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Comparative evaluation of three different membranes for the treatment of a brewery and a dairy treatment effluent

Plevrı A.*[1] , Gkoumas F. [1], Koumakı E. [1], Noutsopoulos C. [1], Mamaıs D.[1] , Nıkolaou M.[2], Margarıtıs M.[2], Malamıs S.[1]

[1]Sanitary Engineering Laboratory, Department of Water Resources and Environmental Engineering, School of Civil Engineering, National Technical University of Athens, Iroon Polytechniou 9, Zografou 157 80, Athens, Greece
[2]Laboratory of Indusstrial and Energy Economics, School of Chemical Engineering, National Technical University of Athens, Iroon Polytechniou 9, Zografou 157 80, Athens, Greece

*corresponding author: Plevrı A.
e-mail:aplevrı@maıl.ntua.gr

Abstract A laboratory-scale system with a capacity of 7L/h consisting of three different ultrafiltration membranes operating alternatively, was designed and installed at the Sanitary Engineering Laboratory (SEL) facilities. The purpose of this membrane system was to test the performance of alternative membranes in terms of secondary effluent treatment from a dairy and a brewery industry located in Patras industrial area. The three membranes selected after a literature review were a PVDF UF tubular membrane module, a ceramic UF tubular membrane module and a polysulfone HF UF tubular membrane module. The batch experiment protocol followed for each membrane consisted of a chemical cleaning procedure and a 5-hour continuous operation with secondary effluent from the two industries. The laboratory results showed that the permeate water complies with the limits set by Greek legislation for unrestricted irrigation. The PVDF membrane showed the best membrane performance in terms of effluent quality with better results in organic load removal. It also showed higher stability with very low standard deviation values. In terms of TMP increase and effluent drop during the 5-hour batch trials, the ceramic membranes showed lower values, while the PVDF membranes were more stable after the first hour of the trial and showed a very low increase for the rest of the trial.

Keywords: cross flow technology; industrial effluent; ultrafiltration.

1. Introduction

The Athenian brewery and Frieslandcampina Hellas Wastewater Treatment Plants (WWTPs) currently use the activated sludge process for wastewater treatment, which does not allow for water reuse. However, an upgrade to the WWTPs is being planned, which will incorporate membrane ultrafiltration and UV disinfection technologies. These new technologies will completely remove organic matter and pathogens from the wastewater, making it suitable for unrestricted irrigation. This upgrade to the WWTPs will allow them to complywith the Greek wastewater reuse legislation, allowing the treated wastewater to be reused for various purposes, such as irrigation or groundwater recharge. The use of membrane ultrafiltration and UV disinfection will ensure that the treated wastewater meets the required standards for reuse, while also minimizing the environmental impact of the WWTPs.

The food and beer industry are known to generate significant amounts of wastewater with high concentrations of biochemical oxygen demand (BOD5) and chemical oxygen demand (COD). As such, effective treatment of this wastewater is crucial to minimize its impact on the environment and ensure compliance with regulatory standards.

Membranes can be classified based on their material of construction. There is a range of materials used to manufacture membrane filters, such as ceramics and polymers. Polymeric materials used in membrane manufacture include cellulose acetate, polyamides, polypropylene, and polysulfone. Ceramic membranes are usually made from metal oxides, such as alumina, often using some form of sol–gel process(Gregory, 2005; Seneviratne, 2006).

Several membrane processes have been proposed for the treatment of dairy wastewater with the aim of producing purified water for reuse or nutrient recovery (Ivnitsky *et al.*, 2005). Membrane technology is advantageous compared to conventional methods since it is tolerant to variable levels of pollutants in the upstream and requires four times less space than conventional WWTPs However, a challenge with using membrane filtration alone for dairy wastewater treatment is that proteinaceous materials tend to accumulate on the membrane surface, making direct treatment with membranes difficult(Bae, Han and Tak, 2003)..Bennani et al. (Bennani, Ousji and Ennigrou, 2014) conducted a study on the treatment of dairy effluent using a Polyethersulfone (PES) membrane through ultrafiltration (UF). The study revealed a promising result of 58% recovery of the effluent after UF treatment. Gong et al.(Gong, Zhang and Cheng, 2012) used a combination of UF and NF90 membranes to treat wastewater, achieving a remarkable outcome of less than 70 mg/L chemical oxygen demand (COD) in the effluent. Zinadini et al.(Zinadini *et al.*, 2015) developed a mixed matrix polyethersulfone membrane by blending various amounts of graphene oxide nanoplates with the phase inversion method (PES/GO). Their results suggest that this process showed exceptional performance for the treatment of milk processing wastewater. Overall, these studies offer valuable insights into the potential applications of different membrane filtration methods for the treatment of dairy effluent and wastewater.

