



Research Paper

Study on Operational Conditions to Minimize Membrane Fouling in Membrane Bioreactor (MBR) System for Wastewater Treatment-Preliminary Pilot Tests

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Highlights

- The effect of antiscalant usage on minimizing fouling in MBR system due to water hardness
- The flux was almost constant up to end of the experiment with tap water in the presence of antiscalant.
- In the absence of antiscalant, the flux decline within ten days in wastewater.
- The flux did not decline until twenty days of operation in the presence of antiscalant.
- A 95% of COD rejection, 98% of total phosphate-P rejection, 40% total N-rejection, 99% of TSS rejection, 98% of color rejection from wastewater.

Abstract

In this study, effect of antiscalant usage on minimizing of membrane fouling due to high water hardness during wastewater treatment tests run by a pilot-scale membrane bioreactor (MBR) system. The membranes used in these studies were Kubota flat sheet MBR membranes made from polyethylene with a pore size of 0.4 micrometer. Preliminary tests were carried out with tap water for sixty days of operation. To investigate the applicability and the effect of antiscalant usage, four experiments (two experiments with tap water and two experiments with wastewater) were carried out and each experiment lasted for 29 days. The tests were carried out in the presence and in the absence of antiscalant. Fouling on MBR membranes was investigated by monitoring flux decline versus time. In tap water tests, unstable flux was observed initially then a flux decline due inorganic scaling. On the other hand, the flux was almost constant up to end of the experiment in the presence of antiscalant. During wastewater tests (in the absence of antiscalant), the flux decline was observed within ten days of operation while during wastewater tests in presence of antiscalant, the flux did not decline until twenty days of operation. The use of antiscalant did not influence the effluent quality. According to the quality analyses results for MBR effluent, removal efficiencies for COD, PO₄-P, and total N were 95%, 98% and 40%, respectively. In addition, 99% of total suspended solid rejection and 98% of color rejection were obtained in the presence or absence of antiscalant.

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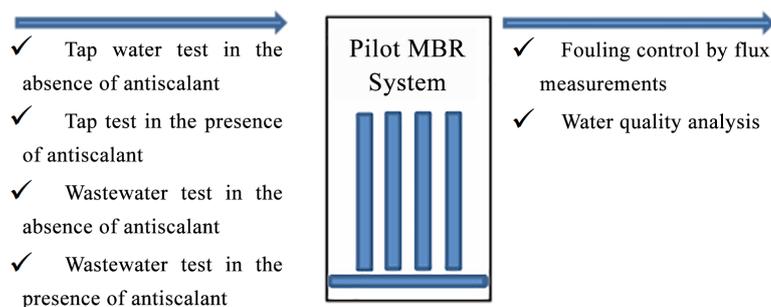
1. Introduction

Membrane bioreactor (MBR) process is the common method used in the last decade for the treatment of industrial and municipal wastewaters. The concept of MBR is similar to that of the conventional activated sludge method used in wastewater treatment in which the removal of dissolved and suspended organic matter are done by the help microorganisms.

During MBR operation, sludge and suspended solids are separated by the help of membranes unlike in the case of conventional method in which gravity plays a vital role in the solid-liquid separation.

MBR technology is not anymore a novel process for the treatment of industrial and municipal wastewaters. The capacity of MBRs nowadays ranges from less than 1 m³/day to 100000 m³/day and above [1]. MBR

Graphical abstract



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technology has so many advantages over traditional activated sludge method for wastewater treatment such as low foot-print, partial virus rejection and ~100% of bacteria rejection, high mixed liquor suspended solid (MLSS) loading, ability to produce high quality effluent, good resistance to organic loading and hydraulic variation [2].

However, membrane fouling remained the bottleneck of this technology. Fouling on MBR membranes is due to the deposition of organic particles on the surface of the membranes thereby reducing water recovery, increasing pressure drop and hence total energy cost. Generally membrane fouling in MBR membranes is attributed to the deposition of sludge particles, adhesion of large particles to the surface of the membranes, pore clogging by fine particles [3]. Cake layer formation is the results of fouling on MBR membranes. This can be removed efficiently by hydrodynamic means, by generating a cross flow across the surface of the membrane. Thus, the lift velocity produced removes the deposited particle from the surface of the MBR membrane [4]. Decreasing MLSS concentration, permeate flux and increasing cross flow velocity are some of the common methods to be applied in the mitigation of cake layer formation [3]. One the other hand, one should be very careful while increasing the cross flow velocity since unnecessary adjustment will result in a sharp increase of the energy cost.

Cake layer formation is not the major challenge in MBR processes since it can be controlled by changing some operational parameters like MLSS concentration, cross-flow velocity, permeate flux, relaxation time etc. However, inorganic fouling remains as the major challenge in MBR process. Inorganic fouling occurs due to the accumulation of inorganic precipitates like metal hydroxides on the surface of the membranes, or blocks the pores of the membranes. The presence of metal ions like Ca^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} , and the anions like CO_3^{2-} , SO_4^{2-} , OH^- can react and cause chemical precipitation. The precipitations are formed when the concentration of the chemical species exceeds their saturation concentrations [5]. Also, biological precipitation of inorganic-organic complexes can be observed.

