Study of the Industrial Wastewater Treatment by a Membrane Bioreactor (MBR) Case Study: Cookie Factory Wastewater

M. Zangouie¹, A. Hemmati²*, M. Kian³, J. Shayegan⁴

¹ Department of Petroleum and Chemical Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran
² Department of Chemical, Petroleum and Gas Engineering, Semnan University, Semnan, Iran
³ Petrochemical Research and Technology Company (NPC-RT), National Petrochemical Company, Tehran, Iran
⁴ Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran

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ABSTRACT
The membrane bioreactor (MBR) is a treatment bioreactor of urban and industrial wastewaters. The advantages of the MBR technology encompass high-quality effluents, less space requirements, and high-speed startups. This study aims to investigate the fouling phenomenon in the flour industry sewage treatment. The pilot has been designed and constructed in line with the research concerning the industrial wastewater treatment. After the adaptation of microorganisms, physical and chemical tests such as chemical oxygen demands (COD), turbidity and total suspended solids (TSS), extracellular polymeric substances (EPS), and soluble microbial products (SMP) were conducted during the process. The concentration of mixed liquor suspended solids (MLSS) in the membrane bioreactor ranged between 5000 and 8500 mg/L. Hydraulic retention times (HRTs) were fixed at 4, 8, and 16 h. Three types of resistance were considered via measuring the leakage current and transmembrane pressure (TMP). Accordingly, the total resistance rates for HRTs of 4, 8, and 16 h were 22.5×10¹⁰, 21.3×10¹⁰, and 20.4×10¹⁰ m⁻¹ respectively. Considering the average organic loading rate (OLR) in three HRTs of 4, 8, and 16 h (8.84, 5.13, and 2.84 kg the COD/m³×day respectively), the daily feed was provided to the bioreactor, and the removal efficiency of COD was assessed. An average removal of 95 % was achieved in the whole process. In this method, the input turbidity of the effluent has been increased to 187 NTU and, then, reduced to less than 3 NTU. It was also observed that EPS, SMP, and the extracted carbohydrates played more vital roles in the membrane biofouling than the extracted proteins.

Keywords: Membrane Bioreactor, Microfiltration, Industrial Wastewater, Membrane Clogging, Extracellular Polymer Material, Soluble Microbial Products

1. Introduction
Emerged as a relatively new treatment processes, the membrane bioreactor (MBR) deals with the system’s performance, filtration profile, specifications of the reactor, and membrane obturation control [1]. The popularity of the MBR technology stems from several factors including its lesser space requirement, high-quality and non-particulate wastewater, high organic loading capacity, production of disinfected wastewater, and the reduction of the sludge production. The
membrane biofouling is an unavoidable phenomenon in the MBRs related to the membrane porosity, pore blocking, and cake layer formation [2]. The most significant factors in membrane fouling include EPS, SMP, hydrodynamic conditions, and physical agents of the membrane. Generally, the MBR is becoming a treatment process used extensively for the treatment of both industrial and municipal wastewaters [2]. The hydraulic retention time (HRT), another key parameter of membrane fouling, is an important factor in MBR operations which can change the properties of the fluid mixture (e.g. the sludge, EPS, and SMP) (Guo et al., 2012). Also, the changes in the solid retention time (SRT) directly affects the MLSS concentration. Chen et al. (2012) asserted that the SRT should be between 20 and 40 days to reduce EPS. Zhang et al. (2015) reported that the SRT in an anaerobic MBR should be 30 days rather than 10 days, while studies would suggest 90 days rather than 30 days [5]. Babatsouli et al. (2014) observed that the rate of fouling and the EPS and SMP concentrations were higher in a pilot industrial wastewater treatment plant at an HRT less than 20 h compared to 24 h.

Different HRTs can eventuate in different OLRs, and short HRTs can create larger OLRs. It depends not only on the wastewater efficiency of the MBR but also on the MLSS concentration. The observations show that the membrane fouling is reduced at a higher HRT (without enhancing the membrane transfer pressure) due to the reduced OLR [5].

