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PERFORMANCE COMPARISON OF MEMBRANE BIOREACTOR WITH DYNAMIC MEMBRANE BIOREACTOR

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LIST OF SYMBOLS

α	Particular Cake Resistance of The Biofilm
ε	Cake Layer Porosity
A_m	Membrane Area
d_p	Diameter of the particle
J	Flux
ΔP	Transmembrane Pressure
ρ_p	Particle Density
R	Resistance
Rm	Membrane Resistance
Rf	Foulant Resistance
Rc	Cake Layer Resistance
Rt	Total Resistance
Rf,t	Total Foulant Resistance
Rf,r	Reversible Foulant Resistance
R,ir	Irreversible Foulant Resistance
η	Water Viscosity
Lp	Permeability
τ	Shear Stress
η	Shear Rate

LIST OF ABBREVATIONS

COD	Chemical Oxygen Demand
CIP	Cleaning in Place
CEB	Chemical Enhanced Backwash
CST	Capillary Suction Time
DMBR	Dynamic Membrane Bioreactor
EPS	Extracellular Polimeric Substances
F/M	Food/Microorganism Ratio
FAS	Iron Ammonium Sulfate
FS	Flat Sheet
GAC	Granular Active Carbon
HRT	Hydraulic Retention Time
HF	Hollow Fiber
LMH	Flux, Liter Meter Hour
MLSS	Mixed Liquor Suspended Solids
MLVSS	Mixed Liquor Volatile Suspended Solids
MBR	Membrane Bioreactor
MT	Multitubular
NF	Nanofiltration
PAC	Powder Active Carbon
PE	Polyethylene
PVDF	Polyvinylidene difluoride
PTFE	Polytetrafluoroethylene
PP	Polypropylene
PAN	Polyacrylonitrile
PES	Polyethersulfone
PS	Polysulfone
RO	Reverse Osmosis
SAD	Specific Air Demand
SRT	Sludge Retention Time
SS	Suspended Solids
SMP	Soluble Microbial Products
SRF	Specific Resistance to Filtration
SF	Sludge Filterability
TMP	Transmembrane Pressure
UF	Ultrafiltration

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ABSTRACT

PERFORMANCE COMPARISON OF MEMBRANE BIOREACTOR WITH DYNAMIC MEMBRANE BIOREACTOR

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Msc. Thesis

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Membrane bioreactors (MBRs) used for wastewater treatment have begun to be used at an increasing rate in developed and developing countries in the last 10 years. It is anticipated that many conventional wastewater treatment plants will convert to the MBR technology in the coming years, and as a result, the final sedimentation basins will come to an end. MBRs are biological processes in suspension growth mode in which purified water and biomass are physically separated by membrane equipment. However, membrane costs, increased energy demand, clogging control and low flow bioreactor operating problems are among the major problems faced by membrane bioreactor systems. Dynamic membrane bioreactor systems (DMBR), due to its low operating cost, have provided a promising approach to solving these problems.

The purpose of this study is to measure the pollution performance of two different membrane types, 0.45 μm and non-woven dynamic membranes, which are operated in the same aerobic membrane bioreactor (AeMBR) and fed with synthetic wastewater. During reactor operation, parameters of COD, turbidity, pH, temperature, electrical conductivity (EC), TMP, SADm and ORP were measured daily. The highest COD removal values were found to be 99.47% and 97.02% and the lowest turbidity values were found to be 0.12 NTU and 1.23 NTU for 0.45 μm real and non-woven dynamic membrane, respectively. The maximum and minimum permeate pH values of the AeMBR operated at room temperature, for 0.45 μm real and non-woven dynamic membrane, were found to be 7.98-7.94 and 7.37-7.43, respectively. The maximum and minimum values for electrical conductivity were measured as 574-577 μS and 470-471 μS, respectively, as 0.45 μm real and non-woven dynamic membrane. As a result of the TMP measurements, both membrane materials were subjected to chemical washing (1 hour 0.5% NaOCl and then 1 hour pH = 2 set in tap water) with the pressure rising 300

mbar or above. It is noted that in the measurements made after washing, the membranes acted as if they were used for the first time in operation. In the ORP measurements made in the reactor, the maximum and minimum values were measured as 177.4 and 114.2 for 0.45 μm real and non-woven dynamic membrane, respectively.

Also, soluble microbial products (SMP) / extra polymeric substances (EPS), specific resistance to filterability (SRF) / supernatant filterability (SF), fourier transform infrared spectroscopy (FT-IR), capillary suction time (CST), scanning electron microscopy (SEM) and denaturing gradient gel electrophoresis (DGGE) analysis were included in this study.

The study consisted of three experimental periods and on the first day of each experimental period, a new membrane was placed in the module. The first experimental period was successfully operated at 10 LMH flux. During this time, approximately 98% COD removal and 1 NTU turbidity values were measured for both membrane types. During operation, the membranes exhibiting high filtration performance with only physical washing were subjected to chemical washing only once, with the pressure reaching 300 mbar and above. During the first experimental study, once in a week SMP / EPS and only once SEM, SRF / SF, CST, FT-IR and DGGE analysis were performed.

In the second period of the experimental run, the flux was increased to 15 LMH and the reactor was run successfully. The average COD removal efficiencies in percentage for 0.45 μm real and non-woven dynamic membrane were recorded as 97% and 90%, respectively. However, physical and chemical washing was applied to both types of membranes against the fouling problems originating from the high flux. The chemical washout was reduced by 97% of the membrane flocking for both membrane types. After chemical washing, the turbidity values of the 0.45 μm real membrane did not change much (around 0.2 NTU) but the turbidity values of the non-woven dynamic membrane gave high values until the cake layer was formed after washing. Minimum turbidity values were found to be between 1-2 NTU for the non-woven dynamic membrane. During the second experimental period, once in a week SMP/EPS and only once SRF/SF and CST were performed and the results compared with the previous experimental period.

In the last experimental period, the flux was increased to 20 LMH, during which time the non-woven dynamic membrane fouled swiftly and thus did not perform a successful filtration process. While the turbidity values of the non-woven dynamic membrane layer reached approximately 8 NTU levels, the turbidity values of the 0.45 μm real membrane remained at about 0.2 NTU. Both membranes reached a TMP of approximately 10 mbar as a result of chemical washing which means 97% of the fouling reduction. During the last experimental period, only once SMP/EPS, SRF/SF, CST, FT-IR and DGGE analyses were performed and the results were compared with the other analyses.

As a result of FT-IR analysis, organic pollutants on the sludge have been assigned on the graph and for the SEM analysis, organic substances on the membrane were identified, thickness of the cake layer formed on the membrane was measured by cross-sectional image, and the types of micro-contamination causing the fouling were observed and significant information was obtained. Within the DGGE study, the numbers of bacterial species in the sludge that cause fouling were determined. Findings in this study showed that the use of DMBR is very low in terms of cost compared to MBRs and is at least as successful as MBRs in terms of functionality. Based on this information it is expected to shed light on DMBR and MBR studies to be made in the future and also benefit on the use of DMBR in real scale installations.

Keywords: AeMBR, DMBR, aerobic membrane bioreactor, dynamic membrane bioreactor, non-woven.

ÖZET

MEMBRAN BİYOREAKTÖR VE DİNAMİK MEMBRAN BİYOREAKTÖRÜN PERFORMANS KARŞILAŞTIRMASI

Mehmet Akif VERAL

Biyomühendislik Anabilim Dalı

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Tez Danışmanı: Prof. Dr. Özer Çınar

Atık su arıtımı amacıyla kullanılan membran biyoreaktörler (MBR) gelişmiş ve gelişmekte olan ülkelerde son 10 yılda artan bir hızla kullanılmaya başlanmıştır. Önümüzdeki yıllarda birçok konvansiyonel atık su arıtma tesisinin teknolojilerini MBR'lara dönüştüreceği ve bunun sonucu olarak son çökeltim havuzlarının ortadan kalkacağı tahmin edilmektedir. MBR'ler membran teknolojileri sayesinde arıtılmış su ve biyokütlenin fiziksel olarak ayrıldığı süspansiyon büyüme modundaki biyolojik proseslerdir. Bununla birlikte, membran maliyetleri, artan enerji talebi, tıkanma kontrolü ve düşük akıda biyoreaktör işletme sorunları, membran biyoreaktör sistemlerinin karşılaşmış olduğu başlıca problemler arasındadır. Dinamik membran biyoreaktör sistemleri (DMBR), işletim maliyetinin düşük olması sebebiyle bu sorunların çözülmesinde umut verici bir yaklaşım olabilme ihtimalini getirmiştir.

Bu çalışmanın amacı, iki farklı membran türünün, 0.45 µm gerçek membran ve non-woven dinamik membran, aynı aerobik membran biyoreaktör (AeMBR) içerisinde işletilerek, sentetik olarak verilen atıksuda beslenen reaktörde bulunan bulunan kirliliğin, membranlar tarafından filtrelenmesi sonucu, kirlilik giderim performanslarının ölçülmesidir. Reaktör işlerimi sırasında KOİ, bulanıklık, pH, sıcaklık, iletkenlik, TMP, SADm ve ORP parametreleri günlük olarak ölçülmüştür. En yüksek KOİ giderim değerleri, 0.45 µm ve non-woven dinamik membran olmak üzere sırasıyla, %99.47 ve %97.02 olarak, en düşük bulanıklık değerleri ise sırasıyla 0.12 NTU ve 1.23 NTU olarak bulunmuştur. Oda sıcaklığında işletilen AeMBR sisteminde, 0.45 µm gerçek ve non-woven dinamik membran olmak üzere, maximum ve minimum çıkış pH değerleri sırasıyla, 7.98-7.94 ve 7.37-7.43 olarak bulunmuştur. Elektriksel iletkenlik için maximum ve minimum değerler, 0.45 µm gerçek ve non-woven dinamik membran olmak üzere, sırasıyla, 574-577 µS ve 470-471 µS olarak ölçülmüştür. TMP ölçümleri sonucunda, basıncın 300 mbar üzerine çıkmasıyla, her iki membran materyali kimyasal

yıkamaya (1 saat %0.5 NaOCl ve ardından 1 saat pH=2 ayarlanmış musluk suyu içerisinde bekletilerek) tabi tutulmuştur. Yıkama sonrası yapılan ölçümlerde membranların, işletmeye ilk alındıkları gibi basınç oluşturdukları kaydedilmiştir. Reaktör içerisinde yapılan ORP ölçümlerinde, maximum ve minimum olmak üzere sırasıyla 177.4 ve 114.2 olarak ölçülmüştür.

Ayrıca çalışma kapsamında, çözünebilir mikrobiyal ürünler (SMP)/ hücredışı polimerik bileşenler (EPS), spesifik filtrasyon direnci (SRF)/süpernatant filtreedilebilirliği (SF), fourier dönüşümü kızılötesi spektroskopisi (FT-IR), kapiler emme zamanı (CST), taramalı elektron mikroskobu (SEM) ve denatürasyon gradient jel elektroforezi (DGGE) analizleri yapılmıştır.

Yapılan çalışma üç deneysel aşamadan oluşmuş ve her deneysel çalışmanın ilk gününde modül içerisine yeni bir membran yerleştirilmiştir. İlk deneysel çalışma 10 LMH akıda başarılı bir şekilde işletilmiştir. Bu süre zarfında her iki membran türü için yaklaşık olarak %98 KOI giderimi ve 1 NTU bulanıklık değerleri ölçülmüştür. İşletme süresinde sadece fiziksel yıkama ile yüksek filtrasyon performansı gösteren membranlar, sadece bir kere, basıncın 300 mbar seviyesi ve üzerine ulaşmasıyla, kimyasal yıkamaya tabi tutulmuştur. İlk deneysel çalışma süresince haftada bir SMP/EPS ve çalışma süresince bir defa SEM, SRF/SF, CST, FT-IR ve DGGE analizleri yapılmıştır.

Deneysel çalışmanın ikinci aşamasında, akı 15 LMH değerine çıkartılmış ve reaktör başarılı bir şekilde işletilmiştir. 0.45 µm gerçek ve non-woven dinamik membranın KOI giderimleri verimleri ortalaması sırasıyla %97 ve %90 olarak kaydedilmiştir. Bununla birlikte yüksek akıda çalışmadan kaynaklı gerçekleşen tıkanma problemlerine karşı, her iki membran türü için fiziksel ve kimyasal yıkama uygulanmıştır. Kimyasal yıkama sonucu her iki membran türünün tıkanıklıkları %97 oranında azalmıştır. Kimyasal yıkamadan sonra, 0.45 µm gerçek membran için bulanıklık değerleri çok değişmezken (yaklaşık olarak 0.2 NTU), non-woven dinamik membran bulanıklık değerleri ilk aşamada yükselmiş, ilerleyen aşamalarda ise 1-2 NTU aralığında seyretmiştir. İkinci deneysel çalışma süresince haftada bir SMP/EPS ve çalışma süresince bir defa SRF/SF ve CST analizleri yapılmış ve sonuçlar bir önceki deneysel faz ile kıyaslanmıştır.

Deneysel çalışmanın son aşamasında, akı 20 LMH değerine yükseltilmiş, bu süre zarfında non-woven dinamik membranın çok hızlı bir şekilde tıkandığı ve dolayısıyla başarılı bir filtrasyon işlemi gerçekleştiremediği görülmüştür. Non-woven dinamik destek tabakasının bulanıklık değerleri yaklaşık olarak 8 NTU seviyelerine ulaşırken, 0.45 µm gerçek membranın bulanıklık değerleri ortalama 0.2 NTU seviyesinde kalmıştır. Her iki membranda da tıkanma %97 azalmış, kimyasal yıkama sonucunda basınç yaklaşık 10 mbar'lık bir TMP'ye ulaşmıştır. Üçüncü deneysel çalışma süresince, bir defa olmak üzere SMP/EPS, CST, SRF/SF, FT-IR ve DGGE analizleri yapılmış, sonuçlar diğer deneysel çalışmalar ile karşılaştırılmıştır.

FT-IR sonuçları neticesinde çamur üzerinde bulunan organik kirleticiler, grafiksel olarak tayin edilmiş, SEM analizi için ise, membran üzerinde bulunan organik materyallerin tayini yapılmış, kesit görüntüsü ile membran üzerinde oluşan kek tabakasının kalınlığı ölçülmüş ve tıkanmaya sebep olan mikro kirleticiler hakkında bilgi edinilmiştir. DGGE çalışması kapsamında, çamur içerisinde bulunan ve tıkanmaya sebep olan bakteri türlerinin sayıları tayin edilmiştir. Bu çalışmada elde edilen bulgular göstermiştir ki DMBR kullanımı MBR'lere kıyasla maliyet açısından oldukça düşük olmasının yanısıra işlevselliği açısından en az MBR'ler kadar başarılıdır. Bu bilgiler ışığında elde edilen bulgular, gelecekte yapılacak DMBR ve MBR çalışmalarına ışık

tutacağı düşünülmektedir. Ayrıca gerçek ölçekli tesislerde de DMBR kullanımı konusunda fayda sağlaması düşünülmektedir.

Anahtar Kelimeler: AeMBR, DMBR, aerobik membran biyoreactör, dinamik membran biyoreactör, dokumasız.

CHAPTER 1

INTRODUCTION

1.1 Literature Review

Membrane bioreactor (MBR) systems are accepted as one of the most critical treatment processes in terms of wastewater treatment operations and environmental health issues. The amount of wastewater utilized for treatment operation is increasing parallel to the world population. In this context, there has been growing rate of interest to the MBR systems to reduce the water pollution caused by not only domestic use but also the industries. In the field of MBR technology, different types of membranes and support materials are employed for treatment processes for reuse of wastewater and resource convalesce. It is known that if the wastewater is discharged as a result of inadequate treatment, there are various problems that show up in receiving water bodies.

Besides being an excellent performer in solid/liquid separation processes, it has also significant advantages such as small footprint and good permeate quality [1]. In spite of its supremacy, there are some primary deficiencies like high operational cost, high membrane cost, low flux and getting membrane fouling under control. Thereby, dynamic membrane formation on the surface of the membrane is an encouraging approach in terms of generating appropriate solution for wastewater treatment operations. [2][3]. Dynamic membrane (DM), also called as secondary membrane, is generated on the surface of the support material which may be sometimes membrane or different types of textile materials such as mesh, non-woven fabric or filter cloth alternative to the microfiltration (MF) or ultrafiltration (UF) membranes. When the wastewater is filtered, colloidal constituents form a cake layer that acts as the secondary membrane and hinders the fouling problem of the support material [4][5]. DM technology, as well as being easy and wide spread, is open for different types of operational modifications.

It is important to indicate that the support layer itself cannot perform the filtration process by itself, but rather the dynamic membrane formed over its surface. When the cake layer loses its permeability due to bacterial or colloidal fouling, the membrane is exposed to a cleaning process that shouldn't be continuously implemented because it removes the secondary membrane [6].

In several experiments, DM technology has been employed for treatment of municipal wastewater in anaerobic membrane bioreactor (AnMBR) [7][8][9] and operational outcomes from the experiments represented that 98% permeate quality has been achieved in the process. After continuous treatment operation, membrane can come across intensive fouling problems, depending on the properties of the system.

Different types of textile materials such as non-woven fabric [10][11][12][13], mesh [14][15][16][17] and woven fabric [18][19] are being used as a support material through experiments. Lately, major portion of the experimental studies have been aiming to use textile materials due to their cost-effectiveness property, applicability during the replacement process and performance during the solid/liquid separation in aerobic environment. Therefore, DM combinations in other operational applications during wastewater treatment have been noted as efficient due to the removal performance of organic and inorganic constituents from the permeate in the range of 95-96% [20]. Extensive assessment of the recent DM operational performances suggests it as a favourable approach to the MBR systems. Performance, applicability and ability for the integration of DM has been examined. Obtained result indicated that porous layer generation act as a barrier which entrammels the transition of colloidal particles in different proportions over the surface of the membrane. Preclusion characteristics of DM application gives superior benefit to the operational output in terms of obtaining good permeate quality during wastewater treatment [20][21].

The quality and strength of DM have been analyzed [20] in AnMBR systems relying upon the disincentive property, that infiltrates the colloidal constituents and very high concentration of wastewater, and fabric consisted of single fiber has been found as useful support material for the formation of the cake layer. AnMBR system has been operated under 20 and 40 days of SRT, respectively, in order to consider the impact of SRT on both DM infiltration feature and biological yield. At the end of operation, over 99% COD removal has been achieved. It has been noted that DM operation for the treatment process of high concentration of wastewater has been found practical and

convenient for acquisition of superior permeate quality and it could be employed alternatively to the MF and UF membranes. As a support material, polypropylene filter cloth has been employed to generate dynamic layer and achieved superior permeate quality [20]. In another experiment [22], generation process of the dynamic layer has been examined at high flux rate of 65 $L.m^{-1}.h^{-1}$. At the end of the operation, it's been noted that dynamic layer has been generated by bacterial flocs and small colloidal particles such as soluble microbial products (SMP) and extracellular polymeric substances (EPS).

Another experimental study [16] has been made on urban wastewater treating it by using DM operation. In the experiment, treatment ability and systematic performance of the DM has been examined and filter cloth has been employed as a support material instead of utilizing MF or UF membrane. Generation and operational performance of infiltration of the DM and operational yield of the DMBR for treating urban wastewater have been evaluated and analyzed. The results showed that generation of the DM over the surface of the support material could be fast and formed much more stable. DM also served of its function in a great way of denying colloidal particles and high concentrated sludge could promote the cake layer generation which directly supports the DM formation. The result of the operation with the DM in the infiltration of the common turbidity represented that DM has had great importance for denying colloidal particles, microbial flocs and microorganisms.

Different types of DM studies have been made relying upon different wastewater types. One of the anaerobic studies that have been operated recently [23] aimed that to enhance anaerobic DM for wastewater treatment with the employment of large pore diameter mesh. It has been also noted that DM has formed by utilizing a mesh with the pore size of 200 μm and with implementation of cross-flow filtration process throughout the generation of DM. Since fouling phenomenon and the operational cost of the MBR system are primary problem [24], DM generation over the surface of the membrane can be an appropriate solution.

Water backwash, air backwash or scrubbing methods can be efficient to clean the dynamic membranes without using chemical substances [25]. Nevertheless, cleaning without using chemical substances may employ transient deprivation of effluent. One of the most critical properties for the dynamic membranes is the preclusion of the solid substances through the surface of the secondary membrane which can be comprised or

regenerated by itself, called self-forming dynamic membrane (SFDM). However, formation and/or reformation of the dynamic membrane layer may diminish the transmissivity of the support layer which is a similar hitch that has been seen in conventional MBRs [26].

Micro/ultrafiltration membranes are overpriced compared to low cost materials like mesh, non-woven fabric and woven wire cloth which can be used as support material for the generation of dynamic layer [16][22][27][28]. In addition, employing low cost materials, which are mentioned above, instead of using traditional materials ensures high rate flow of liquid at lower transmembrane pressure (TMP) in a cost-saving manner [11][19][29].

1.2 Objective of the Thesis

In MBR systems, treatment operation has been done usually by employment of conventional methods. In future treatment operations, with the development of industry, wastewater discharge operation is going to be done at frequent rate and treated wastewater use and reuse processes will increase in value. Due to that, it is predicted that attention to the MBR systems will increase. Beside of currently operated wastewater treatment plants (WWTPs), middle and large scale industries, which will be established in the long term, laboratory scale treatment operations have to be performed.

Utilization of conventional methods creates a financial burden to the WWTPs due to the high configurational and operational cost of the treatment operation, especially in industrial regions. As an alternative to the conventional systems, MBR systems which provide lower installation and operational cost will be financially significant for industrial enterprises. Systems that can be integrated into the treatment plant will play significant role for wastewater return in the following periods. Experience and knowledge about MBR systems is limited. This thesis will try to reduce the weight of financial burden of the industry that aims to install MBR system instead of conventional systems and it is going to be initiative segment of the MBR installation process which is much more advantageous in terms of cost and installation area as compared to existing conventional methods. At the same time, operational and configurational experience and knowledge of the MBR systems will be increased. In this context, the goals of this thesis can be summarized as;

1. When the current WWTPs are considered, although DMBR operating conditions are difficult, it is known that DMBR systems are relatively advantageous to MBR systems. In this context, the efficiency of DMBR systems will be investigated and knowledge and experience relying upon DMBR systems will be increased.
2. Although there is a disadvantage that the operating conditions of the DMBR systems are difficult to obtain with the MBR systems, analyzes have been carried out to show both advantages and disadvantages of these two systems under the same environment conditions.
3. In this context, the first work package will be prepared to determine the minimum SADm value by obtaining the maximum performance while keeping the ventilation cost, which is one of the biggest problems of wastewater treatment plants.

1.3 Hypothesis

MBR systems are widely used in wastewater treatment systems, and feature high initial set-up and module costs, high foaming tendencies and operating costs. It is emphasized that the operation cost of the reactor constitutes the largest share of the total cost, especially the ventilation, and that this cost will be lower during the wastewater treatment if this cost is realized in a single pool. It is thought that DMBR systems, which have relatively low operating costs compared to MBR systems, will play a more active role for the future in wastewater treatment. When the quality of the treatment process is observed, different support materials are used and the thicknesses and filtering performances of cross-sections of the cake layers on these materials are evaluated. Economically, more cost-effective support materials than commercial MBR membranes are promising for wastewater treatment. Within the scope of this thesis, the commercial MBR membrane of 0.45 μm membrane and the DMBR membrane of non-woven mesh were used in a single reactor, and treatment performances were evaluated by providing the same environmental conditions in the same reactor.

That is to say, it is considered to improve the understanding of the problem of fouling, which is a disadvantage in the case of MBR systems, which is becoming widespread in use, and in the case of reactor operating performance, and in this context, it is considered to develop solution strategies to tackle this problem.

It is known that operated reactors are used intensely in aerobic conditions, mainly due to the difficulties encountered during industrial waste disposal, the performance of reactors operating conditions is evaluated primarily by using commercial MBR membranes. In the scope of this thesis, it is planned to carry out analyzes and studies focusing on the problems that can occur during the operation in aerobic membrane bioreactor system and to solve these problems occured due to the employment of the commercial MBR membrane of 0.45 μm membrane and the DMBR membrane of non-woven mesh.

CHAPTER 2

GENERAL INFORMATION

2.1 General Definition of the Membrane Bioreactors

The wastewater produced from factories and other industrial establishments are being treated by using MBR and DMBR systems. In following years, it is estimated that most of the wastewater treatment plants will turn over to MBR and as a result of that the final settling tank will be eliminated. MRBs sustain convenient biological wastewater treatment and also provide physical separation of the water and biomass with the aid of membranes. The main advantage of the MBR systems is the whole process takes place in one tank, while two tanks are used for biochemical oxidation and water/biomass separation processes in conventional active sludge process (CASP) [30]. However, MBRs also provide the conservation of the biomass by employment of the ultra/micro filtration. In that way, total biomass conservation and proceeding the process in high sludge accumulation have been permitted [31]. Throughout the treatment process, wastewater flows across to raw and fine screens and large constituents are eliminated before operation inside of the reactor. While process maintained in aerobic conditions, the influent is exposed to aeration from the bottom part of the chamber. Aeration supports activated sludge inside of the reactor and significantly, released O_2 creates a shear force that hinders the membrane pore plugging, called fouling which will be mentioned in the following sections. However, mixed liquor inside of the reactor exposed vacuum for discharge of treated water to the outside of the reactor. Likewise, same configuration is used for anaerobic membrane bioreactors (AnMBR) which will be mentioned.

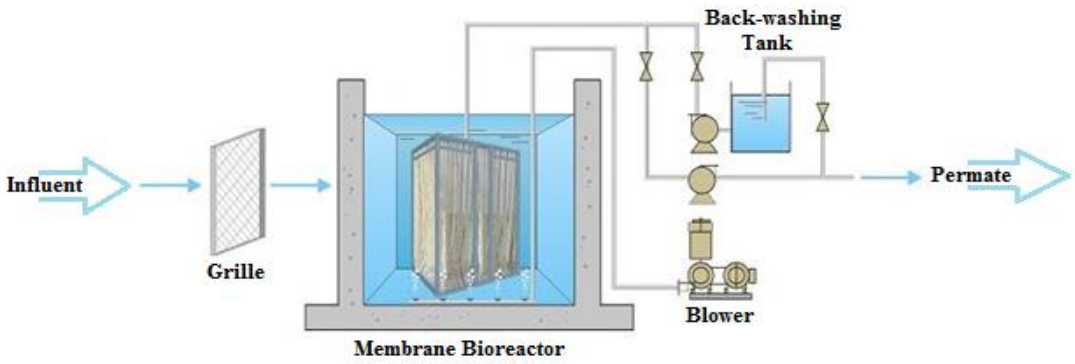


Figure 2.1 General process of membrane bioreactor.

2.2 Main Principle of MBR System

MBR is a system treating wastewater, which is domestic or comes from different kinds of industrial plants, by using diversified membrane types and reactor designs. Since the wastewater treatment process is run by the microorganisms, MBR system's bioreactor has also identical characteristics if it is compared with vented tank of any active sludge process (ASP). In ASP systems, wastewater and microorganisms are separated individually by gravitational force but for distinction of treated water and microorganisms in MBR system 0.05 - 1 pore size μm membranes are employed. Figure 2.2 represents the transportation of the floc, microorganisms and particles.

While small size of particles/microorganisms can pass through the pores, large size particles/microorganisms cannot pass and cause blockage of the membrane pores. However, amount of suspended solids (SS) after the treatment process is almost not determinable and it ensures high quality of treated water. While CAS is performed using two different tanks, MBR systems eliminate the gravity sedimentation tank and operate the process in one tank. If the overall result is compared with the CAS system, MBR systems procures low footprint.

Nonetheless, MBR systems have restrictions like other membrane systems regarding to membrane fouling. It is known that membranes are sensitive materials and can be plugged because of the constituents inside of it (i.e. sludge, colloidal particles, suspended solids, microorganisms, organic/inorganic substances). Controlling the fouling of the membrane is critical for consistent MBR process operation.

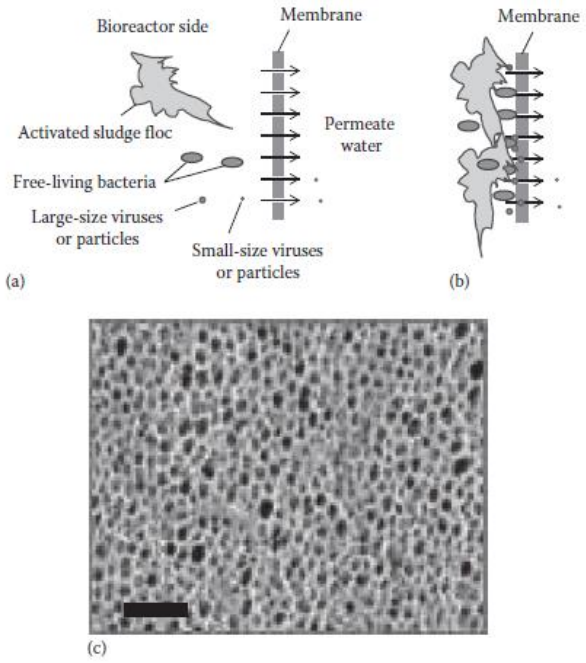


Figure 2.2 (a) Filtration process of the membrane (b) blockage of the membrane and (c) surface image of the Kolon's Cleanfil-S membrane in 1 μm scale [32].

Different kinds of experiment have been done to prevent fouling of the membranes such as manufacturing fouling durable membranes which have been designed in different geometry and enhancing the membranes surface chemistry, while filtration cycles, back-washing and aeration characteristics are procured by process engineers.

2.3 Short History of MBR Technology

First reports of the MBR technology based on the research were made in 1969 (by Smith et al.). Ultrafiltration membrane layers have been used to treat the wastewater for division of liquid (water) and biomass (activated sludge) with elimination of sedimentation tank. A pilot plant has been chosen to treat sewage produced from a manufacturing plant. Membrane cassettes are employed outside of the bioreactor and constituents inside of the reactor was exposed to a flow rate of 1.2 to 1.8 m/s through the surface of the membrane and with the pressure 150-185 kPa to diminish fouling and ensure consistent flow (13.6-23.4 $L/m^2/h$). Through the process, it is succeeded that 100% of the coliform bacteria has been removed through 90% of operation time. Even though, in this process, side-stream MBR design has been tested that brought bright results like high quality permeate, it is only applied for stinted cases (i.e. industrial organization and leachate wastewaters).

Fouling of the membrane pores, high membrane stock cost and circulation of the constituents which give rise to energy cost hindered the sprawl of this application for small-scale applications like municipal wastewater treatment. In 1989, a new MBR technology was reported, which is about solid-liquid separation by utilization of HF membranes in activated sludge aeration tank, generated by Yamamoto et al. [33]. HF membranes with 0.1 μm pore size have been used to excrete effluent in bioreactor that includes activated sludge.

Circulation of the constituents inside of the reactor over the surface of the membrane by suction with a pump which is pressurized and placed outside of reactor were renovated with straight immersion of the membranes inside of the reactor and application of suction pressure to ensure filtration. On the other hand, microfiltration (MF) has been later on used in combination with activated sludge process to improve the purification in domestic wastewater treatment [34].

This MBR configuration is called submerged/immersed MBR (Figure 2.3b) system that has been extensive approach and application for the treatment of wastewater in terms of its low energy cost. While submerged MBR configuration has been used as introduction, a couple of researches have been handled in terms of geometry of the membrane module, membrane pore diameters, processes to reduce the membrane fouling frequency and wiping the foulant away from the membrane.

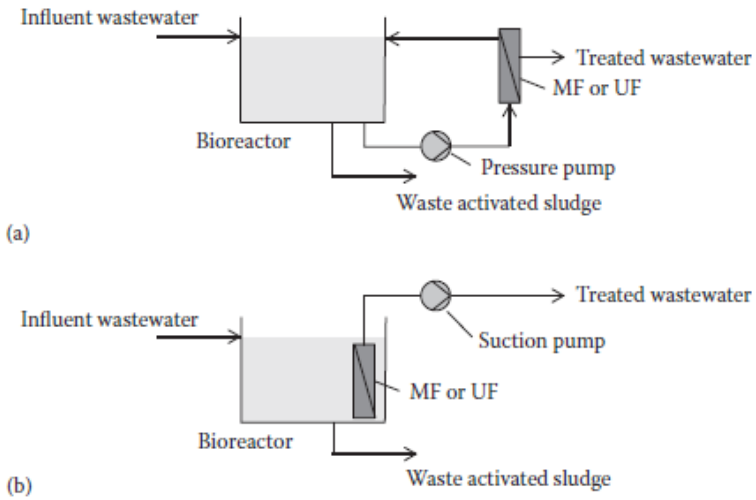


Figure 2.3 (a) Side-stream MBR configuration (b) immersed MBR configuration [32].

MBR configuration providers such as; Zenon, Kubota, Mitsubishi Rayon, and US-Filter, have expedited the implementation of MBR systems practice dated from mid-

1990s. Properties of MBR such as; membrane costs which decreased from 400$ US to 50$ US (through 1992 to 2010); production of qualified membranes; construction of the widescale MBR plants that have a wastewater treatment capacity of over 50,000 m^3/day; has accelerated the establishment of plants that provide wastewater treatment and ensure its reuse in countries like Middle East countries, PRC and US [32].

2.4 Fundamentals of MBRs and DMBRs

Membranes are inclined to fouling due to the permeate flux through its pores. The mixture (solid/sludge and liquid) inside of the reactor diminishes the filtration flux and it has the required membrane area increased [35]. On the other hand, MBRs need different approaches and developments for more global implementations. Fouling of membranes, due to its physical structure consisting of pores, and the high cost of implementation the membrane modules are the major obstacles that actually most of the MBRs systems come across. To reduce the cost and avoid the fouling and forming a shear over the membrane surface, different kinds of materials have been tried within the operations.

Dynamic membrane bioreactors (DMBRs), as distinct from MBRs, are known as formed-in-place (FIP) membrane or with another name used in literature secondary membrane [14]. The formation of the DMBRs is ensured during the diffusion of mixed liquor/solution through the surface of the membrane that filters one/more particular colloidal particles or materials already present in the mixture. Formation is sustained by different kind of materials like mesh non-woven fabric and filter-cloth [11][14]. On the other side, DMBRs come across with fouling intensively, despite aerosol shear employed over the surface of the membrane. The dynamic layer formed on the support layer can be changed by a new deposited layer which itself can be changed with the new one. Major amount of studies center upon employment of the meshes as a membrane for the permeate flux of the mixed liquor [14].

2.4.1 Process Types of MBRs

Activated sludge is sustained by release of O_2 from the bottom part of the chamber and membranes are exposed under suction which aids for absorption of the water from the small pore-sized membrane layers. Thus, biomass that has been aerated is suspended inside of the bioreactor. These types of membrane bioreactors are called immersed or

with another meaning in literature internal membrane bioreactors (Figure 2.1 and Figure 2.4b). Likewise, same bioreactor configurations are used for anaerobic membrane bioreactors (AnMBR). Membranes used for water and wastewater treatment are classified as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF) according to their membrane pore diameter. Generally, UF and MF units are being chosen for MBR applications and operations [36]. Therefore, side-stream MBR configuration where membrane cassettes are outside of the bioreactor is also in use (Figure 2.3a and Figure 2.4a).

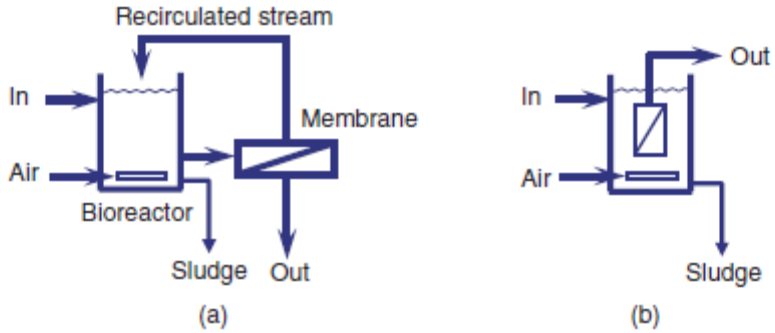
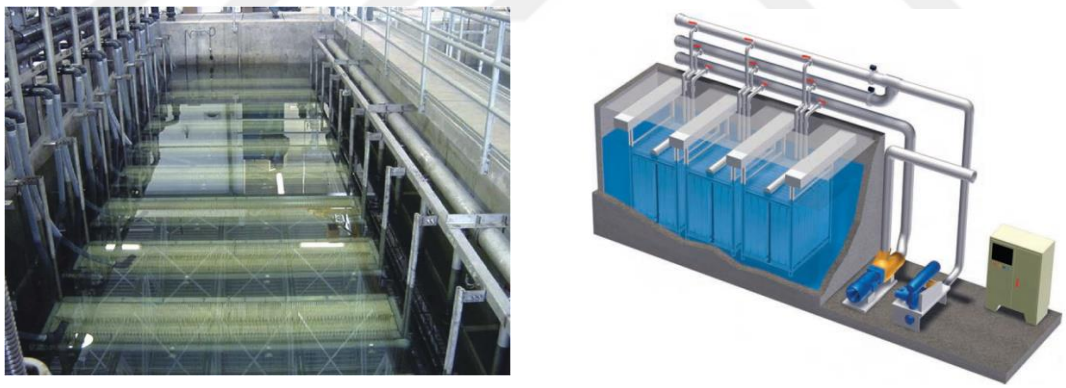


Figure 2.4 Representation of different types of membrane bioreactor configurations (a) side-stream (b) submerged [37].

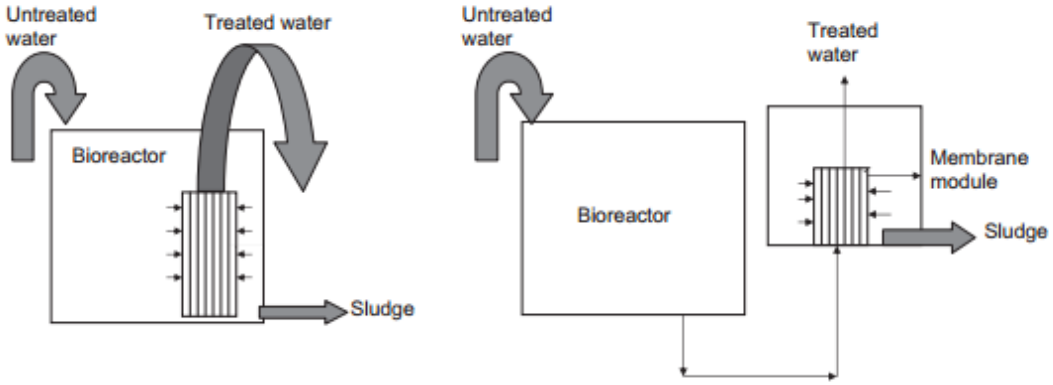


(a) (b)

Figure 2.5 Photographic (a) and schematic (b) representation of submerged/internal MBR configuration [37].

