

Article

Effect of Membrane Type for the Treatment of Organized Industrial Zone (OIZ) Wastewater with a Membrane Bioreactor (MBR): Batch Experiments

Oktay Özkan and İbrahim Uyanık *

Erciyes University, Faculty of Engineering, Department of Environmental Engineering, Melikgazi, Kayseri 38039, Turkey; ozkan@erciyes.edu.tr

* Correspondence: iuyanik@erciyes.edu.tr; Tel.: +90-352-207-6666-7498

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Abstract: Organized industrial zone (OIZ) wastewater is a mixed wastewater that is contributed by both municipal use and from different industrial sectors. Since MBR has advantages over conventional treatment plants, membrane types and fouling become the most important parameters in the treatment of this kind of wastewater. In this study, six different membrane types were used to find the most suitable membrane with the least resistivity to fouling. Three different microfiltration (MF) and ultrafiltration (UF) membranes were operated to estimate their (i) membrane, (ii) cake, (iii) pore, and (iv) total resistances. The highest total resistance was observed in a polyethersulfone (PES) membrane ($3.8 \times 10^{10} \text{ m}^{-1}$), while the lowest one was a UF polyvinylidene fluoride (PVDF) membrane with approximately 20 times lower resistance than the highest one. PVDF membranes showed lower total resistances than PES membranes. An MF or a 250 kDa UF membrane could be operated long-term in a membrane bioreactor with the least fouling potential.

Keywords: MBR; membrane selection; resistance; membrane fouling

1. Introduction

Environmental management of the industrial activities could be better controlled when they are organized in an isolated area in developing countries [1–3]. Centralized and organized industrial zones are common in Turkey, the number of which exceeded 250 [4]. Only one third of these organized industrial zones (OIZs) have their own wastewater treatment plant (WWTP) [4]. The characteristics of the wastewater of OIZs are very different from each other, as their wastewater originates from different sectors. However, the wastewater is similar to municipal wastewater in terms of biological degradation in that their wastewater also comes from the daily water consumption of workers. Industrial water contamination must be controlled, since it affects not only the health of living organisms but also indirectly affects the economy [5,6].

Membrane bioreactors (MBRs) are needed for wastewater to conform to regulations that require high-quality effluents in both developed and developing countries [7,8]. Regardless of the effluent quality of the MBR, it is a good pre-treatment option before a reuse alternative. However, MBR treatment has some technical issues or limitations in operations, and membrane fouling is one of them [8,9].

The fouling problem has been investigated in several studies. Most of the studies are linked with microbial community for the reason of the fouling [10,11]. In a study of MBR treating textile wastewater, microbial composition has been found to be affected by reactor operating conditions [12]. The study further maintains that microbial community may have an impact on biofouling, and each MBR has its own characteristics. Therefore, microbial community structure is the main reason for fouling, regardless of biodegradable type of wastewater to treat. In another study, factors affecting

the biofouling mechanism were reviewed and fouling factors discussed [13]. Biofouling increases as mixed liquor suspended solids (MLSS), organic loading rate (OLR), and food to microorganisms (F/M) ratio are high, and dissolved oxygen concentration, hydraulic retention time (HRT), and sludge retention time (SRT) are low [14]. High salinity and temperature also increase the soluble microbial products and decrease membrane permeability. Although system parameters in MBR can be changed, it still may not be easy to stabilize all the parameters in desired levels. Therefore, membrane fouling is inevitable, but it could be minimized.

While MBR batch studies [15,16] were conducted for the removal of some micropollutants, membrane types were investigated in other studies [17,18]. One study on natural organic matter (NOM) removal investigated using hollowfiber (HF) membranes—two hydrophobic and one hydrophilic. Hydrophobic ones fouled more quickly because hydrophilic compounds formed a gel layer on the surface of the membrane [17]. Another study on membrane type and materials was conducted using three different MF membranes with the same pore sizes. Track-etched polyester (PETE) membrane was the worst one, while the other two were nearly the same in terms of flux decline [18].

The membrane type operated in MBR did not vary widely, since almost 50% of the membranes used in commercial MBR products were polyvinylidene difluoride (PVDF) from among three membrane configurations; namely, flat sheet (FS), hollowfiber (HF), and multitube (MT) [8]. Polyethersulfone (PES) membranes are the second-most-used membranes, and are used only for FS modules. FS module was compared with HF module in a study showing that it could be operated for 6 months without external cleaning compared to HF module (4 months) [19].