The cake layer formation is regarded as a dominant factor in the membrane fouling for a long-term operation [8]. SMP and EPS have often been cited as the primary factors which can influence the fouling in both aerobic and anaerobic MBRs [9, 10, 11]. The F/M ratio affects the content and proportion of the microbial products of the cake layer in a way that high F/M ratio may eventuate in higher SMP and EPS, thereby contributing to considerably severe fouling. Increasing the OLR applied to the bioreactor causes a sudden increase in F/M and, subsequently, in SMP. Increasing the ratio of F/M and the MLSS in industrial wastewater may cause fouling [6]. Increasing the OLR or F/M ratio will heighten the EPS concentration [2, 7]. The membrane blocking reduces the flux of the membrane, which, in turn, increases the resistance against the bipolar concentration. Yong and Chong suggested an effective method to control the membrane deposition and the cake formation mechanism and determined the flux penetration. It was concluded that the cake layer formation was a dynamic process classified into three stages, the pores blocking at the beginning of the filtration, the cakes formation, and the cakes compression [3]. Brink et al. demonstrated that the decrease in temperature caused the polysaccharides to accumulate in the liquid mixture and changed the particle size, provoking the blockage of pores and the deposition of the membrane [4].

The wastewater of cookies factories in Iran is mostly treated by the conventional activated sludge process. This is the first time that this paper has investigated the wastewater of Dorna factory by using a pilot MBR which has been designed and tested different fluxes. The flux should be reasonable because the increase in the flux will cause the membrane to become more clogged. The concentration polarization also has been studied in this article due to its important role in membrane clogging, which causes the formation of a cake layer.
2. Materials and methods

2.1. MBR setup
In this study, the industrial wastewaters have been used as the samples. A plexiglass reactor with 3.9 L of volume has been constructed to perform the experiment. The pilot contained a plate-and-frame type microfiltration membrane made by polyvinylidene fluoride (PVDF) (Fig. 1). The plate membrane module (Sinap, China) with a pore diameter of 0.4 µm and an effective surface area of 0.048 m² was submerged in the filtration zone of the MBR (Fig. 2). The wastewater from the initial filtration unit of the flour treatment plant was introduced into the reactor. Two tanks were also used for loading wastewater into the reactor and the effluent. Two peristaltic pumps (Model: PER-A, 12L/0.5B, Antech) were also employed for the feeding stream and permeate suction. In the MBR input area, sensors with adjustable level controls were employed to control the flow by restricting the input and output to increase and decrease the reactor level respectively. A pressure sensor was used to increase accuracy and determine the transmembrane pressure (TMP) on both sides of the membrane in the suction path. Moreover, two aeration pumps (Model: ACO-6602) were used to supply oxygen to the biomass and create tension around the membrane surface to avoid clogging.

![Figure 1. Plate-and-frame type microfiltration membrane made by polyvinylidene fluoride (PVDF).](image1)

![Figure 2. MBR schematic diagram and experimental set up.](image2)

2.2. Operating conditions
In this research, three HRTs (i.e. 4, 8, and 16 h) have been selected to study the fouling phenomenon. According to the results, the
membrane fouling was separated at an HRT of 4 h. It also increased along with the decrease in the HRT and over the time (an increase in the SRT) thus, determining the optimum and suitable flux and HRT is very important. The experiments were conducted under the following conditions: the TMP range of 1.5-10.5 mbar; pH of ~7; turbidity of ~187 NTU; permeate flux of ~5-21 L/(m²h); HRTs of 16, 8, and 4 h; MLSS of 5.6-7.8 g/L; OLR of 3-9 kgCOD/(m³.d). The dissolved oxygen (DO) of the system was maintained at 2.5 mg/L, and the complete SRT was considered as 30 days. The operational condition during the experiments is summarized in Table 1.

Table 1
Operation parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Hydraulic retention time (HRT)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>16 h</td>
</tr>
<tr>
<td>COD removal (%)</td>
<td>97</td>
</tr>
<tr>
<td>Organic loading rate (OLR) (kg COD/m³.d)</td>
<td>8.84</td>
</tr>
<tr>
<td>Total operation period (days)</td>
<td>10</td>
</tr>
<tr>
<td>Permeate flux (LMH)</td>
<td>20.83</td>
</tr>
<tr>
<td>Mixed liquor suspended solids (MLSS, mg/L)</td>
<td>~7.8</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>24.3</td>
</tr>
<tr>
<td>TMP (mbar)</td>
<td>10.5</td>
</tr>
<tr>
<td>pH</td>
<td>~7</td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>2.5</td>
</tr>
</tbody>
</table>