One of the methods to control inorganic fouling in MBR wastewater treatment process is pH adjustment [6]. Kang et al. [7] reported that acidic medium could be a solution to eliminate the precipitation of inorganic foulants on the surface of the membranes. However, pH has so many effects in the microbial activity in the bioreactor and a microbial activity decline can be obtained when the pH was decreased towards 4.0 [8]. In addition, pH change is considered to have a significant negative effect on flocculation, cell morphology and adhesion phenomena in the MBR reactor [9]. A negative effect on COD removal was observed when mixed liquor pH was increased from 9 to 10 [10]. A decrease in the pH from 8.3 to 6.3 shows a decrease in filtration permeability as a result of the alteration in the extra-cellulose polymeric substances (EPS) and swelling characteristics of the membrane [11]. Increasing pH may cause an increase in cake layer resistance, while decreasing pH has a significant effect on adhesion of sludge on the surface of the membrane [12].

Most of the researches done about fouling in MBR membranes are generally related to organic fouling and its mechanism. However, there is less information to describe inorganic fouling mechanisms on the surface of the membrane and the solutions to eliminate it [13].

In the wastewater treatment plant of ITOB Organized Industrial Zone established in Menderes-Izmir, Turkey, wastewater having both municipal and industrial origins was treated by MBR process. The main problem experienced in the wastewater treatment plant is membrane fouling and flux decline due to the scaling on the surface of the membranes. It was difficult for technical staff to identify the root of these problems and optimize the operational conditions to solve the problems in the full scale treatment system. Inorganic scaling on MBR membranes was dominant problem in flux decline. This study aimed to explore this problem and to find a feasible solution to minimize scaling on MBR membranes and thus flux decline. For this, the effect of antiscalant usage during MBR operation to minimize flux decline due to scaling on MBR membranes was investigated.

2. Materials and methods

A 50-L of MBR tank was outfitted with four flat sheet microfiltration membranes (Kubota, Japan) submerged into the tank as shown in Figure 1. The reactor was equipped with two plates dividing the bioreactor riser and two down-comer, the membranes are submerged in the riser zone. The membranes were made from polyethylene (PE) with a surface area of 0.11 m^2 per module with a nominal porosity of $0.4 \mu\text{m}$. Air was supplied at a speed of 10-12 L/min to the reactor for the biological degradation of the wastewater as well as to create cross-flow velocity in order to prevent accumulation of suspended particles on the surface of the membranes. There are three pumps used as blowers for aeration in the reactor. Air was supplied to the reactor through the diffusers (hole diameters: 1, 3 and 5 mm) located at the bottom of the reactor. Tap water test was first conducted in order to understand the effect of hardness in tap water on membrane scaling. For this purpose, in preliminary tap water tests, pilot MBR system was continuously fed with tap water which is supplied to industries as their process water. In the case of wastewater tests, the feed for the pilot MBR mixed liquor was taken from the MBR unit of existing full scale wastewater treatment plant by the help of a feed pump. During the operation, driving force was the hydraulic pressure head by keeping the water level constant at 0.6 m above the membranes. In this study, suction pump was not used for collection of permeate as recommended by the manufacturer. For this reason, TMP values were not recorded. In a study by Skouteris [14] with similar set-up, an approximate value of 0.118 to 0.104 bar was recorded for the feed height that varied from 2.5 to 2.36 m above the membranes with tap water. However, when wastewater is employed, it may be difficult to calculate the pressure because MLSS is not a Newtonian fluid.

To maintain the MLSS concentration in the reactor, a recycle pump was used to withdraw excess sludge from the reactor. The permeate samples were collected for analyses. The pilot system was equipped with a scada program where the level of the wastewater in the reactor can be adjusted. The parameters such as pH, conductivity, and temperature were monitored at any time from the control panel. Figure 1 shows the flow diagram of the pilot MBR system.

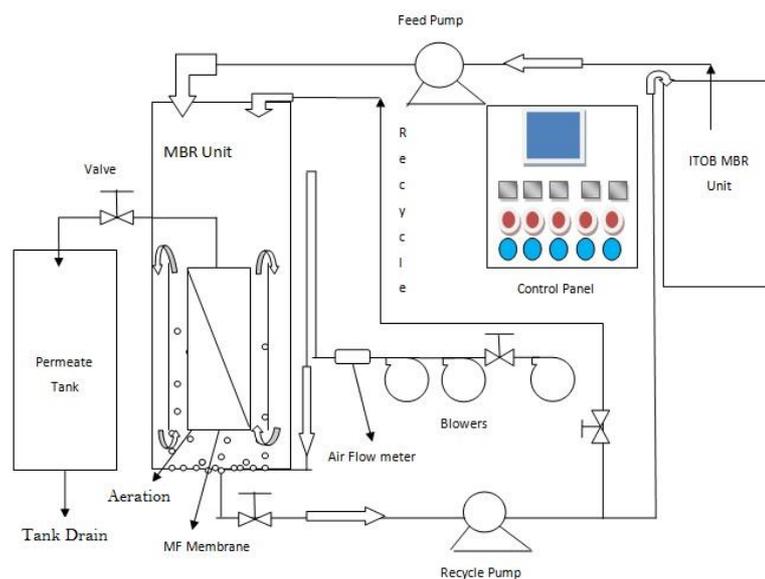


Fig. 1. Flow diagram of the MBR pilot system.