Membrane resistances of the MBR studies have been estimated only for specific resistances in the literature for the prediction of fouling behavior [20–22]. One study shows that cake resistance plays a major role in filtration efficiency [23]. Another one shows that the fouling is irreversible, as the blocking resistance is the major one. Similarly, when cake resistance is the major one, fouling is reversible [22]. However, a pre-study of the membrane resistances is not performed before a long-term operation in MBR.

Selection of membrane type is a hard task for industrial wastewater, since fouling is one of the most important parameters for long-term operations [8]. In this study, membrane types were investigated according to their resistances to an organized industrial zone (OIZ) wastewater using six different MF and UF membranes in MBR.

2. Materials and Methods

2.1. Membrane Bioreactor (MBR)

The reactor used in the study is made of plexiglass with a 20 L of active volume. Real wastewater and activated sludge from the Kayseri organized industrial zone (KOIZ) WWTP were initially fed to the reactor. Then, it was continuously monitored with a programmable logic control (PLC) system as for the dissolved oxygen (DO), oxidation-reduction potential (ORP), pH, temperature, pressure, water level, and flux. Basic influent and effluent parameters of the reactor for one month of operation with a 10 kDa ultrafiltration (UF) FS membrane are given in Table 1.

Wastewater fed to the MBR was from the primary sedimentation tank of the WWTP. Operational parameters of the MBR were stable during each day when the modules were operated. MLSS was 7.2 ± 0.2 g/L, while hydraulic retention time (HRT) was 40 h. A peristaltic pump (Watson-Marlow, Sci-Q 300) with constant speed was used in all experiments to vacuum the filtrate from the reactor. Wastewater of KOIZ mainly comes from textile, paper, recycling, and metal industries, including the wastewater of daily use of 7000 workers, which turns the character of the wastewater into a high-strength domestic wastewater in terms of biodegradability.

Table 1. Membrane bioreactor (MBR) influent and effluent parameters.

Parameters	Influent	Effluent
pH	7.1 ± 0.36	7.9 ± 0.4
Electrical conductivity (EC) (ms/cm)	4.8 ± 0.92	5.1 ± 1.1
Chemical oxygen demand (COD) (mg/L)	471 ± 228	39.5 ± 22.3
Biochemical oxygen demand (BOD) (mg/L)	211 ± 75	0
NO ₂ -N (mg/L)	0	0
NO ₃ -N (mg/L)	<0.01	3.5 ± 2.1

2.2. Membranes

Flat sheet membranes used in the study are given in Table 2. Membrane materials are PES and PVDF (three of each), and membrane types were three microfiltration (MF) and three UF with different pore sizes and molecular weight cutoff (MWCO) values. Membranes are given with increasing pore sizes.

Table 2. Properties of microfiltration (MF) and ultrafiltration (UF) membranes. PES: polyethersulfone; PVDF: polyvinylidene difluoride.

Membrane Type	Brand	Pore Size (μm)	Membrane Material
MP005	Microdyn-Nadir	0.05	PES
UF 4 kDa	Philos	0.07	PES
UF 10 kDa	Philos	0.1	PES
MV02	Microdyn-Nadir	0.2	PVDF
MF	Philos	0.24	PVDF
UF 250 kDa	Philos	0.44	PVDF

2.3. Experimental Procedure

Flat sheet membrane modules used in the study were prepared in the laboratory with an area of 285 cm². Firstly, the modules were submerged into distilled water and vacuumed for 30 min while recording flux and pressure at every min. Secondly, the modules were submerged into the MBR and operated for one day (24 h) without relaxation/backwashing. Lastly, the modules were cleaned only physically and vacuumed again for 30 min with new distilled water to calculate the membrane resistances. Physical cleaning was performed by removing cake layer with a soft sponge and by washing it externally under running tap water. The membrane resistance (R) for each of the resistances can be calculated as:

$$R = \Delta P \cdot \mu^{-1} \cdot J_{ss}^{-1} \quad (1)$$

where R is the filtration resistance (m^{−1}), ΔP is the pressure difference between steady state and the beginning (Pa), μ is the permeate viscosity (Pa·s), and J_{ss} is the steady-state flux (m³/m²·s). From the above experimental procedure, R_m can be calculated as membrane resistance from the distilled water filtration and R_t can be calculated as total resistance from MBR filtration. After cleaning the module with deionized water, the resistance is $R_m + R_p$, where R_p is the pore resistance. The cake resistance, R_c , can be calculated from the difference of steps 1 and 3 as $R_t - (R_m + R_p)$. All experiments were conducted daily, with a total time of 6 days. Figure 1 is illustrated for an easy understanding of the experimental procedure.