An immersed MBR configuration is also shown in Figure 2.5. It should be known that submerged membranes can be internal or external. Briefly, the membranes can be found directly inside the aeration tank or be located in a different tank, which can result in a high pumping cost. In fact, it may be quite advantageous for AnMBR configurations which require cleaning of the membranes without having air inside of the reactor. In

addition, due to high recycle rate, better physical washing can be possible for external membranes [38].



(a) (b)

Figure 2.6 Internal immersed (a) and external immersed (b) membrane bioreactors [38].

While aeration process satisfy the ventilation need of immersed membrane bioreactors by using aerator, it also creates a shear and hinders the generation cake layer over the surface of membrane. Table 2.2 represents the advantages and disadvantages of internal and external MBR systems.

Table 2.1 Advantages and disadvantages of internal and external membrane configurations [36].

Internal MBR	External MBR
High aeration cost	Low aeration cost
Low Pumping cost	High pumping cost
Low flux	High flux (low foot print requirement)
Less cleaning needed	Cleaning needed more often.
Low operational cost	High operational cost
High initial investment cost	Low initial investment cost

2.4.2 Membranes and Separation Processes

Membranes are such materials used for treatment of water and wastewater and due to its physical structure it prevents the transportation of some molecules or particles through the pores. Membranes are called semipermeable because membrane pore diameter doesn't allow the entire micro-molecules or particles pass through, while passed constituents are named as permeate. Small molecules or particles may pass through the pores of the membrane, in proportion to it, some of large molecules, which are called retentate, are denied. The level of particularity depends mostly on the pore size diameter

of the membrane. Insoluble solid particles are retained by coarse membranes which are correlated with microfiltration (MF). Reverse osmosis (RO) membranes have the smallest pore size and can retain the passing of mono charged ions (i.e. sodium (Na^+) and chloride (Cl^-)). Atomic diameter of these ions is less than 1 nm and this can explain how reverse osmosis membranes allow the passing of very particular molecules through the surface of the membrane. Molecules that are able to pass from the membrane can be identified by using super-resolution microscopes. There are four types of membrane separation processes: reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF).

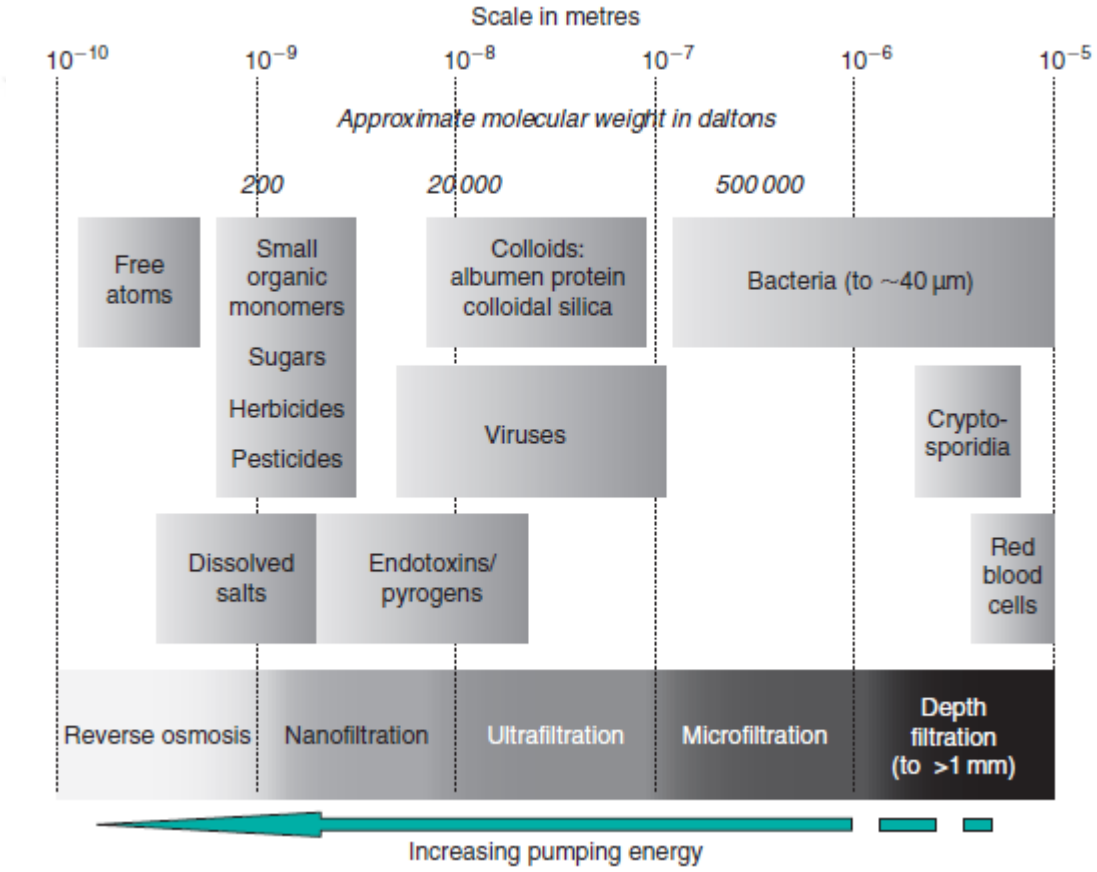


Figure 2.7 General scheme of the membrane separation process [39].

Discrimination process of the operation helps the identification of the membrane and also gives proof about the specification of the pore diameter which is in µm. Therefore, membrane can reject the smallest molecule or particle value in Dalton, while one hydrogen atom stands for 1Da. For ultrafiltration (UF) process, molecules between 2-50 nm can pass through the membrane. If a definition was to be provided for the membrane process, it would be the pressured transportation of water through the membrane.

Table 2.2 Membrane types according to their density and pores in water treatment operation [37].

Pressure Driven	Extractive/Diffusive
Reverse Osmosis (RO) Separation achieved by virtue of differing solubility and diffusion rates of water (solvent) and solutes in water	**Electrodialysis (ED)** Separation achieved by virtue of differing ionic size, charge and charge density of solute ions, using ion-exchange membranes
Nanofiltration (NF) Formerly called leaky RO. Separation achieved through combination of charge rejection, solubility-diffusion and sieving through micropores (<2nm)	**Pervaporation** Same mechanism as RO but with the (volatile) solute partially vapourised in the membrane by partially vacuumating the permeate.
Ultrafiltration (UF) Separation by sieving through mesopores (2-50 nm)*	**Membrane Extraction (ME)** Constituents removed by virtue of a concentration gradient between retentate and permeate side of membrane
Microfiltration (MF) Separation of suspended solids from water by sieving through macropores (>50) nm*	**Gas Transfer (GT)** Gas transferred under a partial pressure gradient into or out of water in molecular form

IUPAC 1985*

Table 1.3 shows the convenient membrane processes. Some of the membrane operations only include pressure-driven procedures and some of them only electrodialysis which is as known as ED and can subtract the ions which cause trouble like nitrogen (N) and other ions that have an interrelation with toughness/saltiness. Municipal field membrane operation is an intensely pressure-driven process. While semipermeable property of the membrane and separation methods can diversify, some of the processes can have mutual results like treated permeate and dense retentate at the end of the operation.

During the process, substances which couldn't get through the membrane and stays on the membrane surface cause a wane called reduction of the flux at a afixed trans-membrane pressure (TMP). On the contrary, a process can go on with an increase in the TMP at a constant flux. That cause considerable decrease in permeability which is critical and consist of the proportion of the flux to trans-membrane pressure. These situations are caused by membrane fouling which is the main restrain in membrane operations. Significant amount of membrane research and development (R&D) methods are carried out for classification and improvement with regards to fouling processes.

Membrane fouling gives rise to biological/physicochemical problems that are associated with accumulation of the solid particles on the membrane and in another definition it plugs the membrane pores and hinders the flow of water, a process called pore restriction/occlusion. This situation should not be related with clogging because clogging is defined as embankment of solids into the spaces between membranes.

However, resistance changes based on the overall quantity of constituent that is in this case fouling material in the reactor. It is dependent to amount of the ingredient and the flow of the mixture over the surface of the membrane and transition of constituents through the pores. Operation performance is affected majorly by the feed water composition and treatment process conditions.

2.4.3 Membrane Materials

Polymeric and ceramic membranes consist of the main types of membrane materials in use. Even though, there are metallic membranes, they are used for different implementations and it is not related with membrane bioreactor technology. A convenient membrane material must be produced/regulated according to the property of appropriate water flux principle. Membrane formation is provided by utilization of different kinds of polymeric and ceramic substances but almost every membrane surface is formed as a thin layer that ensures essential semi-permeability above of much thicker porous sustenance that procures mechanical permanence.

Figure 2.8 represents the anisotropic polymeric and ceramic classic membranes. While polymeric membrane cross-section includes specific geometry that sections reaches out perpendicular to the surface of the membrane, sections of ceramic membrane is contrarily dissipated.

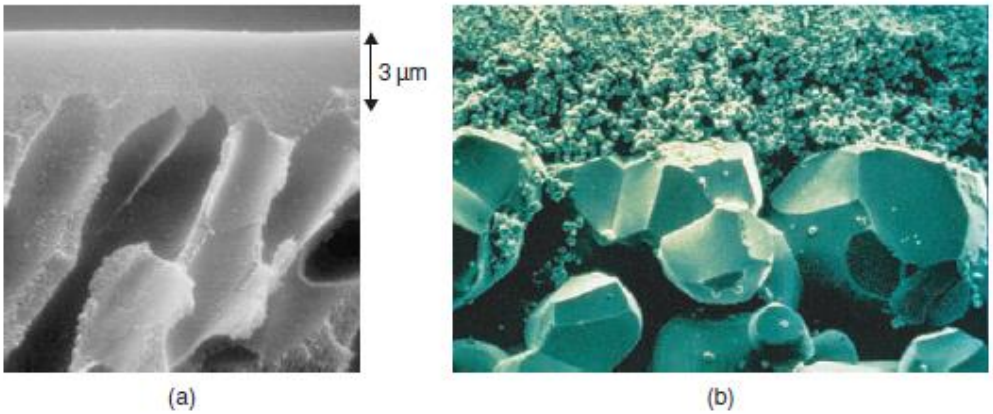


Figure 2.8 Polymeric (a) and ceramic (b) anisotropic ultrafiltration (UF) membranes [37].

It is taken into consideration that polymeric membranes are manufactured in terms of eminent porousness or high sectional area and narrow pore size dispersion of the surface of the membrane for better operational performance (Figure 2.9). On the other hand, mechanical durableness is a must-have property for a membrane.

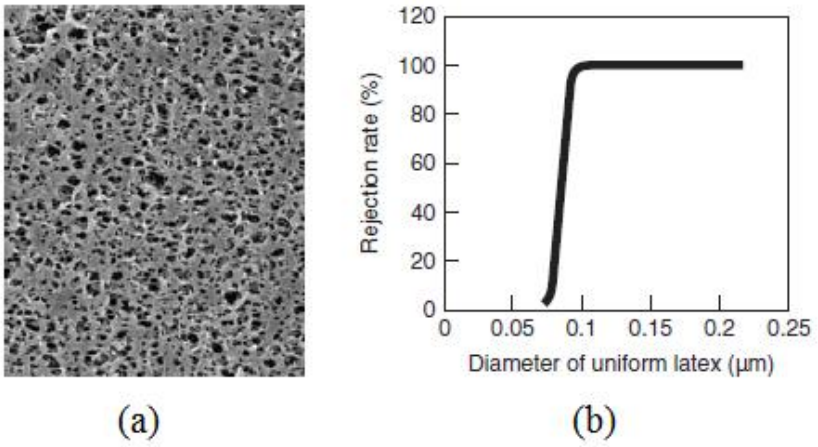


Figure 2.9 Surface of the membrane latex (a) and pore size dispersion with regarding to denial of homodispersed latex [37].

Aforementioned membrane material should have intermediate durability to the warmth and chemicals, during the operational stages, which includes high level of temperature, pH change and concentration related with oxygen. When the membrane is cleaned by using chemicals, properties mentioned above is triggered and augmentation at these values is possibly seen. This should also be a blockage brings resistance to membrane fouling. It should be known that, as a matter of principle, any kind of polymeric substance can be constituted as a membrane layer but not every single material can be

chosen as a convenient candidate membrane. Major mutual polymeric membrane types are as following;

1. polyvinylidene difluoride (PVDF)
2. polyethylsulphone (PES)
3. polyethylene (PE)
4. polypropylene (PP)

By using particular production methods, polymers mentioned above can be produced as a membrane material that we would like to modify with a property intended and every single one have modest characteristic chemical durability. On the other hand, mentioned polymers have hydrophobic property that makes them quite convenient for the applications to reduce the rate of fouling during the filtration process. This process usually requires modification for the surface of the membrane. Providing hydrophobicity depends on chemical methods like; chemical oxidation, organic chemical reaction, plasma treatment or grafting. The most common material for the membrane manufacturing is PVDF and it is usually used for various bioreactors as a membrane.

There are different types of materials, over 130 types, in use for the selection of the membranes but due to the congruity only a few membrane types are widely used and it is known that there are several limitations that diminish the number of materials in use. Through five years of operational experiences, membranes should have high acidic, basic, chemical and mechanical endurance properties and they should perform in the range of pH 4-10. Still membranes are subjected to 1-12 pH during the membrane reuse cleaning and there are unknown toxic chemicals, oxidants are also included, and membranes may be subjected to high shear forces from water and air throughout the process. In this context, resistant material selection should be made like ceramic, plastic and stainless steel to gratify the running performance. Table 2.3 represents the characteristics of polymers for membrane fabrication.

Table 2.3 Properties, advantages and disadvantages of the polymers for membrane fabrication [32].

Polymer	*Fabrication*	*Advantage*	*Disadvantage*
PSF	NIPS	• Easy to form structure • Safe from leaching • High mechanical strength	• Rigid/brittle • Low chemical durability
PES	NIPS	• Easy to form structure • Safe from leaching • High mechanical strength	• Rigid/brittle • Low chemical durability
PE	MSCS	• Low material cost • High elongation	• Wide pore size distribution
PP	MSCS	• Low material cost • High elongation	• Wide pore size distribution
PVC	MSCS	• Low material cost • High elongation	• Wide pore size distribution • Side effect by additives
PVDF	NIPS, TIPS	• Narrow pore size distribution • High chemical durability	• Not easy to form structure • Weak to basic condition
PTFE	MSCS	• High water permeability • Highest chemical durability • Low fouling potential	• Difficult module fabrication • High material cost
CA	NIPS	• Hydrophilic (easily wet) • Easy to from structure	• Low acid/base durability • Low chemical durability

2.4.4 Configurations of Membranes

Configuration of the membrane is one the most essential part in wastewater treatment process, due to the stream of water that can be directly affected from the geometrical shape of the membrane system and also the way of it is application and orientation [37]. There are also different kinds of considerations about the membrane elements, which are about being particularly separated membrane units and organization of the membranes into modules and the formation of cassettes.

As a basis, membranes should have high surface area to process high amounts of water and high level of stream for the mass transfer boost. However, low cost for each unit membrane area, low energy consumption, easy cleaning and convenience for the modularization should be the ideal aim for potential configurations.

If membrane cost is the matter of issue, modularization ensures a little economic contribution, while the cost depends on the membrane surface area which straightly affects the flux. Enhancement of turbulence inside of the reactor cause raise of energy and it should be known that mechanical cleaning, which is cost saving and also known as physical cleaning, is just possible on relatively low area (A):volume (V) unit. Some of module configurations raise the overall expenditure for each membrane unit area but it is indispensable.

However, there are two types of membrane bioreactor configuration that are being commonly operated with pressure and filtration for side-stream MBRs or vacuum-driven membranes submerged in the reactor. The most frequent MBR configuration is the one membrane integrated cassettes are right inside of the bioreactor called submerged but pumping the wastewater to membrane integrated cassettes and make it retrace to the bioreactor configuration is also possible.

Required energy for the filtration of submerged MBRs is visibly lower than the side-stream MBR configuration (Table 1). Both membrane configurations come across with fouling problem which blocks the surface of the membranes and prevents the flow of constituents of mixed liquor. While fouling is preserved by pumping for side-stream MBRs, aeration also plays essential role for the interruption of the fouling for submerged MBRs.

Conservation of the membranes is delicate matter for the fouling that causes serious blockage of the pores and hinders the flow of the liquid inside of the reactor but it should be known that, prevention from the fouling requires energy and this may be the reason why submerged MBR configuration have actually strong influence. Likewise, fouling in side-stream MBR configurations is quite apparent, because of high liquid flow penetration. When the sludge inside of the reactor is pumped or stirred, it causes protection of the membrane to bacterial flocs which reduces the foulant material transition and also the amount of small particle drift autonomously [33].

Table 2.4 Comparison of the side-stream tubular and submerged MBRs' membrane filtration condition [37].

	Side stream tubular membrane	Submerged membrane
Manufacturer	Zenon	Zenon
Model	Permaflow Z-8	ZeeWeed ZW-500
Surface area [m^2]	2	46
Permeate flux [L m^{-2} h^{-1}]	50-100	20-50
Pressure [bar]	4	0,2-0,5
Air flow rate [m^3 h^{-1}]	-	40
Energy for filtration [kWh m^{-3}]	4-12	0,3-0,6

For this reason, membrane fouling more often comes off and occurrence rate of fouling critically increases. Table 2.4 represents the filtration conditions of the both MRBs configurations. The forms of MBR are founded on planar or cylindrical structure. Currently, there are 6 major membrane configurations used in practice and only the first three configurations suit to the MBR technologies [32]:

1. Plate-and-frame/flat sheet (FS)
2. Hollow fiber (HF)
3. (multi) tubular (MT)
4. Capillary tube (CT)
5. Plated filter cartridge (FC)
6. Spiral-wound (SW)

Plate-and-frame configuration consists of flat sheet (FS) membrane module. They can be with support material, separator or both. Every single sheet piece is interlocked to the plate and process works by using vacuum. The water flows through the membrane and filtrated water is transported by pipes and gathered [40].

In hollow fiber (HF) configuration, major number of hollow fiber (HF) membranes create a sheaf and closely knocked together. Therefore, edges of the fibers are adhered to each other. Membranes, which can also work under pressure and vacuum, allows the flow of water from inside to outside and also outside to inside and they are produced by the way of how manufacturers desire.

For nanofiltration (NF) and reverse osmosis (RO), mostly spiral-wound configuration is chosen. It is easier to install and membrane production costs less. Systematically, membranes are wrapped around throughout the wimbled tube that discharges permeate

out and they can be installed together correspondingly or serially. Therefore, production of the spiral-wound module is standard and not variant.

Generally, tubular or multi tubular membranes are covered up in pressurized pipes and mixed constituents (sludge, water, bacteria) are pumped to them. Side-stream MBR configuration is a convenient setup to use it. Hollow fiber (HF) and flat sheet (FS) configurations are submerged right inside of the reactor and processed flux is carried by vacuum pumps. Membranes can come across stringy substances during the process and it significantly increases the rate of cleaning surface of the membranes.

Employment of 0.8 μm to 1.5 μm pore sized membranes provides better performance and it is also advised for the protection of the membrane dirtiness. Generally, 2-3 μm pore sized membranes are employed for the flat sheet (FS) membrane systems. Turbulence promotion and/or membrane cleaning are indispensable parameters for a membrane module. Because turbulence promotion enhances the passing of feed and water/air mixture helps the flux of permeate.

Table 2.5 Configuration, cost, turbulence promotion, backflushable and applications of the membranes [37].

Configuration	**Cost**	**Turbulence promotion**	**Backflushable?**	**Application**
FC	Very low	Very poor	No	**DEMF, low TSS waters**
FS	High	Fair	No	**ED**, UF, RO
SW	Low	Poor	No	**RO/NF**, UF
MT	Very high	Very good	No	**CFMF/UF, high TSS waters**, NF
CT	Low	Fair	Yes	**UF**
HF	Very low	Very poor	Yes	**MF/UF**, RO

In table 2.5, different types of membranes are represented in terms of their configuration, cost, turbulence promotion, backflushable property and their applications through the operations.

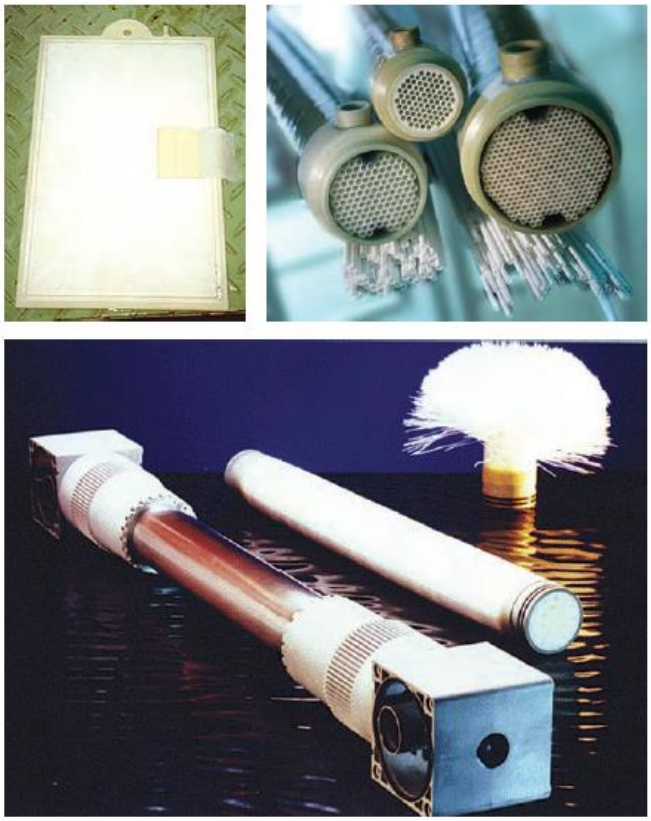


Figure 2.10 Flat sheet (FS), multi tubular (MT) and hollow fiber (HF) modules, clock-wise from the top [37].

It should be known that modules will be performed with the reactor should allow turbulence promotion and should be convenient for the physical cleaning methods. However, turbulence promotion gives rise to the passing of air/water mixture over the surface of the membrane and it also aids the passing of feedwater during the process. This operation is commonly integrated in many different processes and MBR systems.

2.4.5 Flux, Pressure, Resistance and Permeability

Essential parameters for the membrane process operation on permeate flux are resistance of the membrane, operational running force, hydrodynamic status at interface between membrane and liquid, membrane surface fouling and the cleaning later on.

Amount of water passing along the unit surface area of membrane per unit of time is simply called flux and generally unit of flux is given as L/m^2/hour (LMH). Therefore, flux has a SI unit like $m^3/m^2/s$ or basically s^{-1}, this is every so often related with permeate/filtration velocity. MBR systems are operated at the rate of 10-100 LMH flux rate and this rate is straightly related with the propulsive power. TMP is a basic example

for this power in conventional MBR systems. Flux and propulsive power terms are interrelated and hydraulic resistance property given from the membrane and interfacial area batch to it.

Propulsive power of MBRs through the operation is the TMP for conventional biomass separation (CBS). It is concentration pressure gradient for extractive MBRs and for diffusive MBRs. In conventional MBR systems, permeate is called purified product, for extractive MBRs substances that result contamination are abolished from the water over the membrane surface under the impact of density inclination and they are afterwards biologically treated material that cannot pass from the filter.

Neither water nor contaminants permeate the membrane for diffusive bioreactors. In this situation, gas is transported over the membrane and the membrane itself is used for the transportation of the gas in the reactor.

Resistance (R, 1/m) and permeability K (LMH/bar) are closely correlated. The resistance formula is;

$$R = \frac{\Delta P}{\eta J} \tag{2.1}$$

In this formula η represents the viscosity (kg/(m s2)) and ΔP, stands for pressure drop, can indicate the TMP or particular constituent that conduce to the pressure drop. Resistance includes couple of parameter like membrane resistance, fouling layer resistance and membrane: solution interfacial region resistance.

Permeability is;

$$K = \frac{J}{TMP} \tag{2.2}$$

In classical operation, membrane itself and substances cause fouling which in turn reduces the permeability of the water. Thus, total resistance is divided into two subcategories as: membrane resistance and resistance of foulant. These equations are derived from the well know Darcy Law [41] which is;

$$R_t = Rm + Rf = TMP/\eta J \tag{2.3}$$

In this situation, R_t is the total resistance, R_m is the membrane resistance and R_f is the resistance of the foulant. However, membrane durability is sustained by the membrane material itself and also durability property is supported by pore size, surface porosity (surface percentage which is covered by the pores) and membrane transverse density.

Fouling layer resistance is involved in filtration procedure that will later on be related with the membrane and property of the solids which will be retained on the surface of the membrane. Steadiness of interfacial region between membrane and solution is related with the concentration polarization (CP), such as performing RO method for more sensitive semipermeable operations, and it generates osmotic pressure regarding the solution at the surface of the membrane. Osmotic pressure on the membrane surface area is higher than the pressure into the bulk solution.

Factors that cause membrane fouling can be divided into different subcategories. Cake layer on the membrane causes loose surface contamination which can be easily removed by physical cleaning methods. This type of fouling is called removable fouling, controversially, fouling at the pores which can be cleaned by using specific chemicals is named irremovable fouling which are going to be mentioned afterwards. Besides of all, if the membrane pores are plugged and it is not possible to clean in any way mentioned above, it is called permanent membrane fouling which results with the replacement of the membrane with a new one. In terms of these subcategories of the fouling circumstances, the formula of the foulant resistance that is the total resistance of all can be defined as [42];

$$Rf = Rc + Ri + Rp \tag{2.4}$$

In this context, 'Rf' is the resistance of the foulant which cause the main fouling problem, 'R_c' is the resistance of the cake layer, 'R_i' is irremovable resistance and R_p is the permanent resistance.

2.4.6 Dead-end and Crossflow Operation

Classical way of pressure-driven filtration operations over the surface of the membrane processes can be performed by using two types of modules. If non-filterable part's flow doesn't exist, the following procedure is called dead-end or with another definition in the literature full-flow. In fact, if non-filterable part nonstop runs-off through the process then the operation is called crossflow (Figure 2.11).

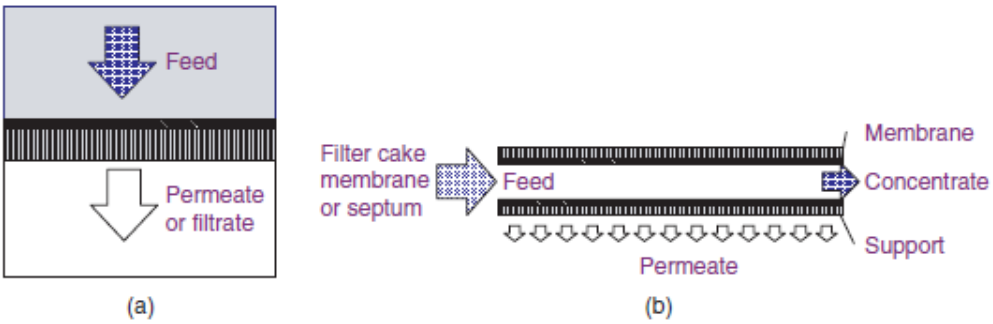


Figure 2.11 Dead-end (a) and crossflow (b) operations [37].

Crossflow operation indicates that, one-off transition of feed over the surface of the membrane, only fraction is transformed into non-filterable constituent. This transformation operation is named as 'conversion/recovery'. The recovery is usually reduced when membrane is tried to clean and the non-filterable product delays or decelerates the operation sturdy.

Filtration process normally causes to the opposition to the run-off. If the matter of issue is dead-end filtration, steadiness increases regarding to the denseness of the cake layer on the membrane which is about proportional in terms of the total volume of filtrated substances. Swift permeability reduction affects the concentration/density of the solid proportion and flux, and requires cyclical cleaning (Figure 2.12).

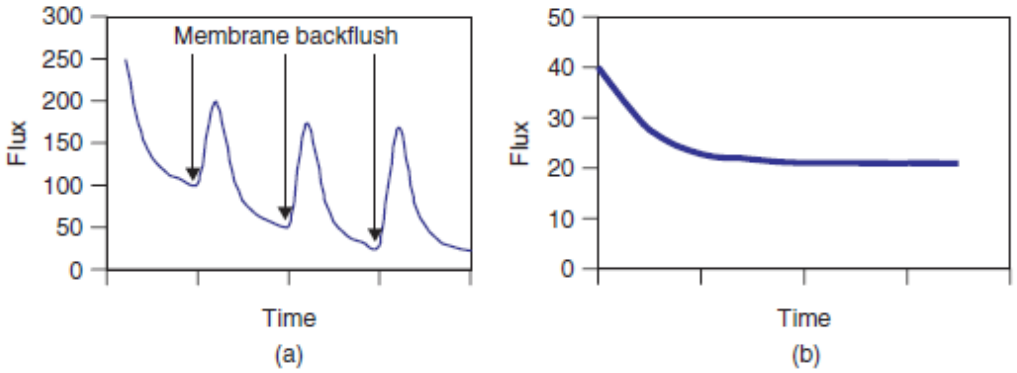


Figure 2.12 Flux transition for Dead-end (a) and crossflow (b) filtration processes for operations that are performed at constant pressure [37].

In the case of crossflow operations, sludge goes on until agglutinant forces connecting the cake layer to the membrane are compensated by the scour force of the liquid or air/liquid mixture passing through, over the surface of the membrane.

In the field of application, just stabilized situations are sustained to provide the inevitable accumulation. With the help of mostly used and known mechanisms that leans on to the former studies, filtration processes encapsulate:

1. complete blocking
2. standard blocking
3. intermediate blocking
4. cake filtration

Figure 2.13 represents the fouling mechanisms of complete blocking, standard blocking, intermediate blocking and cake filtration. Models mentioned above indicate an dependence of flux reduction on the proportion of particle size to the caliber of the pore. Throughout the colloidal particles filtration [43], standard blocking and cake filtration representations seem the most appropriate methods for the operation (including proteisn). [44]. Filtration models are endured to the empirically sprouted up knowledge and some of them have been chosen to include in the scope of other essential predictive factors

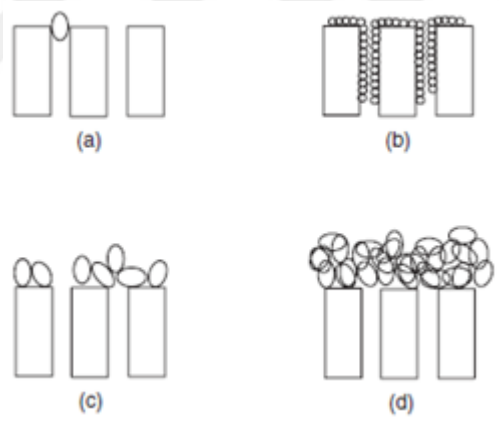


Figure 2.13 Complete blocking (a), standard blocking (b), intermediate blocking (c) and cake filtration (d) [37].

Besides that, different kinds of approaches for matrices and applications or both have been examined from several empirical and heuristic expressions. If there is a chance to calculate the undeposited solute constituent, traditional dead-end filtration representation can be transcribed for the crossflow operation.

2.5 Dynamic Membrane

In biological treatment and its substantial application processes and operations which involve solid-fluid separation, membranes and membrane support materials have been used through many years. It's obvious that MBR treatment operations increasingly catch the attention due to its low footprint, high permeate quality primarily [37]. However, dynamic membrane biological reactor (or bioreactor), called DMBR, could be another promising approach for treatment operations. Dynamic membrane (DM) is generated on support material, such as; membrane, mesh etc., in the case of filtration process of the mixed liquor, which comprises suspended solids (SS) or microbial cell cultures.

Throughout the process, organic constituents and colloidal granules are attached to the surface of the membrane. Therefore, captured constituents cause fouling phenomena [17][45][46]. Generation of the cake layer through superficial area of membrane has chance to deny constituents succumbed to the suction force. Cleaning methods such as air backwash, water backwash, or scrubbing can be sufficient for the cleaning process of DM without employing chemical constituents [25].

Therefore, on the basis of support material, cleaning operation of the cake layer from the support material may result to transient loss of permeate quality. Since solid particles are denied by secondary membrane, which has chance to reform as a SFDM (self-forming dynamic membrane) in situ experimental studies, membrane itself might not be required any more. Rehearsed operations of DM generation and elimination might diminish membrane permeability which has been seen as an example in the experiment [26].

Different types of cost-effective supplies, mesh or non-woven fabric for instance, have chance to be employed as a support layer in the place of MF or UF membranes for forming dynamic layer [16][27]. Replacing the conventional membranes by cost-saving support materials possibly tenders effective flux ratios at lower TMP [11][19]. Many of DM experiments were carried out by proceeding of physical infiltration experiments to MBR practices.

2.5.1 Brief History of Dynamic Membrane

First experimental trial has been tried to advance in 1966 by employing zirconium oxychloride for detention of salt molecules in RO operation [47]. Later on, there has been different types of studies made for the rejection of the salt molecules throughout the filtration process by using RO [48][49]. However, UF operations have got off the ground in 1980s. The main objective of those researches was throwing a light to the wastewater treatment process, dye operation and protein removal [50]. Therefore, UF membranes have been tested by some research specialists in food industry [51]. Eventhough, UF operations provide high retention capability, high investment and configuration cost of support material and low permeability sufficiency hindered further implementations of DM operations on a sheer scale. Wastewater treatment operation by using MF processes has been used since 1990s but first aerobic wastewater treatment operation has been done at the middle of 1990s. In most of the experiments through that time period, significant amount of COD, BOD and SS has been eliminated regarding upon the UF and MF operations. [11][14] Nonetheless, infiltration process with employing DM has been noted as encouraging method, particularly for small WWT systems, which request minimum capital outlay and operating cost. Since 2007, different types of experiments have been made to proceed the operations at the ideal phase relying upon DM approaches [28][52].

2.5.2 Dynamic Membrane Theme

Dissimilarly well-liked sense, pore size isn't an essential parameter influencing permeate composition in micro filtration and ultrafiltration with probable exemption with very firm membranes, for instance molecular weight cut-off, which is also called as MWCO, should be less than 100 kDa. When microfiltration and ultrafiltration membrane types with several pore diameters were collated in aerobic digester liquid feed location filtration, there was no distinguishable variation in permeate standard [53]. Congener investigation was preceded in viral expurgation from the effluent [54].

This situation is due to the cake layer emerged at the start of the filtration cycle behaves as a novice membrane surface of which efficient pore diameter is enacted by the colloidal particles in feed water. Thenceforward small colloidal particles in feed water focuses on only the cake formation, leading filtration in efficient way for quality of permeate. Composed cake layer on the surface of membrane (DM) it can be eliminated

through physical operation. Technically, it refuses most of the colloidal particles for instance; single-celled bacterium and virus but it might not properly refuse comparatively little macromolecules

One of the most important deductions of dynamic membrane formation is the characteristic of the feed matrix supplied and correspondingly the problem caused fouling due to that feed matrix. This congestion can be eliminated at a lower feed concentration and by pre-treatment feed matrix. If the formation of cake layer is on membran surface through the specification, colloidal particles smaller than membrane pore can be refused by the cake formation. In this context, pore diameter can be negligible.

Figure 2.14 represents the impact of dynamic layer generation on the permeate composition. The research includes 0.45 µm flat sheet type submerged membrane, manufactured by Yuasa, were utilized to filter 1 g/L very small constituents of 0.05 µm. At first, turbidity value of permeate was calculated at about 100 NTU, yet it increasingly reduced to below 10 through 6 hr. In the meantime, trans-membrane pressure increment from 5 kPa to 55 kPa at constant flux of 25 LMH has been noticed. Results that are obtained from this experiment represents that the cake layer composed on the surface of membrane provides opportunity to the membrane with 0.45 µm sized pores to deny 0.05 µm small particles at the diminution of high filtration stress/compression.

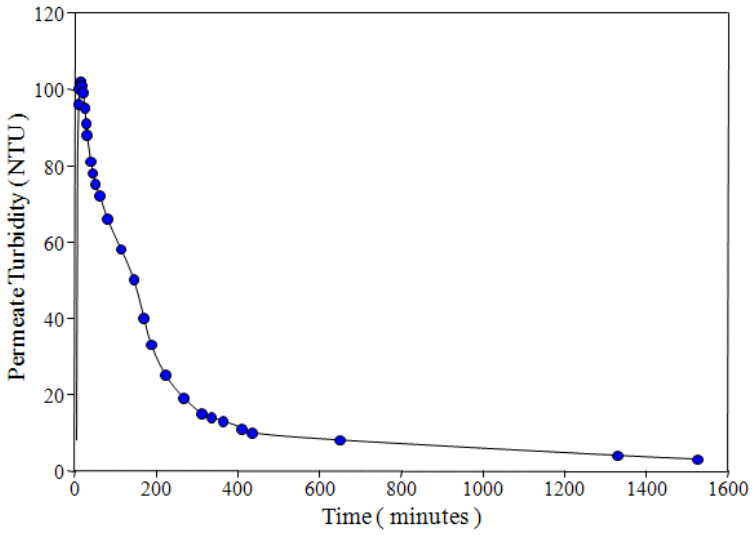


Figure 2.14 Permeate turbidity regarding to time through filtration of 0.05 µm small silica substances by using flat sheet submerged membrane with 0.45 µm pores (Yoon, 2002).

One of the significant property of the dynamic membrane is that it can induce the rate of membrane fouling by creating a cake layer directly on the membrane surface area with relatively eminent permeableness at initial filtration turn that not just hinders the small colloidal particles transition through over membrane surface, but also makes the cleaning process of the membrane convenient and simple. When bovine serum albumin, which is also called in literature as BSA, filtered in the existence of yeast cell culture by using microfiltration membrane exposed cross-flow process, originally constituted yeast cell layer not just induced flux reject but also provided a convenient approach to the membrane cleaning process, which became easier [55]. Flux boosting impact was discovered when BSA had been filtered by the pre-coated yeast cell membranes [56].