The MLSS of pilot MBR system was maintained as 10-22 g/L which was approximately same with full scale MBR system of wastewater treatment plant. Hydraulic retention time (HRT) was maintained at 3 h where solid retention time (SRT) was 37 days. The properties of the pilot MBR system and the conditions employed were summarized in Table 1.

Table 1
Properties of the pilot MBR system

Property	Value
Reactor capacity (L)	50
Membrane active area (m ²)	0.11
Nominal pore size of membrane (micron)	0.4
Membrane type	Plate and frame
Membrane material	Kubota-PE
Diffuser diameter (mm)	3 mm
MLSS (g/L)	10-22
HRT (h)	3
SRT (day)	37

To make sure that the addition of antiscalant does not affect the treatability of the wastewater by MBR system, some analyses were carried out. Ready-prepared Hach Lange test kits were used to determine COD, Phosphate (PO₄-P), Nitrite (NO₂-N), Nitrate (NO₃-N), Total Nitrogen (TN) and Ammonium (NH₄-N) in MBR influent and effluent samples. Before analyzing COD, PO₄-P and total nitrogen, a Hach Lange LT200 thermo-reactor was used for digestion, while Hach Lange DR3900 Bench top VIS spectrophotometer was used to carry out the final reading. A portable Hach-Lange multi-meter was used to measure conductivity, TSS and salinity while a portable Hach-Lange pH meter was used to measure pH of samples. The colorimetric method was used to determine the color in MBR influent and effluent samples. Table 2 shows the results of quality analyses of ITOB MBR influent.

Table 2
Properties of ITOB influent wastewater.

Parameter	Influent
Conductivity (mS/cm)	2.25-3.58
pH	7.05-7.69
Calcium (mg/L)	140-160
Salinity (%)	1.52-2.05
TSS (mg/L)	580-1341
NH ₄ -N	19.70-44.30
PO ₄ -P (mg/L)	2.12-18.20
Total Nitrogen	35.8-75.30
NO ₃ -N (mg/L)	0.514-10.956
NO ₂ -N (mg/L)	0.112-0.921
COD (mg/L)	262-1006
Color (Pt-Co)	1697- 2304

Due to the change in the ambient temperature, we need to recalculate the flux values since it changes with temperature as reported [15]. Equation 1 given in Appendix part was used to calculate the temperature corrected flux. The membrane recovery was calculated with the Equation 2 given in the Appendix.

Following experiments were run using pilot MBR system:

1. Preliminary tap water test.
2. Study with tap water in presence of antiscalant
3. Study with tap water in the absence of antiscalant
4. Study with wastewater in the presence of antiscalant
5. Study with wastewater in the absence of antiscalant

The antiscalant used during MBR tests in the presence of antiscalant was Ropour (RPI-3000 A). The dosage of antiscalant solution during MBR tests was 5 mL/min while the concentration of the antiscalant solution for tap water test was 45 mL antiscalant/50 L tap water and 90 mL antiscalant/50 L wastewater for the wastewater test. In MBR tank, the hole diameter of diffuser used was 3 mm. MLSS value in wastewater was 12-19 g/L during MBR tests run with wastewater. As explained in next session, different membrane cleaning procedures were implemented during pilot MBR tests.

3. Results and discussion

3.1. Preliminary tap water test

In order to understand the effect of hardness in tap water on the scaling of the MBR membranes, tap water test was carried our first for a period of 2 months. Initially, flux of the virgin membrane in tap water was measured after membrane conditioning and the initial flux value was 190 LMH. In the second day, the flux decreased to 180 LMH. The flux continuously decreased until 1.92 LMH after 60 days of operation. After the preliminary tap water test, the membranes were removed from the bioreactor. As shown in Figure 2, the fouled membranes have a chalky color indicating an inorganic fouling due to mainly CaCO₃ deposition after 2 months of operation with tap water.

Since MBR membranes were not contacted with wastewater, it was considered that only inorganic fouling exists on MBR membranes and only acid cleaning can remove the foulants. Generally, the membrane manufacturers recommend a cleaning procedure for MBR membranes. However, this may vary according to wastewater treatment plant since the characteristic of wastewater cannot be same everywhere. However, one should be careful with the recommended pH and temperature during operation because these parameters affect the chemical structure of the MBR membranes thereby decreasing the performance of the membranes. To find the optimum condition of membrane cleaning, a trial and error method is generally adopted [16].