2.3. Analytical methods
All experiments were performed based on the Standard Methods (APHA, 2005) in which there was a steady-state operating condition and the COD removal variation was less than 10 %. The COD was examined with a COD meter (Model: DRB200 from HACH, Germany), and DO was measured with a DO meter (Model: HQ40d Multi from HACH, Germany). The turbidity and pH were monitored by the turbidity sensor (Model: TURB 355IR ) and pH meter (Model:p15). MLSS and mixed liquor volatile suspended solids (MLVSS) tests were performed in accordance with Standard Methods (ASTM 2540D) and, then, the sludge volume index (SVI) was checked. The viscosity was measured by a viscometer (Model: Anton Paar, SVM 3000). In addition, the total EPS and SMP concentrations, containing carbohydrates, proteins, and humic acids, were examined via the Lowry method. The DR 5000 spectrophotometer (HACH, USA) was also used to determine the concentration. Samples were taken from the feed, permeate tank, and the bioreactor.

2.4. EPS and SMP characterizations
To measure the EPS and SMP, a 50-ml sample from the bioreactor was collected and centrifuged with 3200 rpm for 30 minutes. Then, two phases were separated (i.e. the liquid phase and the solid phase) to measure the SMP and EPS.

2.5. The microstructure of the sludge flocs
In wastewater treatment plants, handling the sludge is typically the main challenge of the treatment process. Therefore, the picture of
the sludge in the bioreactor was taken with a light microscope with a magnification of X40 (Model: Olympus, CX31).

2.6. Membrane resistance analysis
The analysis of the membrane biofouling has been performed by measuring the hydraulic resistance to permeation based on the membrane permeability.

Where \( R_t \) (1/m) is the total filtration resistance, \( \text{TMP} \) (Pa) is the transmembrane pressure, \( J \) (L/m².h) is the measured permeate flux, and \( \eta \) (Pa.s) is the supernatant viscosity (\( R = \frac{\Delta P}{\eta J} \)). The total resistance (\( R_t \)) includes three types of resistance, \( R_m \), \( R_p \), and \( R_c \). \( R_m \) (1/m) is the membrane resistance, \( R_p \) (1/m) is the pore blocking resistance with the irreversible nature, and \( R_c \) (1/m) is the cake filtration resistance with the reversible nature. The resistance determination was conducted as follows: (1) \( R_m \) was determined by filtering water with the fresh membrane at the beginning of the process, (2) \( R_t \) was measured at the end of the process, (3) \( R_p \) was determined after the physical removal of the cake layer, and (4) \( R_c \) was determined under the steady state condition (\( R_c = R_t - (R_m + R_p) \)).

2.7. Membrane cleaning
The purpose of washing the membrane module is to reclaim the permeability of the membrane. The cake layer created on the membrane surface was removed by the physical washing using distilled water, while the suspended particles inside the membrane pores and cavities were removed with chemicals. During the process, the chemical membrane cleaning was done because the membrane was clogged by the suspended materials. Accordingly, the membrane was first put in distilled water for 10 minutes and, then, in a mixture of NaOCl (5000-2000 ppm), NaOH solutions (1000 ppm) for 30 minutes, and in the oxalic acid solution (1000 ppm) for 30 minutes. Afterward, the membrane was washed with distilled water for 10 minutes [12].