When water containing small particles is exposed under filtration process by application of ceramic membranes in cross-flow operation condition, upper flux rate can be get at nominal cross-flow pace in some circumstances. Description represents proportionally big particles that constitute a cake layer at a reduced flow circumstance and subsequent membrane fouling is induced by the formation of the cake layer [57].

Under high flow-off circumstance, in comparison, proportionally little particles are predominantly existing in the cake layer since bigger colloidal particles are scoured. In this way, the opposition of the cake layer is able to be higher at the supernal flow circumstance even though the cake layer is slim. Congener investigation had been done when a mixture of two diverse colloidal particles were filtered, where actually flux was higher with reduced cross-flow pace [58]. Therefore, inferences made according to these investigations where primarily constituted cake layer intervention formed due to the accumulation. Predominantly, higher cross-flow paces end up with superior flux in many conditions.

Circumstance which don't include cake/gel layer, superior particle density close to the membrane surface can give reason to the high colloidal particle deprivation through membrane because of the superior chance of colloidal particle transition through the membrane surface. Specific type of bacteriophage *Qβ,* has been suspended in the pure water, filtered by a 0.1 μm membrane that is consisted of ceramic, retention proficiency raised with enhanced cross-flow pace as represented in 2.15 [59]. It was ascribed to the poor colloidal particle concentration in the polarization density layer at rich crossflow pace on the surface layer of the membrane. It should be accentuated that this situation can be seldomly seen in applicable operations.

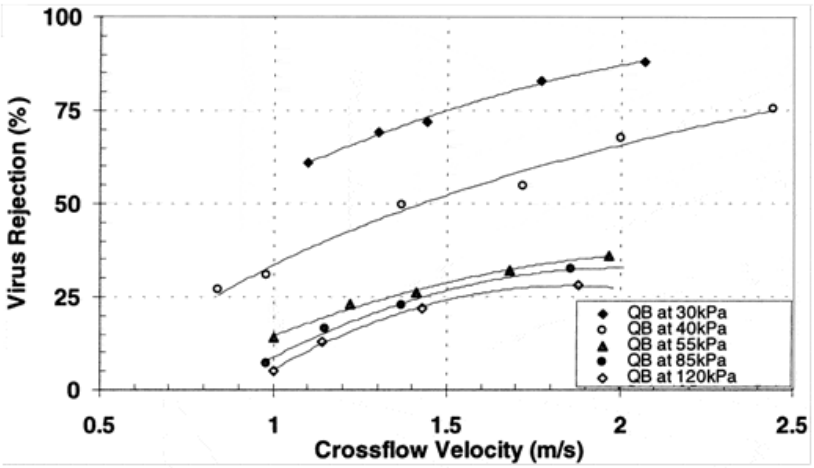


Figure 2.15 Bacteriophage Qβ rejection as a function of crossflow velocity at constant flux levels (Urase, 1993).

2.5.2 Dynamic Membrane Forming Materials

Self-forming and pre-coated dynamic membranes can consist of the main category of dynamic membranes (DMs). Self-forming dynamic membranes (SFDM) are formed by permeate flux through the membrane and constituents of mixed liquor creates a layer during the process, i.e. suspended solids (SS) in wastewaters. However, pre-coated dynamic membranes (PDM) or also named formed-in-place (FIP) are consisted of the transition of the mixture or liquor, which includes one or more colloidal substances, through the porous material [60][61]. During the process, while soluble substances inside of the mixture can pass through the pores, the other insoluble materials stays at the surface of the porous material. Due to the need of external material, SFDM has a kind of handicap.

On the other hand, single additive and composite (bi-layer) membranes are the subgroup of the pre-coated membranes (PCM). In solitary stride, single additive membranes can be generated by using single material. In 2006, powdered activated carbon has been used to form single additive dynamic membrane [61]. Bi-layer membranes are formed more than one process [62]. Formed layer over the membrane turns into flocs in SFDM with the employment of aerobic membrane bioreactors and returned promotive outcomes [17][19]. At the same time, pre-coated dynamic membrane configuration has been employed to form layer in aerobic DMBRs. Some of the substances, which are PAC [61], kaolinite [63] and bio-diatomite [25], have been used to create pre-coated membranes. Although self-forming dynamic membrane procedure has been used for anaerobic implementation [28], polytetrafluoroethylene has been used for the surface

change-over. It is also known that in physical dynamic filtration, zirconium oxide (ZrO_2) is thriving widespread chemical to create dynamic membrane layers [64][65].

To obtain better filtration results and enhance the filtration characteristics of dynamic layers, zirconium oxide (ZrO_2) has been modified with specific polymer, poly acrylic acid (PAA), and performed through the process [66]. There are also different kinds of materials utilized to generate dynamic membranes such as; Manganese oxide [60], Titanium dioxide [67], Magnesium hydroxide [68], gelatin [69], ovalbumin [70], kaolin [71], kaolin/manganese oxide bi-layer [72], polyvinyl alcohol [73], dextran [74] and non-coagulating and hydrophlized coagulating polymers [75].

2.5.3 Dynamic Membrane Support Materials

As a dynamic membrane, different kinds of membrane materials have been chosen through the researches; particularly selection process has been carefully and sizably made but the support material of interest has been mostly mesh, woven and non-woven fabrics. Different kinds of mesh fragments can be found because the main material inside of the mesh can be fiber, metal or other non-rigid/tensile substances. The physical structure of the mesh may be disadvantageous for the MBRs, in terms of inadequate amount of sludge accumulation [17].

However, a woven fabric can be generated from single type of string called monofilament, which has glabrous surface, and it can also be generated from multiple strings called multifilament which are consisted of several monofilament strings spun together and exist as one individual yarn. A non-woven fabric can be human-made or natural and also it can be in sheet form or in web form. Paper is omitted because it cannot be produced as a spun or string [76]. It is known that non-woven strings are quite slim, and accumulation of the sludge can be seen at the pores and also in the midst of string matrix. Due to its matrix structure, the sludge cannot be easily fended off, which is a kind of difficulty, in long run processes [17]. Different kinds of materials such as; ceramic membranes [63], woven fabrics [19], meshes [15][52] and non-woven fabrics [10][11] have been stated for an/aerobic DMBRs and liquid-solid dispersement.

When the physical integrations of the DMs examined, it will be seen that they have greatly comprised as of in/organic support materials like; stainless steel tube [77], MF membrane [51][73][78], RO membrane [79][84], ceramic tube [65][72], polymeric membrane [80], UF membrane [80] [82] [83] , woven and non-woven fabrics [66][81].

In physical dynamic membrane practices, particularly the early ones, ceramic tubes and stainless steel have been more ordinarily used but the main dilemma was the cost of these materials and it was quite disadvantageous to practice. This situation let the other materials, which are cheaper like woven and non-woven fabrics, to be tested in practice.

2.6 Different Wastewater Types in MBR and DMBR System Applications

2.6.1 Different Wastewater Types in MBR Systems

Synthetic wastewater treatment in aerobic conditions has been performed as a research made by Hong *et al*. In the experiment, factors that trigger the plugging have been tried to identify to form and develop a convenient strategy. Immersed ultrafiltration and microfiltration hollow fiber membranes have been employed. As a result of the study, it is achieved that membrane plugging was critically affected by the membrane porous space, membrane configuration and trans-membrane pressure also called TMP. The result of the study illuminated that amount of 3600-8400 mg/L suspended solid didn't critically affect the value of flux. Beside of that, in the situation of discontinuous process, higher flux values would be achieved [85].

High effluent quality has been obtained on MBR systems and following studies aimed on fouling and reducing the fouling problems and finding appropriate solutions for it.

However, some of the pilot scale works directed the researches and scientists to make research on concentrated domestic wastewater [86]. In the research, reactor has been operated sequential and under discontinuous condition. Therefore, it is exposed to low speed of aeration and nitrification/denitrification processes, simultaneously. Especially, in concentrated domestic wastewaters, COD and TN/COD ratio is high and both as carbon and as nitrogen removal is important. Although, simultaneous nitrification and denitrification processes has been employed with the reduced aeration, the most important handicap of that system is membrane fouling which has been caused by the such aeration conditions.

Membrane fouling caused by soluble microbial products (SMP) is going to be mentioned in the following chapters in details. In high concentrations products expressed by bacteria cultures sticks to the surface of the membrane and forms gel-like constituent, which tends to plug the membrane pores. Moreover, soluble microbial products plug the pores of cake layer formed on the membrane surface and increase the

specific cake resistance. Thus, addition of powder active carbon and different types of coagulant substituents are employed to reduce membrane fouling for the MBR operations [87]. Yet, experiments are generally executed in laboratory and pilot scale reactors which actually limits the studies that may be operated in real scale. In the scope of a doctorate thesis made by Köseoğlu [88], plugging of the membranes in MBR systems are studied with addition of different chemical constituents. The best result had been obtained, which is around 70%, with the addition of Biofloc in terms of SMP removal. With the addition of $FeCI_3$ and PaCl which is a polymeric salt, 55% and 60% SMP removal yield has been achieved, respectively. Results have been additionally summarized in Figure 2.16

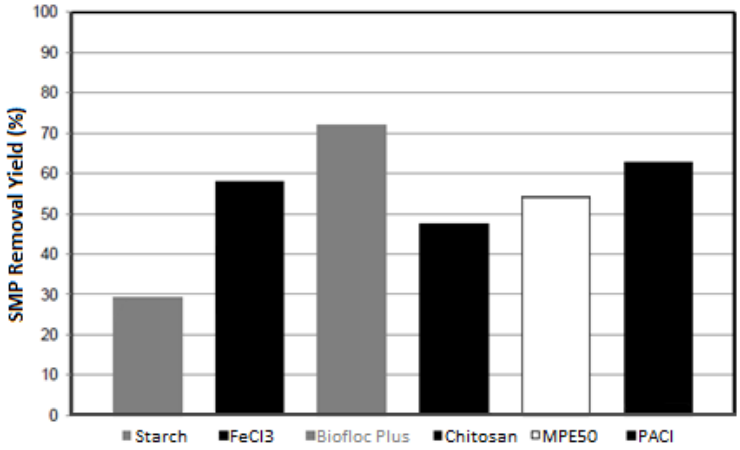


Figure 2.16 SMP removal yields in MBR systems with addition of different chemicals [88].

When the critical flux results have been examined, 50 LMH critical flux, which is quite much, obtained with the addition of MPE50. Figure 2.17 represents the 40 LMH and 35 LMH scores with the addition of Biofloc and $FeCI_3$, respectively. As a result, MPE50 and Biofloc additions were successful and $FeCI_3$ was proposed for experimental use due to its cost-effectiveness and efficiency.

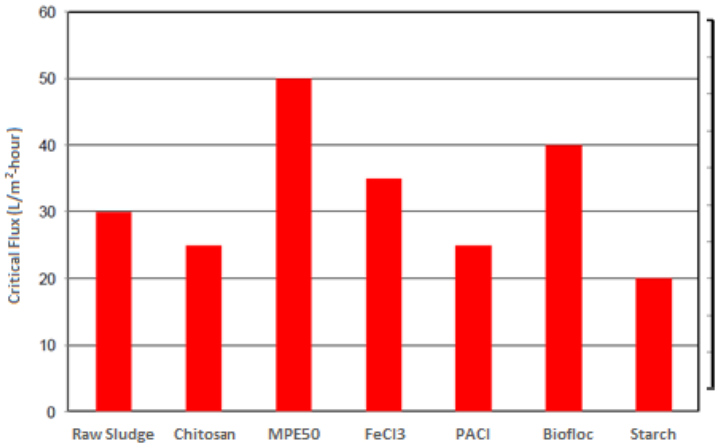


Figure 2.17 Effects of different types of chemicals on critical flux in MBR systems [88].

Anaerobic processes are not only stays at the production of methane but also effective for operational processes in terms of less energy requirement, if it is compared with aerobic operations. However, the property of less sludge production reduces the difficulties seen in sludge production. Yet, conventional anaerobic treatment technologies cannot full fill the requirements of stiff wastewater discharge standards only by itself and it is required another additional treatment technology [89].

Conventional anaerobic membrane bioreactors generally at mesophilic temperatures which is around roughly 30-35 ^{o}C are not able to give appropriate desired performance. However, wastewater temperature is generally between 15-20 ^{o}C and it is needed to heat. The gas formed after the treatment of domestic wastewater under anaerobic processes isn't sufficient for heating up processes and it barely is going to be cost-effective, if it is operated under convenient temperature.

Anaerobic baffled reactor experiment was performed for the diluted wastewater at different temperatures [90]. At 35^{o}C and 10 HRT hour operational conditions, COD removal performance was 80%. When the temperature is reduced to 20^{o}C and then 10^{o}C, COD removal performance reduced to 70% and 60%, respectively. The reason why removal performance of the process is declined is low SMP production under low temperature conditions.

Attendantly, conventional anaerobic membrane bioreactors don't give appropriate results for the domestic wastewater treatment under low temperature condition and for this reason, researches made on membrane bioreactors became much more intensive than before. Anaerobic bacteria population has low growing rate because of low amount

of energy when they are exposed under substrate. Due to that, it is required to establish a new reactor type to distinguish HRT and SRT values in each other.

In recent years, operating MBR system under low HRT and low footprint ambition gave great importance to the AnMBR applications. AnMBR operations are roughly the derivative of AeMBR systems which have significantly important disadvantages. First of all, high energy requirement and energy cost and high sludge requirement. For this reason, significance of AnMBR applications is increasing day by day. Nonetheless, AnMBR systems increase the recuperation probability of water and nutrient [91].

Because of the membranes employed in anaerobic MBRs, some of the dissolved or colloidal particles inside of the mixed liquor, just like in conventional systems, stay in the system as near as HRT and the residence time of the constituents inside of the liquor has been measured as SRT. Thereby, degradation of some dissolved colloidal or organic molecules, methane production and wastewater treatment performance is increased.

Two-phased anaerobic fluidized bed membrane bioreactor (FBR) is developed to prevent membrane plugging and to reduce the energy spent for plugging control [89]. This type of system is consisted of fluidized bed reactor which is interrelated in series and second reactor contains immersed membrane that is 1.9 mm, 0.1 nominal pore-sized hollow fiber type. In lab scale work, domestic wastewater, which passed from secondary clarifier, is used. Reactor is operated through 192 days at 6-11 $L/m^2.h$ flux and TMP value was generally at 0.1 bar. In the condition of 2.3h HRT and 25 ^oC, COD and BOD concentrations were 25 mg/L and 7 mg/L, respectively. Thereby, COD and BOD removal performance were 84% and 92%, respectively. 5% of the removed COD was transformed into biomass and biomass production value determined as 0.049 g VSS/g BOI_5. It is designated that system has required 0.047 kW hour/m^3 water and net produced electrical power has been 0.082 kW hour/m^3 water which means 33% of the energy saving.

In the study, furthermore, tests have been made on membrane plugging control and appropriate membrane flux. Without return and relaxation, providing the flux at 9 LMH $L/(m^2/h)$, TMP has increased to level of 0.1 bar. When the flux has changed to 6 LMH $L/(m^2/h)$, TMP directly reduced to 0.06 bar and after 15h relaxation flux decreased to 0.02 bar. So, it is noticed that elusion of membrane with granular activated carbon (GAC) has significant importance.

Hence, it is distinguished that elusion of the membrane with powdered activated carbon without exposing the water suction has been found important. Thereupon, flux has been moved to 9 LMH and subjected to 2 hours relaxation with precise gaps. In this case, flux has been stayed at 0.05 bar through 60 days which is called mod III. At the second phase, flux has been moved to 12 LMH to identify maximum applicable flux. So, TMP has been increased over 0.1 bar and leaped forward to 0.2 bar level. After then, in the case of water suction from membrane for 11 minutes filtration and 1 minute relaxation, TMP has been employed around 0.1 bar pressure through 23 days without changing and not exposing back washing. Lastly, flux has been moved to 13 LMH and filtration and relaxation periods set to 13 minutes and 1 minute, respectively. In this case, effective operational process has been obtained and pressure has been moved to 0.25 bar level.

In AnMBR applications, when methane and energy production were the focal point, methane at liquid phase and influent sulfate concentration is important because production of the methane is limited for the treatment of the diluted wastewater. Most of the time, liquid phase methane is equal to the half of total methane and solubility increases when the temperature reduces. Another important factor is sulfate. Reduction occurs for the sulfate inside of the water in anaerobic conditions and due to that sulfur forms. There are two essential parameters which is important for the formation of sulfur process. First of all, some of the organic material inside of the water is utilized for the reduction of sulfate. Second of all, removal of the sulfur at liquid phase (and methane as well) requires additional investment and operational cost.

Nonetheless, synthetic wastewater experiments in AnMBR systems run on in another experiment at 35^{o}C with the amount of 460 mg/L COD [92]. Gas produced through the experiment employed for the cleaning of the membranes. Since it is 3 L laboratory scale reactor, speed of the biogas employed for the physical cleaning is 5 L/minute.

In another experiment, performance of powder active carbon, which is called PAC in the literature, was searched in anaerobic MBR system [93]. Feed water, which represents average polluted industrial wastewater, includes 4 g/L COD. Even though high removal performance has been obtained for each reactor, powdered activated carbon addition enhanced the removal performance and flux. Two different powdered activated carbon concentrations which are 1.67 g/L and 3.4 g/L performed and it is noticed that concentration at 1.67 g/L represented the optimum result in terms of performance and operational cost. In high concentration, it is designated that flux has

decreased because of increased viscosity with the addition of powdered activated carbon. Removal of the COD at significant rate with the addition of PAC has also been observed. It is because of the adsorption of SMPs with the addition of PAC. It is also important to state that, SMP adsorption has reduced the TMP value. Therefore, lower TMP value has obtained at 1.67 g/L PAC included reactor. Thereby, it is emphasized that addition of PAC to anaerobic MBRs systems increase the performance and flux values.

The research showed that organic molecules inside of the reactor generally 30 kDa molecular weight and it is noticed there is no that heavy organic molecules at permeate. Thereupon, even though the membrane used is micro filtration membrane, the cake layer on the surface of the membrane forces the membrane act as a UF.

Unification with discontinuous filtration and gas washing in anaerobic MBR operations has been operated by utilization of synthetic domestic wastewater [41]. In lab scale upflow anaerobic sludge blanket (UASB), tubular membrane has been employed and reactor operated at room temperature with 8 HRT. In continuous filtration mode, filtration proceeded through 20.3 hours. Operated through 32 hr. and 52 hr. with 10 min./1 min. and 4 min./1 min. operating and relaxation process, respectively, without gas back washing. It is noticed that, when gas filtration is added, operational duration is increased 10 times more than normal. The research also indicated that, COD removal performance was around 97% [41].

In another research, lab scale immersed anaerobic MBR has been operated 106 days and removal performance of the domestic wastewater has been tested [94]. Since the capacity of the reactor was determined as 60 L, flat sheet polyvinylidene fluoride (PVDF) membranes have been employed.

Molecular weight cut-off value of the membrane employed for the operation is 140 kDa and effective filtration area is 0.6 m^2. Membrane has been operated according to filtration and relaxation procedure which is 9 min. and 1 min, respectively. Temperature inside of the reactor was kept at 30 ^oC, HRT at 10 hr. and flux at 10 LMH. Suspended solid concentration inside of the reactor has been stabilized at 6.4-9.3 g/L. In the research, duration of the start-up has just taken 12 days and during that time period, influent and permeate COD concentration has been noted as 425 mg/L and 40 mg/L, respectively. It is also emphasized that, lower COD thematic domestic wastewater

treatment systems requires short start-up period in anaerobic MBR systems. The amount of methane produced through the process is 0.24 L CH_4/g COD and it is lower than the theoretical value which is labeled in the literature as 0.382 L CH_4/g COD at 25 ^oC.

The reason is that the some of the methane gas produced has stayed at the liquid phase and a far amount of the organic material consumed for the reduction of the sulfate. The speed of gas used for the membrane washing is 5 L gas/(L reactor.hr) and maximum flux value has noted as 11 LMH. Throughout the operation, permeate average COD concentration has stayed at 51±10 mg/L (%88±2 removal). At the end of the process, investment and operational costs have been measured. In the experiment, unit investment cost has been calculated by taking into consideration of flow amount at results have been represented at Figure 2.18.

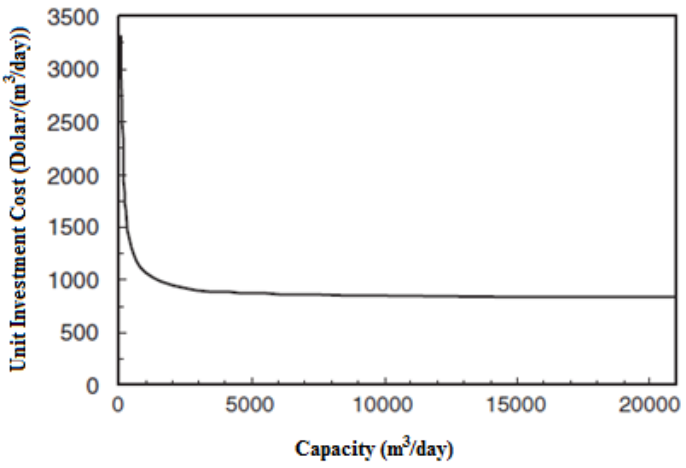


Figure 2.18 Unit investment cost for AnMBR operation changing with the flow [94].

As is seen from the figure above, the cost decreases as the flow rate increases and it remains stable at 800 Dolars/(m^3/day). This value is close to the value given in the literature for AnMBR systems.

According to the layout flow, cost of the membrane inside of the total cost has been showed at Figure 2.19.

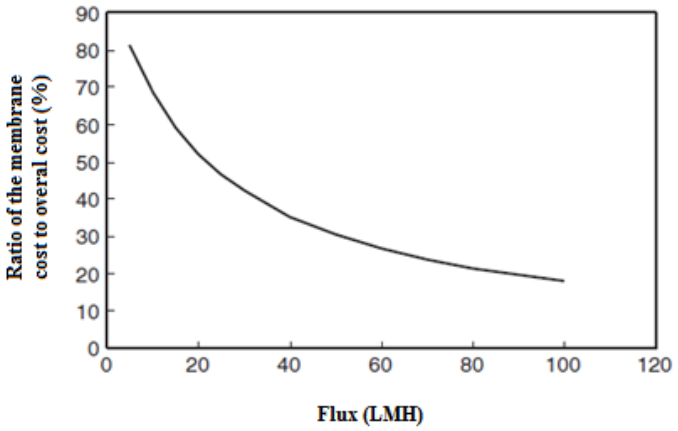


Figure 2.19 Effect of flux on the membrane cost [94].

As it can be seen from the figure, increase in the flow reducing the investment cost at considerable rate. Since, it is possible to have much more reduced flux rates in AeMBR systems, in some circumstances investment costs are considerably low regarding to anaerobic MBR operations.

In another experiment, under mesophilic and psychrophilic circumstances, anaerobic external MBR system has been operated. Bioreactor active volume is 350 L and 38 nm pore size flat-sheet membrane has been employed for the operation. Total membrane area is 3.5 m^2. Reactor has been fed with glucose and domestic wastewater mixture together and reactor performance and plugging properties has been examined at 35-20^oC. Flux has been stabilized at 7 LMH and at 35 ^oC TMP has been around 0.17 bar. When the temperature has been reduced to 20 ^oC, pressure has increased to around 0.25 bar. Besides, as the reactor temperature drops, an increase in COD in the reactor was observed, although the permeate COD value doesn't change.

Reactor influent COD value was 630 mg/L and permeates of COD and BOI_5 values were stayed at 80 mg/L and 25 mg/L throughout the operation, respectively. The results have also showed that, permeate itself could be employed for the irrigation.

In another research, paper mill wastewater has been treated by using activated sludge and correspondingly pilot MBR systems by employment of flat sheets membranes. The influent wastewater was provided from an anaerobic bioreactor which is used for the treatment purpose of paper mill wastewater [95]. The wastewater treatment plant (WWTP) contains equaling tank with the volume of 750 m^3 and the anaerobic reactor established inside of the treatment plant is an UASB with a lengthwise reactor with the volume of 1,200 m^3. Therefore, aerobic AS facility contains totally mixed aeration basin

with the volume of 8500m^3 which is equipped with aerators. Table 2.6 represents the average parameters of MBR and AS systems.

Table 2.6 Average parameters of MBR and AS systems [95].

Parameter	MBR (lab scale)	AS (full scale)
1 Flow rate, m^3/day	30	6,100
2 Volume of basins, m^3	24	8,500
3 HRT, hr	19	33
4 MLSS, gr/L	15	6
5 MLVSS, gr/L	8.7	4.1
6 DO in aeration basin, mg O_2/L	3.0	2.5
7 F/M, kg BOD_5/kg MLVSS * day	0.04	0.06
8 SOUR, mgO_2/gr MLVSS * hr	5.7	6.1
9 SRT, days	24	31

Empirical pilot scale MBR has been ordered from Kubota and it is operated correspondingly with the AS configuration which operates at full-scale. Membrane type has been chosen as flat-sheets made of poly-olefin with pore size of 0.1 to 0.4 microns, which makes the process type micro-filtration. The total amount of membrane employed for the operation is 75 with a whole surface area of 60m^2. Pilot scale reactor that has been ordered from Kubota consisted of four different chambers as; anoxic, aerobic, membrane and permeates with the volume of 5, 11, 9 and 7 m^3, respectively. Figure 2.20 represents the chambers of the reactor.

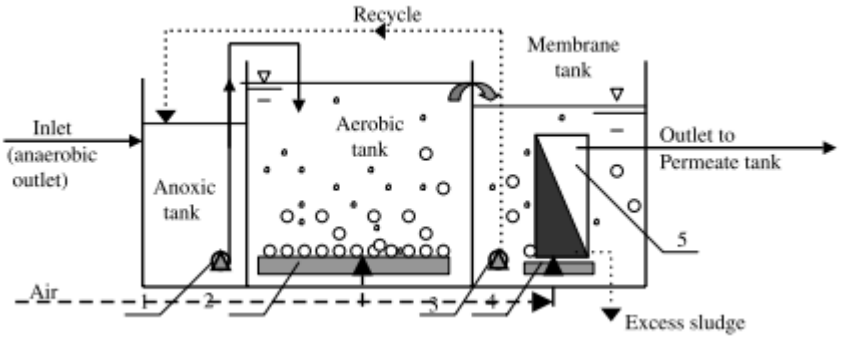


Figure 2.20 Submerged membrane bioreactor employed for the operation. (1) Submerged pump, (2) Air diffuser, (3) recycle sludge pump, (4) coarse bubble air diffuser, (5) membrane unit [95].

Nonetheless, some of the chambers, which are aerobic and membrane, were regulated with dense and rough aeration diffusers and the operational flux has been set to 20.8 L/m^2 p hr.

The research showed that, average permeates concentration of MBR and AS has been found as 105 mg/L and 102 mg/L, respectively. In a similar manner, BOD removal performances were 1-5 mg/L and 3-7 mg/L for MBR and AS, respectively. In terms of suspended solid removal performance, MBR has showed better results than AS configuration. Total suspended solid (TSS) removal for the MBR system was very close to the 100% with permeate quality values equal to or less than 1 mg/L without any alteration.

Therefore, sludge retention time of AS has been found as higher than MBR systems like 25-40 days and 24 days, respectively. The data for the residence duration provided from the average values. Organic matter removal performances of COD and BOD have been represented at Figure 2.21.

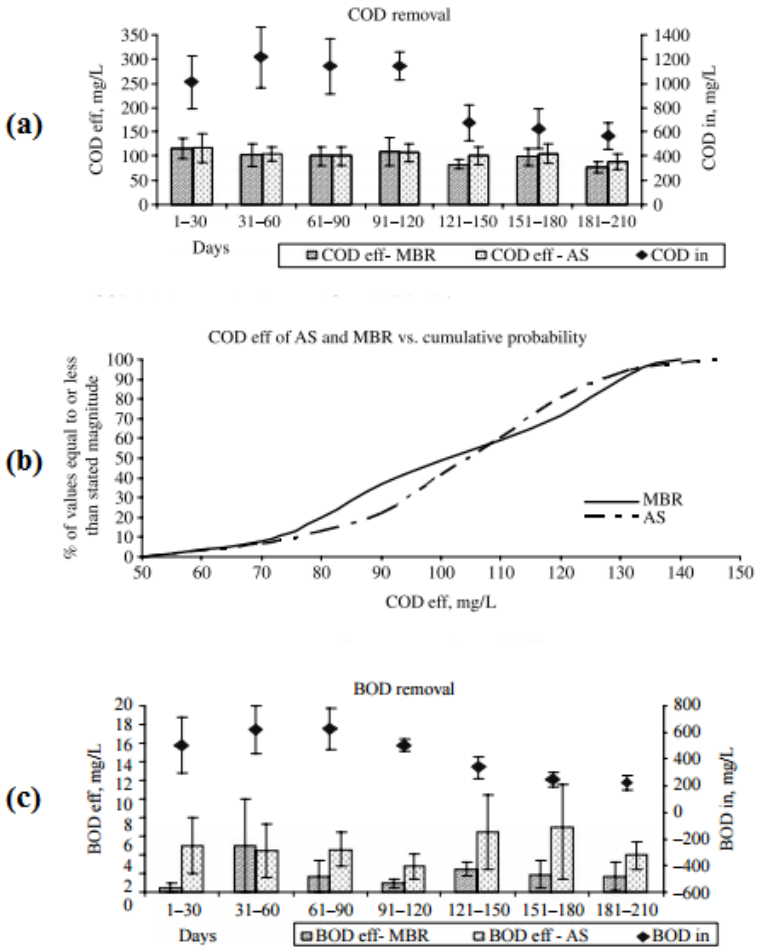


Figure 2.21 (a) COD in influent and effluent of AS and MBR pilot, (b) COD in effluent of AS and MBR pilot vs. Cumulative probability and (c) BOD in influent and effluent of AS and MBR pilot [95].

There are different wastewater types examined in MBR operations which throw light the capability of the treatment process in terms of the removal of organic soluble materials. One of the researches has been operated as multi-stage aerobic and anaerobic MBR treatment of soft drink industry wastewater (SDIW) [96]. In the study, wastewater produced through the production process of soft drink industry has been categorized as medium to eminent wastewater with contaminating constituent of vitriolic soda that comprise pH of between 6.1 – 11.8, sucrose, COD which is between 2242 and 11.717 mg/L BOD of up to 1150 mg/L.

Throughout the operation, temperature was kept between 35 – 37 °C, HRT has been between 12 – 60 hr. and upflow velocity, which is labeled in literature as V_{up}, were between 0.59 – 1.1 m/h. It is noted that COD removal performance of the operation was around 93% at HRT of 12 hr., upflow velocity of 0.85 m/h and organic loading rate of 11 COD/m^3 d. Figure 2.22 represents the multi stage aerobic and anaerobic MBR configuration for the soft drink industries wastewater treatment.

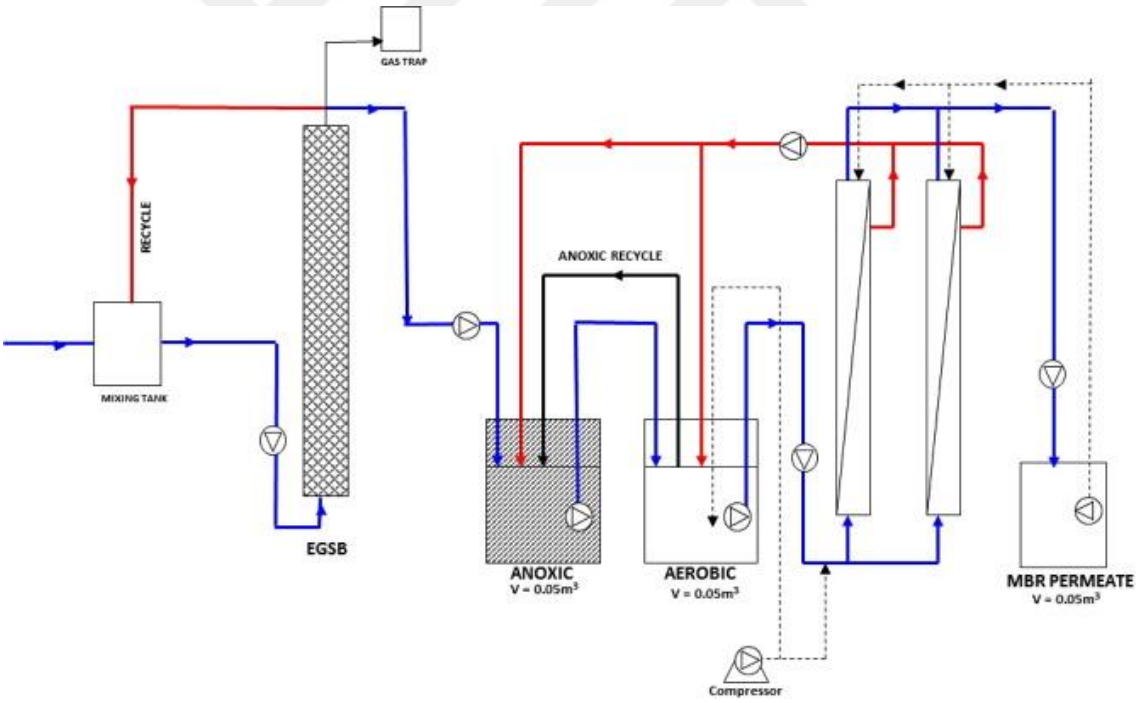


Figure 2.22 Schematic representation of the multi-stage hybrid anaerobic expanded granular sludge bed and ultrafiltration membrane bioreactor system employed in the treatment of soft drink industry wastewater treatment [96].

Therefore, anaerobic expanded granular sludge bed have played essential role for the production of the methane around 70% and nitrogen around 41%. Feed water of the bioreactor has been set to 12 – 50 L/d, dissolved oxygen (DO) value has been between 2

– 3.7 mg/L in the aerobic chamber. Through the operation HRT and membrane flux values have been 3.3 – 14 hr. and 3.4 – 17 L/m^2h, respectively.

As a result of the treatment of soft drink industry wastewater, COD removal has been around 87% at a feed flow of 34 L/d, an organic loading rate of 2.3 – 3.1 kg COD/m^3d for anoxic and aerobic chambers, respectively. HRT for both corresponding chambers has been set to 0.41 h. Nonetheless, membrane flux and TMP parameters have been adjusted to 12 – 15 L/m^2h and 60 – 100 kPa, respectively. It has been also noted in the research that the treatment able to obtain COD, TE around 95% and also COD removal in the effluent has been reduced to 253 mg/L with all the nourishments such as; NH_4^+, NO_3^- and PO_4^{3-} at macro scale and underneath the evacuate standards. It's been also indicated that the MBR system itself couldn't reduce all the nutrients which exist in the liquor at macro scale.

Another study has been put through for the consideration of the winery wastewater treatment by employment of MBR pilot scale reactor and comparison has been made with full-scale CAS system [97]. Pilot scale MBR reactor was continuously fed with real winery wastewater from the obtained from wine production procedure in in Bodegas Torres facilities (Catalonia, Spain).

However, total volumes of the bioreactor and membrane have been 11 – 17 m^3 and 3.5 m^3, respectively, and membrane surface area has been designated as 20 m^2. System has been operated discontinuous and it is performed as 9 min. of working and 1 min. relaxation. While inflow and outflow rates of the set-up have been the same 6 m^3/day, permeated flux value has been noted as 12.5 L/m^2h and recirculation flow rate (%) range has been between 100 – 400. Figure 2.23 represents the schematic view of the MBR and CAS systems.

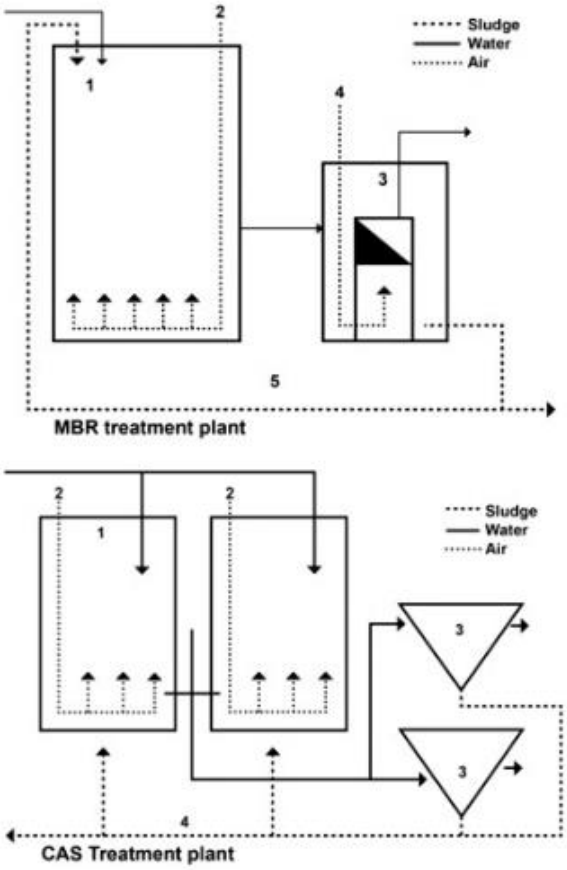


Figure 2.23 Scheme of MBR treatment plant for winery wastewater treatment. : 1. Aerobic reactor, 2. Fine bubble aeration system, 3. Membrane reactor, 4. Coarse bubble aeration system, 5. Recirculation and purge; and scheme of the CAS system: 1. Aerobic reactors, 2. Fine bubble aeration system, 3.Clarifiers, 4. Recirculation and purge [97].

Winery wastewater from Miguel Torres S.A. facilities showed very high temporal variability. COD removal was 95% and 97% for the CAS and MBR systems, respectively. MBR produced a very high quality treated wastewater in terms of COD, suspended solids and microbiological contamination. MBR treated wastewater meets the requirements for reuse in agricultural practices. Water permeability in the MBR system was correlated to the presence of EPS. After 6 months of perpetual operation duration, physical and chemical and also microbial parameters of the bioreactor have succeeded the indications identified for urban employment which plays essential role for the agricultural utilization. The MBR plant operated have represented very steady and responsive operation throughout the experiment. An important and crucial at the same time, interrelation between EPSc and permeableness affirmed the effect of the hydrophilicity on the membrane fouling potential.