Here, the membranes were cleaned ex-situ with citric acid solution (3000 mg/L) at pH 2.5 for 150 min at 7°C in a cold winter day. After treatment with citric acid, rinsing with tap water was carried out and the membranes were inserted back to the reactor.

In the first acid cleaning trial, the membranes were physically cleaned but the flux in tap water was still 22.5 LMH. This showed us that a lot has to be done since the flux recovery was only 11.8% although the initial flux was 190 LMH. It was considered the concentration of citric acid used was not enough to remove the inorganic scaling from MBR membranes. Temperature has also a significant role in membrane cleaning as it increases the rate of the reaction between the chemical reagent and the foulants. Bearing this in mind, the temperature of cleaning solution was increased to about 20°C in order to increase the speed of the reaction in the next step. Also, another trial was performed in order to find the optimum acid concentration that can remove the inorganic foulants from the surface of the membrane by changing acid concentration and contact time. However, when the acid concentration used was 10000 mg/L, the cleaning operation has to be stopped because a small deformation was observed on some part of the membrane surface even though the flux was still 47.8 LMH. This finding contradicted the results obtained by Wang et al. [17] which stated that up to 1.5% of citric acid was good enough to clean MBR membranes while there was not any damage on active layer of the membranes.

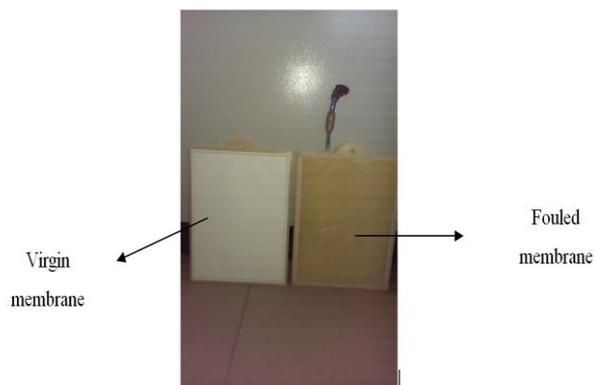


Fig. 2. Virgin membrane before and after the operation in tap water.

3.2. Study with tap water in the absence of antiscalant

After preliminary study and acid-cleaning, another test was carried out with tap water in the absence of antiscalant. From Darcy's law for filtration it is well known that flux is directly proportional to driving force (pressure difference), inversely proportional to absolute viscosity of the fluid and total hydraulic resistance. Temperature has significant influence on viscosity and hence it affects the flux in an inverse proportion (temperature effect on flux equation is given in Equation 1 in the appendix). For this reason, all flux values were recalculated according to the reference temperature of 20°C. The temperature corrected flux and flux values at ambient temperature versus time plots were shown in Figure 3. As can be seen in Figure 3, temperature has a significant effect on flux values, while ambient temperature fluctuated from +1 to +25°C.

Immediately after the chemical cleaning, it was observed that the measured flux decreased rapidly, then almost a constant flux was obtained and finally the flux decreased again. After the chemical cleaning, the membranes were cleaned but when they are inserted into water, accumulation of flocs on the pores of the membrane occurred. That was the reason of the sharp drop in the flux immediately after chemical cleaning [18]. After rapid build-up of the flocs, the system reached a steady state in the 14th day of operation and after that the flux was almost constant until 21th day of operation. After 21 days, the flux began to decrease that means, during the steady state of operation there was an accumulation of foulants on the membrane.

After the second test with tap water in the absence of antiscalant, the color of the membranes seems to be different than observed in the preliminary study as shown in Figure 4. In order to understand the reason the scaling on membrane surface, EDX (Energy Dispersive X-ray spectroscopy) method was employed. According to the result of analysis summarized in Table 3, the main component of the precipitate was determined as CaCO_3 (21.5 wt %).

Table 3

The results of EDX analysis.

Element	Concentrate (wt%)
Ca	8.614
Si	0.168
K	0.062
Zn	0.059
Fe	0.052
Cu	0.021
Br	0.017
S	0.011
Sr	0.05
Ti	0.003
C	91
Total	100.057

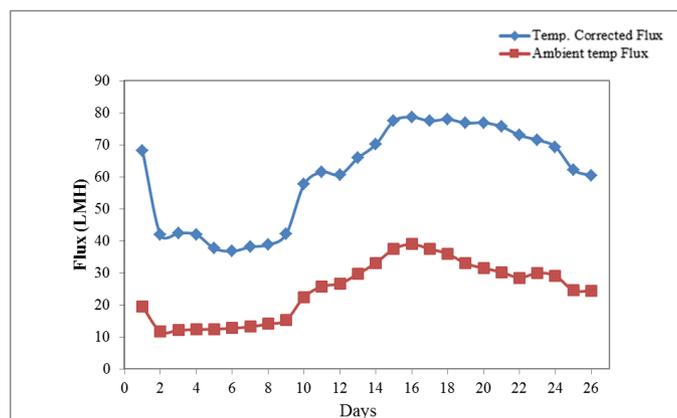


Fig. 3. Temperature corrected and ambient temperature flux values vs. time plots for the study with tap water in the absence of antiscalant.