3. Results and discussion
The SRT is one of the most important factors affecting the membrane biofouling in the MBR. Studies have shown that there is a relationship between the membrane deposition and SRT deficiency. The cake resistance is significantly reduced due to the increase in the SRT in the MBR. At the SRT infinitely, the membrane fouling is reduced due to the small particle size and low EPS concentration. The selection of the SRT depends on the membrane pore size, HRT and type of wastewater. The concentration of the MLSS was low in the early days. It was initially 5080 (mg/L), and gradually increased to 8940 (mg/L). The concentration of the MLSS in membrane bioreactor operations varies on different days, which is normal, due to the proper performance of the microorganisms and the variability of feed in the bioreactor. The concentration of the MLSS increases by decreasing the HRT because of the optimal soluble oxygen, increased OLR of the bioreactor, and high hydraulic retention time (the biomass aging), which has a significant impact on the growth of microorganisms. In general, a higher MLSS results in a better bioreactor performance in eliminating contaminants (the efficiency of the COD removal). Fig. 3 shows the percentages of the COD removal at different HRTs. In HRTs=4, 8, and 16 h, the average percentages of the removal were 97±2.04, 95±2.32, and 94±3.14 respectively. The average percentage of the COD removal
during the total process was 95 %. Thus, the highest COD removal occurred at the HRT=4 h (99 %). Gökhan Balçoğlu et al, also achieved 99 % of the COD removal in an anaerobic MBR for the confectionary wastewater treatment [13]. On the other hand, it was found that in low HRTs and high MLSSs, the bioreactor had a better performance in the removal of contaminants (the efficiency of the COD removal). The organic loading rate (OLR) could change microbial behaviors, microbial properties, and biomass characteristics in mixed liquors (e.g. the MLSS, particle size, viscosity, floc structure, EPS, and SMP), and membrane biofilms, thereby causing the membrane biofouling. Under the steady-state conditions, the membrane fouling didn’t happen in the low OLR in the MBR (2.84 kg COD/m³.d and 5.13 kg COD/m³.d), while the MBR biofouling was observed in the higher OLR (8.84 kg COD/m³.d). Wu et al. (2011) also reported that, in the OLR, different F/M ratios and DO levels might change the number of bacteria and the EPS which were produced under operating conditions [14]. While the sustainable OLR was determined as 4.4 kg COD/ m³.d for anaerobic conditions [13].

The sludge volume index (SVI) was used to assess the quality of the sludge sediment in the MBR and the typically-activated sludge system. The SVI determined the sludge stability/instability and its quality. The smaller volume index of the sludge causes a better sedimentation and flaking. According to the results of this research, a decrease in the SVI has been observed as a result of the higher MLSS concentration, lower HRT, and passage of time. The amounts of the SVI at the HRT=4 h and HRT=16 h were 121 (ml/g) and 167.5 (ml/g) respectively. Therefore, good sedimentation of the flocs was observed. However, a decrease in the SVI occurred when the sludge was dispersed in the mixed liquor. To conduct a precise investigation, a picture of the sludge was taken by a light microscope with a magnification feature of X40 and methylene blue staining.

Nitrification, which occurs inside the bioreactor and results in the growth of small organs, is the process of oxidation of ammonia to nitrite by nitrosomona and nitrification to nitrate by nitrobacter. Throughout the entire process in the reactor, the color of
the reactor changed with the passage of time and the nitrogen concentration was increased. Thus, at the beginning of the period (the sludge rearing period) the sludge was dark black or gray, but gradually, following the removal of ammonia and nitrite, the sludge changed to brown. According to the depletion diagram of the total nitrogen, the removal efficiency decreased by decreasing the hydraulic retention time and increasing the nitrogen organic charge (Fig. 4).

The oil removal effect of the lipids varies depending on the pollutant density, pH, etc. Fat and oil adhere to the activated sludge masses in the aeration units, reducing the oxygen supply for microorganisms and reducing the efficiency of the effluent treatment. Due to the reduced hydraulic retention time, water and oil have a higher contact surface and particles adhere to the microorganism masses which lead to a better removal of them. The results showed that by decreasing hydraulic retention time, the percentage of the oil removal increased (Fig. 5).

When the F/M ratio is low, it simply means that the influent of the bioreactor is low for the microorganisms. However, the F/M ratio increases due to an increase in the amount of the COD input (the input organic load) or a decrease in the HRT (Fig. 6). In this case, biomasses were added to the bioreactor and increased the concentration of the suspended solids. To study the membrane biofouling, changes in the TMP with different residence times were monitored under three constant-flux conditions (5-10.42-20.83 LMH). Fig. 7 shows the change of the TMP in the MBR. At the beginning, the TMP rises directly and slowly. Then, following the severe fouling, the TMP begins to rise quickly, and the membrane fouling causes a detour from the straight line. At HRTs of 8 and 16 h, no considerable fouling was observed in the membrane, not to mention that the TMP diagram was a straight line. However, at an HRT of 4 h, biofouling occurred in the membrane, and the TMP diagram deviated from the straight line. At that HRT (i.e., 4 h), chemical cleaning was done on the membrane.
Among the extracellular polymeric materials, EPSs containing multifarious types of macromolecules (e.g. carbohydrates, proteins, nucleic acids, phosphorus lipids) and polymer compounds inside or outside of the cell surface and in the intercellular space, have a significant role in the membrane fouling, particularly in the cake layer formation. This phenomenon occurs because high EPS levels reduce the floc permeability, and the membrane is also affected by the bulky sludge due to the prevalence of stranded bacteria and the presence of the EPS [15]. In addition, the high protein-to-carbohydrate ratio in the EPS may cause sludge bubbles and the membrane fouling. There is a close relationship between the EPS concentration and the specific resistance of the cake layer, in a way that the special resistance is likely to increase the EPS concentration and increase the TMP. The soluble EPS is always used for centrifugation. Thus, SMPs create a gel layer, block the membrane pores, and penetrate into the pores and spaces between the particles. For example, Geng and Hall [5] concluded from their studies that the size of flocules and SMP concentrations were absolutely essential in the membrane fouling. According to the studies, the SMP concentration, similar to the EPS, decreases with an increase in the SRT.