In another pilot scale study, pharmaceutical wastewater treatment has been examined in Taiwan [98]. A 10 m^3/day content MBR tank includes aeration tank and membrane bioreactor have been employed to exclude organic constituents which has been examined in terms of COD and the operation has been conducted through 140 days.

Operation regulation willed to discharge COD amount under 450 mg/L for tertiary treatment plant. In this context, permitted COD amount has been determined as 50 mg/L for the treated wastewater discharge. Figure 2.24 represents the schematic representation of the system.

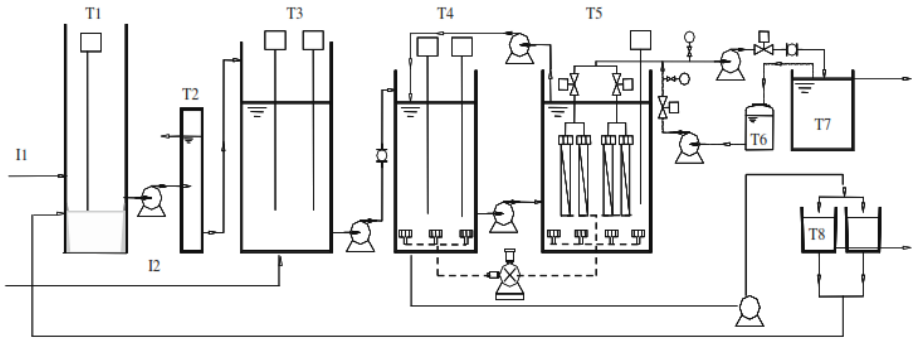


Figure 2.24 MBR configuration of the pharmaceutical wastewater treatment. I1: Representation of permeate comes from the pharmaceutical's production; I2: influent which comes from the septic tank permeate; T1: wet well; T2: separation process of the solvent–liquid; T3: equalization tank; T4: biological tank; T5: MBR; T6: backwash tank; T7: permeate tank; T8: sludge drying bed [98].

However, operation has been done by using PVDF hollow fiber membrane with 650/1000 μm internal external and diameters, respectively. Therefore, poresize of the membrane has been determined as 0.1 μm and as a specific membrane area optimized as 12.1 m^2/g. 4220 membrane fibers have been employed with the length of 90 cm for each. Operation has been determined as continuous and it was performed with 4 minutes of working and 30 seconds of relaxation.

Two membrane modules have been employed in the secondary tank to alternatingly associate with the pumping and relaxation mode operation interchange. Every single membrane operation with 12 cycles of suction and relaxation has been performed through 54 minutes of operation time and 6 minutes of backwashing by permeate. Throughout 30 days of sowing and operating, MBR mechanism was followed-up continuously for 140 days. The HRT values of the aerobic and MBR tank were adjusted to the same value which is the value of 24 h. Recirculation ratio of the mixed liquor was arranged to 500% of the mean influent flow rate.

Wastewater used for the treatment operation has been provided from real pharmaceutical manufacturing plant and permeate comes from the septic tank. The MBR plant operated discontinuously. Fluctuating wastewater flow off with the changing wastewater constituent materials hinged upon the operational production. In the regime of operation, temperature of the raw wastewater has been kept at 18.5 – 25.1 °C and the pH around 6.6 – 9.4. Therefore, the amount of the suspended solid inside of the mixed liquor, amount of the COD and BOD has been determined as 60 – 360 mg/L and 800 – 11800 mg/L and 100 – 6350 mg/L, respectively. Conductivity confirmed as 518 – 284 µs/cm.

However, specific characteristics of the MBR power plant has been determined as following, design flow is 10 m^3d^{-1}. Membrane/biological tank volume and aerobic tank/membrane tank HRT has been determined as 10 m3 and 24 h, respectively. Solid retention time specifically adjusted to >40 days and mixed liquor recycle ratio has been given as 5. Since the temperature of the reactor kept at 16 – 28 °C, food/microorganism ratio in terms of biological tank and membrane tank has been 0.014 – 0.65 and 0.003 – 0.079 kg COD kg ML VSS^{-1} d^{-1}, respectively. Therefore, volumetric loading rate of biological tank and volumetric loading rate of membrane tank determined as 0.099 – 6.844 and 0.11 – 0.408 kg COD m^{-3} day^{-1}, in turn. Membrane surface area and flux have been specified as 24 m^2 and 0.384 – 1.536 m^3 m^{-2} d^{-1}.

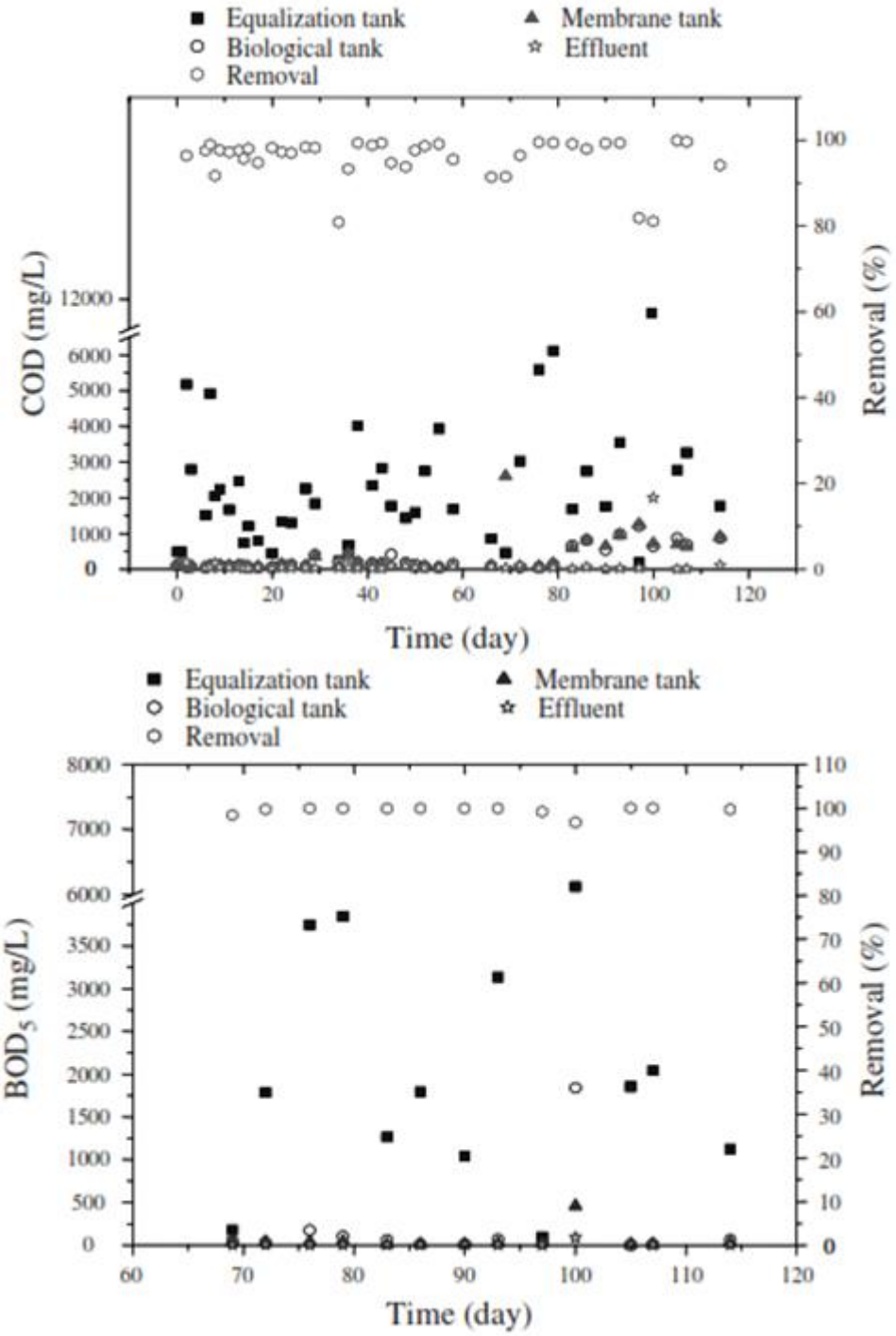


Figure 2.25 Variations and treatment performance of the COD and BOD removal operations, respectively [98].

Each sample taken from the influent and effluent tanks has been gathered two or three times per week. The analysis containing COD, BOD, MLSS, MLVSS and turbidity were analyzed in suitability with the standard methods (APHA, 1993) and the related devices using the accompanying manuals. The mixed liquor viscosity was measured by

a TVC-5 type viscometer. Figure 2.25 represents the COD and BOD removal of the operation.

Throughout the operation, analyzes made on the permeate water showed that 96% of the organic chemicals inside of the wastewater has been removed. Nonetheless, the average BOD removal rate has been noted as 99% and among of all results the best BOD removal rate has been found as 100%, which is represented in Figure 2.25.

It can be noticed from the operation that process can be continued with high biomass concentration addition for the sludge separation. MLSS concentration inside of the tank has been stabilized 6000 – 17.000 mg/L and excess sludge has been eliminated in accordance to the sludge growth rate such that the average SRT rate is maintained higher than 40. It is achieved that, this operation has represented great way to treat pharmaceutical wastewater in terms of its BOD and COD removal rates which have been 95% and 99%, respectively. Thereby, it is also noticed that MBR systems have great potential and are appropriate to treat the wastewater with stable operation standard, configuration and substantial removal performance.

In another research, high-concentration food wastewater treatment has been operated by using an AnMBR system configuration [99]. Sustainability of the processed high concentration food wastewater by an AnMBR system has been operated by employment of the PES UF membranes which can be literally names as PES200, PES300, PES500 and Pes700 with normal MWCO range between 20.000 – 70.000 Da. HRT and SRT values, that have critically affected the removal success of the AnMBR, have been kept at 60 h and 50 days in the study. The four membranes examined under similar circumstance such as; removal of suspended solids, color, COD and bacterial. However, operated system has been consisted of 13 different sections which are represented at Figure 2.26.

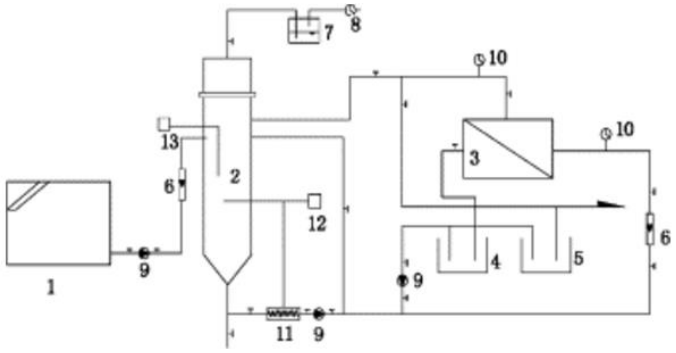


Figure 2.26 Configuration of the AnMBR for food wastewater treatment (1) Storage tank, (2) anaerobic reactor, (3) membrane module, (4) hydraulic cleaning tank, (5) chemical cleaning tank, (6) liquid flow meter, (7) water seal, (8) air flow meter, (9) pump, (10) pressure meter, (11) heating equipment, (12) temperature controller, (13) pH controller [99].

The raw wastewater has been screened to exclude SS which are larger than 1 mm and sent to the tank where wastewater stored. The total volume of the tank has been determined as 0.7 m^3 that wastewater stored and mixed to homogenize the constituents. Afterwards, wastewater has been pumped inside of the aerobic reactor, an air-proof cylindrical shaped reactor with the total volume of 0.5 m^3 and working volume of 0.4 m^3. Nonetheless, pH has been stabilized at 7±0.2 with the help of automatic pH controller. Temperature has been kept at 37.0±0.5 °C with the benefits of automatic heat and temperature controller and gas production operation and measurement has been conducted with a gas flow meter.

A flat-sheet membrane module, which has 0.32 m^2 area, has been employed for the separation process. Operation has done with 8 channels which are parallel to each other and set up with the dimensions of 300 mm×68 mm×0.7 mm for channel length, width and height respectively, and each individual channel could be controlled and monitored. Configuration of the system has made the sample taking operation easier. The rate of the flow-off has been noted as between 1.4 – 1.5 m^3/h resulting in a cross-flow speed of 1.02 – 1.09 m/s and a number of Reynolds of 1300. It has been identified that power of the pump that provides pressure for the operation has been 0.75 kW and the applied pressure has been 0.2 MPa. Besides, all membranes have been run under same operation conditions for instance; temperature, feed liquid, cleaning, cross-flow velocity and pressure. The sludge that stayed at the surface of the membrane has been reused in the anaerobic system.

Flat sheet membrane module has been washed every day 30 minutes by reusing the membrane effluent at a running pressure of 0.14 MPa. The module has been chemically clarified by recycling 0.5% NaOH solution for every 10 days for 1-hour operation. It has been noticed from the experiment that when the volumetric loading rate has been under 4.5 kg/m^3d, removal performance of the COD founded between 81 – 94% and the gas production fixed at 0.136 m^3/kg COD. Throughout the assessment process, effects of MWCO, hydrophobicity and membrane fouling surface morphology cleaning has been analyzed. When the membrane has been examined closely, it has also seen that reduction in the flux coincided with the generation of the coarse biofouling layer.

However, nitrogen and carbon removal from the wastewater has been a concern of matter in the lab-scale MBR operations. Operation and process configuration of the MBR system represents the empirically instrument employed for the MBR operation, that includes normally of an anoxic reactor and AnMBR. Both anoxic reactor and MBR configuration have circular shape columns with the operational volumes of 10 and 30 L, respectively. For the MBR operation, 0.22 μm pore-size, PVDF HF membrane which has 0.2 m^2 filtration area has been immersed inside of the reactor. Figure 2.27 represents the schematic view of the MBR configuration.

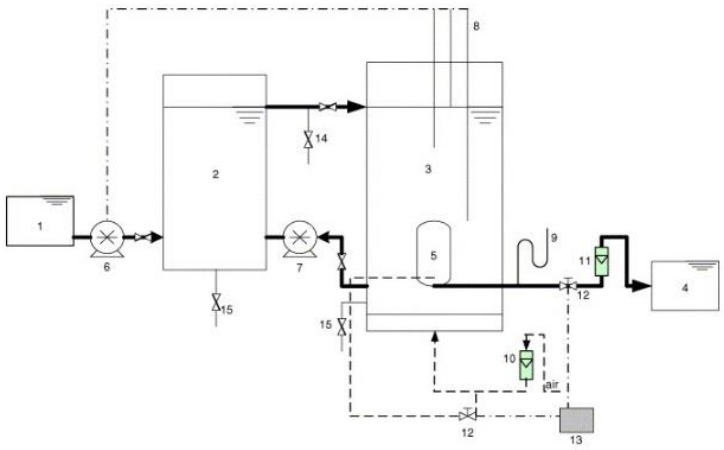


Figure 2.27 Anoxic MBR configureation for carbon removal from the food processing wastewater [100]. (1) Raw wastewater tank (2) anoxic tank (3) aerobic MBR (4) effluent tank (5) membrane module (6) feeding pump (7) recirculation pump (8) water level sensor (9) pressure gauge (10) air flow meter (11) water flow meter (12) electromagnetic valve (13) control system (14) sampling valve (15) sludge discharge valve.

Titanium plate, which has the size of 15 μm and placed at the bottom of the reactor to provide oxygen for the microorganisms inside of the tank, has been used for the air enlistment. DO in the MBR system has the range of 2–3 mg $O_2\,l^{-1}$. In the experiment

continuous process has been employed for the COD, NH_4^+– N and TN elimination which have been over 94, 91 and 74%, respectively. COD removal for the anoxic reactor determined as 40–63% and for the MBR it's been 29–46%. Nonetheless, NH_4^+– N elimination have been 31 – 43 and 47–64%, respectively. With the addition of some carrier molecules, nitrification process in the MBR could be increased when the operation has done at a shorter SRT. COD and TN maximum values have been noted as high as 3.4 kg COD m^{-3} day^{-1} in terms of N it has been 1.26 kg m^{-3} day^{-1}. When the results are examined, nitrification process for the sludge activity has shown steady results in terms of effluent NH_4^+– N density change.

In another point of view, MBR treatment systems and operations have been employed for removal of the organic and inorganic materials that can also critically affect the health condition of the individuals inside of the population [101].

Different types of pharmaceuticals, personal care products and their ingredients are called endocrine disrupting compounds (EDCs) and they can be usually found in surface water. Endocrine system is responsible from the hormonal circulation inside of the body and thyroid, parathyroid, hypophysis, epiphysis glands are the member of this system. So it has earned great significance to identify the amount of endocrine disrupters inside of the reservoir [102][103][104]. Adverse effects of the EDCs has also noted at previous researches [105][106]. It has been also the matter of issue for the drinking water that has been contaminated by pharmaceuticals that cause endocrine disruption and also trace of some obstinate molecules have been followed from sewage to drinking water chambers [107]

A pilot scale MBR system and three WWTPs have been employed for the treatment operation. At the first stage of the operation, solid-liquid separation has been made and wastewater has been pumped inside of the feed tank where actually denitrification process occurs. Before the treatment operation, wastewater exposed to 1 mm strainer to eliminate undesirable materials Table 2.7 represents the features of the researched pilot plant and the samples CAS WWTPs.

Table 2.7 Qualification of the researched MBR pilot plant and the sampled CAS WWTPs. [101].

	T (°C)	SRT (d)	HRT (d)	TSS ($g\,l^{-1}$)	VSS TSS^{-1} (–)	F/M ($g\,COD\,g\,TSS^{-1}\,d^{-1}$)
MBR						
1st sampling	22.2	10	0.5	6.3	0.75	0.24
2nd sampling	27.2	27	1.2	4.5	0.71	0.16
3rd sampling	5.5	55	4.0	11.8	0.79	0.03
WWTP1						
1st sampling	16.8	114	13.3	4.9	0.65	0.02
2nd sampling	22.1	237	12.5	4.0	0.60	0.02
3rd sampling	6.8	52	13.6	4.0	0.68	0.02
WWTP 2	13.5	2	0.08	4.0	0.80	1.70
WWTP 3	10.4	46	1.20	3.1	0.65	0.04

The sludge has pumped from nitrification tank to the cross-flow membrane module which has settled externally. The sludge inside of the chamber exposed to the recycling operation and the effluent has been stocked in different tank called permeate tank. Membrane module itself exposed to the back-washing operation with the processed wastewater from the effluent tank. An interior sludge reuse relates nitrification and denitrification to hinder the biomass accumulation in the nitrification tank. This process ensures future nitrogen removal. Excessive amount of sludge has been removed from the interior sludge recycle. Since, both nitrification and denitrification tanks have the volume of 2.5 m^3, the nitrification tank has been exposed to the aeration and denitrification tank has been mixed by an electric mixer. Throughout the operation no phosphorous constituent precipitation has occurred and MBR system has been operated with a particular setting. Diversified SRTs has been mounted through the three experimental periods. Significant data about the MBR operation has been represented in Table 2.7.

However, conventional WWTP has the capacity of 100 g COD pe^{-1} d^{-1} (pe: population equivalents) and plant itself has been loaded with the domestic sewage from a distinct sewer system. Each WWTP includes screening and grit holding sections, two aeration tanks (with the capacity of 1546 m^3 for each) and two secondary clarifier for final sedimentation. In order to make an analogy between the results of STRs in MBR, two CASP operating diverse SRTs have been sampled. Automatic sampling instruments have been employed for the operation which gives an opportunity for composite sampling. While WWTP2 has been designed and highly loaded only for carbon removal, WWTP3 has been designed for low loading and nutrient elimination.

Result of this experiment showed that some of the constituents like antiepileptic drug carbamazepine has not been eliminated in any of the treatment facility. Additionally, concentration of permeate has been gauged in the range of influent in terms of the concentration of chemical constituents mentioned above. However, some of the compounds such as bisphenol-A, the analgesic ibuprofen or the lipid regulator bezafibrate has almost eliminated which is more than 90%.

WWTP operation is convenient for the elimination of the N at the temperature of 10 °C and SRT>10 and increment at the elimination potential has also seen for the chosen micropollutants. There hasn't seen any distinction in the removal performance between the treatment methods. It has also noticed that, both conventional WWTP and MBR performance has been dependent on the SRT and UF membranes haven't permitted any additional inhibition of the examined constituents because of magnitude dispensation. Nonetheless, high SRT values could be obtained in MBR systems inside of the compressed reactor. Nonylphenolpolyehtoxylates has also been eliminated in considerable amount at low amount of loading in CAS WWTPs.

2.6.2 Different Wastewater Types in D-MBR Systems

Dynamic membrane operations and applications dominates the MBR operations in terms of its low operational and module cost and normal physical disinfection performance which is going to be mentioned at following section (advantages and disadvantages of DMBR, MBR and CAS systems). However, DMBR operation, especially crossflow dynamic membrane (CDMBR) operation, has been researched by curing caprolactam wastewater through 180 days [63].

Removal yield of the organic constituents and amount of nitrogen inside of the wastewater has been noted as over 99% and 80%, respectively. Monitored sludge performance has only been 0.14 g SS gx^{-1} CODxd^{-1} at SRT rage of 30 days. Therefore, organic sludge loading has been around 0.3 g COD g^{-1} SS·d^{-1}. According to the measurement of TOC, congestion of SMP in the upstream region, also called supernatant, has given rise to the membrane separation that has been observed through beginning of the operation. SMP inside of the supernatant has been confirmed as biologically degradable afterwards throughout its molecular weight distribution (MWD) essay.

Table 2.8 Characteristics of the caprolactam wastewater used in the experiment [63].

Quality of Caprolactam Wastewater					
Items	$COD_{Cr}(mg.L^{-1})$	$BOD_5(mg.L^{-1})$	pH	TP ($mg.L^{-1}$)	TN ($mg.L^{-1}$)
Conc.	1800-2000	1370-1530	6.8-7.2	20-30	100-130

Textile wastewater Caprolactam ($C_6H_{11}NO$) has been challenging and difficult to treat because of the high nitrogen density inside of the liquor. Table 2.8 gives the essential features of the caprolactam wastewater which is synthetically produced in this experiment.

Anoxic reactor that has effective volume of 8 L has been filled with the caprolactam wastewater with a magnetic stirrer which fits inside of the reactor. Stirred wastewater has been cultivated gravimetrically to the aerobic reactor which has ascendant volume of 20 L and inserted inside of the circulated anoxic reactor for denitrification process. The schematic representation of the CDMBR employed in this experiment has shown in Figure 2.28.

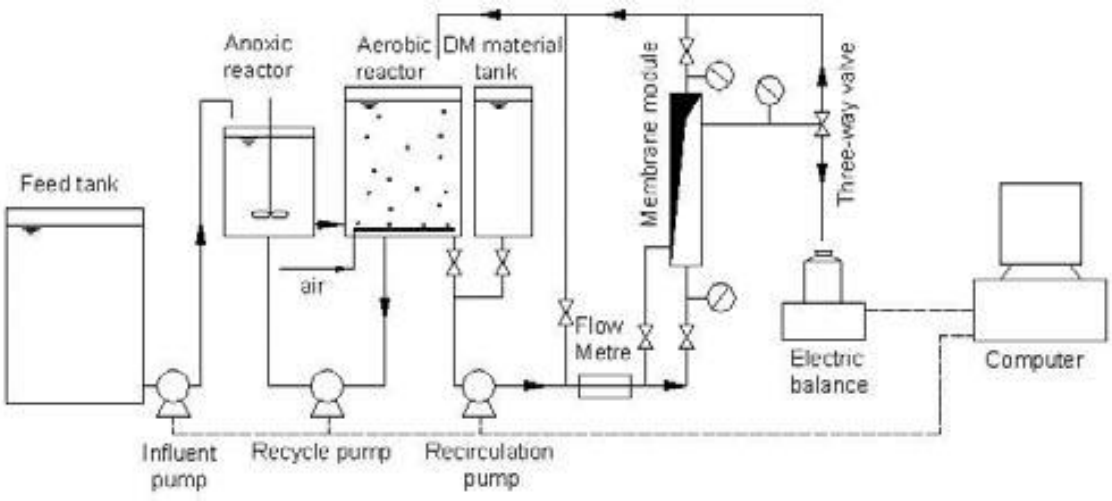


Figure 2.28 CDMBR configuration of the system employed for the operation [63].

The rate of the circulation and recirculation for the influent flow rate has been kept at 3 to 1 along examination. Temperature has been checked and stabilized at 30°C with a heat modifier and DO density at the rate of upward 3 mg L^{-1} in the aerobic reactor. TMP has been supplied by the utilization of a centrifugal pump. Both excessive effluent and the region which cannot be filtrated have been returned to the aerobic reactor to maintain the volume of the reactor stable. There has been no excessive sludge release seen throughout the operation until suspended solid had been augmented to 4500 mg L^{-1}

and, therefore, SRT has been controlled for 30 days. HRT has been set to 33 to 66 hours to protect the mean sludge loading about 0.3 g COD g^{-1} SS d^{-1}. Throughout the experiment, embraced TMP value has been in the scale of 0.1-0.2 MPa and crossflow speed in the range of 1-2 m s^{-1}. Stainless steel cylindrical shape membrane module has been utilized and tubular ceramic membrane employed with the pore size of 2 μm. Each membrane module has consisted of 6 tubes with an interior diameter of 9mm, length of 400 mm and with the overall membrane surface area of 0.0672 m^2.

Dynamic membrane has been formed on the surface of the membrane by circulating the kaolinite solution with the amount of 0.5 g^{-l} over the membrane module with the effluent outrun under the designed circumstance. Mean particle size of the kaolinite has been noted as 2 μm. Programmed cleaning operation has been done by employment of backwashing operation as the flux reduces less than 20 L m^{-1} h^{-1}.

The result of the experiment showed that, COD concentration of the liquor has been maintained beneath 100 mg L^{-1} while effluent value under 50 mg L^{-1} d, and even less than 20 mg L^{-1} d, after 100 days of operational time which represents the perfect membrane disentanglement has been achieved. When the TN removal and nitrification yield has been examined, it has been found as 80% and density of the TN in the membrane effluent has been less than 20 mg L^{-1}. The NH_4^+-N density has been kept at low level which has changing the range between 1-3 mg L^{-1}.

After the initial phase of the operation, increment in MLSS concentration has been observed. Throughout 45 days, excessive sludge release has seen and SRT has maintained at 30 days. Density of MLSS accrued until concentration attained 9213 mg/L and it has fixed at that rate. Monitored sludge performance has been noted as 0.14 g SS g^{-1} COD d^{-1} that is lower than the conventional sludge processing.

In another research, biodiatomite dynamic membrane (BDMB) has been examined on residuals of surface of the membrane and characteritics of high porosity has been noticed [108].

The rate of VSS inside of the liquor has been found as lower than SS amount regarding to BDMB. Support material has been made of 74 μm stainless steel mesh. It has been stabilized in immersed mode with bivious efficient a filtration at course of 0.084 m.

However, the quality of the raw municipal wastewater has been noted in terms of its organic and inorganic values. COD and NH_4^+-N values have been noted in the range of

260 – 600 and 7.6 – 11.2, respectively. Amount of SS inside of the mixed liquor has been noted as 30 – 360 and water temperature and pH values have been 23 – 33 °C and 6.5 – 7.4, respectively. MLSS concentration inside of the mixed liquor has been 11000 mg/L and flux has been set to 50 – 130 L/m^2h. Nonetheless, SRT and HRT values have been noted as 70d and 2.8 – 7.1h, respectively. Temperature of the liquor inside of the reactor has been maintained at 26 – 32 °C. Amount of dissolved oxygen in aerobic tank and anaerobic tank has been noted as 3 – 4 and <0.15 mg/L, respectively.

Experimental results have represented that hydraulic impression scouring effect of precoating phase has led to grow microorganism beside of the cake layer close to the support material, which has been mesh in this case. Elusion of the biolayer from the support material and augmentation in the porosity has enhanced. This situation gave rise to the asymmetric pore structure formation in the structure of the cake layer. The essence of the biodiatomite which has been also called as diatomite has been the essential parameter for the dynamic semi-compressibility of the BDDM. Hereby, performance of the BDDM has shown fine retention convenience, high filterable flux and facile backwash operation.

In another experiment, organic matter (OM) (such as nitrogen, phosphorus and carbon) recovery has been tried to sustain from the municipal wastewater with employment of dynamic membrane separation processes [3].

Configuration of the upflow dynamic membrane separation (DMS) operation has been developed for organic constituent recovery from municipal wastewater which has had low strength. Operational duration has taken 300 days and 81.6% of the organic substance has been recovered at the flux of 60 L/(m^2h). Chemical approaches and batch assays showed that recovered organic matter (ROM) has had broader C/N ratio, in addition to that, waste activated sludge has been compared with the advanced fermentation capacity. Change occurred in the organic matter has been paved the way to the DMS process for polyferric sulfate (PFS) coagulation, anaerobic metabolism and membrane retainment. Recovery of resolvable organic constituents has been facilitated by coagulation and the change has been noticed in the sludge region because of the anaerobic metabolic activities. Even though, DM has less efficiency to eliminate small molecules, it has permitted a retainment of particulate remainder and biopolymers, allowing comparatively excess ROM recovery in the DMS operation. Therefore, the total process spending for new wastewater treatment method has been around 0.24 kW

h/m^3 which is lower than traditional methods employed in the wastewater treatment operations cost 1.10 kW h/m^3. Results showed that the up-flow DMS operation has been an up-and-coming option for wastewater treatment operations in terms of their sustainability.

Different wastewater types employed for the treatment operation. One of the significant and critical wastewater treatment operations is the treatment of the polluted surface water. In another pilot-scale study, hybrid bio-diatomite/dynamic membrane reactor has been employed for slightly polluted raw water purification [109]. Experiment has indicated the operational yield and process of a new pilot-scale BDDMR for partially contaminated surface water therapy in perpetual flow mode. Pilot scale BDDMR has been found as significantly effective method for attenuation of particle number and eliminating turbidity, COD, UV absorbance at 254 nm, NH_3-N and trihalomethane generation potency with HRT of 8 hours.

DM-TPM has been stationary for every single selected flux parameter which are 30 L/m^2h, 50 L/m^2h and 80L/m^2h. At the early phases of filtration operation, TMP increased 4.5 kPa swiftly in the conclusive phase of the process term. The results showed that, aromatic protein-like constituents in permeate have been eliminated instrumentally, according to the 3D-EEM methodology employed for the operation. Therefore, separation of the SS, the BDDMR could partly eliminate MW which is between 1000 – 3200 Da of dissolved organic matter. Three specific effects which are responsible for pollution elimination have been examined. Also three PCR operations have been applied with the denaturing gradient gel electrophoresis called DGGE to validate the relocation of microbial organisms in the mixed liquor.

However, experimental analyses not only made on raw wastewater types taken from industrial environments but also synthetic wastewater prepared in laboratory [60]. In that context, generation of the MnO_2 on the dynamic membrane has been examined. The MnO_2 employed in the investigation has been settled from $KMnO_4$ solution utilizing HCOONa. However, generation of dynamic membrane with granule dimension less than the pore size of the primitive membrane has been contrived to perform according to the standard statue of filtration which occurs in the early periods of membrane generation.

In the experiment, tubular, 20 – 40 μm polyester woven fabric has been employed. Length, cross-sectional area, total surface area and wall thickness values of the fabric have been given as, 4x0.98 m, 4.597 cm^2, 0.295 m^2 and 0.34 – 0.375 mm, respectively. Nonetheless, characteristics of the wastewater have been defined in the laboratory. Turbidity, pH and density results have been given as 22 NTU, 7.45 and 1001.84 g/L, respectively. COD, BOD and TOC results have been given as 130, 20 and 86 mg/L in order. On the other hand, as small colloidal particles initiate to link the pores and settle on surface of the membrane, dynamic membrane generation has been constituted follow the orders of cake filtration model. Therefore, standard equation to identify every single incidence of dynamic membrane generation has been achieved. When the wastewater is purified from the undesired components by using the dynamic membrane, it is determined that the components are located in the same wastewater as in the production of the dynamic membrane.

Another synthetic wastewater examination has been made in lab-scale MBR configuration. Change in operational conditions may differ the operational output but employment of the fabric and microfilter materials directly influence the performance of the system. So, characteristics of flux and quality of gel layer on microfilter (MF) and non-woven fabric filter (NWFF) surface have been examined [110]. NWFF and microfilter bioreactor modules have been practiced utilizing 100 μm polypropylene and 0.25 μm polyethylene substance, respectively. Yield and methodology of these two operations have been examined, subsuming additional batch infiltrating examinations to study out the function of the dynamic gel layer on the surface of the membrane. Both configuration have been set to 9h HRT and the permeate flux that has been operating has been 13 $L/m^2/h$. The two bioreactor systems comprise aerobic and anoxic reactor and, therefore, NWFF or MF has been immersed in every oxygen dependent reactors. Synthetic wastewater including 250 ± 30 mg/L COD based upon glucose, at 30 ± 5 mg/L TN (NH_4Cl), 4 ± 0.5 mg/L TP (KH_2PO_4), 200 ± 30 mg/L alkalinity ($NaHCO_3$) and trace elements like Mg, Fe, Ca, Mn has been synthesized and perpetually fed to both bioreactor systems.

The undisturbed batch cell trials have been carried out parallel to the uninterrupted two bioreactors. In these batch operations, for fabric filter and microfilter, MLSS density and TMP impact on the flux excursion properties have been examined. 180 mL of broad volume solution from the aerobic reactors, including 10,000 ± 2,000 mg/L suspended

solids, has been positioned into a 200 mL stamped vessel where NWFF and MF have been mounted. N_2 with fixed pressures of 0, 10, 20 and 30 kPa repressed the fluid out of the stamped vessel by favor of particular gas compressed stock system. Effluent volume has been noted automatically by software throughout operational duration. To monitor the flux semblance employing just soluble components, the permeated sizeable solutions in the NWFF and MF aerobic reactor of the lasting bioreactors have been syringed into 200 mL of the stamped vessel after eying through over 0.45 μm membrane pore size diameter. Alternative 180 mL of broad volume from two aerobic reactors has been centrifuged to spare the solids and solution, which is named mixed liquor.

Separated solid particles have been exposed to washing process a few times with pure water to achieve small sole sludge substances. Accumulated sludge granules have been suspended again in distilled water and attenuated to small sludge substance. The gathered sludge substances have been suspended again in pure water and attenuated to sludge colloidal particles densities of 20.000, 10.000, 5.000 and 2.500 mg/L. The flux gets changed under stable air stressed nitrogen at 0 kPa and 10 kPa, regarding to NWFF and MF, respectively.

The two bioreactors consisted of an anoxic reactor tracked by aerobic bioreactor where NWFF/MF has been immersed. The mean suspended solid concentration of the effluent from the NWFF has been consistent below 2 mg/L, even though, the pore diameter of the NWFF has been leastwise 400 times greater than the MF. Table 2.9 represents the removal performances of the operation regarding to suspended solids, organic constituents and nitrogen in the NWFF and MF.

Table 2.9 Removal performances of suspended solids, organic matters and nitrogen in the NWFF- and MF-MBRs [110].

	Influent		Effluent of NWFF		Effluent of MF	
	Range of variation	Average value	Range of variation	Average value	Range of variation	Average value
SS (mg/L)	0	0	0.6-4.2	1.9	0.1–1.8	0.8
COD (mg/L)	201–372	270	4.1–10.2	7,5	3.2–6.8	4,9
DOC (mg/L)	32–120	65	1.6–2.8	2	1.2–2.1	1,6
TN (mg/L)	14–30	22	4.7–7.5	6	5.0–10.1	6.6

The elaborated yarn mould of the NWFF has been formed the channels much more complex, and filtrated most of the SS out. Moreover, cake formation on the surface of the membrane played a significant role as a blockage depending upon a similar result of the former examinations [15].

Also it has been found correct when the monitored biofilm has been a matter of issue, in terms of low suspended solid density in effluent as well as apparent investigation with a microscope. However, COD removal performance of the bioreactor system has been achieved around 97%. Similar outcome has been obtained for the MF. Therefore, both MBR configurations have ensured similar performance in terms of other organic substances, suspended solids and nitrogen. Generation of the cake layer on the NWFF contributed to primary resistance, while gel layer occurred on the surface of microfilter or interior fouling of the pores that had an important role in the fouling process of the membrane. Quantity of the EPS has been measured as 13 mg/L which is greater than the quantity of EPS attached to the NWFF. The functional thick gel bed has been formed on the connection amongst the EPS, TMP and MLSS.

NWFF system has been stated as the variance in the water level because of the suction occurred due to the gravitational force. Throughout the filtration time, nearly 0.1 – 0.3 kPa head drop-off has taken place. In this context, the head drop-offs have been only kept below 0.1 kPa after the beginning term when the flux has been noted as 14.8 $L/m^2/h$.

In another experiment, filtration ability and operational features of dynamic membrane bioreactor for municipal wastewater treatment has been examined [16]. In the experiment, industrial material which is filter-cloth in this context has been employed instead of utilizing conventional MF or UF membrane types to create an MBR for the treatment operation. Generation and filtration capability of the dynamic membrane and the success of the DMBR for eliminating the organic substances inside of the municipal wastewater treatment have been investigated. Result of the batch test has revealed that dynamic membrane could be generated on the filter-cloth face level swiftly and improved stably. It has significant role to deny particulate material. Superior sludge density had chance to make a contribution to the generation of dynamic membrane but spearhead to enhanced suspended solid concentration in the permeate and lower penetration flux. For municipal wastewater treatment operation serially, in the effluent turbidity has been less than 9 NTU and suspended solid has been zero at the many of

operation time under the MLSS concentration of less than 6000 mg/L^{-1}. At 6.9 HRT and temperature of 9 – 13 °C, total COD and ammonia elimination has been noted as 72–89% and 66–94%, respectively. It has been also noticed that, dynamic membrane total resistance has been revealed lower than the MF or UF membrane. Major resistance in the experiment has been esteemed to the resistance of the cake layer.

Formation mechanism and structure of dynamic membrane related to this formation in DMBR has been a matter of examination in lab-scale studies [111]. Bioreactor adjusted volume of 7.5 L has been produced from polyethylene and separated into 3 sections which are labeled as left, right and middle part. Aeration instruments, which are literally called as lateral aeration, have been placed to the on the bottom left and right side of the reactor. Aeration of the middle part has been provided by the underside aeration set-up. Throughout the regular operation, lateral aeration has been run to ensure DO for microorganisms, mixed liquor, generates cross-flow on the surface of the membrane and expedites the circular flow.