Fig. 4. Fouling on MBR membranes after 29 days of operation in tap water in the absence of antiscalant.

After the operation, the membranes were cleaned ex-situ with citric acid solution (4000 mg/L) and pH was adjusted to 2.5 during cleaning. For this, the membranes were soaked into a citric acid solution (4000 mg/L) for 3 h. The initial temperature corrected flux in water after acid cleaning was 140 LMH. As we cleaned the membranes frequently, the remaining foulants from the previous study were possibly removed also. The increased temperature was also another important factor decreasing the solubility of CaCO_3 in the second trial.

3.3. Study with tap water in presence of antiscalant

Figure 5 shows temperature corrected and ambient temperature flux values of tap water study in the presence of antiscalant. In this study, ambient temperature flux values at 14–22°C were almost the same with the normalized flux values calculated for 20°C. The flux values shows a similar trend with the previous study (without antiscalant) in the sense that, the immediate flux after chemical cleaning was high then shows a fluctuation for two days after that the flux values were almost constant. This means that the system has reached a steady state. Up to 29th day of operation, there was no flux decline, for this reason the test was terminated at that point for the next study.

Chemical cleaning after this study was the same as in the previous study (tap water test in the absence of antiscalant). However, the acid concentration used was 2000 mg/L since the membranes were less fouled compared to the previous study and the measured flux was 184 LMH.

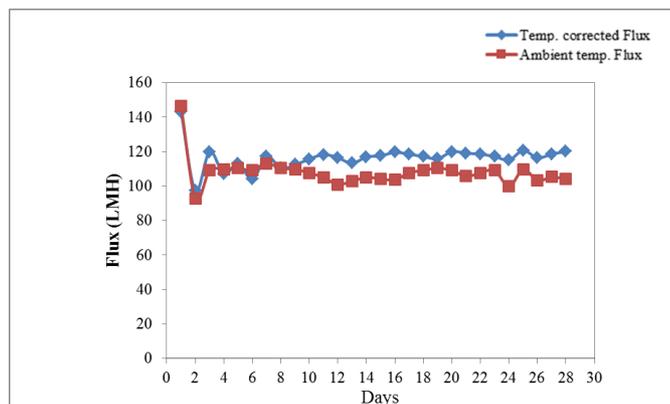


Fig. 5. Temperature corrected and ambient temperature flux values vs. time plots for the study with tap water in the presence of antiscalant.

3.4. Study with wastewater in presence of antiscalant

Figure 6 shows the temperature corrected flux of the study performed with wastewater in the presence of antiscalant. At the beginning of the experiment, the calculated flux was 84 LMH. A day after start-up of the system, a sharp drop in the flux was observed due to the accumulation of colloids and biomass on the surface of the membranes. The operational temperature flux between 18 to 25°C was almost same with the reference temperature flux. That's why the effect of temperature on membrane fouling was not discussed. However, one should keep in mind that when temperature

decrease is far below the reference temperature, the MLSS viscosity will increase and hence there may be a high tendency of membrane fouling as reported by Skouteris [14]. This was followed by a gradual decrease in the flux until 21st day of the experiment in which a second sharp drop began to appear with a flux of 8 LMH indicating that the membranes are fouled. A chemical cleaning was considered in the 21st day of operation in order to restore the flux for the continuation of the experiment. The test was continued with the wastewater in the presence of antiscalant and the flux measured with the wastewater was 92 LMH after chemical cleaning which is greater than the flux at the beginning of the experiment. This happened due to the decrease in the MLSS in the reactor. A day after cleaning, we experienced a sharp drop in flux which may be due to presence of fine particles in the biomass. In the presence of antiscalant, the membrane seems to be less biofouled. However, this was attributed to the decrease in the MLSS in the reactor.

When the effluent quality was analyzed, it was obtained that color was highly rejected from wastewater in the presence of antiscalant and almost all the rejections were above 98% indicating well function of the MBR operation. The minimum color in permeate was 19 Pt-Co while the maximum color was 35 Pt-Co. The TSS rejection was also high in the presence of antiscalant. The results showed a similar trend with color rejection in which TSS was highly rejected by MBR process (not less than 99%, even 100% in some cases). The rejection increased when the membranes were fouled due to the biolayer formed on the membranes during the process.