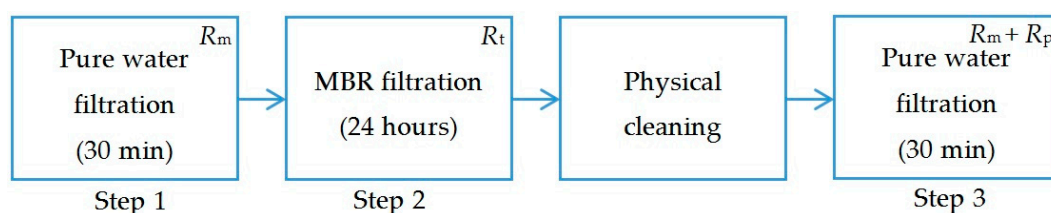


Figure 1. Flow diagram of the experimental procedure.

2.4. Analytical Methods

All parameters were analyzed according to Standard Methods [24]. In the MBR, all parameters mentioned above are measured online. Permeate analysis was made using a HACH multimeter (pH, temperature, electrical conductivity (EC)), while turbidity analysis was made with a HACH 2100AN laboratory turbidimeter. Chemical oxygen demands (CODs) of the permeate samples were analyzed using titrimetric method (Standard Methods 5220 C). Membrane fluxes were measured as $L \cdot m^{-2} \cdot h^{-1}$ (LMH).

3. Results and Discussion

Basic water quality parameters of the effluent of membranes operated in the MBR were not significantly different from each other, as shown in Table 3. The treated water had high EC, low COD, and low turbidity. Although this wastewater had higher organic and pollutant loading rate, these values are consistent with other MBR studies treating municipal wastewater treatment plants in terms of average COD and turbidity removal [25,26]. Since the membranes are MF and UF membranes, EC values do not reduce as expected.

Table 3. Permeate analysis results after MBR operation.

Membrane	Effluent pH	EC (ms/cm)	COD (mg/L)	Turbidity (NTU)
MP005	8.10 ± 0.12	4.06 ± 0.08	19 ± 7	0.42 ± 0.25
UF 4 k	8.19 ± 0.24	4.23 ± 0.06	32 ± 11	0.36 ± 0.18
UF 10 k	8.10 ± 0.09	4.62 ± 0.11	38 ± 4	0.72 ± 0.09
MV02	8.16 ± 0.17	4.41 ± 0.10	66 ± 14	0.88 ± 0.13
MF	8.01 ± 0.05	5.02 ± 0.27	67 ± 9	0.96 ± 0.07
UF 250 k	8.41 ± 0.10	4.65 ± 0.18	21 ± 16	0.21 ± 0.16

3.1. Resistances

Membrane, pore, and cake resistances of the membranes are given in Figure 2. PVDF membranes showed lowest membrane (R_m) and pore resistances (R_p), while PES membranes demonstrated high pore resistance. The highest pore-sized membrane showed the lowest pore resistance. Membrane resistances (R_m) of the PVDF membranes were lower than PES membranes because of the hydrophobicity of the membrane structure. An inverse relationship with the R_m of the PES membranes and their pore sizes may be originated from the membrane fabrication, as the contact angles differ. The UF 10 kDa membrane with 0.1μ pore size showed the highest membrane resistance with distilled water.

MP005 (PES) with the lowest pore-sized membrane indicated approximately 60% more cake resistivity in MBR. The hydrophobicity of this membrane causes organic matter to form a cake layer on the membrane surface. This type of membrane is not a good choice because of a very high potential of a cake layer being formed. Additionally, this cake layer may block the pores of the PES membranes.