When the fouling occurred on the surface of the membrane which makes the membrane slender to operate, the lateral aeration has been stopped. In fact, the underside aeration has been run to eliminate membrane fouling with the impact of powerful gas-water multiphase flow. However, membrane partial montage which is like plate-frame membrane has been employed. While height of the membrane has been adjusted as 0.1 m, surface area of the membrane which has been made of silk with the pore size of 0.1 mm has been 0.01 m^2.

The effluent has passed over the surface of the membrane and removed to outside of the reactor. Diversely, DMBR could be performed progressively through few months until the membrane lose its permeability and attain the restricted level. The feed water used in the operation has been sustained from the municipal raw sewage that has been monitored via 1 mm pore size holes. Nonetheless, amount of COD and NH_4^+–N have been 78 – 126 mg/L and 9 – 19 mg/L, respectively. In addition to the characteristics to the wastewater utilized inside of the reactor, total phosphorus, turbidity, temperature and pH values have been noted as 1 – 3 mg/L, 56 – 84 NTU, 15 – 24 °C and pH of 6 – 8.

In another examination, operation has been separated into two phases which are named as low MLSS and high MLSS. At the low MLSS phase which have been noted as 3000

mg/L dynamic membrane have been consistently operated for few months without cleaning operation and excellent division capability of dynamic membrane that could be achieved in 30 minutes, which has been reported in previous research [112]. Nevertheless, when the concentration of the MLSS has been about 3000 mg/L, dissolved oxygen and pH have been 2 – 3 mg/L and 6 – 7. Describing the generation process of dynamic membrane more apparently, the MLSS has been enhanced for compressing the operation loop of dynamic membrane. It has been noted that, COD and turbidity contexts in the permeate have attained to a fixed rate after 5h of operation, referring that overall dynamic membrane generation has been ensured in 5h. Nevertheless, in the system of DMBR, it has been very significant to control MLSS within an influential range.

Dynamic membrane has been generated through the filtration operation and showed difference due to the change in operational time. Hereby, it has been difficult to state the generation process of dynamic membrane by utilizing mathematical models. Based on the attitude of flux under stable filtrating pressure, the generation process of dynamic membrane has been enhanced by separating generation process into 4 phases that has been later on performed by 4 filtration rules. Furthermore, dynamic membrane from interior section to exterior has been separated into 3 sections which have been known as substrate layer, separation layer and fouling layer. Thereafter, association of the generated process with the rule of hydrokinetic restrictive layer, the methodology for calculating the favorable cross-flow proportion on dynamic membrane surface has been enhanced, and the method for calculating the suitable aeration quantity to handle with membrane fouling has been constructed.

In another experiment, inwardly recirculating dynamic membrane bioreactor employing sieve silk as membrane support material has been used to treat domestic wastewater [113]. Operational condition has been set to 6h of HRT and membrane flux parameter has been noted as 66.2 L/(m2·h). However, it is critical to mention that biological dynamic membrane (BDM) formation of the reactor has taken 120 minutes to constitute. After the formation of the DM, mean removal rates of the COD, NH_3^+-N, TN and TP of the bioreactor have been 94.0%, 97.6%, 49.2% and 83.7% respectively. Aeration in the invert direction of permeate has been embraced to perform with utilization of online backwashing. Throughout 5 minutes of backwashing and 3.2 m3/(m2·h) of airing intensity, BDM renewal has required 30 minutes to accomplish.

Utilized bioreactor has been run steadily for 60 days and backwashing cycle could be fixed over 50h. It is quite common issue to keep dynamic membrane stable and throughout the cleaning operation such as physical and/or chemical cleaning membrane can be harmed, deformed or ripped. Result of the electron microscopy has monitored that operation of backwashing cycle had chance to destroy BDM critically.

Characteristics of the dynamic membrane have been examined and subjected to research that involved in municipal wastewater treatment [15]. Membrane has been made of 100-μm Dacron type mesh material. Membrane module has been submerged into the reactor that has total volume of 140L. There have been 18 modules mounted into the reactor and permeate of these modules could be operated individually. Each individual module had the filtration area of 0.15 m^2 and total filtration area has been noted as 2.7 m^2.

Two aeration diffusor have been used for the operation. Therefore, while one of the aerators has been chosen as lateral aerator which service as oxygen vendor and it is involving a cross-flow filtration over the surface of the DM modules, the other aerator has been chosen for cleaning of the modules that have been plugged. Feeding has been stopped during the load which has taken 5 minutes. After 5 minutes of waiting, feeding has begun and DM formation has run on.

The quality parameters of COD, NH_3^+-N, SS and pH have been noted as 97.9-371.7 mg L^{-1}, 39.65-59.89 mg L^{-1}, 45-290 mg L^{-1} and 6.8-7.2 in the raw domestic wastewater, respectively. Wastewater has been sustained after passing through 1 mm bar screen and released into the tank where actually wastewater stored with the help of electromagnetic pump. Nonetheless, MLSS concentration, DO and operation flux have been 7500 mg L^{-1}, 3-5 mg L^{-1} and 14.8-33.3 L m^{-2} h^{-1}, respectively. SRT of the operation has been 56 d and HRT has been 3.5h. Through the operation, temperature has been kept at 27 °C and it has been measured and periodically controlled. In addition, lateral and bottom aeration fluxes have been 30 and 120 m^3 m^{-2} h^{-1}.

The influent, ML and permeate have been synchronously sampled. The supernatant region of the liquor has been procured with the benefit of centrifuge at 4000 rpm for 15 minutes and 0.45 μm membrane filtration has followed. COD has been analyzed with $K_2Cr_2O_7$ oxidization method and DOC value has been measured with TOC analyzer. Through the operation, the mean COD concentration of permeate has been 28.2 mg L^{-1} with mean removal performance of the entire system of 84.2% and also the mean value

of NH_3^+-N concentration of permeate has been 0.80 mg L-1 with the mean removal performance of the entire system of 98.03%. It has been noted that, DM has made contribution around 9% to the entire system COD elimination but this contribution has been a little in terms of NH_3^+-N elimination and COD removal from the supernatant has been 34.3%. It has been noted from the previous studies that MBR operations have been found advantageous in terms of their complete solid-liquid separation effect, high organic matter removal, high nitrification efficiency, etc. This experiment has proved that DM can subrogate traditional MF/UF membranes to establish a MBR process.

In another lab-scale experiment, removal yield of the TOC and COD have been concerned [114]. Throughout the experiment, 0.1 mm Dacron type mesh membrane has been used instead of using static membrane, such as; HF membrane, to provide appropriate ground for the dynamic membrane formation and also to enhance an immersed DMBR. At 3.5h HRT, operation has shown great performance in terms of permeate quality. It has been also noted that, DM could work stably at a stress not above several centimeters water head drop. The maximum SS concentration in the permeate has been 4.05 mg/L, in fact the gauged SS concentrations have been zero in many situations. The concentration of MLSS has been 7000-8000 mg/L, the permeate head drop has only been 5.8 mm when the flux equaled to 14.9 L/(m^2.h) and it has had small interchange through a perpetual operation process of 27 days. At the end of the operation, DM has removed meanly 28.74% of COD and 36.9% of TOC in the supernatant, respectively. It has also been noted that, dynamic membrane could eliminate NH_3^+-N more than 96% when DO in the mixed liquor not fewer than 2-3 mg/L.

In another study, impact of mesh size and air scouring on the generation and fixation of the cake formation has been examined in a lab-scale DMBR application for treatment of the municipal wastewater [115]. In different periods of tests, two 20 and 50 μm pore size nylon meshes have been utilized under aerobic operational condition and three diversified air flow ratios have been examined for filter surface area scouring. Each experimental period, the legibility of permeate and the cleaning necessities have been appraised under steady state circumstances. The main purpose of the experiment has been valuation the impacts of mesh volume and air scouring on the success of the SFDMBR.

Operating volume of the MBR system has been set to 4.6 L. A mesh module, which has been used for the filtration process and one side surface area has been 6x6 cm, has had total surface area of 72 cm^2 and immersed into the reactor to promote of the cake formation. Permeate of the bioreactor has been withdrawn with employment of the peristaltic pump. Operational volume of the reactor has been fixed through a level check attached to the feed pump. The reactor has been perpetually aerated and the mesh has been exposed to the air scouring. Due to these objectives, two diverse aeration routes have been utilized. In order to change the air flow rate of the process and keep the air supply for the bio-process constant, the air flow is reduced by providing it along the secondary vent line. This has minified the contrast of DO, in the scale of 2-3 mg/L, in the bioreactor.

Two different meshes made support material which had 20 and 50 μm pore size and four different air scouring instruments at different flow rates like; 0, 150, 250, and 500 mL_{air}/min have been tested. Besides, to sustain better operational performance, 8 probatory set of run have been constituted. It is critical to implement that, each individual run have been initiated with a brand-new filtering mesh support material.

For instance, the examination with 50 μm mesh and 250 $mL_{air}\ min^{-1}$ have been indicated by R50-250. TMP has been screened by online reading during every two hours. Cleaning of the mesh support material has been performed when the TMP has been higher than 100 mbar. When an increment has seen during the analysis of TMP through non-monitored term such as; nights or weekends, operation has maintained the TMP value which has been higher than 100 mbar up to the next membrane pressure investigation through 16h to 64h. Cleaning operation has included the disintegration of the module from the reactor and jet swilling the mesh superficial area. In addition, there has been no chemical addition found, in order to form an estimate of probable insistent plugging of the mesh.

Each phase of the operation has been started with a biomass of 1.5 g TSS/L (1.3 g VSS/L) and has been maintained under fixed temperature of 20°C. Therefore, volumetric loading rate of 1.25 kg COD $m^{-3}\ d^{-1}$ has been used and a SRT of 16 days has been set for the operation. The flow rate has been fixed at roughly 16.4 L/day, regarding to a flux of 95 L $m^2\ h^{-1}$ and a HRT of 6.7h. Reduction in flow rate has taken place through the non-screened terms because of increment in TMP. Thereby, the actual generated effluent volumes have been gauged. The feed gathered weekly at a local

WWTP, reserved at 4 °C, stirred continuously, and subtilized with tap water to sustain the constant volumetric loading rate of 1.25 kg COD m^{-3} d^{-1}.

In order to attain and pursue the fixed state circumstance, all operational states have been operated four times the SRT, excluding for the tests without air scouring which have been R20-0 and R50-0 and abandoned in time because of their restricted performance.The fundamental water qualification changeable have been gauged in both the influent and the permeate of the reactor. Electrical conductivity, temperature and pH have been screened carefully. The permeate turbidity has been gauged at least three times which includes leastwise three copies.

Throughout the operational conditions continued for the bioprocesses, which are SRT of 16d and volumetric loading rate of 1.25 of kg COD m^{-3} d^{-1}, each individual phase arrived to stable phase concentration of solids in the mixed liquor that includes 2.1 ± 0.4 g TSS L^{-1} and 1.8 ± 0.4 g VSS L^{-1}. Operational success of the system has been primarily utilized according to mesh plugging and consistent cleaning necessity. After a few days of the operation, development of the cake layer resulted in fractional fouling of the mesh, as discovered by increment of suction pressure. Nonetheless, augmentation of TMP and flux between two cleaning operations has been noted in Figure 2.30 for two incidences, regarding to operational conditions such as R20-500 and R50-500. It has been noticed that membrane pressure values have been around 900 mbar and increment in the TMP has stopped. However, pores of the mesh support material have been continuously plugged and caused a thematic deduction of the membrane flux. Nonetheless, the biomass layer has been cleaned at certain intervals. The interval rate of the cleaning has been concluded by both air scouring and mesh pore diameter. After the cleaning operation of the mesh support material, membrane pressure turned back to the null and the flux has again almost been 95 L m^{-2} h^{-1}, emphasizing the basic operation of jet rinsing has been found as efficient for the elimination of the mesh support layer plugging. Figure 2.29 represents the membrane pressures of R20-500 and R50-500. In addition to the TMP values, flux measurements regarding to the R20-500 and R50-500 mesh pore size-air scouring rates have been typified.

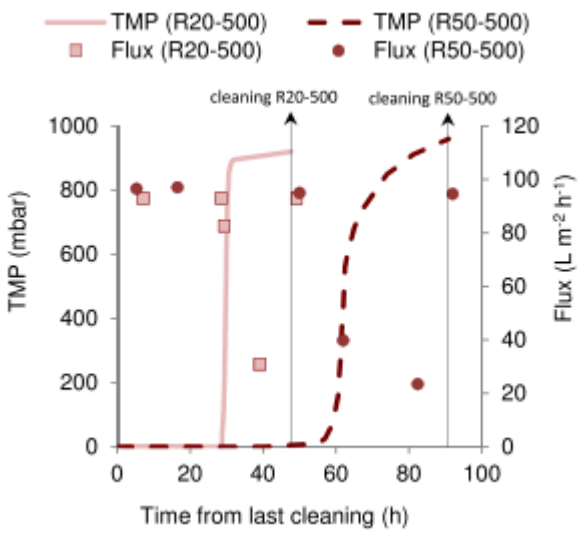


Figure 2.29 Development of the TMP that has been denoted as certain value and membrane flux between the following cleaning cases [115]. Two different specimens (R20-500 and R50-500) regarding to operation.

The 20 μm mesh support material has had much higher purging necessities than the 50 μm mesh support material. At fixed state of the operation, 20 μm mesh support material has required cleaning, crossbench air scouring and flow rate. In fact, the 50 μm mesh support material has been only elutriated between 1.0 and 2.6 times per week. The result of this process has shown that much more limited maintenance for the reactor operation.

Operation R50-150 has been noted as the most fruitful run due to its cleaning necessities. In all operational phases, excluding the R20-250, the cleaning interval has risen throughout the experimental term. Nonetheless, the whole flux recovery of the mesh support material after jet flushing has just referred the brief period performance restoration. In fact, increment of the mesh cleaning frequency has shown the probable formation of insistent fouling. This circumstance has been affirmed by the microscopic investigation of mesh samples pre and post operations. Nevertheless, this incident has not influenced the mean performance of the entire operation under unplugged circumstances and membrane pressure has been noted as lower than 100 mbar. Figure 2.30 represents the experimental duration regarding upon the flux and in terms of its sustainability and stability as well.

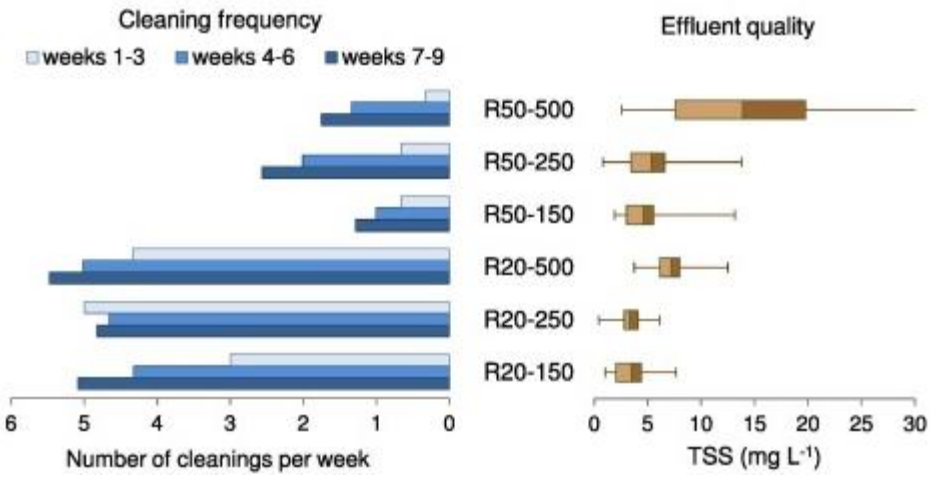


Figure 2.30 Operational performance of each one of the samples regarding upon their cleaning necessities and permeate quality [115].

The mean physical and chemical features of permeate formed under fixed phase through each of experimental interval have been reported. Under all experimental circumstances, COD removal concentration has been found as 87% and 93% which represents ascendant elimination ratio and success in terms of exact nitrification.

2.7 The Comparison of MBRs, D-MBRs and CAS in Terms of Advantages and Disadvantages

Biochemical reaction of the activated sludge is provided completely mixture with aeration and mixing in the bioreactor in the conventional activated sludge system (CAS). The reaction is eventually needed to secondary clarifier for separate microorganisms and processed wastewater. The membrane bioreactor (MBR) is used to separate solid and liquid constitutents in the bioreactor, and the operation eventually doesn't require a secondary clarifier. In this context, when compared with conventional activated sludge processes (CAS), MBR and D-MBR, MBRs use membrane filtration for solid–liquid separation, supplying higher effluent quality for wastewater reclamation and reuse.

The MBR and D-MBR systems have attracted increasing interest both academically and commercially in wastewater treatment as an alternative of CAS systems. MBR and D-MBR have many advantages such as, higher biomass concentration, smaller footprint, lower sludge production and rejection of SS (effluent SS is close to zero) [116]

Although many researchers now reconsider whether MBR has been the best choice for various treatment methods, choosing between MBR and CAS for wastewater treatment

remains ambiguous [117]. MBR and D-MBR systems have been widely applied in full scale and laboratory scale wastewater treatment process thanks to supply higher MLSS concentration, better control of SRT, higher volumetric loading, production of high-quality effluent when compare with CAS. However, the application of MBR is restricted by its high membrane module cost and membrane fouling [11]. So, many researchers attempted to use cheap covered material for replacing the expensive micro-/ultra-filtration membrane for decrease the high cost [15].

Despite it is claimed advantages of better treatment method performance and occupation of much less land, broader application of MBRs is still hindered by their relatively high construction cost and energy consumption [118]. For these reasons, in recent years done extensive research on D-MBR instead of MF and UF membrane is trying to eliminate the cost of the MBRs. Dynamic membrane is formed on the underlying a support materials when filtering the wastewater from the reactor, so is also called secondary membrane [119]. Mesh, woven and nonwoven fabrics are used instead of MF or UF [26] in the D-MBR, by this means operating costs of DMBR are much lower than the CAS and MBR systems.

Membranes need physical and chemical washing due to often fouled by microorganisms. The main fouling reason was reported in the previous studies due to increased bacterial growth [120]. So, they do not frequently need chemical and physical cleaning [25]. Although physical operations such as water backwashing, air sparging, brushing, intermittent suction (relaxation) and cross-flow are enough for MBR and D-MBR systems, these operations temporarily result in low effluent quality (high MLSS). In the light of all these findings, although D-MBRs are more advantageous compared to MBR and CAS, some disadvantages are associated with the initial cake layer development on the membrane surface.

This layer causes a considerable reduction of the permeate flow [121] and increase the trans-membrane pressure (TMP). So, a well-defined and systematic comparison of D-MBR, MBR and CAS about wastewater treatment, must be of fundamental importance, thoroughly and meticulously [122]. Based on the findings of several studies in the literature about the considering the relative advantages and disadvantages of MBR, D-MBR and CAS systems general information are tabulated in the Table 2.10.

Table 2.10 The comparison of comparatively advantages and disadvantages of MBR, D-MBR and CAS [123].

MBR		D-MBR		CAS	
Advantages	**Disadvantages**	**Advantages**	**Disadvantages**	**Advantages**	**Disadvantages**
High MLSS (5,000–20,000 mg/L)	O_2 Supply	High MLSS (5,000–20,000 mg/L)	O_2 Supply	—	Lower MLSS (3,000–5,000 mg/L)
Low footprint	—	Low footprint	—	—	Large footprint
Higher volumetric loading	—	Higher volumetric loading	—	—	Lower volumetric loading
Fine control of SRT	High sludge flow	Fine control of SRT	—	—	Workload for SRT control
—	Greater operational and process complexity	—	Greater operational and process complexity	—	Easier operational and process complexity
Lower sludge production	—	Lower sludge production	—	—	Higher sludge production
—	Higher capital Low operational costs	Low capital Low operational costs	—	—	Higher capital High operational costs
—	Greater foaming propensity.	—	Greater foaming propensity	Lower foaming propensity	—
Treated water that reusable	—	Treated water that reusable	—	—	—
Unlimited by settling due to gravity	—	Unlimited by settling due to gravity	—	—	It is limited by settling due to gravity
—	High Module Cost	Low module cost	—	—	—
Simple TMP control based on constant flow	—	—	Complex TMP control based on constant flow	—	Not applicable
Simple fouling control	—	—	Complex fouling control	—	Not applicable
Chemical wash easer applied	—	—	Chemical wash not easily applied	—	Not applicable
Very high physical disinfection performance	—	Normal physical disinfection performance	—	—	Not applicable
Affected indirectly by Bulking problem	—	Affected indirectly by Bulking problem	—	—	Affected directly by Bulking problem
—	Cake formation/reformation	—	Cake formation/reformation	—	—

2.8 Membrane Fouling

Membrane fouling is one of the most challenging problems through the separation processes that have been done by using membranes in water and wastewater treatment. Just like other pressure-driven filtration operations, there are innate problems and the major constrictive factor in MBR systems is fouling of the membrane. However, the operation quality and achievement is majorly related to successful membrane fouling management. Fouling of the membrane can be affected by several factors like; the water quality of influent wastewater, membrane feature, bioreactor process stage, and cleaning methods (physical or chemical) of the membrane.

Fouling of the membrane can cause the reduction in permeation flux or it can also cause to the increment in transmembrane pressure (TMP) depending on operation method which can be under constant flux or constant pressure. Transmembrane pressure affiliated to the membrane fouling and pressure directly increases when fouling occurred to sustain particular operation flux. On the other hand, under fixed pressure manner when permeate flux reduces, it points to the membrane fouling.

For comprehension of the fouling in MBR systems, two different variants which are TMP in the fixed flux mode and flux in the fixed pressure mode should be followed up throughout the operation execution time. It can be directly notified that the lines in Figure X (a) and (b) are contrary to each other.

However, many of the wastewater treatment plants are predominantly run in constant flux mode and fouling is later on noticed by tracking the transmembrane pressure difference with time. First operational nuisance in MBR systems are slow and piecemeal increment in TMP which are also called the early symptoms of the operation. Convenient cleaning methods have been applied to the MBR operation and sudden growth in transmembrane pressure is going to be seen.

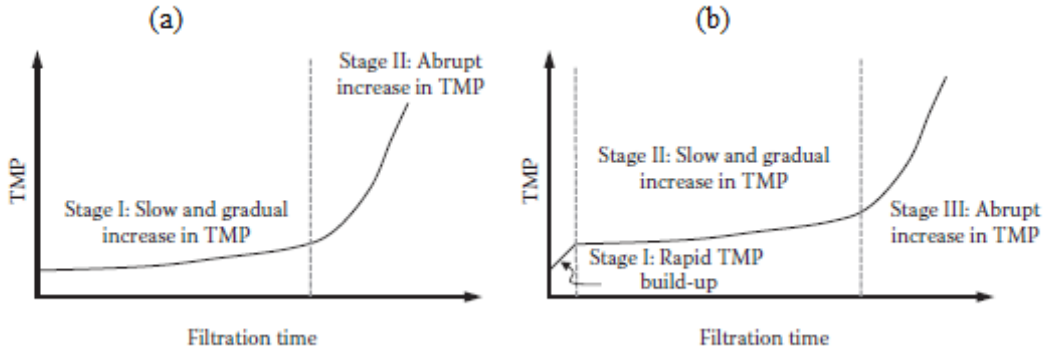


Figure 2.31 Sudden TPM increase contrived in MBR processes: (a) two phase of TMP change and (b) three stage of TMP change [32].

Figure 2.31.a represents the two different process of gradual TMP increment and sudden change of the TMP. These types of sudden changes are generally called two-phase of TMP step-up. The elapsed time to the broken point of gradual line is dependent to the cleaning strategy and how actually this strategy is set up. Favorable cleaning methods can extend the time of sudden change moments in TMP and also increase the time of occupancy of membrane.

Figure 2.31.b shows the sudden changes in three steps. In the beginning of the MBR process, little and swift TMP increments are generally controlled. That type of changes mentioned above can occur due to the swift plunge of the membrane and membrane pores by sludge grains, concentration polarization, and compaction of the membrane becoming at matutinal phases of the filtration operation. The first sudden change in the TMP is once in a while veiled by the sequent second stage increment. Therefore, three phased sudden TMP change can be seen as two staged TMP profile. In this context, residuary second and third phases becomes identical with contrivance referred before.

Slow and piecemeal increment in TMP is seen at the second phase of the TMP accrue because of the storage of microbial flocs and particles over the surface of the membrane, in fact first phase of plunge is the passive coherence of solvated substances to the membrane surface and walls of the pores. Swift TMP increase at the last phase, regarding the third phase, is recognized to be related with a deduction in porosity ascending from pressurization which is seen through the duration of the process on the cake layer in tandem with enhanced components of EPSs internal to the cake layer.

2.8.1 Fouling Rate

The rate of fouling is a term used as a principle for the membrane fouling and generally it is mentioned as a membrane fouling criteria. There are four sequential phases can be identified during the process of fouling. Those are:

1. Plugging of the tiny pores
2. Coverage of the bigger pores' internal facet
3. Overthrust of small particles and straight-forward plugging of the bigger pores
4. Formation of the cake layer

While every individual step is not easily defined or identified the amount, confirming the total fouling tendency is usually tested instead of describing each fouling step.

The easiest way to have an insight into the fouling propensity is to express the fouling rate.

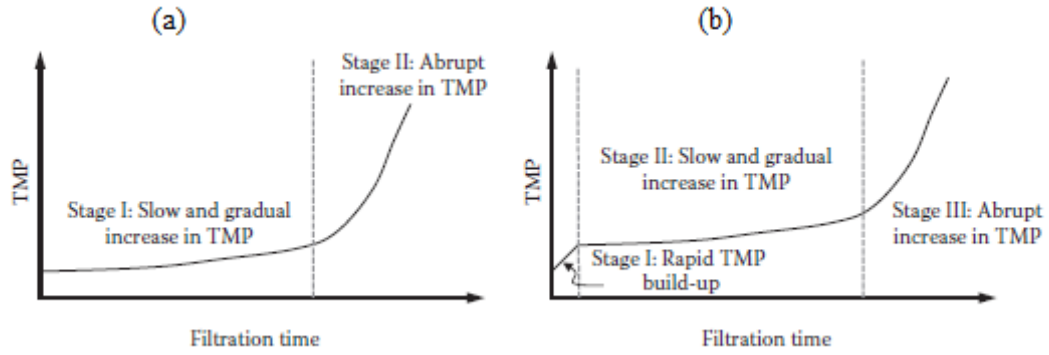


Figure 2.32 Typical TMP increment template (a) and fouling rate as a function of flux (b) [32].

According to the Figure 2.32a, the derived format of the TMP grow at a significant time (dTMP/dt for example) is the usually used term to present the rate of fouling. However, the unit, which will be used for the derived pressure process, ought to be kPa/h or psi/h. In terms of making calculation for the resistance of fouling, which is called as capital letter 'R', instead of TMP could be utilized to express the fouling disposition at a significant time. In this circumstance, fouling rate unit should be m-1 h-1.

Nonetheless, the rate of fouling is dependent on flux rate of the operation that has been shown in Figure 2.32b. If the flux rate of operation is high, faster fouling rate can be seen. As operating flux rises gradually from J4 to J1, the rate of fouling steps up until the turning point flux, $J_{critical}$, that is known as the critical flux. The rate of fouling goes

up suddenly further the mentioned critical flux which is known for supracritical flux zone. Typical critical flux values are generally between 10 – 40 LMH and makes critical flux value differentiated from sub and supracritical area in MBR plants for domestic wastewater refinement. If the bioreactor plants refine industrial wastewater or the other highly variable influent feed water stream, the critical flux might differ because of the types of influent operated inside of the reactor.

2.8.2 Classification of Fouling

Membrane fouling process cannot be explained by a sole procedure and the fouling process itself is difficult to fully understand. Different kinds of calssification of membrane fouling in bioreactor systems have been made by researchers, but fouling phenomena have not been explained yet fully. However, fouling of the membrane in bioreactor mechanisms can be graded into severe predicament according to what kinds of classification measurements have been employed and convenient for the application.

Table 2.11 represents the ordination of the membrane fouling in bioreactors. The most elementary and simplest method to categorize fouling is to pay regard to reversibility of the flux just right after an ordinary cleaning process. Therefore, the fouling operation is severed into three categories as; reversible, irreversible, and irrecoverable fouling. Depending upon the second criteria, where actually fouling problem happens, fouling can be graded into the plugging, formation of the cake layer, and interior pore plugging.

Table 2.11 Classification of the membrane fouling in MBRs [32].

Criteria Classifying Fouling	*Fouling Phenomena*	*Description*
Flux recovery after cleaning	Reversible fouling	Flux is recovered after simple or chemical cleaning.
	Irreversible fouling	Flux is not recovered by any kind of cleaning.
	Recoverable fouling	Flux is recovered after simple cleaning such as backwashing or relaxation.
	Irrecoverable fouling	Flux is recovered only by chemical cleaning.
Places of fouling occurrence	Clogging	Sludge accumulation between hollow fibers and flat sheet membrane channels inside the module.
	Cake layer deposition	Sludge deposition on the membrane surface.
	Internal pore fouling	Adsorption of solutes smaller than the pores to the membrane pore walls.
Solids deposition pattern	Cake layer formation	Vertical buildup of layer on the membrane surface.
	Pore narrowing	Narrowed pore size due to the accumulation of solutes inside pore walls.
	Pore blocking (or plugging)	Particle blockage of the entrance of pores or pore walls.
Solute fouling	Concentration polarization	Concentration gradient of solutes near the membrane surface.
Solute fouling	Concentration polarization	Concentration gradient of solutes near the membrane surface.
	Gel layer formation	Consolidation of the initially adhered solutes (as well as solids) on the membrane surface.
Nonfouling	Compaction	Compression of membrane structure by the applied pressure.

However, plugging of the membrane or the blockage of the membrane channels as well, virulently amassed suspended solids inside of the mixed liquor is not classified as membrane fouling because it happens outer surface/layer of the membrane.

Therefore, it reduces the membrane performance and makes the membrane worse so it is quite usual to strive together with the fouling. The algorithm of the solid formation is the last criteria. Composition of the cake layer, reduction at the diameter of the pore size or pore straitening, and pore blocking go in for this fouling classification. Even though

compaction of the membrane is not graded as a type of fouling, it degrades the filtration performance of the membrane like plugging.

2.8.3 Reversible versus Irreversible and Recoverable versus Irrecoverable Fouling

Conventionally, ordination of the membrane fouling into reversible and irreversible is communal and it is even simple. Reversible and irreversible membrane fouling classification is based upon the aptitude of flux recovery later on traditional cleaning processes. The meaning of reversible fouling is that the flux is recovered after an ordinary cleaning method like; backwashing, relaxation with the usage of the pressure, and air expurgating but it should be known that when the irrecoverable fouling happened the flux is recovered solely after certain chemical cleaning. In other perspective, flux cannot be saved by employment of any kind of cleaning method (Figure 2.33).

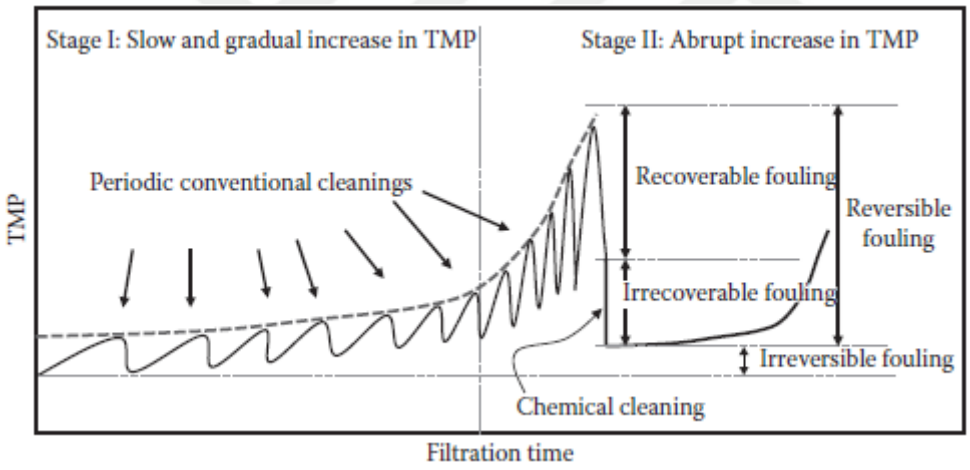


Figure 2.33 TMP profile in compliance with the fouling classification.

The following equation below for fouling phenomena can be denoted as:

$$Total\ fouling = reversible\ fouling + irreversible\ fouling \quad (2.5)$$
$$= recoverable\ fouling + irrecoverable\ fouling + irreversible\ fouling$$

When the membrane filtration operation begins, TMP also starts to increase until the end of stage I where later on the line rapidly scrambles up. Cleaning in apple-pie order, characteristically backflushing, keeps the TMP as low as doable. By employment of ordinary cleaning method, recoverable fouling can be easily restored, for instance; backwashing or air expurgating, during this period. Gel layer, which has been unified at

the interface between surface of the membrane and the formation of the cake layer alongside from the powerful adherence to the surface of solutes to the pores and/or pore walls, can stir up the irrecoverable fouling problem. Traditional cleaning methods are not conveniently capable for the gel layer and the absorber layer in the pores but they are needed to be removed by employment of the chemical cleaning. At the initial phase of the Figure 2.33, irreversible fouling is comparatively smaller than reversible fouling but subsequent frame of the process, piecemeal increment is going to be seen.

Membrane pressure greatly increases at the beginning of second phase and swiftly arrives to the maximum potential. Fouling has taken place throughout this period that is quite short as compared to the first phase, which is usually reversible fouling. If some specific chemicals are used as an oxidizing agent, e.g. sodium hypochlorite, in terms of chemical cleaning approach, the TMP will be diminished yet. There are different types of membrane fouling patterns which are represented in Figure 2.34. Proportion of reversible fouling to total fouling, a/(a+b) is not identical for the two diverse types although the total volume of fouling (a+b) is at the same ratio.

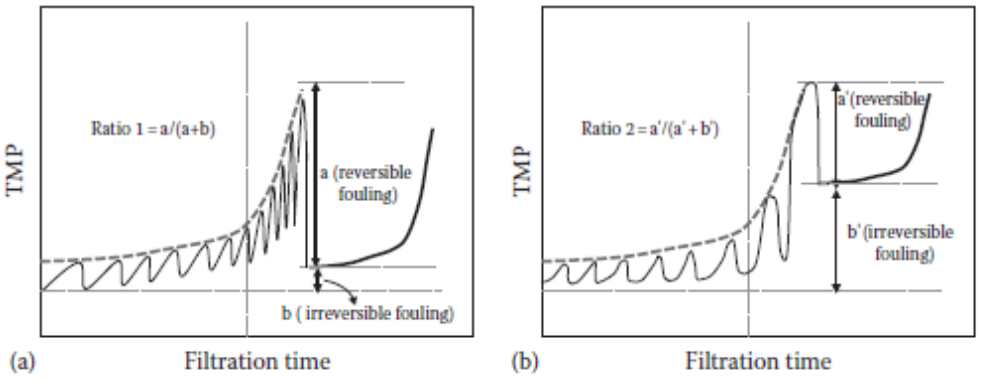


Figure 2.34 TMP profile in compliance with the fouling classification: Dominant reversible fouling (a) and big irreversible fouling [32].

Regarding to the Figure 2.34, it is obvious that the Ratio 1 is greater than ratio 2. That means reversible fouling is further savant in Fugure 2.34a contrasted with b. This proportion is dependent on how devoutly and/or usual practice backwashing have been proceeded before employment of chemical cleaning method and what type of chemical cleaning procedure is used. More compact and steady backwashing method before chemical cleaning operation is going to end up in higher ratios.

2.8.4 Classification of Fouling by Location of Fouling

Membrane fouling can be categorized according to the place where actually fouling come off which is actually another criterion for fouling problem, for instance: clogging, formation of the cake layer, and fouling of the internal pores. Outer space of the membrane batch is the place where actually clogging takes place and mostly between the channels of the membrane. As it is known, formation of the cake layer arise from the membrane surface and cake formation itself makes contribution to the most essential fouling, however, pore fouling at internal environment comes along inside the membrane.

2.8.4.1 Clogging

Rubble, small substances and sludge flocs, which are in the bulk solution, can migrate with relative ease and pile up to the gaps in the HF or FS membrane types inboard of a membrane module. In this way, flow of the water to the surface of the membrane is seriously plugged.

Clogging is primarily due because of the lack of efficient treatment of SSs and debris inside of the mixed liquor. Defectively formed membrane modules or membranes integrated inside of the cassettes can also give opportunity for clogging. However, if there is no clogging, the configuration of the membrane module is appropriately planned to sustain convenient flow from the bulk solution to the surface of the membrane and accrued solid substances. Nonetheless, accumulated colloidal particles, sludge and other small constituents are possible to accumulate inside of the membrane module. Clogging ought not to be categorized under the fouling title, but it apparently leads to identical results, for instance: the flux degradation or membrane pressure formation just like other fouling problems.

2.8.4.2 Cake Layer

Generation of the cake layer on the surface of the membrane has been recognized to be a dominant fouling process in bioreactor systems on no account of membrane kind, characteristic property of the wastewater, and the operational states. Suspended solids and mixed liquor in the aeration reservoir commence to precipitate on the surface of the membrane from the beginning of decantation because of the convective stream from the collective solution, which is also known as bulk solution, to the membrane. Coarseness

of the cake layer on membrane surface area grows at the beginning of the cake formation. Later on, the larger-sized aeration bubbles do not permit the cake layer to build up further. Cake layer coarseness can diverse from several to hundreds of micrometers, and primarily it is depending upon the membrane applied air stress (pressure) and aeration density. Usually, thickness of the cake layer could cause high cake resistance. Notwithstanding, coarseness of the cake layer is not the only component discriminating membrane filtration ability.