The $\text{NH}_4\text{-N}$ was removed from wastewater with more than 98% of efficiency. According to Huang et al. [19], $\text{NH}_4\text{-N}$ is usually removed with no dependency on STR. However, $\text{NO}_3\text{-N}$ in the effluent was greater than that in the influent. The reason behind the increase in the $\text{NO}_3\text{-N}$ instead of decrease was due to inefficient denitrification in the MBR tank. This can be enhanced when aeration is done at intermediate rates so that some part in the tank will operate as anoxic chamber [20]. The $\text{NO}_2\text{-N}$ was highly rejected and this is due to the fact that $\text{NO}_2\text{-N}$ is removed by converting $\text{NH}_4\text{-N}$ into $\text{NO}_2\text{-N}$ in anoxic process since air is continuously supplied into the MBR chamber. In wastewater treatment, nitrogen is usually removed by the conversion of $\text{NO}_3\text{-N}$ into N_2 gas and this requires an anoxic process which does not exist in the MBR chamber. That is why we could not achieve a high total nitrogen removal in our system and an average of only 33% of rejection was obtained. Phosphorus in wastewater is usually found in phosphate form and it is usually removed by adsorption on the biomass or by precipitation [20]. Both precipitation and adsorption require a pH adjustment or the presence of calcium ion. In our wastewater, the calcium concentration was above 140 mg/L. That is the reason of high $\text{PO}_4\text{-P}$ rejection in our system. COD is a measure of organic matter in the wastewater. For this purpose, its removal will improve the quality of the effluent water in wastewater treatment processes. In our study, an average COD removal of 94% was achieved. In most cases, COD removal is related to MLSS concentration. In the study carried out by Skouteris [14], COD removal efficiency has increased from 71.4% to over 90% when MLSS concentration increased from 4.643 g L^{-1} to 9.658 g L^{-1} . Summary of the effluent properties of pilot MBR effluent was given in Table 4. However, the mechanism of COD removal in wastewater is scarce, but generally the removal efficiency is greater than 90% at MLSS concentration of 9.5 g L^{-1} and above it [20].

After MBR test with wastewater in the presence of antiscalant, a physical cleaning was employed to remove the reversible fouling. This was done by hand without applying much pressure on the membranes in order not to cause any damage on the membranes (only a soft brush was used). After physical cleaning, the measured flux measured in tap water was 72 LMH.

Later, the membranes were soaked into a hypochlorite solution (300 mg/L) for 45 min followed by 15 min backwash (by gravity). After rinsing with tap water, the temperature corrected flux in tap water was 147 LMH. Finally, the membranes were submerged into a citric acid solution of 2000 mg/L for 45 min and then back-washed with this solution for 15 min by gravity force followed by rinsing with tap water. At the end, the measured flux in tap water was 188 LMH which is very close to the measured flux of the virgin membrane.

3.5. Study with wastewater in absence of antiscalant

Figure 7 shows the flux profile of the study carried out with wastewater without using antiscalant. As can be seen in Figure 7, the flux dropped in the first 10 days of the operation from 84 to 8 LMH unlike in the case of the study with antiscalant. The reason of the sharp flux drop may be due to the presence of the fine particles or inorganic foulants. So, the membranes were cleaned in order to restore the flux for the continuation of the experiment. The initial flux after chemical cleaning and the initial flux at the beginning of the experiment were different. The reason might be due to incomplete removal of the foulants. The system continued to work without antiscalant until 21st day of operation in which the flux dropped from 46 to 8.18 LMH (which means

cleaning is required). The membranes were cleaned for the completion of the experiment. After the second cleaning, the experiment continued until 29th day of operation (the end of the experiment) and the flux dropped from 27.3 to 9 LMH during this stage.

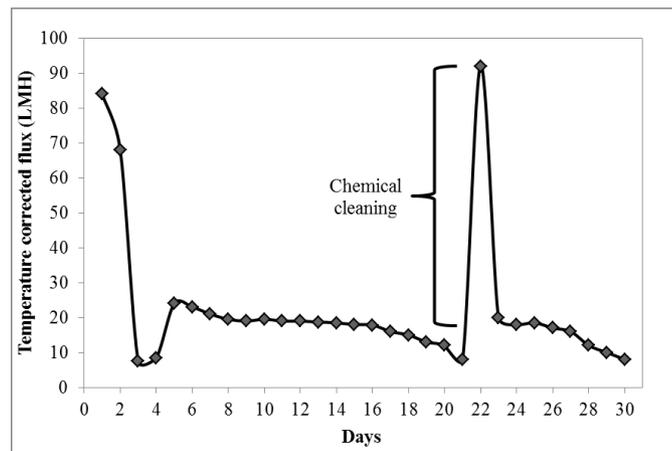


Fig. 6. Temperature corrected flux for the study with wastewater in the presence of antiscalant.

Table 4
Properties of MBR effluent.