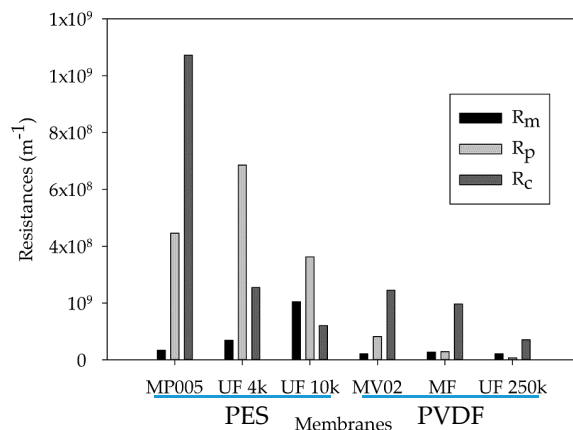


Figure 2. Membrane, pore, and cake resistances of the membranes.

Another significant result in Figure 2 is the pore resistances, which are very high in PES membranes compared to PVDF ones. The cake resistances of PDVF membranes were higher than the pore resistances. This data indicates that the cake layer is removed by physical washing. However, pore resistances of PES membranes are higher than the cake resistances, except for MP005 membrane, which indicates that the pores of the membranes fouled irreversibly. This type of fouling can only be cleaned by chemical cleaning agents, but not physically. This finding is consistent with previous studies. Pore blocking is found to be irreversible, while cake blocking is easily removed by simple backwashing, and irreversible blocking may be formed due to the organic macromolecules [22]. However, in another study, PVDF membranes showed a removable fouling character, with flux being nearly the same as before the operation [27]. Other studies of cake and pore blocking of the membranes also showed that pore blocking and cake formation are the dominant fouling mechanisms in PES membranes [28].

Although the UF 4 kDa membrane showed the highest pore resistance, it had lower total resistance (Figure 3) than the MP005 membrane, both of which are the same material (PES). This could be due to both the pore sizes and the manufacturing processes of different membrane suppliers. Total resistances of the membranes were inversely proportional to their pore sizes. The lowest total resistance was seen in the UF 250 kDa membrane with the highest pore size. However, that alignment was not reflected on the water quality, as it has better COD and turbidity removal than the other membranes. The effect of pore sizes is discussed in another study, which suggested that larger pore sizes exhibit faster flux decline, while having better flux recovery in different UF membranes [21]. The study also showed that hydrophobicity is the second unwanted property in terms of fouling. Membranes with lower MWCO and high hydrophobicity demonstrated the worst performance, as in the current study, with the hydrophobic membrane (MP005) with the smallest pore size.

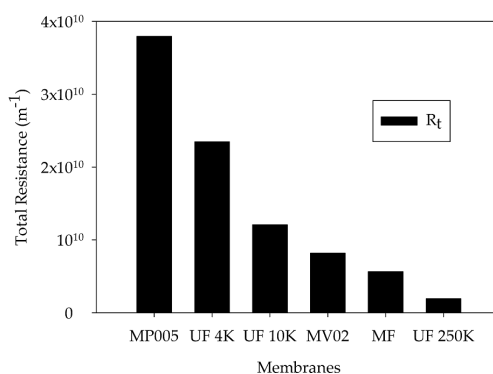


Figure 3. Total resistances of the membranes.

3.2. Flux Pressure Profiles

Flux pressure profiles of the membranes are shown in Figures 4 and 5 for only MP005 and UF 250 kDa, respectively. These membranes showed the highest and lowest total resistances, respectively. For the MP005 membrane, flux rapidly declined in 15 min in MBR (Step 2), while it was stable in distilled water before and after the operation in the MBR. Almost no pressure rise was observed in distilled water filtration (Step 1). However, it reached steady state at 0.8 bar for both the MBR and after the cleaning operation (Step 3). A rapid rise in pressure indicated that the membrane surface was clogged by soluble foulants such as soluble microbial products (SMPs). This was also indicated in a fouling study conducted in a submerged MBR [29].

However, flux was almost recovered after simple physical cleaning of the MP005 membrane. This is due to the cake layer formed on the membrane surface in MBR operation, as shown in Figure 2 (MP005 membrane has the highest cake resistance). Fouling of this membrane can be related to high pressure during filtration caused by cake formation. Cake layer on the membrane surface acts as another filter layer to increase the pressure and the resistance. The easier cleaning of the cake layer can be related to the hydrophobic nature of the membrane. In a membrane fouling study, it is suggested that increasing surface hydrophilicity cannot mitigate membrane fouling in MBRs [29]. High zeta potential and roughness of membranes alleviate membrane fouling, as stated earlier [29]. Therefore, the PES membranes used in this study are not proper for an MBR filtration of OIZ wastewater, as they show high potential of fouling.