For instance, resistance of the cake (R_c), which is intimately concerned with the ability of membrane filtration, is a function of the specific cake resistance (α) of a cake layer and the heaviness of the biomass (M) on the membrane surface:

$$R_c = \frac{\alpha.m}{A_m} \tag{2.6}$$

In this context,

α represents particular cake resistance of the biofilm, m/kg
m typifies the mass of the biofilm, kg
$\mathbf{A}_m$ is the membrane area, m^2

As to Carmen-Kozeny equation, particular cake resistance of the cake layer is determined both particle extent, for instance microbial flocs, and the porosity and it can be formulated as:

$$\propto = \frac{180(1-\varepsilon)}{\rho_p d_p^2 \varepsilon^3} \tag{2.7}$$

In this regard,

ε is the cake layer porosity
ρ_p is the particle density, kg/m3
$\mathbf{d_p}$ is the diameter of the particle, m

It is typically known that density of the activated sludge in most of the wastewater treatment plants does not indicate remarkable changes and the most dominant effect influencing the particular cake resistance is literally size of the particles and the porosity itself. However, the ability of the filtration of a coarse cake would be larger than that of a slim cake if the latter consists of qualified and tiny particles than the predecessor.

2.8.4.3 Internal Pore Fouling

Dissolved solute constituents and particulate adsorption of good quality to interior pore walls manage interior fouling. From the early phase of filtration, adhesion happens when dissolved substance and small colloidal particles in mixed liquor start to stick to the pore entry and membrane pore walls, straitening the diameter of the pore. Later on, adequate cake formation on the surface of the membrane, the dissolved matter and small good quality of particulates are tent to link favorably to the adhesive cake layer primary to start delivered to the membrane walls, however it is named cohesion. In general, the dominant fouling opposition is the cake layer resistance which has been formulated as (R_c) instead of the interior fouling (R_f). A few to ten of times greater cake resistance compared to interior fouling was reported in most of situations of bioreactor systems.

2.8.5 Factors Affecting Membrane Fouling

Even though it is quite hart to build up a general order about the fouling of the membrane in bioreactor systems, the nature and drive of fouling are stiffly affected by three factors, which has been represented in Figure 2.35.

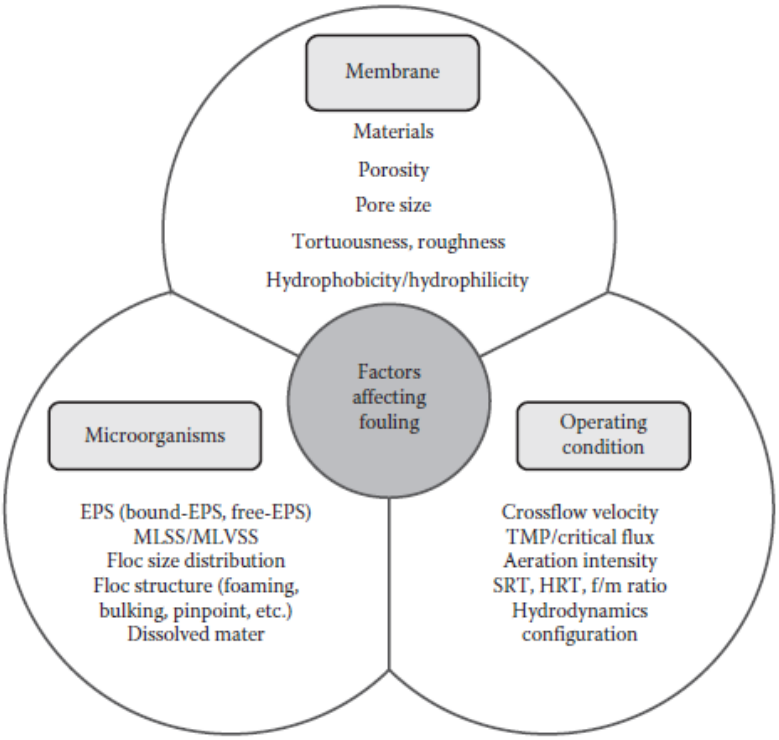


Figure 2.35 Factors influencing the membrane fouling in bioreactor systems [32].

Singular fouling affects the fouling of the membrane individually and/or reciprocatively. They affect each other which have been represented in figure. For instance, significant operating circumstance like hydraulic retention time (HRT) and SRT affect fouling of the membrane straightly. They influence the microbial property contemporaneously for instance EPS make-up or concentration of the MLSS, which are essential factors supervising the fouling of the membrane.

2.8.5.1 SMP/EPS

EPSs are synthesized by microbial organisms as a mucous-like constituent and well-known molecule due to its high weight. They have critical role in the formation of floc generation and contain nonhomogenous polymeric matters encapsuling DNA and RNA in a small portion and proteins, polysaccharides, lipids and humic acid in a large portion. Some of these materials have a critical role in the membrane fouling. EPSs are water-rich and they are substantial components for the flow of effluent throughout the operation. Accumulation of SMP molecules also causes increment in TMP through the infiltration process. When the concentration of SMP increased, it also raises the fouling rate due to the existence of proteins, polysaccharides etc.

However, bound EPS molecules inside of the flocs exist in accumulated solution in a soluble state. Pores can be blocked because of the foulant material's stopper activity which also cause internal fouling problem in the case of pore narrowing. This situation can be avoided when the selection of membrane or support material has been made properly. Dominant infiltration opposition has leant on to the cake formation over the surface of the membrane. As a basis of the process, bound EPS molecules closely keep the internal construction of the cake layer and plays important role for the flow of permeate through the membrane surface. For this reason, bound EPSs are one of the most accentuated molecules in MBR systems.

CHAPTER 3

MATERIALS AND METHODS

3.1 Membrane Bioreactors

Within the scope of the work, two different membrane modules were performed and one lab-scale aerobic membrane bioreactor (AeMBR) tank was designed and operated at three different operatonal conditions. Operational details will be given in the following sections.

The aerobic membrane bioreactor was made of plexiglass material with the dimentions of 8x14x38 cm. According to this, reactor total volume is 3 L. However, reactor was operated with the active volume of 2.5 L.



Figure 3.1 Reactor setup and instruments before the operation.

It was covered with an aluminum foil to protect from external disturbances like flies and dust. Water level sensor was mounted to the interior region of the reactor and marked for the level of active volume verge. Feed and effluent port, aeration ports were drilled to the top of the reactor. Reactor was fully mixed with the impact of the aeration pipes lies down at the bottom. Suspended solids concentration was stabilized at 4000 mg/L. Reactor instruments and reactor configuration has been represented at Figure 3.1.

Membranes are exposed to the air for scouring and applying physical cleaning and skinning the sludge over the surface of the membrane. Some of the qualities like pH, temperature, turbidity, ORP, electrical conductivity, were measured manually and noted transiently. Therefore, temperature changes in the system was manually controlled each day and chemical and/or physical cleaning process were applied when it reached to specific limits. Operational image of the reactor has been represented at Figure 3.2.

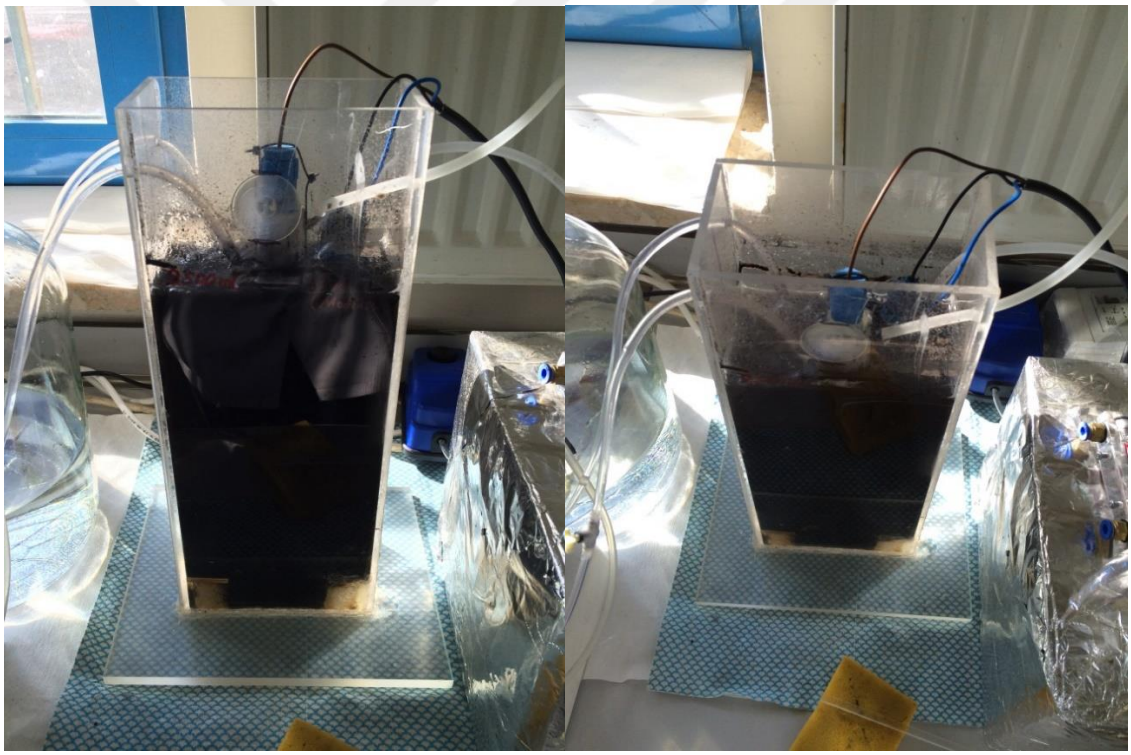


Figure 3.2 Reactor image during ther operational process.

3.2 Reactor Setup and Operation

Discontinously operated AeMBR system was filled with the sludge taken from İstanbul Ambarlı İleri Biyolojik Atıksu Arıtma Tesisi and initial bacterial concentration inside of the tank was 4000 mg/L.

Inside of the tank, two different membrane types, non-woven flat-sheet and 0.45 μm pore size polyethersulfone (PES) microfiltration membrane were employed for the operation and double-sided support layer was utilized for the membrane stableness. Each membrane module, made of 12x12 cm plexiglas, was volume of 217 ml and active surface area was adjusted to 7.5x7.5 cm. Figure 3.3 represents the membrane modules.

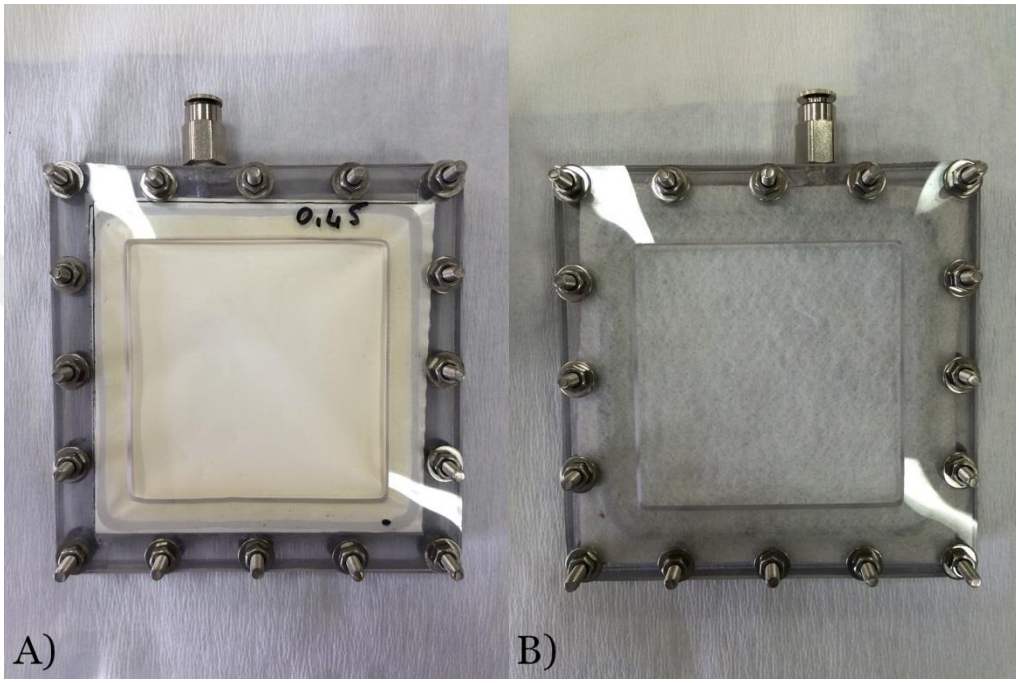


Figure 3.3 0.45 μm membrane (A) and non-woven support layer (B).

MBR system was operated at 11.11 LMH flux and 10 LMH net flux. SADm value and membrane suction pumps' flow rate was 1 Nm^3 (air)/m^2.hour and 2.08 ml/minute, respectively. Membranes were operated 4.5 min. and kept 0.5 min rest. When the membrane pressure reached over 250 mbar pressure, dynamic membrane and real module was subjected to physical cleaning process.

Every day, air backwash operation implemented to the dynamic membrane (22.5 L (air)/hr) to reduce plugging. It was noticed that physical cleaning and air backwash pressure values were at desired level, in terms of transmembrane pressure (TMP). Figure 3.4 represents the schematic view of the MBR operation.

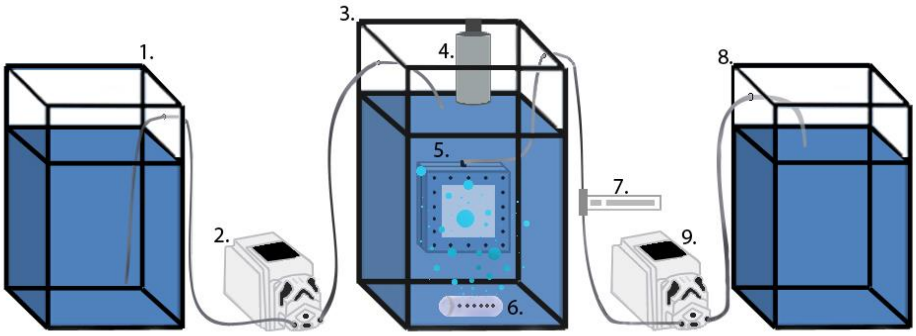


Figure 3.4 Schematic representation of MBR system. 1. Feed Tank, 2. Feed Pump, 3. Reactor, 4. Level Sensor, 5. Membrane Modules, 6. Air Diffuser, 7. Air Flow Regulator, 8. Permeate Tank, 9. Suction Pump

3.2.1 Synthetic Wastewater Characteristics and Operation Procedures

The feed water of the MBR system was synthetic wastewater and feed chamber was filled regularly as 7000 ml every day. Chemicals of synthetic wastewater were represented at Table 3.1 and sucked permeate accumulated into two different tanks. Established AeMBR was operated with infinite sludge retention time and throughout its operation no kind of sludge elimination process was employed.

However, pumps were adjusted 4.5 minutes of suction pressure so as to apply 30 seconds rest. This is one of the methodologies widely used to prevent fouling. To prevent clogging, non-woven dynamic membrane was employed for daily backwash operation for a minute and 0.45 μm pore size membrane was not employed for the same operation.

Table 3.1 Synthetic Wastewater Content.

Chemicals	Concentrations(mg/L)
$C_6H_{12}O_6.H_20$	500
$NaHCO_3$	2754
NH_4Cl	230
K_2HPO_4	37
KH_2PO_4	67
$MnSO_4.H_2O$	0.4289
$ZnSO_4.7H_2O$	0.1053
$NaSO_3$	0.2811
$CuSO_4.5H_2O$	0.0556
$FeSO_4.7H_2O$	5.92
$NiSO_4.6H_2O$	0.1
$CoCl.6H_2O$	1

Throughout the experiment, three different operational LMH changes employed. At the first stage of the experimental work, flux was set to 10 LMH and different analytical methods were applied to represent the qualities of the wastewater and the process. Theoretically, no sludge was discharged from the reactor, meaning the reactor is operated at infinite SRT. Daily and weekly experimental work and the amount of sludge taken from the reactor as a result of the repetition of these studies compensates the SRT period of this study. Therefore, the reactor was maintained for 30 days until the stabilization stage was reached, and after the waiting period, experimental work was started to take place.

At the second period of the study, flux was set to the 15 LMH and at the final, third period, it was set to 20 LMH and instrumental analysis were made to obtain information about the characterictis of the sludge and operational work. Experimental periods listed in Table 3.2.

Table 3.2 Planned operation of the AeMBR system.

AeMBR Operational Conditions			
Periods	**Days**	**COD (mg/L)**	**Flux (L/m^2.hour)**
I	0-45	500±25	10±0,5
II	46-91	500±25	15±0,5
III	92-137	500±25	20±0,5

3.2.2 Membrane Plugging and Cleaning

Throughout the membrane operations, vacuum impact was applied and stable flux suction and correspondingly pressure change observation principal was employed. In this context, during the vacuum, TMP machine was used and the data were noted. For each period of the experimental work, membrane pressure was controlled manually with a manometer daily and when the pressure reached to the 300-350 mbar ,whihc means membrane was found barely plugged with the bacterias and the other organisms, physical and chemical cleaning operations were employed.

For the first period, through 10 days, real membrane exposed to the physical cleaning and after 10 days it was exposed to chemical cleaning. For about dynamic membrane, it was tried to apply physical cleaning but membrane itself directly plugged with the sludge over the surface of the membrane. Therefore, chemical cleaning operation

directly employed for the clenaning. At the end of the period, new membrane materials were put to the modules.

Second period of the experiment, since the LMH increased to 15, more physical cleaning processes were made for the real membrane due to the speed of suction by membrane modules. When the pressure increased physical cleaning was seen as not efficient, chemical cleaning was used to clean the membrane. On the other hand, at the second period of the experiment, dynamic membrane were not exposed to the physical cleaning. When the pressure increased, the cake layer over the membrane surface skinned and washed with the tap water. The bacteria excreted from the operation were reused and dynamic membrane module was put to the chemical clenaning tank. At the end of the period, new membrane materials were put to the modules.

At the third period of the operation, flux increased to 20 LMH and plugging occurred much more often for both dynamic and 0.45 μm membrane. Since physical washing process could be employed for the real membrane, it still could not be employed for the dynamic membrane. Due to the increased amount of permeate and pressure, it was barely found difficult to manage and operate the dynamic membrane.

Physical cleaning was applied to remove the surface contamination by rubbing the surface of the membrane with the sponge slowly under the tap water. In this cleaning, only the cake / gel layer was cleaned from the membrane surface, trying to reduce the pressure generated in the membranes and to regain the flux.

Chemical cleaning was applied when the frequency of membrane occlusion was increased. In this cleaning, the membranes were first cleaned physically under the tap water as described above. The membrane was then allowed to stand for one hour in basic and acidic solutions, respectively. 300 mg / L NaOCl as a basic solution, tap water reduced to pH 2 with sulfuric acid as an acidic solution was used. Membranes deposited in the solutions were settled in the system after being immersed in tap water. The process represented at Figure 3.5.

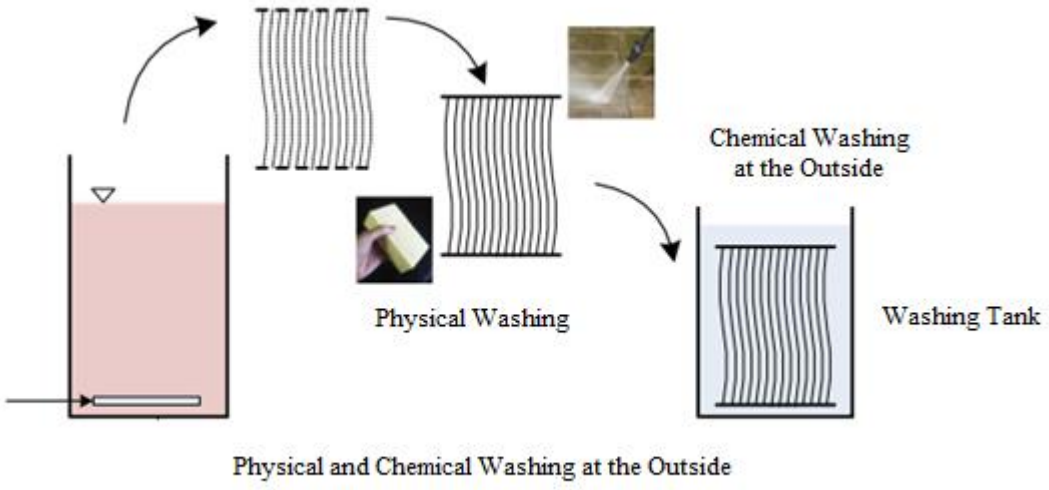


Figure 3.5 Physical and chemical methods employed for the membrane clenaning processes. (Wang et al, 2014).

3.2.3 Net Flux Calculations

Amount of water passing along the unit surface area of membrane per unit of time is simply called flux, J. In this context, flux can be formulated as;

$$Flux = \frac{Flow}{Area} \qquad J = \frac{Q}{A} = \frac{Volume}{Time\ x\ Area} \tag{3.1}$$

MBR system was operated in 5 minutes periods, as 4.5 min. working and 0.5 min. rest. Net flux is represented with the following formula;

$$Net\ flux = flux \times \frac{running\ time}{waiting\ time + running\ time} = 11{,}11 \times \frac{4{,}5\ min.}{(0{,}5+4{,}5)\ min.}$$

$$\cong 10\ LMH \tag{3.2}$$

3.2.4 Surface area, Flow and SADm Calculations

Dimensions of the membrane were 7.5cmx7.5cm. Active surface area calculation is presented with an equation below;

$$Active\ surface\ area = 7{,}5\ cm\ \times 7{,}5\ cm \times 2(membrane\ modules), = 0{,}01125 m^2$$

Flow, can be calculated by multiplying the flux and membrane surface area. Active surface area and flux are calculated as 0.01125 m^2 and 11.11 LMH (L/m^2.saat), respectively. Flow is calculated by the following equation [3];

$$Flow = 11{,}11 \frac{L}{m^2.hour} \times 0{,}01125\ m^2 = 0{,}125\ L/hour \quad (3.3)$$

Volume of permeate which should be evacuated from the operation and volume of flow that should be sucked by the pumps were computed via following balance, respectively;

$$Permeate = 0{,}125 * 24 = 3000\ L$$

(3.4)

$$Flow = \frac{Volume}{Time} = \frac{3000\ L}{1440\ min.} = 2{,}083 \cong 2{,}08\ ml/minute \quad (3.5)$$

System was operated under 1 Nm^3xhr/m^2 SADm value and required oxygen amount is calculated as;

$$SADm = \frac{Q(air)}{Area} \qquad SADm = \frac{Nm^3/hr}{m^2} 1 = \frac{Nm^3(air)}{0.1125 \times 1hr} \quad (3.6)$$

Amount of air for a membrane module calculated as 11.25 L/hour. In our system, two membrane modules were operated, so total amount of air for the reactor was calculated as 22.5 L/hour.

3.3 Analytic Methods

COD Analysis

COD is one of the most important parameter in determining the degree of organic pollution in wastewaters.

In the work done, the COD experiment was carried out from the inlet feed line and the 0.45 μm membrane and the sample from the outlet line of the non-woven dynamic membrane. The samples taken from the inlet feed line were diluted 2-fold and the effluent drained from the membranes was used in the experiment without dilution. Therefore, COD analyzes were carried out using the micro-digestion and titration method specified in the standard methods [124].

Four COD test tubes were reserved for the experiment. For the blank, 2.5 ml of pure water was taken, 2.5 ml of samples were taken from real and dynamic membrane filtrate water, 1.25 ml of synthetic feed wastewater was sampled and diluted 2-fold with 1.25 ml of purified water. These are placed in four COD tubes. 1.5 ml of potassium dichromate solution and 3.5 ml of silver sulphuric acid solution shown in Figure 3.7

were added and the tubes were sealed. The thermoreactor was placed at 150C for 120 minutes. A WTW CR 3200 thermoreactor is used and is shown in Figure 3.6.

After 2 hours, the tubes were removed from the thermoreactor and allowed to cool. For titration, the beaker is placed on the mixer shown in Figure 3.6 and the magnet is thrown in it. The COD tubes are poured into the beaker respectively and the inside of the tubes are washed with pure water and this is poured into the beaker. Subsequently, 2 drops of ferroin indicator were added to the mixture while stirring the beaker on the one hand. It was then titrated with FAS solution and the consumptions were noted.



Figure 3.6 WTW CR 3200 Thermoreactor and WiseStir MSH-20A Magnetic Stirrer.

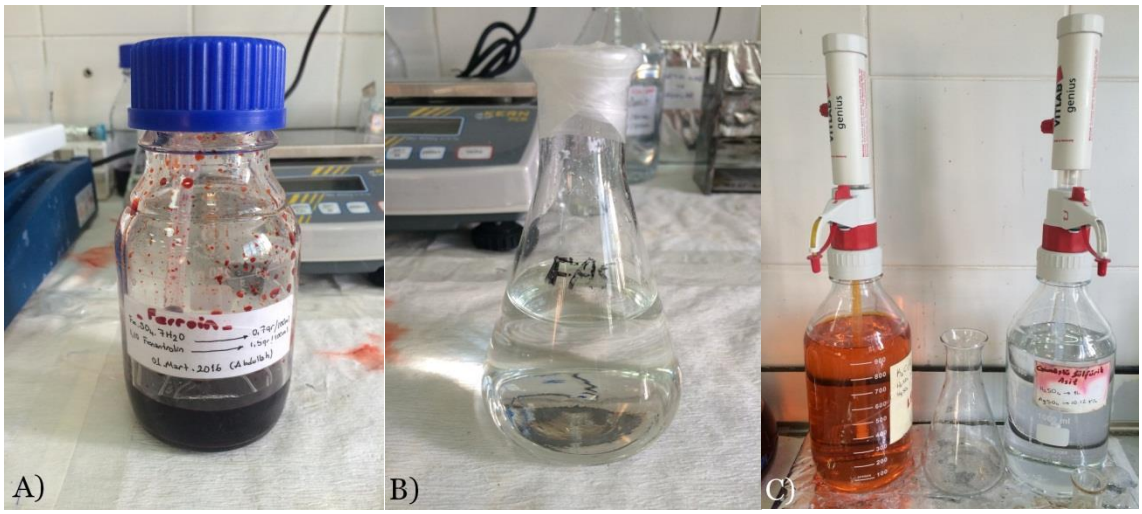


Figure 3.7 Ferroin (A), FAS solution (B), Potassium dichromate ve Silver Sulfuric Acid solutions (C).

MLSS, Electrical Conductivity (EC), pH and Oxydation/Reduction Potential (ORP) Measurements

Throughout the analysis, pH, EC, ORP and temperature parameters were daily measured with the instrument HACH HQ40D Multimeter.

Turbidity Analysis

Turbidity is primarily esthetic in importance. Suspended solids and dissolved organic matter in the water cause blur. Turbidity unit is NTU in nephelometric turbidimeters. The WTW TURB 550IR turbidimeter device shown in Figure 3.8 is used for turbidity measurement in operation.

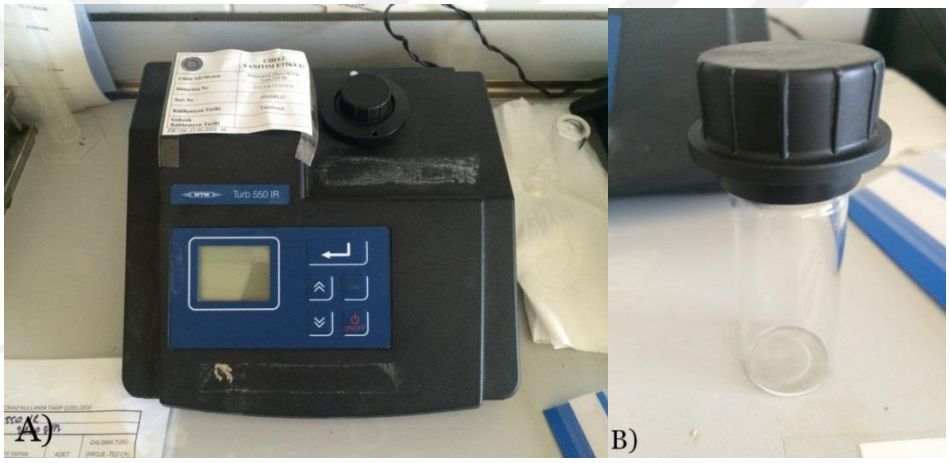


Figure 3.8 WTW Model TURB 550IR turbidymeter instrument (A), 25 ml glass tube for the samples (B).

The samples going to performed were taken from the 0.45 μm membrane and non-woven dynamic membrane as 35 ml into the 50 ml falcon tube without making dilution.

Before using the turbidimeter, the glass tubes with standard solutions of 1000 NTU, 10 NTU and 0.02 NTU shown in Figure 3.9 were thoroughly cleaned with glass cloth and placed in the device, respectively, and the device was calibrated. The glass tube used for the specimens of the turbidimeter shown in Figure 3.8 was first cleaned by rinsing with soap and rinsing with pure water. After that, the sample was shaken twice with water to make the measurement ready. The sample was filled with 25 ml glass tube. The glass tube was thoroughly cleaned with a glass cloth and then shaken and placed in the measuring device. The values read for both samples are noted.



Figure 3.9 Standard solutions fort the turbidity (C and D).

TMP Analysis

During the study, pressure measurements were made daily with the TMP meter. After the dynamic membrane pressure reached 300-400 mbar, physical or chemical wash was employed. The increase in pressure indicates that the membrane fouling is taking place. All pressure measurements were performed with a programmable digital manometer (KELLER-Leo record, Switzerland) and InstallerLogger5 software. Digital manometer is represented at Figure 3.10.



Figure 3.10 TMP measurement instrument.

Capilary Suction Time Analysis

The CST is used to determine the sludge characterization, and the water that separates from the mud is once timed to take a 1 cm path on a membrane with a capillary gap. In the studies, the capillary suction time was determined using the CST device to determine the sludge filtration properties and the relationship between the clogging and the capillary suction time. As shown in Figure 3.11, the Triton 304M capillary suction

time device is used. In aerobic systems, as shown in Figure 3.12, a long tub is used. The experiment is carried out using mixture samples as shown in Figure 2.15.



Figure 3.11 Triton brand CST instrument.

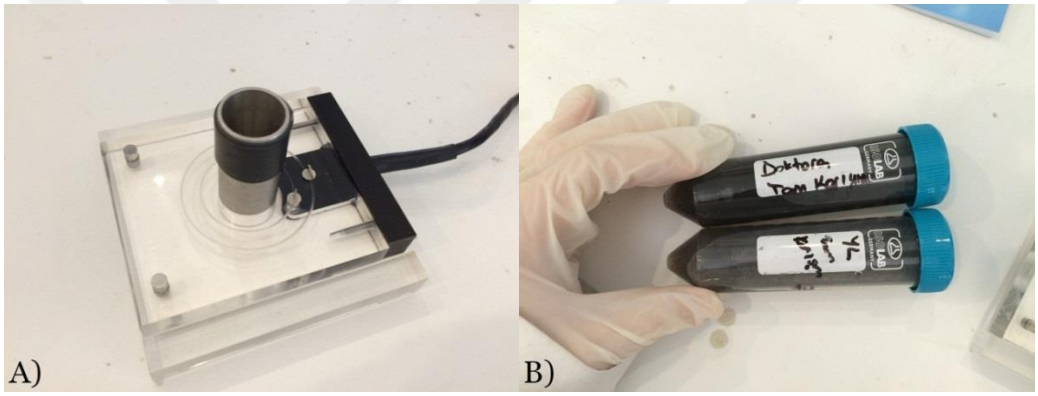


Figure 3.12 Long bathtub for aerobic mud of CST (A) and complete mixture samples used in the experiment (B).

SMP and EPS Analysis

The SMP was determined by looking at the protein and carbohydrate in the filtrate samples obtained from the filtration of the reactor sample and the filtration of the in-reactor sample and filtrate from the supernatant after 10 minutes of centrifugation at 4000 rpm. For EPS analysis, the samples from the reactor were centrifuged and the EPS in the biomass was extracted. EPS extractions were done by heating as described in Judd [37]. Protein and carbohydrate were measured in the obtained extract and expressed as EPS, protein and carbohydrate concentration. Protein and carbohydrate analyzes were performed using Bradford [125] and Dubois [126] methods, respectively.

SRF and SF Analysis

Specific Resistance to Filtration (SRF) and Supernatant Filterability (SF) analyzes were conducted to obtain more detailed information on the filterability of the sludge and sludge resistance over the membrane. In the scope of the analysis, 100 ml of sludge was taken from the reactor. This sludge was poured onto a 0.45 µm membrane placed on the bottom of the Sterlitech brand (P / N HP4750) dead-end mechanism, and then the valves of the nitrogen (99.95% Pure) tube were opened. When the filtration process was carried out, the effluent was weighed by AND EK-3000i brand weighing. The weighing instrument was integrated to computer with the RsMulti Ver1.10W software. The measurement results were recorded simultaneously by the program. Figure 3.14 represents the dead-end mechanism and the nitrogen tube.

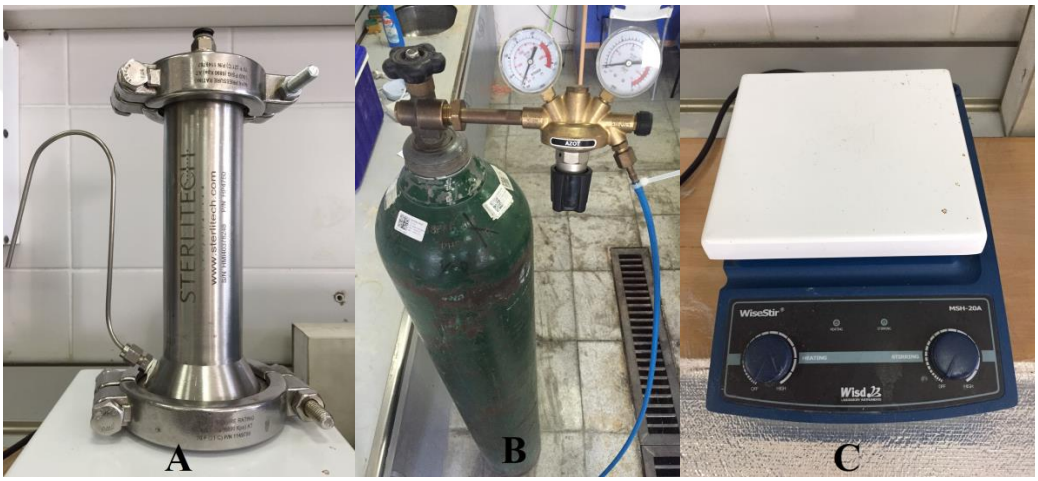


Figure 3.13 The dead-end mechanism (A), the nitrogen tube used in the experiment (B) and the magnetic stirrer (C).

For SF analysis, 0.22 micron membrane was used. 110 ml slurry was withdrawn from the reactor and centrifuged for 10 min at 4000 rpm using a Hettich Rotofix32A centrifuge. The supernatant part is poured into the dead-end system. The magnetic stirrer is thrown into the dead-end system and the lid is closed. The filtration process was started and the results were recorded simultaneously by the same software. Figure 3.15 shows the other instruments and the computer software used during the experiment and 3.16 demonstrates the experimental scheme.



Figure 3.14 Weigh (A), Centrifuge device (B) and a capture from the software used for simultaneous data recording (C).

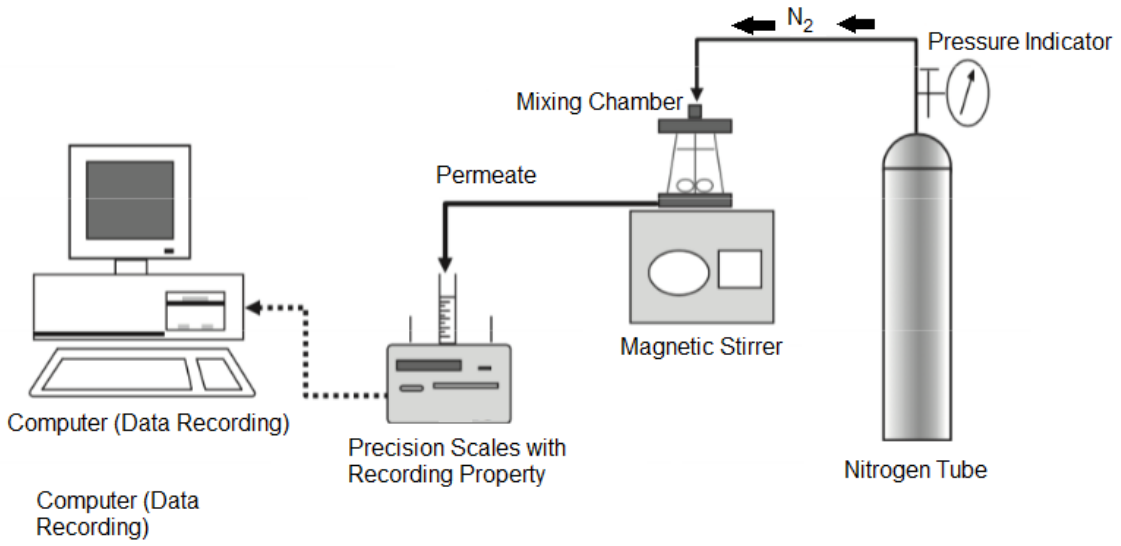


Figure 3.15 Schmatic representation of the SRF/SF operation.

Fourier Transformed Infrared Spectrophotometer- Attenuated total reflectance (ATR/FT-IR) Analyses

ATR-FTIR analyzes of contaminated and clean membranes, SMP and EPS produced in the reactors were also performed to determine the pollutants causing membrane contamination. For this purpose, the Thermo iS10 instrument in YTÜ Chemistry Faculty laboratory was used. The images of the FTIR device used for this purpose are presented in Figure 3.17. Analyses are done by the procedure made Zhu et al. [127]. Both liquid samples and membranes were dried at 50 °C for two days prior to FTIR assays. Subsequently, the obtained samples were pulverized by pouring in special air. The powder and KBr obtained were mixed in a weight ratio of 2: 100 and pelletized under pressure. Then, important functional groups were characterized using FTIR device.