According to research conducted by (Dai *et al.*, 2010) Dai et al., membrane technology is a viable option for treating brewery wastewater. Their findings indicated that membrane filtration could remove up to 96% of the COD present in the wastewater. Similar studies have also reported successful COD removal efficienyof up to 90% using membrane filtration for brewery effluent treatment and reuse (Lom, 1977).Furthermore, (Daufin *et al.*, 2001) Daufin et al. found that dynamic filtration or cross-flow could be a significant technological alternative to conventional solid and liquid separations in the brewing industry. Another study conducted by Chen et al. tested three PES UF membranes, namely PES5, PES10, and PES30, with different molecular weight cut-off (MWCO) values of 5 kDa, 10 kDa, and 30 kDa. Their results showed that the PES30 membrane had the lowest fouling rate and produced high-quality effluent.

Most of the membranes used in the literature for the treatment of industrial wastewater are polymeric membranes (Chen and Liu, 2012; Buntner, Sánchez and Garrido, 2013). However, ceramic membranes have several advantages over polymeric membranes. They have good thermal and chemical stability, high resistance to corrosion, abrasion, and fouling, resulting in high backwashing efficiency and making ceramic membranes more durable. In addition, ceramic membranes can achieve much higher flow rates than polymer membranes due to weaker bonding between foulants and the membranes (Lee *et al.*, 2013). Thus, although polymeric membranes have lower initial costs, it is worth investigating ceramic membranes as their operating advantages may result in been more competitive than polymeric membranes in the long term.

Although there have been some studies on the filtration of dairy wastewater using ceramic membranes (Farizoglu and Uzuner, 2011), there is still limited knowledge on the reduction of fouling mitigation and COD and suspended solids removal during post-treatment of secondary effluents with tubular membrane modules containing ceramic membranes. Even with the use of ceramic membranes, fouling remains a problem, which means that membrane filtration is limited by the clogging of the membranes with pollutants. This leads to a decrease in flux and shortens the filtration cycle and membrane lifetime.

A ceramic tubular membrane was tested for the treatment of dairy wastewater, and the results indicated that the membrane had high rejection efficiency. Over 87% of COD was removed, as well as over 96% of color, and almost all of TSS and turbidity. Coagulation had no effect on the total removal of pollutants in the systems and was not an effective factor in controlling membrane fouling (Zielińska and Galik, 2017).

Overall, the purpose of this study is to examine the performance of three alternative UF membranes in terms of secondary effluent treatment from a dairy and a brewery industry located in Patras industrial area in terms of membrane fouling and effluent drop. The three membranes selected after a literature review were a PVDF UF tubular membrane module, a ceramic UF tubular membrane module and a polysulfone HF UF tubular membrane module. The lab-scale UF system serve as a promising step towards the successful upgrade of the Athenian brewery and Frieslandcambina Hellas WWTPs, while also contributing to the broader field of wastewater treatment research.

2. Materials and methods

2.1. Lab-scale UF/UV system description

A laboratory-scale ultrafiltration (UF) system consisting of three different membrane modules was designed and installed at the Sanitary Engineering Laboratory (SEL) of the National Technical University of Athens (NTUA) (Figure 1 left). The membranes included a polyvinylidene fluoride (PVDF) tubular membrane module from KOCH US with a surface area of 0.1 m^2, a ceramic tubular membrane module from LIQTECH with a surface area of 0.063 $m^{2,}$ and a polysulfone hollow fiber tubular membrane module from KOCH US with a surface area of 0.1 m^2, all operating with cross-flow technology (Figure 1, right).

Figure 1:Presentation of the UF systm installed(left) and the three membranes examined (right).

The laboratory scale unit installed has a capacity of 7L/h effluent. It consists of two 110 L tanks (supply and filtration), a stainless-steel supply pump for the recirculation of feed wastewater. Low-cost sensors have been installed in the inlet and outlet tanks for quality control of the process (pH, turbidity, temperature, total dissolved solids. The values of the low-cost sensors are transmitted directly to an online platform. The unit has the ability to operate each membrane separately by opening and closing valves.

2.2. Batch experiments protocol

The batch experiments involved a well-defined protocol for each of the three membranes tested. Firstly, a chemical cleaning procedure was performed. Subsequently, a 5-hour continuous operation using wastewater from the two industries was carried out at the maximum flow rate for each membrane to assess membrane fouling. Each cycle began with water to determine the initial permeability of the membrane. Following the 5-hour experiment, a chemical cleaning procedure was carried out to restore the permeability of the membrane before retesting. During each experiment, various parameters such as feed pressure, recirculation pressure, pressure drop, outlet pressure, feed flow, and outlet flow were monitored. Additionally, laboratory analyses were conducted to verify compliance with Greek irrigation standards.

This study examined three cleaning cycles (alkaline, acid, and disinfection) for membrane cleaning, with flushes of water and measurement of flow and transmembrane pressure between each cycle. Results showed all cycles were effective, but the alkaline cycle was most efficient in restoring membrane performance. Regular cleaning and maintenance are crucial for extending membrane lifespan and performance.

After 5 hours of continuous operation, laboratory analyses were conducted to investigate the water quality of the effluent and its compliance with Greek legislation. The conventional parameters that were tested include COD total and soluble, BOD, TKN, NH_4-N, PO_4-P, pH, conductivity, and turbidity, as well as microbiological parameters TC and E. coli.