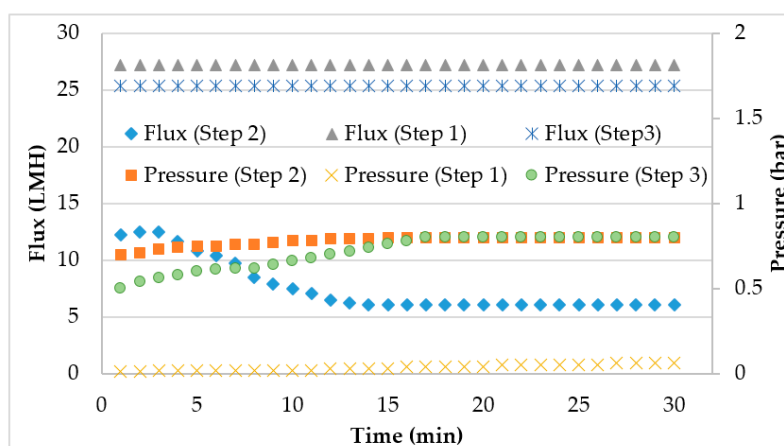


Figure 4. Flux pressure profile of MP005 membrane. LMH: $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$.

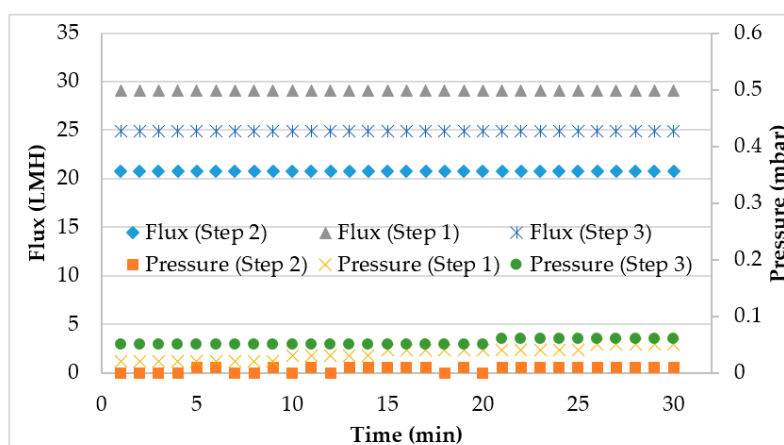


Figure 5. Flux pressure profile of UF 250 kDa membrane.

The UF 250 kDa membrane, with the best performance in the current study, showed little or no pressure rise in all steps. This membrane also had little or no flux decline when operated in the MBR (Figure 5). MBR flux of this membrane reached as high as 25 LMH, while the worst one (MP005) declined from about 12 LMH to 6 LMH.

Resistances and flux-pressure profiles of PVDF membranes showed less resistivity to OIZ wastewater than PES membranes. Both membrane types are known to be hydrophobic; however, the PVDF membranes used in this study seem to be less hydrophobic than PES membranes. The membrane with the best performance was a UF membrane (MWCO of 250 kDa), which has hydrophobic nature and PVDF material. Therefore, hydrophobicity may not be a fouling parameter in the MBR filtration of OIZ wastewater.

4. Conclusions

MBR treatment of industrial wastewater is not a novel subject; however choosing the right membrane in a long-term operation is essential for maintenance, investment, and operation costs. Membrane resistivity is the key parameter for the treatment of mixed industrial wastewater in terms of fouling for operation. This study showed that for a high-strength industrial zone wastewater, membranes with high pore size showed low resistance with PVDF membranes. A UF membrane which had a 250 kDa MWCO value and highest pore sized membrane demonstrated the best performance in terms of resistance. Water quality of this permeate was also much better than other types of membranes. Tertiary treatment of this wastewater for reuse will be investigated with different nanofiltration (NF) and reverse osmosis (RO) membranes in our further studies.

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Author Contributions: Oktay Özkan conceived and designed the experiments; İbrahim Uyanık performed the experiments, analyzed the data, provided membrane materials, and wrote the paper.

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