Parameter	Effluent
Conductivity (mS/cm)	2.58-3.58
pH	7.12-7.59
Salinity (%)	1.58-2.01
TSS (mg/L)	0.00-3.00
$\text{NH}_4\text{-N}$	0.021-0.075
$\text{PO}_4\text{-P}$ (mg/L)	0.016-0.121
Total Nitrogen	21.63-45.20
$\text{NO}_3\text{-N}$ (mg/L)	20.84-40.40
$\text{NO}_2\text{-N}$ (mg/L)	0.008-0.028
COD (mg/L)	18.70-32.40
Color (Pt-Co)	21-61

As we obtained in the previous study with wastewater in the presence of antiscalant, color rejections were above 98%, indicating well function of the MBR membranes. However, the minimum color in the permeate was 21 Pt-Co while the maximum value was 61 Pt-Co in this case. The reason why there was poor performance in this study compared with the previous study run with wastewater in the presence of antiscalant was due to the decrease in MLSS value which makes it difficult for the membranes to reject small particles. TSS rejection results showed a similar trend with color rejection and TSS was rejected with a rejection of more than 99%. Also, the rejections for $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, $\text{PO}_4\text{-P}$, and COD were similar to the results obtained in the studies performed in the presence of antiscalant.

At the 10th day of operation after starting the experiment, membranes were cleaned in-situ with hypochlorite solution (300 mg/L) when the flux dropped from 84 to 8 LMH through a chemically enhanced backwash (CEB) for 30 min followed by in-situ washing with citric acid (300 mg/L) for 30 min. The flux after chemical cleaning was 46 LMH.

The second cleaning was carried out at the 21st day when the flux was dropped from 46 to 8.2 LMH. The membranes were again cleaned in-situ (chemically enhanced backwash) using hypochlorite solution (500 mg/L) for 30 min followed by a cleaning with 500 mg/L of citric acid for 30 min. The concentrations of hypochlorite and citric acid were increased from 300 to 500 mg/L considering more fouling on the membranes was expected compared to the previous fouling. The flux after CEB was 27.3 LMH.

After second cleaning step, the experiment continued until 29th day which is the end of the experiment. The flux dropped from 27.3 to 9 LMH during this period. Then, the membranes were cleaned ex-situ with the same procedure before starting the next experiment like in previous case. In this case, the membranes seem to be more fouled unlike in the presence of antiscalant.

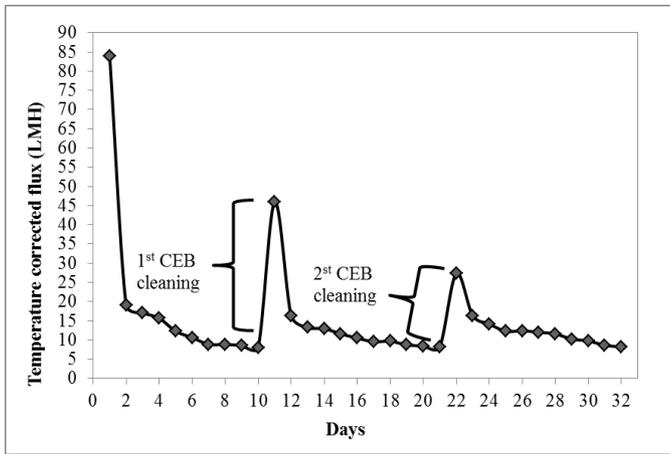


Fig. 7. Temperature corrected flux with wastewater in the absence of antiscalant.

4. Conclusions

MBR pilot tests were conducted with tap water first to understand the source of scaling on MBR membranes. The pilot MBR tests were carried out in the presence/absence of antiscalant. In the presence of antiscalant, the MBR system worked longer with less decrease in flux. It was concluded that the use of antiscalant in MBR system does not affect the bio-oxidation of the organic matter in the reactor. If proper cleaning (either physical or chemical) is not applied, it will lead to the deterioration of the active layer on the other hand. When we used citric acid at high concentrations, we observed some membrane ageing. Therefore, low acid concentration should be used while cleaning the membranes, thereby increasing the life time of membranes.

It was understood that operating MBR membranes at flow rates above 20 LMH is not sustainable because higher flux can cause membrane fouling within short period of time. Therefore, the operational flux should be kept in the range of 10-15 LMH.

According to the quality analyses results for MBR effluent, a 95% of COD rejection, 98% of total $\text{PO}_4\text{-P}$ rejection, 40% of total N-rejection, 99% of TSS rejection and 98% of color rejection in the presence or absence of antiscalant were obtained in the studies with wastewater.

The amount of antiscalant was 389 mL during wastewater tests with antiscalant. The cost of antiscalant was 6.61 €/L (tax is included). The cost of antiscalant per each experiment was calculated as 2.57 €.

Future study will be on optimization of antiscalant type and concentration along with diffuser diameter employed in MBR tank.

5. Appendix

$$J = \frac{\Delta p}{\mu(T) * R_t} \quad (1)$$

where

ΔP = Pressure difference (transmembrane pressure (Pa))

$\mu(T)$ = Absolute viscosity as a function of temperature (kg/m.s)

R_t = Total hydraulic resistance (1/m)

$$J(20^\circ\text{C}) = \frac{Q_p \times \text{Exp}^{-0.0239 \times (T-20)}}{A} \quad (2)$$

where J is the temperature corrected flux at 20°C, Q_p (L/h) is the flow rate of the permeate, T (°C) is temperature and A is the membrane area (m²).

$$\text{Membrane Recovery} = \frac{J}{J_0} \times 100 \quad (3)$$

where J and J_0 are the fluxes of cleaned and virgin membranes, respectively.