According to the results obtained in this study (Fig. 8), the concentration of the EPS and SMP is reduced due to a reduction in the HRT. This reduction occurs due to the passage of time and, consequently, an increase in the concentration of the MLSS in the mixed fluid that enters the self-feeding stage, leading to the lack of growth of the microorganisms. Over time, with the aging of the sludge, microorganisms need more dissolved oxygen, which reduces the EPS and SMP. Nevertheless, some believe that the EPS is independent of the SRT. As shown in

**Figure 6.** Ratio of the OLR to the F/M at different HRTs.

**Figure 7.** TMP at different HRTs.
Fig. 8, the concentration of the extracted carbohydrate is higher than the protein concentration, highlighting the role of carbohydrates in the membrane blocking related to the proteins. In addition, by increasing the EPS, the fouling and cake formation may occur due to the EPS adhesion to the biofilm, which mainly contains the carbohydrates. It is of note that, in the application of the heating method, the least amount of carbohydrates was observed. The low ratio of protein to carbohydrate in the SMP causes irreversible fouling. According to the data shown in Table 2, the EPSp/EPSc ratio is increasing, and the SMPp/SMPc ratio is decreasing, which, in turn, exacerbates fouling.

Table 2
Ratio of the EPS, SMP (P/C).

<table>
<thead>
<tr>
<th>HRT=16 h</th>
<th>HRT=8 h</th>
<th>HRT=4 h</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.38</td>
<td>0.39</td>
<td>0.41</td>
<td>EPS (P/C)</td>
</tr>
<tr>
<td>0.05</td>
<td>0.047</td>
<td>0.035</td>
<td>SMP (P/C)</td>
</tr>
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</table>

4. Conclusions
A pilot MBR was designed and constructed for the wastewater treatment of Dorna cookies factory for the first time. The results of this study have showed that at HRTs of 4, 8 and 16 hr, the percentage of the COD removal
was quite high with a mean COD input of 1500 (mg/L) and mean COD of 72 (mg/L), and 95 % removal rate. Therefore, the system performance in this range is less sensitive to the hydraulic lifetime. In addition, there was no remarkable change in the COD removal as a result of a short hydraulic residence time. The average MLSS for this experiment have ranged from 5000 to 8500 mg/L. The study showed that pH and opacity values for the MLSS were also high. The average opacity of the input was 187 NTU, and that of output was 3 NTU. The efficiency of the system in the opacity removal was estimated to be 98.5 % on average. At HRTs of 4, 8, and 16 h, the total resistance rates were, 22.5×10¹⁰, 21.3×10¹⁰, and 20.4×10¹⁰ respectively. The cake layer resistance (Rc) had the highest share of the total resistance. The concentrations of the EPS and SMP and their respective compounds were strongly influenced by the melting temperature and the membrane function. The extracted carbohydrates were more prominent in the membrane fouling than in the extracted protein. The most significant factors that may influence the reactor performance include, inter alia, the increased number of the EPS, the increased SMP, and the F/M ratio. Therefore, considering the results obtained in this study, as well as studies carried out by researchers in this field, the MBR can be considered as the most suitable option for the treatment of wastewater and reusing wastewater. Although the membrane bioreactor process is more hydraulically sensitive (due to the clogging of the membrane) than the conventional activated sludge, it is more efficient than the active sludge process in terms of the high-quality wastewater production, especially for reusing wastewater in agriculture and other industries, and compliance with stringent drainage standards.

References