3. Results and discussion

In terms of effluent quality, results indicate that the filtrated effluent water meets the limits set by Greek legislation. The effluent was found to be free of suspended solids and had a turbidity of less than 1 NTU for all three membranes. Additionally, E. coli was completely removed, while TC showed a very low presence in the effluent.

Regarding membrane fouling and TMP, there was a significant increase in the first hour, followed by a decrease in flux. However, after the first hour, TMP and outlet flux tended to stabilize. This phenomenon is due to the cross-flow technology and is called a quasi-steady state. The balance between the transport of particles to the cake layer and the return transport of particles to the feed stream contributes to this fact.

3.1 Frieslandcampina's effluent batch experiments

Figure 2 shows the transmembrane pressure rise and therefore membrane fouling after 5 hours of operation for all three membranes.

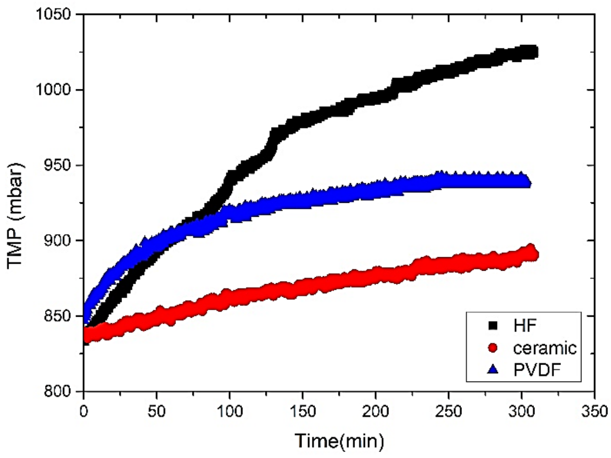

Figure 2 Presentation of the TMP after five hours of operation of the three membranes (Frieslandcampina's effluent)

The performance of different materials in a filtration process was compared and the results are as follows: Ceramic material showed a 6% increase in TMP and a 12% drop in effluent. PVDF material showed an 11% increase in TMP and a 29% drop in effluent. On the other hand, HF material demonstrated the highest increase in TMP, with a 23% rise, but also the highest drop in effluent, with a 32% reduction. These findings suggest that the choice of material can significantly impact the efficiency of the filtration process, and careful consideration should be given when selecting the most appropriate material for a specific application.

3.2 Athenian Brewery's effluent batch experiments

Figure 3 shows the transmembrane pressure rise and therefore membrane fouling after 5 hours of operation for all three membranes.

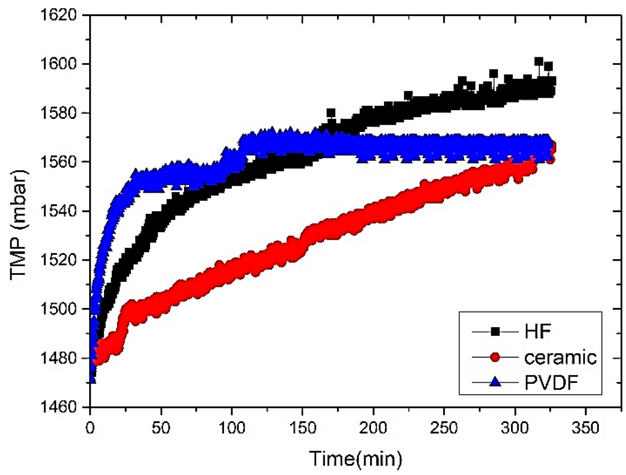

Figure 3 Presentation of the TMP after five hours of operation of the three membranes (Athenian Brewery's effluent)

Specifically, Ceramic material showed a 6% increase in TMP (transmembrane pressure) and a 16% drop in effluent flow, while PVDF material demonstrated a 7% increase in TMP and a 21% drop in effluent flow. HF material, on the other hand, showed a higher increase in TMP at 8% but also had the largest drop in effluent flow at 30%. Therefore, the selection of the most appropriate material should be carefully considered to achieve the desired filtration outcomes. Ceramic and PVDF are potential material choices for applications that require moderate TMP increase and a relatively larger reduction in effluent, while HF may be better suited for specific applications that do not prioritize a lower increase in TMP.

4. Conclusions

The results in terms of effluent quality, showed that the polyvinylidene fluoride (PVDF) membrane had a COD removal efficiency of 66% for FCH and 84% for AB. The hollow fiber (HF) membrane had a COD removal efficiency of 56% for FCH and 77% for AB. Finally, the ceramic membrane had a COD removal efficiency of 51% for FCH and 74% for AB. Based on these findings, it can be concluded that the PVDF membrane was the most effective in removing COD from the wastewater, followed by the HF and ceramic membranes, respectively.

The experimental results showed that the membranes exhibited similar fouling behavior when used to treat two different industrial effluents. However, the starting TMP for the AB effluent was twice as high as those for the FCH effluent. HF material exhibited the highest increase in TMP, followed by PVDF material, while ceramic demonstrated the lowest increase. Despite these differences in TMP increase, the PVDF membrane demonstrated greater stability after the first 100 minutes of operation. Moreover, in addition to superior effluent quality, PVDF was selected as the optimal membrane material for both industries.

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