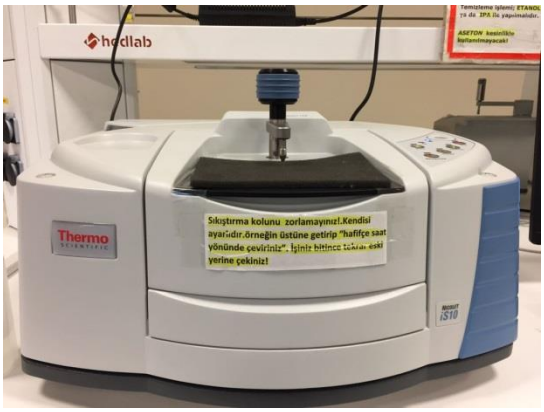


Figure 3.16 Thermo iS10 instrument used for GPC analysis.

Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS) Analyses

During the operation of the reactors, SEM and SEM-EDX analyzes were carried out on clean and dirty membranes in order to have more information about the contaminants on the membrane. Analyzes were made with service procurement at Gaziantep University – SEM Lab. Different angles were taken from both sides of the membrane as a sectional view. SEM images were taken using the SEM microscope JEOL 6390LV instrument after Au / Pd (gold-palladium) coating on the membranes. In addition to SEM, EDS analyzes were performed for both membrane types for the detection of inorganic contaminants in the cake layer.

Microbiological Analysis

Microbial species identification was consisted of determination of nucleic acid extraction, PCR (Polymerase Chain Reaction), DGGE (Denaturing Gradient Gel Electrophoresis). Received samples were prepared for use in molecular techniques. Nucleic acids were first extracted from the samples. Extracted DNAs were stored at -20 ° C. The 16S rRNA genes of the extracted DNA mixtures were amplified by Thermal Cycler using the PCR method. After this process microbial species diversity was detected by DGGE and DNA sequence analysis [128]. Therefore, PCR1 and PCR2 procedures were edit according to the procedure made by Lee et al. [129].

In molecular studies; PCR (Bio-Rad Mycycler Thermal Cycler System), Electrophoresis Device (SCIE PLUS), DGGE (Bio-Rad D-Code Universal Mutation Detection System) and Gel Imaging System (WiseDoc) was used.

DGGE studies will illuminate which bacterium species are responsible for the clogging of the mud or which bacterial species are dominant and occluded in the reactor periodically. It was consisted of determination of nucleic acid extraction, PCR (Polymerase Chain Reaction), DGGE (Denaturation Gradient Gel Electrophoresis). In the scope of the study, bacterial 16S rRNA genes was isolated with the PowerSoil DNA isolation Kit (Cat 12888-100, Lot PS11D19) MO BIO Laboratories Inc. CA, USA and stored at -20°C. After the centrifugation process, DNA extract was first run on the gel without making PCR just to be sure that there was enough DNA or there was a DNA at all. After the first run, DNA extract was amplified by Thermal Cycler using the PCR method (Bio-Rad Mycycler Thermal Cycler System). Table 3.3 shows the PCR1, PCR2/3 experimental procedures. (Forward and reverse primers concentration was 10 µM.)

Table 3.3 PCR1, PCR2 and PCR3 procedures.

PCR1		**PCR2**		**PCR3**	
Reagents	**Amount**	**Reagents**	**Amount**	**Reagents**	**Amount**
dH_2O	33,3 µL	dH_2O	32,8 µL	dH_2O	32,8 µL
10*Rxn. buffer	5 µL	10*Rxn. buffer	5 µL	10*Rxn. buffer	5 µL
dNTP	1 µL	dNTP	1 µL	dNTP	1 µL
F. primer (27F[a])	1 µL	F. primer (357F-GC[c])	1 µL	F. primer (PRB 357F[e])	1 µL
R. primer (1492r[b])	1 µL	R. primer (R518[d])	1 µL	R. primer (R518[d])	1 µL
Polymerase	1,2 µL	Polymerase	1,2 µL	Polymerase	1,2 µL
BSA	-	BSA	0,5 µL	BSA	0,5 µL
$MgCl_2$	1,5 µL	$MgCl_2$	1,5 µL	$MgCl_2$	1,5 µL
Extract	6 µL	PCR1 product	6 µL	DGGE product	6 µL
Total	50 µL	Total	50 µL	Total	50 µL

[a] 27F: 5'-AGAGTTTGATCCTGGCTCAG-3'
[b] 1492r: 5'-GGYTACCTTGTTACGACTT-3'
[c] 357F-GC:5'-CGCCCGCCGCGCGCGGCGGGCGGGGCGGGGGCACGGGGGGCCTAC GGGAGGCAGCAG-3'
[d] R518: 5'-ATTACCGCGGCTGCTGG-3'
[e] PRB 357F: 5'-CCTACGGGAGGCAGCAG-3'

The products obtained as a result of the PCR1 procedure were subjected to electrophoresis under a condition of 100 Volts and 1.5 hours on a 1% agarose gel (5 µL of sample mixed with 1 µL of dye). The product obtained from step 1 of PCR1 was subjected to the procedure in Table 3.4., which was progressed to step of PCR2, and the second step of electrophoresis was carried out with the obtained products of PCR2. In the second electrophoresis step the same procedure as in the first step (100 V - 1.5 hours - 1% agarose gel) was carried out.

Table 3.4 PCR cycles set during the operation.

PCR1				PCR2 – PCR3			
Procedure	**Temp.**	**Time**	**Cycle**	**Procedure**	**Temp.**	**Time**	**Cyle**
Initial denaturation	94°C	3 mn	1	Initial denaturation	94°C	3 mn	1
Denaturation	94°C	30 sc		Denaturation	94°C	30 sc	
Elongation	55°C	30 sc	30	Elongation	65°C*	30 sc	20
Extension	72°C	2 mn		Extension	72°C	45 sc	
Final extension	72°C	5 mn	1	Denaturation	94°C	30 sc	
Final	4°C	∞	1	Elongation	55°C	30 sc	10
				Extension	72°C	45 sc	
				Final extension	72°C	10 mn	1
				Final	4°C	∞	1

* The elongation temperature is reduced by 0.5 ° C in each cycle.

The species differences of the samples before the sequence analysis were determined by the DGGE technique. Different types can be confirmed by sequential analysis method. In this study, sequencing was not performed after DGGE. It has been attempted to analyze whether the bacterial species for different base lengths have changed during operation or whether they have been dominant over any other species. In this context, the type of dominance in the reactor can also be a major cause of the problem of fouling.

One high and one low denatured solution for DGGE should be prepared in 50 mL tubes. While preparing 20% APS, 0.1 g APS (ammonium persulfate) eppendorf tube is weighed, then 0.5 mL sterile Milli-Q (ultrapure water) is added and rinsed to dissolve. While preparing the gel, 5 µL TEMED is added to each of 16 mL denaturing solutions (high and low) and mixed. Then 50 µL of 20% APS to each denaturing solution is added and mixed. These solutions should be filled into DGGE glasses (sandwich) within 10 minutes. The prepared DGGE glasses are left to stand for 2 hours at 30 ° C. 3 mL of ultra pure distilled water is added to the casting gel to allow the gel to cool properly. After freezing, ultrapure water on the casting gel is first drained. When preparing the stacking gel, 1 mL of 40% acrylamide/bis, 100 µL of 50 × TAE, 3.9 mL sterile Milli-Q (ultrapure water) is added to the small falcon tube and mixed. 5 µL TEMED and 50 µL APS (20%) are added to this solution. 4-5 mL of this solution is added between DGGE bands (on top of Casting gel) with a pipette. The comb is placed into the gel so that the bubble is not left. The prepared DGGE glasses are left to stand for 30 minutes at 30 ° C. At the end of 30 minutes, the combs between the DGGE glasses are removed and the grooves of the skins are cleaned 3 times with the help of a syringe with 1xTAE.

Sample loading is done by mixing 25µL sample + 5 µL loading dye. The ladder is applied as 10 µL. During the operation 60 ° C - 60 V - 30 minutes and 60 ° C - 120 V - 4 or 20 hours (optimize). Staining is carried out by adding 10 µL of Sybr GOLD into 100 mL of 1 × TAE for gel processing. Dyeing is carried out for at least 30 minutes. For the incubation procedure, the bands cut from DGGE are placed in a 0.2 mL microcentrifuge tube. 20 µL of DNA-free water is added to each well. Incubated for 24 hours at 4 ° C. PCR2 is applied to the samples. Picture 3.18 represents the instruments used through the experiment.

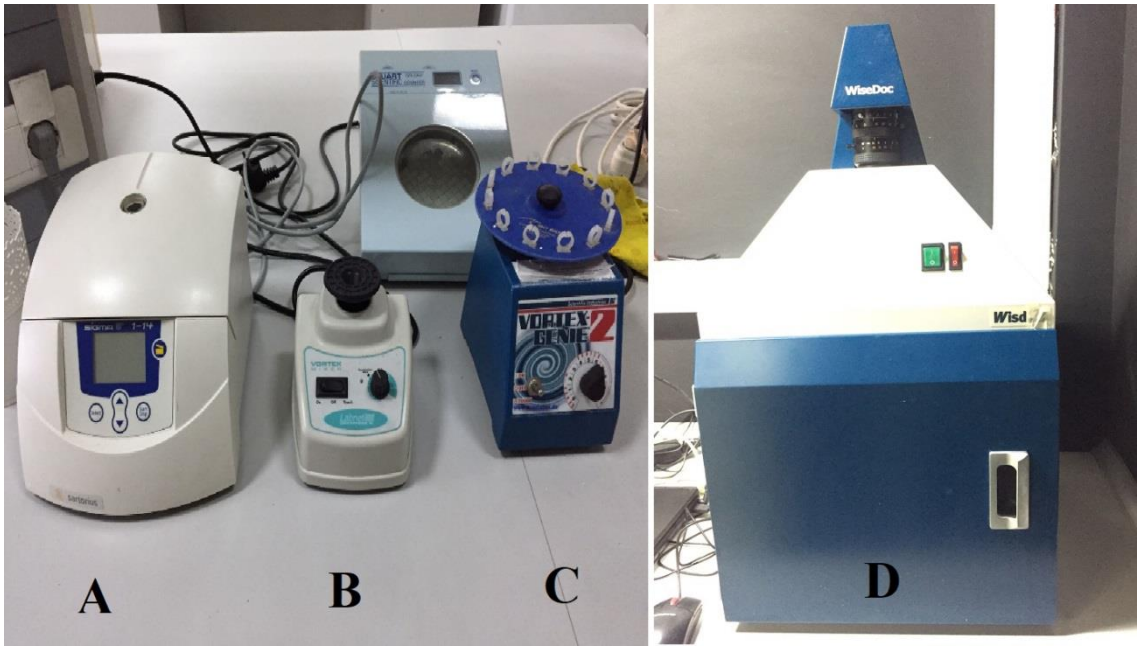


Figure 3.17 Instruments used during the DGGE experiment.. Micro-centrifuge (Sartorius Model:1-14)(A), Vortex (Labnet)(B), Horizontal centrifuge for DNA extraction (Vortex Genie 2, Scientific Industries)(C) and UV-Cab (Gel Documentation System, WGD30) (D).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Analytical Results

4.1.1 COD Experimental Results

The AeMBR system was fed with synthetic wastewater containing glucose in the first period as 500 mg/L COD as organic carbon source (Table 3.1 and Table 3.2). AeMBR showed rapid carbon reduction and, however, removal efficiencies ranging from 92% to 98% were obtained and the permeate COD values were generally observed at levels below 50 mg/L for 0.45 μm membrane and generally around or below 10 mg / L. However, non-woven dynamic membrane COD removal efficiency was found 50-100 mg/L, especially it was found around 100 at the final stage of the experimental period.

Each period lasted for 45 days and the reactor was operated at steady state for 30 days. After 30 days of steady state operation, 15 days of data collection was carried out.

In the first period of operation, average COD concentrations of 0.45 μm and non-woven dynamic membrane; were determined as 3.8 ± 1 mg / L and 25 ± 3.6 mg/L, respectively. As seen in Figure 4.1, although the COD concentrations in both membranes are quite low, in the first period, 0.45 μm membrane has been found to perform better filtration compared to dynamic membrane and thus to achieve better COD removal. Another second important point is that the COD concentration in the filtrate is lower for both modules, although it was filtered with 0.45 μm injector filter sample taken from the reactor. The reason for this is the cake layer developed on the membrane surface. However, in the firt period of the experimental study, the maximum COD removal efficiencies of 0.45 μm membrane and non-woven dynamic membrane were 99.47% and 97.02%, respectively.

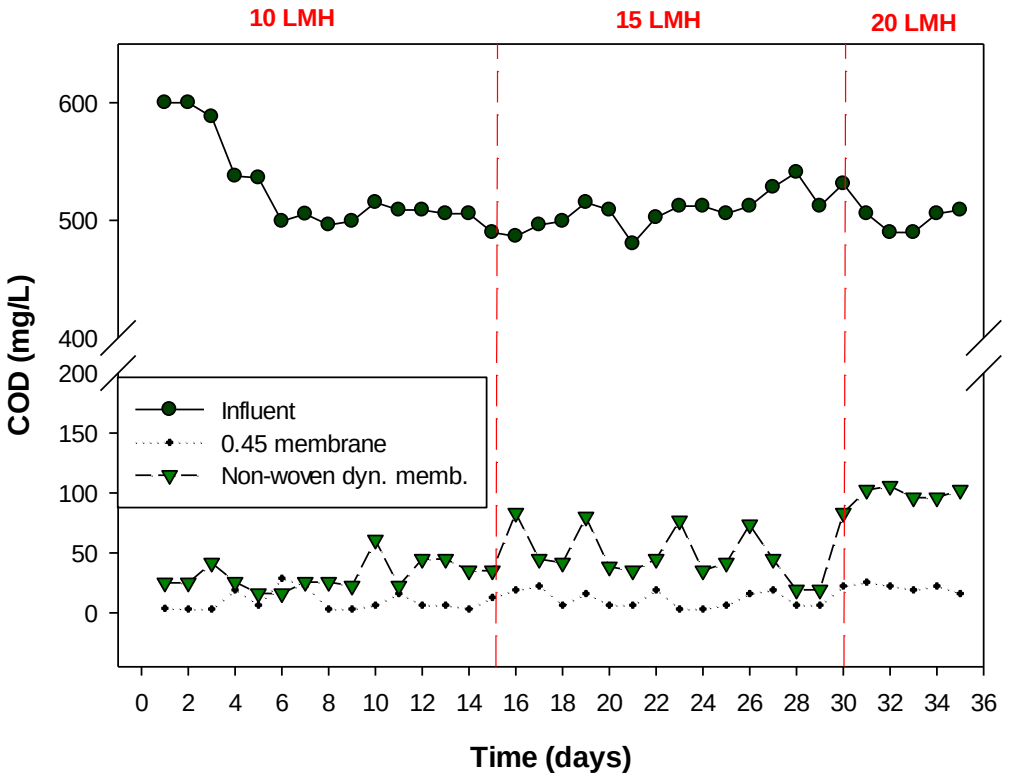


Figure 4.1 COD removal performances of the 0.45 µm and non-woven dynamic membrane throughout the periods. 1-15 represents the first, 16-30 represents the second and 30-35 represents the last experimental period.

In the second period of the experiment, membrane modules were opened and new membranes were placed and closed inside the modules. Despite the new additions of the membrane materials, no change was observed in the COD removal, demonstrating similar removal performance to the previous period of the operation. Average COD concentrations of the 0.45 µm and non-woven dynamic membrane were 11.9±5 and 50.87±15 mg/L, respectively. On the other hand, the non-woven dynamic membrane showed low efficiency in the first day of the 2nd period, in terms of COD removal, compared to the previous period. First COD removal efficiencies in the 2nd period for 0.45 µm membrane and non-woven dynamic membrane were 96.05% and 82.89%, respectively. The reason for the partially poor performance of the dynamic membrane is that the cake layer has not yet formed over the surface of the membrane. It has been observed that the formation of the cake layer in the following days showed more severe COD removal performance. However, with the increase of the flow of the dynamic membrane module from 10 LMH to 15 LHM, the membrane is more often blocked. Therefore, as a result of the chemical washing, the cake layer was cleaned from the

membrane surface and the COD removal efficiency decreased at certain intervals. The details of the chemical wash will be given in the following section. Although 0.45 μm membrane was not significantly affected by the actual membrane chemical washout, similar COD removal yields have been shown when the first period of the experimental work is considered. In the second period of the experimental work, the maximum COD removal efficiencies of 0.45 μm membrane and non-woven dynamic membrane were 98.82% and 96.45%, respectively.

At the end of the final experimental period, the flux was increased from 15 LMH to 20 LMH, resulting intensive fouling problems in the dynamic membrane. While average COD concentrations of the 0.45 μm and non-woven dynamic membrane were 21.12±10 and 100.87±21 mg/L, respectively. In terms of COD removal due to the high fouling rate and daily washing of the membrane, yields were not obtained as high if it's compared with other experimental periods. It should be noted that 0.45 μm is affected by the fact that the actual membrane flux is increased to 20 LMH, but less than the fouling problem. In the other experimental periods, about 98% yield was achieved, whereas in the last experimental run, 95% yield was obtained despite the chemical wash (Figure 4.1). Throughout the experimental periods, the intra-reactor COD concentration remained the same throughout all periods and the output COD concentration varied between 3.2-100 mg/L, including the first two experimental runs. However, in the process of transitioning between experimental periods, it was found that new membranes are deposited and thus the COD removal is reliably removed in the process of cake layer formation. As a result, the average performance of 0.45 μm membrane and non-woven dynamic membrane COD removal in the first and second experimental period was 98% - 94% and 97% - 90%, respectively. In the final period of the experimental study, flow-induced, high TMP and turbidity results were obtained, thus indicating that the output COD values were not at the desired efficiency. The last experimental period showed 95% and 79% COD removal, respectively, as 0.45 μm membrane and non-woven dynamic membrane. It should be noted that the COD concentrations are lower than the COD concentration in the filtered reactor mixed liquor. Because of the 0.45 μm membrane used in the filtration and filtration stages, some of the dissolved COD is filtered by the membrane. The reason is that both the SMPs of the cake and gel layer on the membrane are biodegraded and the effective pore diameter on the membrane decreases as the cake layer develops. Similar findings have

been reported by other researchers [92][93][94]. In addition, about half of the dissolved organics by the membrane are trapped in the reactor and hence stayed longer in there. Thus, the treatability of slowly disintegrating dissolved organics is increased.

4.1.2 Mixed Liquor Suspenden Solid (MLSS), Electrical Conductivity (EC), pH and Oxydation/Reduction Potential (ORP)

MLSS concentration was made once in a week through 15 days of the experimental periods. Through 0-15 days, MLSS concentrations were measured as 4050 mg/L for the first week and 4131 mg/L for the second week. For the second experimental period the MLSS concentrations of the reactor were measured as 4127 mg/L and 4133 mg/L as first week and second week respectively. For the last experimental period the MLSS concentration was found as 4177 mg/L. During the each experimental run, it was observed that the concentration of the bacterial sludge was increasing slightly.

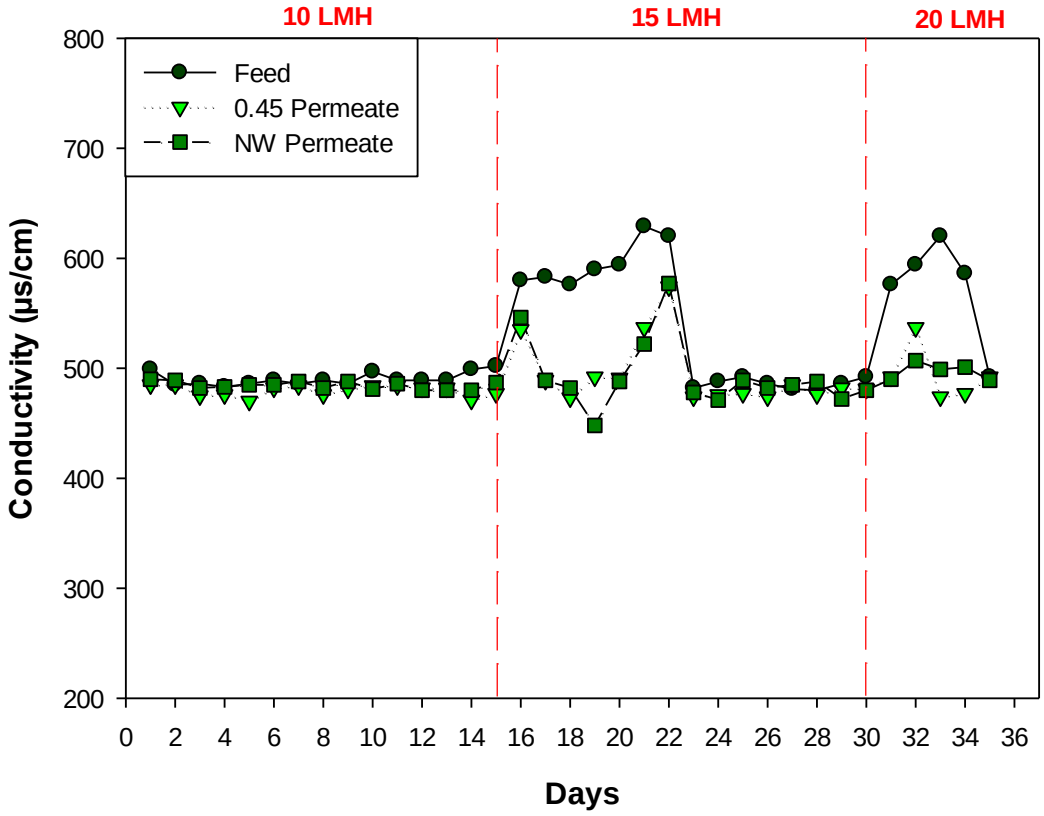


Figure 4.2 EC values of the influent, 0.45 µm membrane and non-woven dynamic membrane. 1-15 represents the first, 16-30 represents the second and 30-35 represents the last experimental period.

The results of EC are represented at Figure 4.2. In the first period of the experimental study, the influent electrical conductivity value approximately 490 μS/cm. However, the electrical conductivity averages of 0.45 μm membrane and non-woven dynamic membrane permeate were measured as 479 μS/cm and 484 μS/cm, respectively. At this stage of the work, results were very close to each other.

In the second period of the study, the average influent EC was measured as approximately 536 μS/cm. Besides, the averages EC of 0.45 μm membrane and non-woven dynamic membrane permeate were measured as approximately 494 μS/cm and 493 μS/cm, respectively. During this period of the study, the COD values prepared daily increased more than 500, thus increasing the conductivity values of the materials in the feed. However, fluctuations were observed in the output conductivity values. At the end of the experimental study, it was observed that the influent and permeate EC values gave stable results as the correct COD values were improved.

In the final period of the experimental study, fluctuations in EC values were observed. Average, influent EC value was noted as 580 μS/cm. On the 32nd day, 0.45 μm membrane read 537 μS/cm. In the following days, this value decreased to 475 μS/cm. On the other hand, dynamic membrane average EC value was noted around 490 μS/cm.

The results of the pH and ORP values are represented at Figure 4.3. Input and output values at each stage of the experimental run did not show much variation. The input pH value was measured around 7.2 on average during the study. In addition, the pH values of 0.45 membrane and non-woven dynamic membrane were measured as 7.62 and 7.76 respectively. Besides, the ORP values showed changes in the operating period. In the first period of the experimental study, averages of 176; 143 in the second period; and 157 mV in the last period were noted.

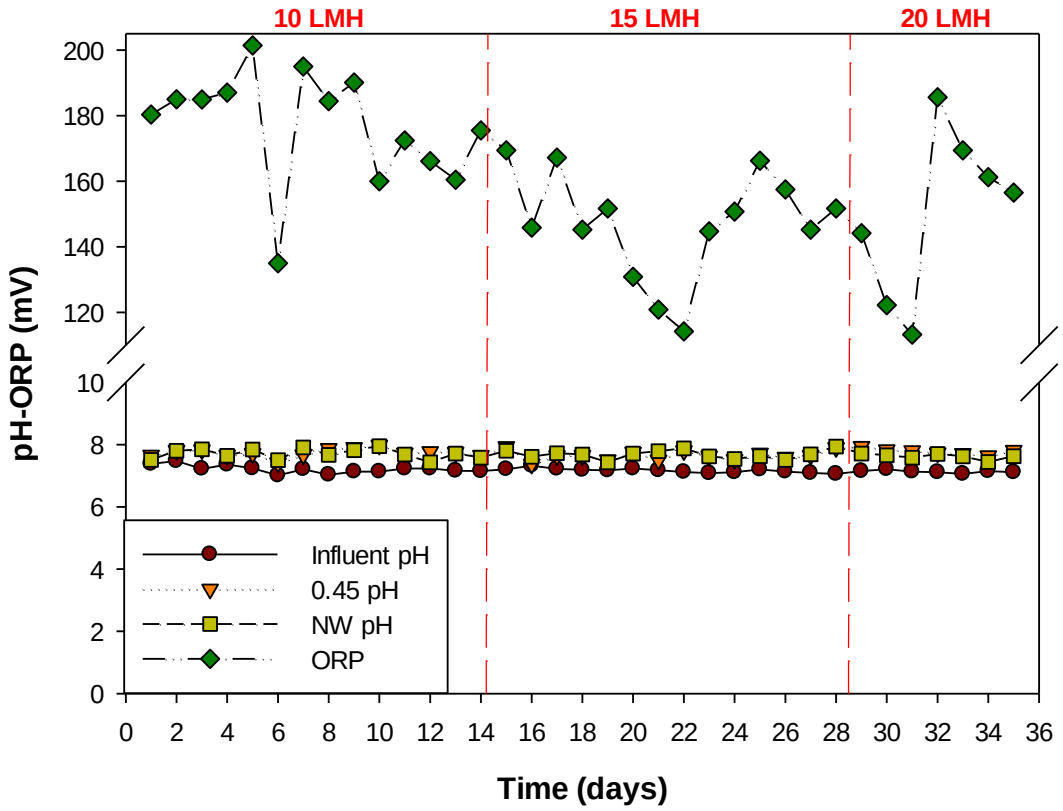


Figure 4.3 pH (downside) and ORP (upside) values observed throughout the experimental periods. 1-15 represents the first, 16-30 represents the second and 30-35 represents the last experimental period.

4.1.3 Turbidity Results

Turbidity is the loss of transparency of water and the presence of invisible solid matter in the particulate level. The excess particulate matter in the water causes the water to appear more blurred, which makes the water more turbid. For each experimental period, the turbidity results were studied until the reactor reached stabilized level, and turbidity results were recorded daily from the moment the stabilization level reached.

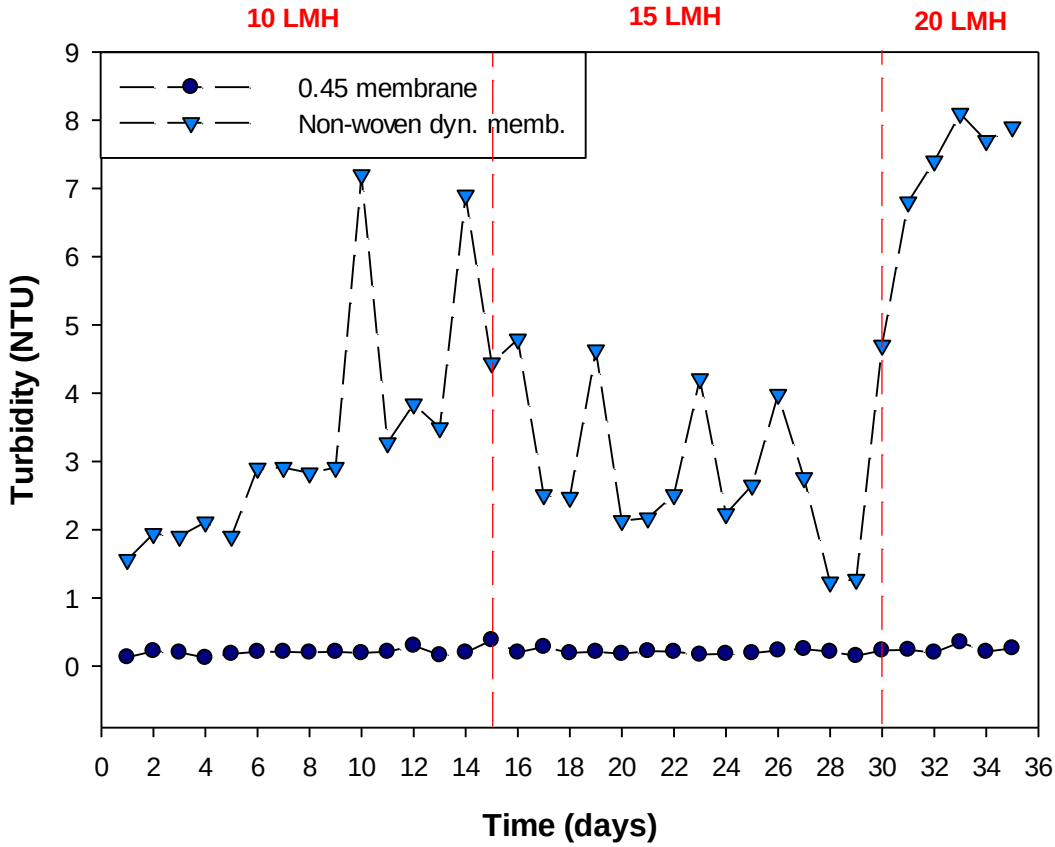


Figure 4.4 Turbidity results of 0.45 µm and non-woven dynamic membrane in aerobic reactor during MBR operation. 1-15 represents the first, 16-30 represents the second and 30-35 represents the last experimental period.

In the first period of the experiment, when the permeate parameters of the 0.45 µm membrane were examined in the 15-days period of the study, it was observed that on the average, the output was turbid around 0.2 NTU. However, chemical washing was performed once on the 12th day for 0.45 µm membrane. In studies conducted on the output values of the washing result, the filterability decreased and thus the turbidity values increased due to the cleaning of the membrane pores (Figure 4.4). On the other hand, non-woven dynamic membrane turbidity values were higher than 0.45 µm membrane due to pore diameter. At increasing pressure values, the membrane was chemically washed on the 10th day of the experiment and turbidity values were found to be 7.2 NTU when the reactor was operated after chemical washing. The highest and lowest turbidity results for non-woven dynamic membrane were found as 7.2 and 1.5 NTU, respectively.

In the second period of the experimental study, the flux was increased to 15 LMH and no significant critical changes were observed in the 0.45 µm membrane turbidity values.

In addition, non-woven dynamic membranes, along with increased flux, were frequently subjected to chemical washing and increased turbidity values were observed. In the second experimental period, the highest and lowest turbidity values for non-woven dynamic membranes were 6.7 and 1.2 NTU, respectively. In addition, on the 19th, 23rd and 26th days of the second experimental period, non-woven support layer underwent chemical washing and higher turbidity results were obtained.

In the final period of the experimental run, the flux has been increased to 20 LMH and therefore, it has been observed that the output values are greatly altered when considering non-woven dynamic membrane. The membrane was chemically washed in parallel with the flux increase, so that high values were obtained in turbidity analysis after washing. It was determined that turbidity results did not show intensive variation for 0.45 μm membrane. However, non-woven support layer underwent chemical washing every day due to the high rate of flux and inefficient turbidity results were obtained. The average turbidity value for the non-woven support layer was noted around 7.5 NTU.

As a result, the membranes were subjected to chemical washing in order to restore functionality, given the increasing pressure values. After this process, the membrane pores were opened and thus the turbidity values were increased. Although the 0.45 μm membrane turbidity values were not affected by the washing process and showed averagely 0.2 NTU, the non-woven dynamic membrane was highly influenced by this process. Due to the inability to form the cake layer over the surface of the membrane and proper filtration, the dynamic support layer cannot be properly operated at 20 LMH flux.

In a study in literature, at the first stage of the operation, the initial non-woven fabric filter performance has shown high turbidity values in terms of NTU. In the following stages, turbidity values decreased in a gradual manner, taking into account the intra-reactor SS values. In addition, the bacteria in the reactor flocked on the membrane ın very short time and the resulting turbidity values decreased [13]. In another study, it was noted that with the formation of dynamic membranes, the turbidity values decreased by 99% [9].

As a result of the experimental study, it was observed that the turbidity values decreased due to the formation of the cake layer. It was also determined that the cake layer was

not formed or very thin depending on the increase of the turbidity values for non-woven dynamic membrane material. On the other hand, it was noted that, the turbidity result of the 0.45 μm membrane were not dynamic and through the operation, it was found as stable.

4.1.4 TMP Results

The flux and TMP changes of both membrane modules in the same reactor are given in Figure 4.5. Prior to the experimental run, pure water was passed through both membrane modules, with pure water fading into the reactor. As a result of this procedure, the resistance of the membranes to pure water was recorded as mbar. In the later stage, pure water was evacuated, bacterial sludge was poured into the reactor, and the first period of the experimental work was taken into operation.

In the first period of the experimental study, both membrane modules were operated at 10 LMH flow. 0.45 μm membrane showed higher TMP values as initial pressure than non-woven support layer. These values are 36 and 24 mbar, respectively, with 0.45 μm membrane and dynamic membrane. In addition, the filtration process would start directly, since no secondary layer will form on the real membrane. On the 5^{th} and 8^{th} day of the study, real membrane was subjected to physical washing due to increased pressure. As a result of the first wash, the pressure dropped from 307 mbar to 124 mbar, while the second wash resulted in a pressure drop of 315 mbar to 180 mbar. On the 12^{th} day of the operation, the real membrane was subjected to chemical washing due to pressure increase and the pressure decreased from 310 mbar to 14 mbar. After 3 days of chemical washing, the pressure increased rapidly and rose to around 150 mbar. The dynamic membrane reached 310 mbar level within the first 6 days and was physically washed for 6 days and the cake layer on the membrane was carefully peeled off so as not to block the membrane. After stripping, the membrane was washed with pure water and the pressure dropped to 114 mbar. After 4 days of washing, the pressure increased to 320 mbar and the dynamic membrane was chemically washed. During the study, it was observed that the physical washings blocked the membrane pores to a large extent and the turbidity values measured after washing were high, so no physical washing was carried out in the following stages. On the 11^{th} day of the study, the membrane pressure started at 96 mbar and reached to 320 mbar pressure until the final period of the

experimental work. On the 15th day, the membranes were separated from the modules and replaced with new membranes.

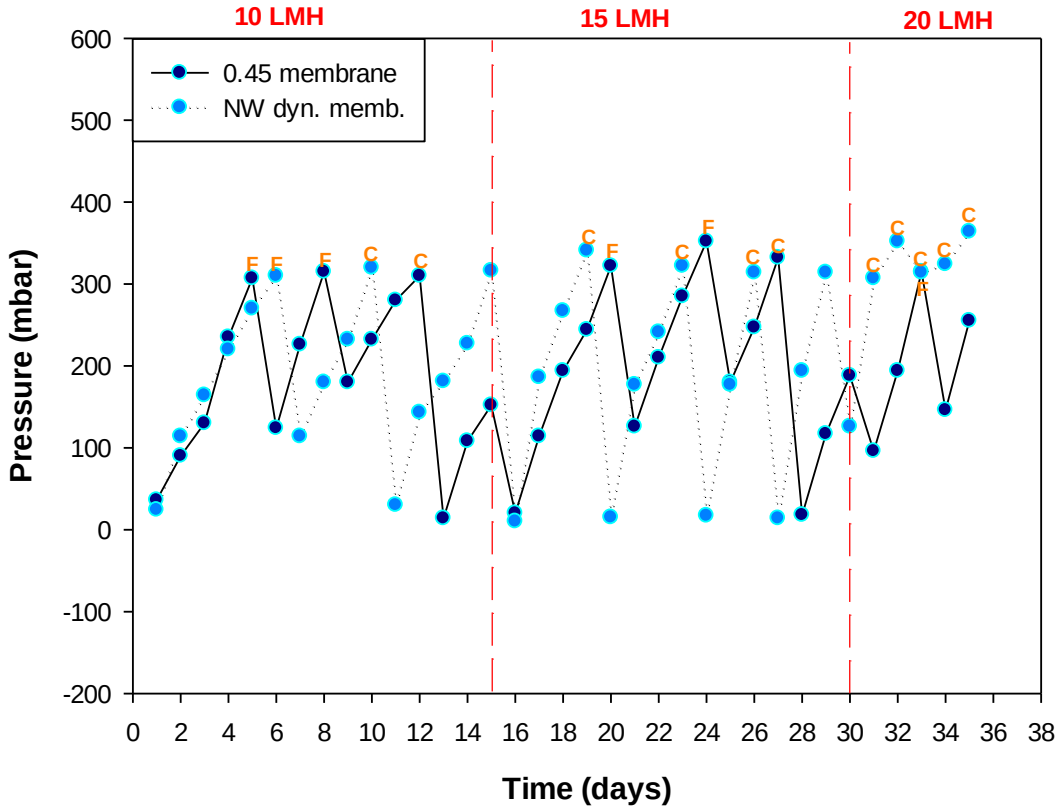


Figure 4.5 0.45 µm membrane and non-woven dynamic membrane TMP values throughout the reactor operation. 1-15 represents the first, 16-30 represents the second and 30-35 represents the last experimental period.

In the second period of the experimental run, the flux was increased to 15 LMH and the initial pressure values were found to be higher than the initial run. On the 20th and 24th days, real membrane underwent physical washing and the pressure drop from 322 mbar to 126 mbar and 352 mbar to 180 mbar, respectively. On the 27th day, the membrane was chemically washed due to the pressure increase and the pressure dropped from 332 mbar to 31 mbar. In addition, the dynamic membrane quickly clogged with high flux, chemically washed on 19th, 23th and 26th days of the operation. The dynamic membrane pore diameter is larger than the real membrane pore diameter. Therefore, it is normal to see low pressure increase and intense turbidity results in the first steps. In the course of the proceeding, high pressure and low turbidity values were obtained with the formation of the cake layer. Therefore, after chemical washing of the membrane, the pressure and turbidity values are inversely proportional. In addition to the information given, the

physical and chemical wash results due to the pressure increase were interpreted on a single plot with the pure water membrane pressure recorded at the beginning of the experimental work.

Physical scrubbing and chemical washing were carried out several times during the study. Cleaning type was chosen as CIP which is called Cleaning in Place. Due to the high pore size of the dynamic membrane, it was observed that the membrane quickly clogs after chemical washing. However, after physical washing the membrane pressure increased very rapidly. Due to the fact that the dynamic membrane is not suitable for physical scrubbing and the fibrous structure and the cleaning process is chemically made in the 2^{nd} and 3^{rd} experimental periods.

