ultrafiltration experiments (Fig. 5/b.), the lowest rejection of 14 % shortest was observed with the sample of dairy control *UF* experiments, while the highest rejection of 74 % for the bakery *UF* with stirring case. In general, the stirring increased the rejection values, but the spacer and stirring together decreased compare to stirring cases.

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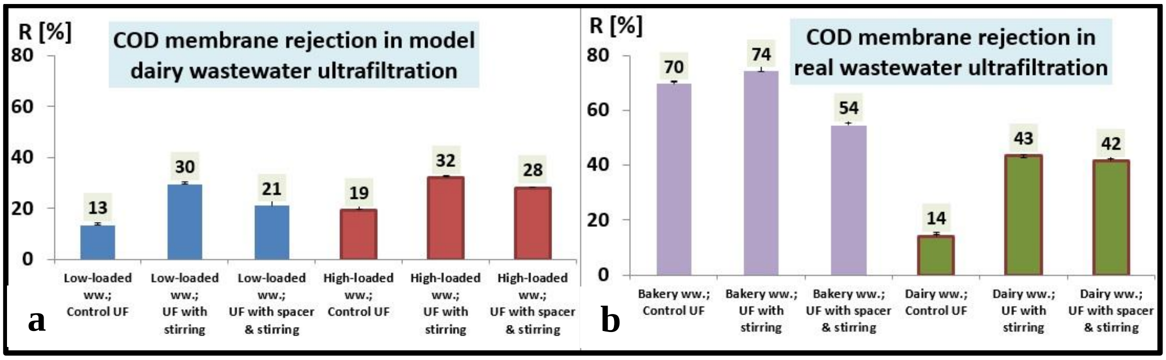

Figure 6. The organic content, chemical oxygen demand (COD) percentage membrane rejection of the model dairy wastewater (a) and real wastewater ultrafiltration (b) experiments.

It can be observed that the real, industrial wastewater samples had significantly higher membrane rejection values than the model wastewater samples, because their content were more heterogeneous. Furthermore, the real bakery wastewater had much higher rejection of control *UF* experiment of about 70 % than the dairy wastewater sample control with 14 %, even it had two times higher initial *COD* value, 2800 compare to 1400 mg/L. All samples had very similar changes in total salt rejection measured by conductivity measurements. It can be observed that the experiment with stirring lowered the conductivity values the most in all types of wastewater. But turbidity values were lowered approximately 99 % and there was not a significant difference between experiments or different types of wastewater.

4. CONCLUSIONS

The results of this research have shown that the use of a 3D printed spacer and stirring at a high velocity have increased the efficiency of membrane separation of all types of wastewater and resulted in the highest flux values and the lowest resistance values in all wastewater ultrafiltration experiments. The high-loaded model dairy wastewater type had a higher permeate flux decline ratio compared to the low-loaded model dairy wastewater and therefore tendency for membrane fouling was higher in those experiments. Which was proven by the resistance results also.
According to the membrane percentage removal of *COD*, the samples of industrial wastewater types had significantly higher membrane rejection values than the model wastewater samples. Moreover, the industrial bakery wastewater samples had much higher rejection values than industrial dairy wastewater samples. The experiments with stirring had the highest rejection values in all the wastewater types, but the experiments with spacer and stirring together had comparable rejection values.

Acknowledgments: Thanks the support of the János Bolyai Research Scholarship of the Hungarian Academy of Sciences (BO/00576/20/4) and the New National Excellence Program of the Ministry of Human Capacities (UNKP-21-5-SZTE-550). Additionally, many thanks to the project "Building Entrepreneurial Ecosystem – Student entrepreneurship beyond borders" acronym BEE-Student of the Interreg IPA CBC Programme (project no. HUSRB/1903/43/0012) for the support.

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DOI: https://doi.org/10.14232/analecta.2022.1.129-135