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7. References

- [1] J. Zhang, H.C. Chua, J. Zhou, A.G. Fane, Factors affecting the membrane performance in submerged membrane bioreactors, *J. Membr. Sci.* 284 (2006) 54-66.
- [2] S. Judd, *The MBR Book: Principles and Applications of Membrane Bioreactors for water and Wastewater Treatment*, 2nd ed., Elsevier, Amsterdam, 2011.
- [3] R. Liu, X. Huang, F. Sun, Y. Qian, Hydrodynamic effect on sludge accumulation over membrane surfaces in a submerged membrane bioreactor, *J. Process Biochem.* 39 (2003) 157-163.
- [4] Y. Shimizu, YI Okuno, K. Uryu, S. Ohtsubo, A. Watanabe, Filtration characteristics of hollow fiber microfiltration membranes used in membrane bioreactor for domestic wastewater treatment. *Water Res.* 92 (1996) 30-2385.
- [5] J. Zhang, W.L.C. Loong, S. Chou, C. Tang, R. Wang, and A.G. Fane, Membrane biofouling and scaling in forward osmosis membrane bioreactor, *J. Membr. Sci.* 403 (2012) 8-14.
- [6] S. Sanguanpak, C. Chiemchaisri, W. Chiemchaisri, K. Yamamoto, Influence of operating pH on biodegradation performance and fouling propensity in membrane bioreactors for landfill leachate treatment, *Int. Biodeter. Biodegrad.* 102 (2015) 64-72.
- [7] I.J. Kang, S.H. Yoon, C.H. Lee. Comparison of the filtration characteristics of organic and inorganic membranes in a membrane-coupled anaerobic bioreactor, *Water Res.* 36 (2002) 1803-1813.
- [8] J. Wu, Y. Zhuang, H. Li, X. Huang. pH adjusting to reduce fouling propensity of activated sludge mixed liquor in membrane bioreactor, *Sep. Sci. Technol.* 45 (2010) 890-895.
- [9] J.E. Baily, D.F. Ollis, *Biochemical Engineering Fundamentals*, McGraw-Hill, New York, 1986.
- [10] W.J. Gao, H.J. Lin, K.T. Leung, B.Q. Liao. Influence of elevated pH shocks on the performance of a submerged anaerobic membrane bioreactor. *Process Biochem.* 45 (2010) 1279-1287.
- [11] A. Sweity, W. Ying, S. Belfer, G. Oron, M. Herzberg. pH effects on the adherence and fouling propensity of extracellular polymeric substances in a membrane bioreactor. *J. Membr. Sci.* 378 (2011) 186-193.
- [12] Y. Zhang, M. Zhang, F. Wang, H. Hong, A. Wang, J. Wang, X. Weng, H. Lin, Membrane fouling in a submerged membrane bioreactor: effect of pH and its implications. *Biores. Technol.* 152 (2014) 7-14.
- [13] S. Shirazi, C.J. Lin, D. Chen. Inorganic fouling of pressure-driven membrane processes – a critical review. *Desalination* 250 (2010) 236-248.
- [14] G. S. Skouteris, *Low Energy Membrane Bioreactors For Decentralised Waste Water Treatment*, PhD Thesis, Department of Chemical Engineering, University of Bath, United Kingdom, 2010
- [15] N.Ö. Yigit, *Membran biyoreaktörü ile (MBR) evsel atıksu arıtımı*, PhD thesis, Suleyman Demirel University, Isparta, Turkey, 2007.
- [16] C. Kappel, *An integrated membrane bioreactor–nanofiltration concept recirculation for wastewater treatment and nutrient recovery*, PhD Thesis, University of Twente, Enschede, The Netherlands, 2014.
- [17] W. Wang, J. Ma, Y.C. Tang, K. Kimura, Q. Wang and X. Han, A review: Membrane cleaning in membrane bioreactors, *J. Membr. Sci.*, 468 (2014) 276-307.
- [18] F. Meng, S.-R. Chae, A. Drews, M. Kraume, H.-S. Shin and F. Yang, Recent advances in membrane bioreactors (MBRs): membrane fouling and membrane material, *Water Research*, 43 (2009) 1489-1512.
- [19] X. Huang, P. Gui and Y. Qian, oxidation of organic matter in anoxic condition, *Process Biochem.*, (2001) 36-100.
- [20] J. Radjenovic, M. Matosic, I. Mijatovic, M. Petrovic, and D. Barceló, Membrane Bioreactor (MBR) as an Advanced Wastewater Treatment Technology, *Env. Chem.*, 5 (2007) 37-101.