At the final experimental period the flux has been increased from 15 LMH to 20 LMH. The initial pressure measurements of the real and dynamic membranes were 96 mbar and 307 mbar, respectively. Since real membrane showed very effective results in terms of turbidity, dynamic membrane fouled daily and required chemical washing. One of the reasons is that sludge might be acclimated in the first place and the microbial culture changes in the MBR caused instability in the process. The other reason is the low MLSS concentration. In literature, there are different types of MLSS concentration results found to criticize the results of membrane filtration performance [130]. It has also been observed that at low MLSS concentrations (<6 g / L MLSS) fouling is caused [131]. Therefore, MLSS concentration should be at least 6 g / L in order to observe stable state operation in MBR. In our reactor, the MLSS concentration was fixed to the 4 g / L and this might be a reason for the fouling.

4.1.5 Capilary Suction Time Results

CST is used to identify the sludge characteristics and it measures the time of water drop from the sludge moved 1 cm path in a porous membrane. CST results of fully mixed liquor samples are represented at Figure 4.6.

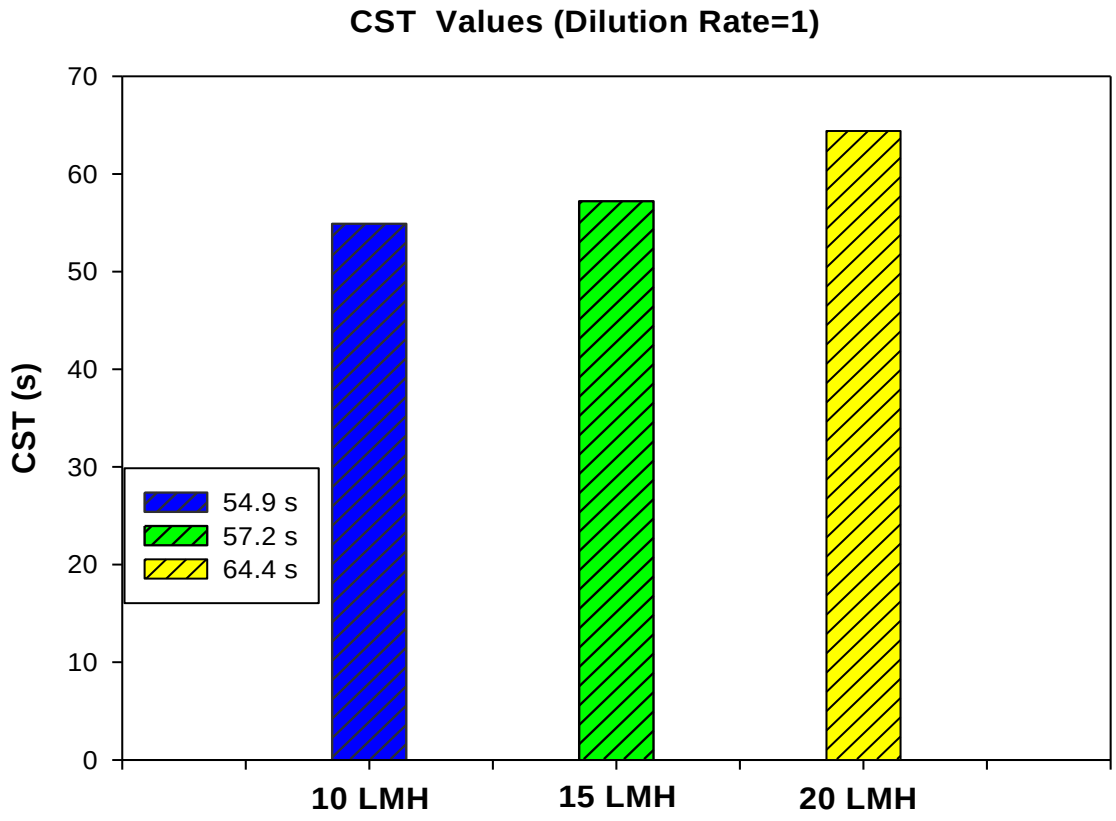


Figure 4.6 The result of the CST analysis. 10 LMH represents the first experimental period result between 0-15 days (A), 15 LMH represents the second experimental period result between 15-30 days (B) and 20 LMH represents the last experimental period result between 30-35 days (C).

In the first experimental study, CST analysis was performed once over a period of 15 days. During operation, a ring was placed on the membrane and all the samples were taken directly from the reactor and poured into the ring without dilution (Figure 3.12.A). The results, 10-15-20 LMH, are shown in Figure 4.6 above the 10-15-20 LMH tag. Directly taken sludge sample through the reactor showed a value of 54.9 seconds for the first experimental period. However, the other two samples showed 57.2 and 64.4 seconds, respectively.

As a result, the samples taken from the reactor and diluted at a certain rate gave almost similar results into the each other because of analyzes that were made on different days of the experimental work. As seen in Figure 4.6, there is no significant difference comparing with diluted and non-diluted samples. This difference may be due to an increase in the biological activity in the reactor, an increase in the bacterial population and, concomitantly, an increase in the amount of protein and carbohydrate in the reactor. Information on protein and carbohydrate quantities will be provided later.

Along with the increase in the amount of protein and carbohydrate, however, the density in the reactor also increases. This increase will be discussed later in the viscosity experiments. Therefore, the temporal difference in which the CST membrane was exhibited in this study was due to this density.

4.1.6 SMP and EPS Results

SMP and EPS analyzes were carried out for one week in the first period of the experimental study (0-15 days) (Table 4.1). In the second period of the study, these experiments were repeated.

Table 4.1 SMP and EPS results from the first experimental period between 0-15 days of the operation.

	Non-Woven Permeate		**0.45 Mem. Permeate**		**Supernatant of the Sludge**		**Sludge from the MBR**	
	SMP		SMP		SMP		EPS	
0-15 Days	**Prot.** (mg/L)	**Carb.** (mg/L)	**Prot.** (mg/L)	**Carb.** (mg/L)	**Prot.** (mg/L)	**Carb.** (mg/L)	**Prot.** (mg/L)	**Carb.** (mg/L)
1st Week	0.413	11.46	0.362	17.52	0.328	24.048	0.724	24.169
2nd Week	0.424	10.07	0.488	16.19	0.409	26.402	0.803	23.122

In MBR and DMBR, SMP and EPS are important in terms of congestion and cake formation. The extracellular polymeric substance of microorganisms, called EPS, is formed in the support layer, as well as the formation of the EPS floc. SMP and EPS values are directly related to many parameters such as sludge viscosity, CST, sludge resistance etc. In addition, SS, VSS and COD removal profiles affect SMP and EPS values. In this context, when COD removal of microorganisms is taken into consideration, it is observed that as the COD removal increases, the SMP values also increase. In addition, the EPS value obtained by fragmenting the structure of the microorganism confirms this data, which is not the sum of the carbohydrates, proteins and humic acids, which were stored in the microorganism during the COD recovery. Since humic acid values range from 1% to 4% in a slurry, in many studies in the literature SMP and EPS, values are given as protein or carbohydrate or as COD values of these two parameters.

In the first period of the experimental study, the average protein and carbohydrate amounts were found to be 0.4040 mg/L - 17.62 mg/L and 0.531 mg/L and 18.946 mg/L in the first and second week studies, respectively. However, after centrifugation of the sludge sample taken as a complete mixture from the reactor, bottom sludge was accumulated and this sludge was used for EPS analysis. As a result of EPS analysis, the total average protein and carbohydrate amounts were found to be 0.7635 mg/L and 23.6455 mg/L, respectively (Table 4.1).

The results of the SMP and EPS protein and carbohydrate determinations for the second study are given in Table 4.2.

Table 4.2 SMP and EPS results from the second experimental period between 15-30 days of the operation.

	Non-Woven Dyn. Memb. Perm.		**0.45 Memb. Permate**		**Supernatant of the Sludge**		**Sludge from the MBR**	
Time	SMP		SMP		SMP		EPS	
15-30 Days	**Prot. (mg/L)**	**Carb. (mg/L)**	**Prot. (mg/L)**	**Carb. (mg/L)**	**Prot. (mg/L)**	**Carb. (mg/L)**	**Prot. (mg/L)**	**Carb. (mg/L)**
1st Week	0.701	21.609	0.648	34.064	0.612	41.024	1.171	41.307
2nd Week	0.729	22.162	0.764	33.817	0.675	40.253	1.201	43.430

In the second period of the experimental study, the mean protein and carbohydrate portions were found to be 0.6883 mg/L-32.1548 mg/L and 0.84 mg/L -34.91 mg/L in the SMP experiments performed in the first week and the second week, respectively. However, the total average amount of protein and carbohydrates in the EPS were noted as 1.186 mg / L and 42.3685 mg / L, respectively.

Table 4.3 SMP and EPS results from the last experimental period between 30-35 days of the operation.

	Non-Woven Dyn. Memb. Perm.		**0.45 Memb. Permate**		**Supernatant of the Sludge**		**Sludge from the MBR**	
Time	SMP		SMP		SMP		EPS	
30-35 Days	**Prot. (mg/L)**	**Carb. (mg/L)**	**Prot. (mg/L)**	**Carb. (mg/L)**	**Prot. (mg/L)**	**Carb. (mg/L)**	**Prot. (mg/L)**	**Carb. (mg/L)**
	0.9305	41.315	0.719	53.172	0.847	62.142	1.722	53.178

In the last period of the experiment, average SMP for proteins and carbohydrates were found as 0.83 mg/L and 52.20 mg/L for non-woven and 0.45 μm membrane permeate, respectively. For the MBR sludge, SMP value was found as 1.72 and EPS value found as 53.178 (Table 4.3).

In this context, it was noticed that SMP and EPS values increased through out the experimental periods. In a study found in the literature, information about the low SMP and EPS values in the reactor is given as a result of the study in low SRT [132]. Also, it has been noted that when the amount of SMP increased inside of the reactor, the rate of fouling also increases [133]. In the first period of the study, due to the low SMP concentration there were no TMP to employ chemical cleaning. After a certain period of time, the SMP value of the sludge in the reactor was increased, so that high TMP values were obtained as a result of the measurements made [134]. The interpretation of EPS as one of the reasons for the reduction of the filtration resistance has also been verified and parallel to our study. In another study, it was reported that the rate of membrane occlusion would increase with increasing polysaccharides [135][136]. In another study, it was mentioned that the increase in EPS was caused to increment the resistance of the membrane [137]. It was observed that the results obtained from the operation are in accordance with those found in the literature.

4.1.7 SRF and SF Results

The values of the two experimental periods are given in Figure 4.17. At the first period, 100 ml of the supernatant sample given for the SF1 operation and 100 gr supernatant were obtained after the filtration process. At the second period of the SF analysis which is called SF2, 100 ml of the supernatant given into the dead-end chamber and 96.6 gr permeate was measured. The reason for this may be explained by the wetting of the

membrane paper by the sample loaded at the beginning of the experimental run, or the reduction of the amount of solids after the centrifugation step during operation, and thus the sample we have taken may be seen as reduced. In the SRF period of the both experimental work, sample was taken directly from the reactor and poured into the dead-end system without any treatment. The results for the SRF1 showed that 57 gr of permeate was measured out of 100 ml of the sample. In addition, for the SRF2 experimental run, 15-30 days, 100 ml sample was poured into the system and 48 ml of the sample was weighed.

During the study, SRF measurements were performed every 1 minute on 1 hour measurement and SF measurements on every 1 second on a minute. As a result of the study, the SRF and SF results showed small differences as the output values. In literature, there have been different types of analysis made to understand the reason why sludge filtration over the surface of the membrane reduces. One of the reasons is the acclimation of the sludge. Sludge acclimation can floc the the bacteria and causes flocing. The other reason is the increased amount of SMP and EPS inside of the reactor. When the protein and carbohydrate concentration inside of the reactor increases, the sludge gets concentrated and dense. Due to that property, it makes the filtration process difficult to proceed.

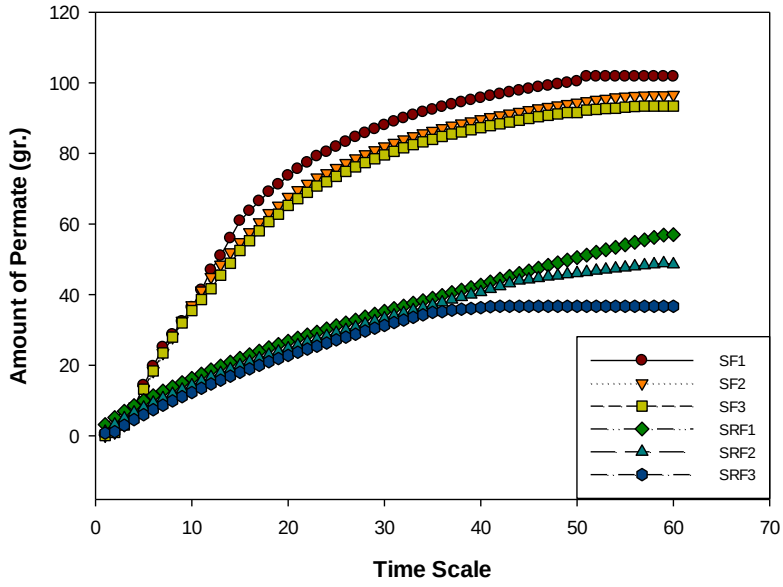


Figure 4.7 SRF and SF analysis of the experiment. SRF1 and SF1 represent the first experimental period between 0-15 days. SRF2 and SF2 represent the second experimental period between 15-30 days. SRF3 and SF3 represent the last experimental period between 30-35 days.

4.1.8 FT-IR Results

During the experimental study, 0.45 µm membrane and non-woven dynamic membrane were chemically washed several times. During this time, the organic components and organic micro-molecules in the reactor were attached to the membrane surface due to filtration and eliminated after the cleaning. As a result of long-term operation, these organic materials cause membrane fouling except the membrane not washed physically or chemically.

ATR / FT-IR studies are used to identify organic compounds. At the basis of the ATR technique, instead of being absorbed and reflected by the sample, the scatter of the beam from the sample is measured. ATR technique is very effective in the analysis of coating materials such as polymer, foam, textile, paint, and glaze. The IR spectrum of all compounds other than optical isomers is different from each other. The IR region is located between the visible region of the electromagnetic spectrum and the microwave region. The results of the, 10 LMH, ATR/FT-IR analysis, between 100-4000 wavelenght, carried out in the study are given in Figure 4.8 and Figure 4.9.

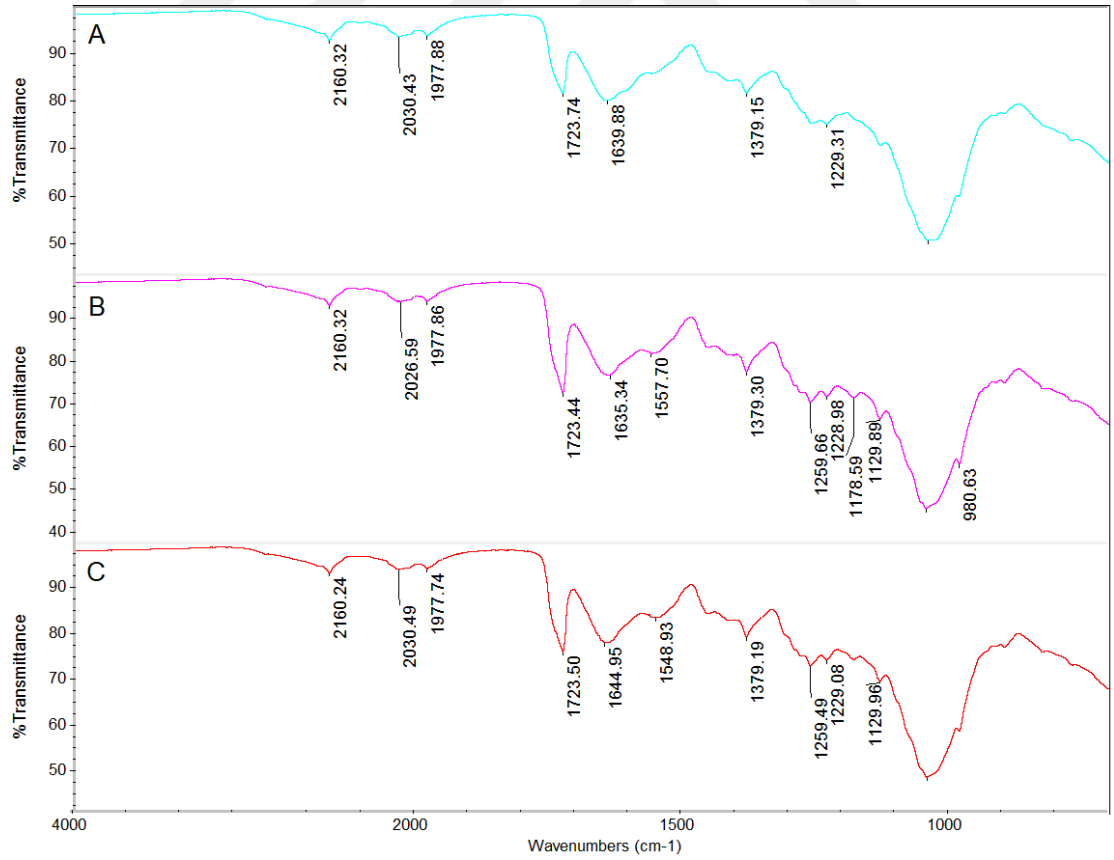


Figure 4.8 ATR/FT-IR result of the 0.45 µm membrane powdered cake layer (A), non-woven dynamic membrane powdered cake layer (B) and reactor sludge sample (C).

When the results of the experimental study were analyzed, values of 1557 and 1548 were read in the parameters of cake layer and reactor sludge sample, respectively, around 1500 wavelengths. On the other hand, 0.45 µm membrane did not peak at the same wavelength. A similar difference was observed in 1259 wavelengths. The 1178 wavelength value was only found in the dynamic support layer powdered cake, while the 1129 wavelength value was observed in the dynamic support layer powdered cake and the sample taken through the reactor. Very differently, it was only seen on non-woven support layer powdered cake on 980 wavelength value (Figure 4.8).

On the other hand, a peak was observed on non-woven dynamic membranes with 1548 wavelength spectra when comparing ATR / FT-IR result with 0.45 µm membrane. In addition to these, different values were read in wavelengths of 1229, 1179, 1129 and 980 (Figure 4.9) for non-woven dynamic membrane material.

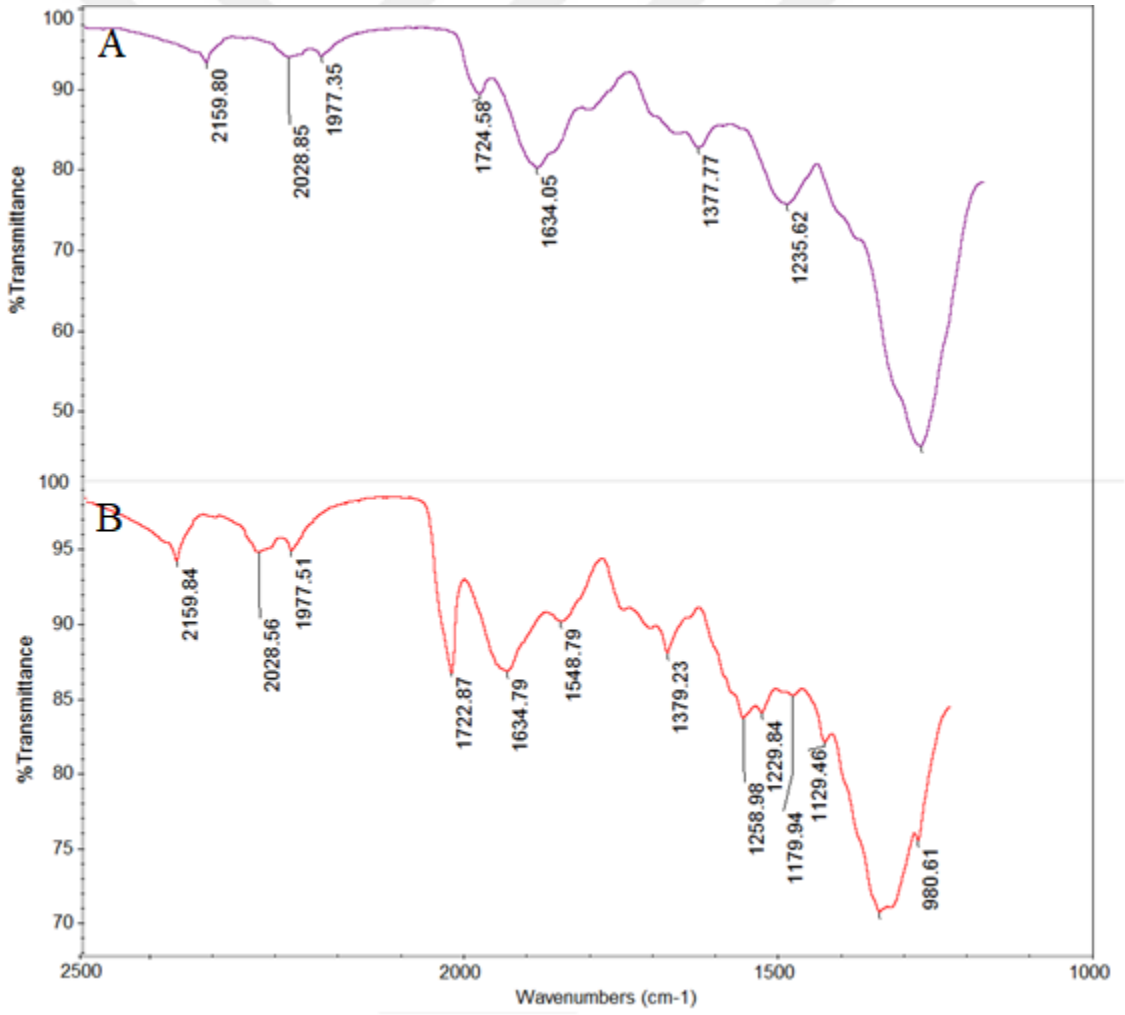


Figure 4.9 ATR/FT-IR result of the 0.45 µm membrane with cake layer (A) and non-woven dynamic membrane with cake layer (B).

On the other hand, the last experimental period of the study (30-35 days) another FT-IR analyzes were made and membranes and membrane cake layers were subjected to the experiment. Experimental work was done between the wavelengths of 650-4000. Figure 4.10 represents the both membrane cake ATR/FT-IR analysis on 0.45 and dynamic membrane cake for the last period of the experiment, respectively.

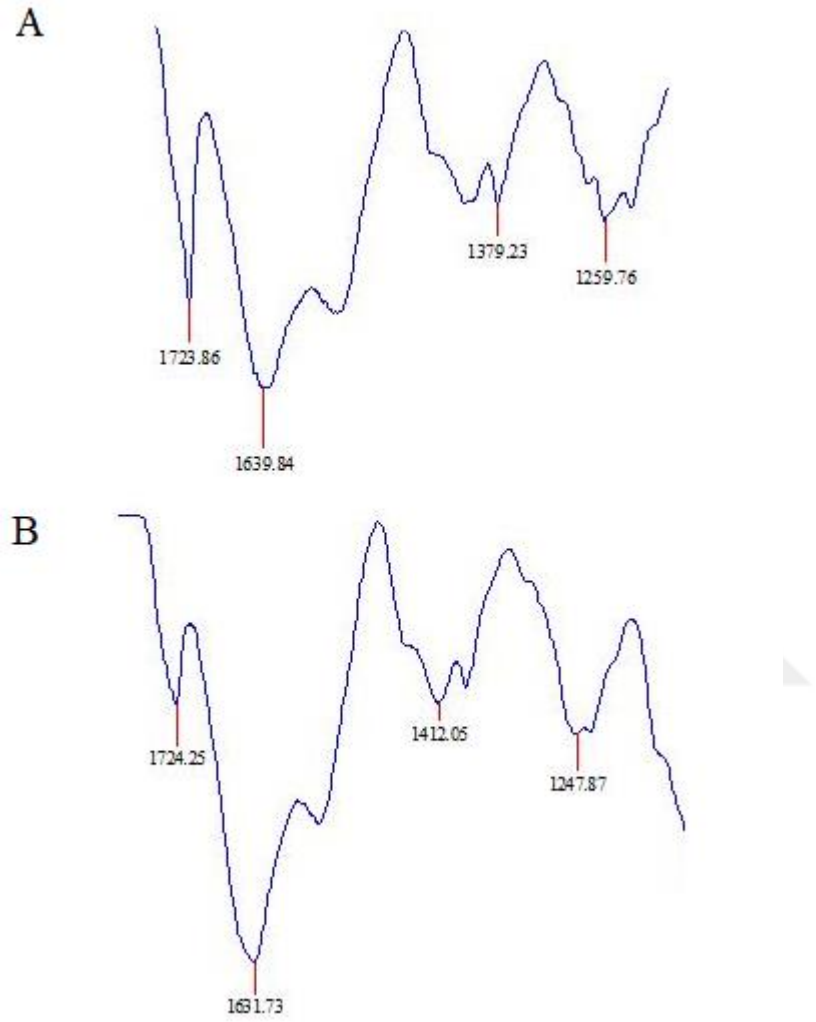


Figure 4.10 ATR/FT-IR result of the 0.45 µm membrane cake (A) and non-woven dynamic membrane cake (B).

Both membrane cakes were taken at the final stage of the experiment (30-35 days). When the results were compared with the first experimental period ATR/FT-IR results, it is going to be noticed that there is no significant differences in terms of the peaks obtained. 0.45 µm membrane cake results showed the peaks as; 1723, 1639, 1379 and 1259. However, the peaks obtained from the dynamic membrane is as following; 1724, 1631, 1412 and 1247. Therefore, membranes were taken from the modules, cut and subjected to the ATR/FT-IR analyzes. The results were represented at Figure 4.11. 0.45

μm membrane cake was given the peaks at 1727, 1635, 1379 and 1249. However, for dynamic membrane examination three different peaks (1734, 1647 and 1257) were observed.

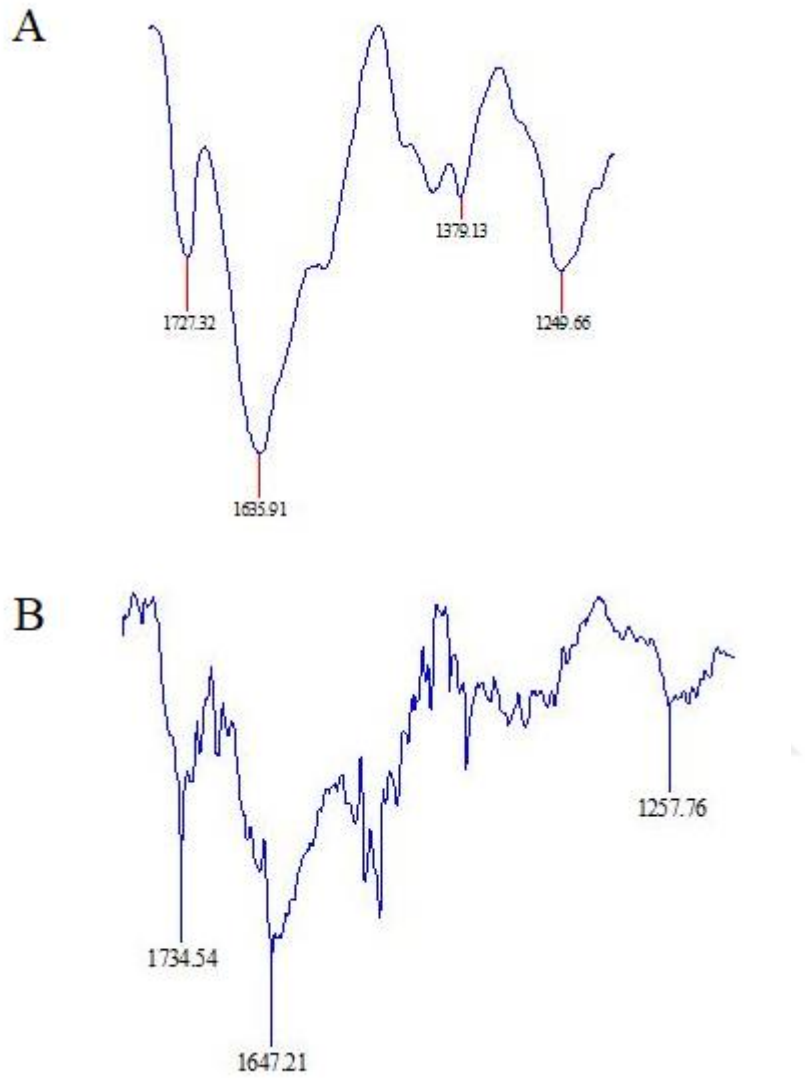


Figure 4.11 ATR/FT-IR results for the 0.45 μm membrane with cake (A) and non-woven dynamic membrane with cake (B) for the last experimental period.

In general, 0.45 μm and dynamic membrane FT-IR results showed that membrane foulants that are majorly spread over the membrane surface are protein and carbohydrate [138].

In literature, there have been different types of MBR studies done to examine the peaks observed through the FT-IR analysis. In one experiment, it has been found that 1548,79 and 1557,70 represents the unique protein secondary structure called amides II (N–H in

plane) [139]. The values in our study in this context are consistent with the literature in terms of sludge characterization.

In a study done in the literature, it has been determined that the value found near 1160 wavelengths (COH stretch) are indicative carbohydrates (representing polysaccharides) [140][141]. In our work, the value of 1178 and 1179 wavelengths on the dynamic support layer powdered cake is considered to be this value. Also, in another study, it has been found that the range between 1350 and 1215 is called amide III [142].

4.1.9 SEM Results

At the last period of the operation, SEM images of the membrane samples taken are presented in Figure 4.12 and Figure 4.13 for 0.45 µm membrane and non-woven dynamic membrane. As can be seen from Figure 4.12 and Figure 4.13, a thick and dense cake layer was observed on the membranes. The thickness of the cake layer formed on 0.45 µm membrane and non-woven dynamic membrane was measured as 121.83 µm and 316.16 µm respectively. In this context, it is seen that the cake layer formed on the dynamic support layer is thicker than the cake layer formed on the real membrane. The structure of the dynamic membrane has a spongy-like texture and the developing cake layer attracts attention with its tight and non-porous structure. According to the results, cake layer formed on the dynamic support layer showed more resistance than 0.45 µm membrane and showed swift increase of TMP in a short time. The TMP and cake resistance values obtained also support these findings. However, as understood from the 100 µm scale images of the membranes, the dynamic support layer has a mountainous network structure, while the real membrane support layer has a more flat structure (Figure 4.12.A and Figure 4.13.A).

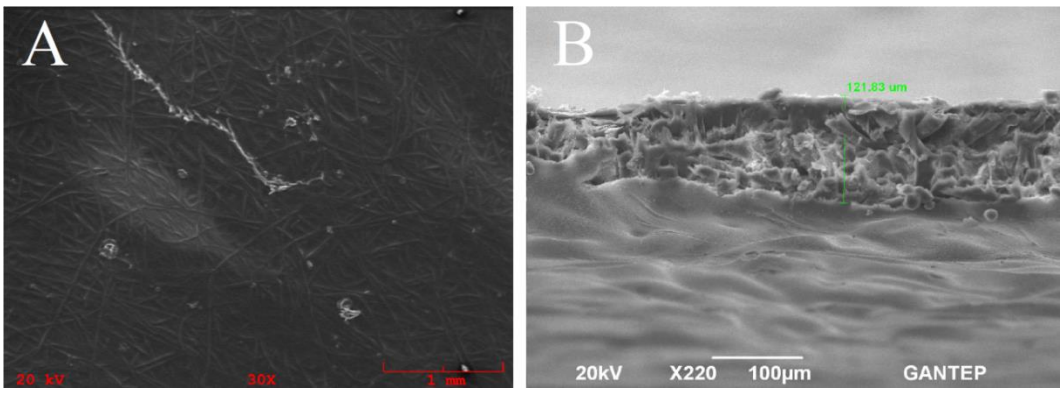


Figure 4.12 SEM picture of the 0.45 µm membrane. Top view of the membrane (A) and the sectional view of the cake layer (B).

However, on the cake layer, different micro-contaminants were observed that cause membrane fouling. As a result of SEM studies on the cake layer, it is possible to learn about the morphology of the pollutants. It is reported in the literature that the membranes are porous materials and can be plugged by the micro- pollutants. It has been reported that these micro-pollutants are biopolymer-coated and consist of biocompatible clusters [143].

In order to perform material studies on the membranes, the surface of the membrane is covered and the elements found at the base of the cake are defined as a result of EDX analysis. The results of the EDX are represented in Figure 4.14 and Figure 4.15. Within the scope of this study, the elements detected on 0.45 µm membrane cake layer with EDX analysis were; C 46%, O 36%, Cl 12%, Si 1.5%, Na and Ca 0.8%, Mg and Al 0.2%, S 0.9%, Ni 0.08%.

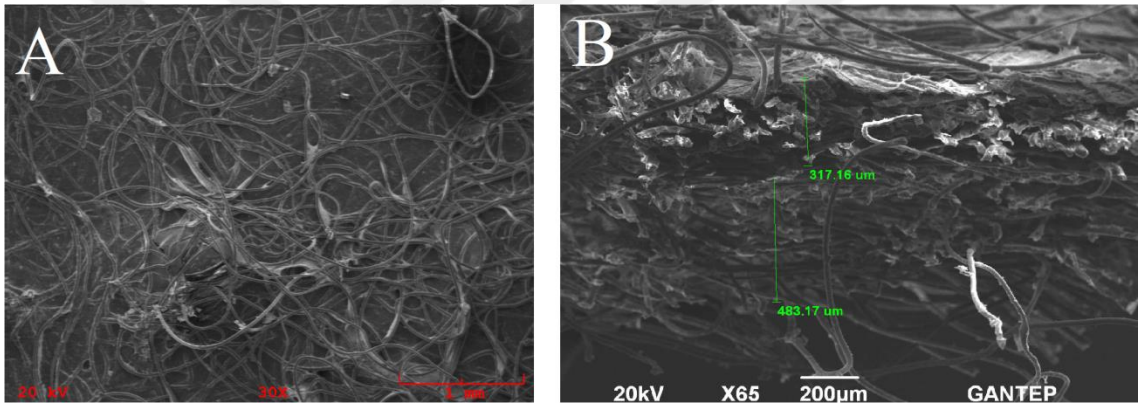


Figure 4.13 SEM picture of non-woven dynamic membrane. Top (A) sectional view (B) of dynamic membrane.

On the other hand the elements detected on non-woven dynamic membrane cake layer with EDX analysis were; C 48%, O 44%, Na 0.7%, Mg 0.2%, Al 0.3%, Si 1.1%, S 1.6%, Cl 0.1%, Ca 1.4% and Zn % 1. The content of S in the cake is approximately 1.3% on average. The reason for this is that under aerobic conditions, a few sulphides are oxidized in elemental sulfur. C and O observed in the cake layer developed on the membranes are generally thought to originate from the bacterial mass. When the results are examined, S is close to 1% by weight and Ca close to 1%. With the sulfur compounds formed, metals can easily form metal sulfide compounds and collapse. For this reason, metal sulfide compounds can easily form by entering into the sulfur reaction. Observed S and metal ratios are proof of this.

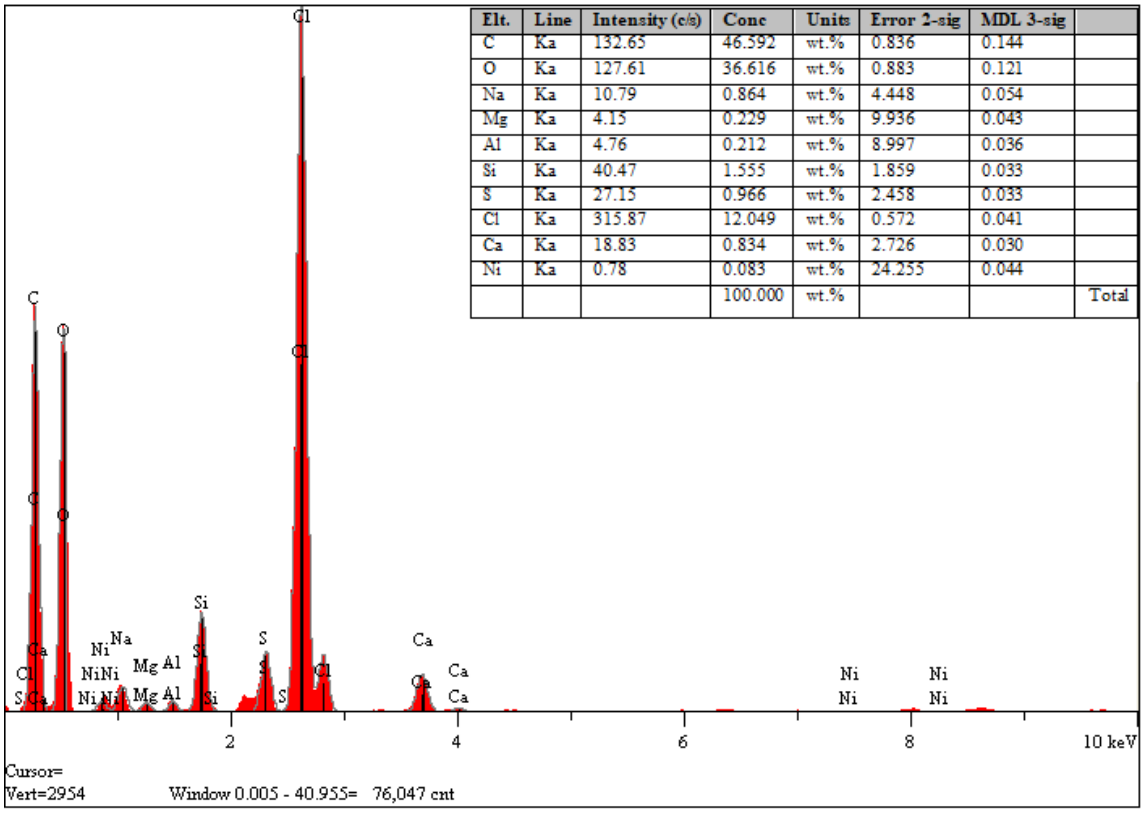


Figure 4.14 SEM-EDS image obtained from 0.45 µm membrane.

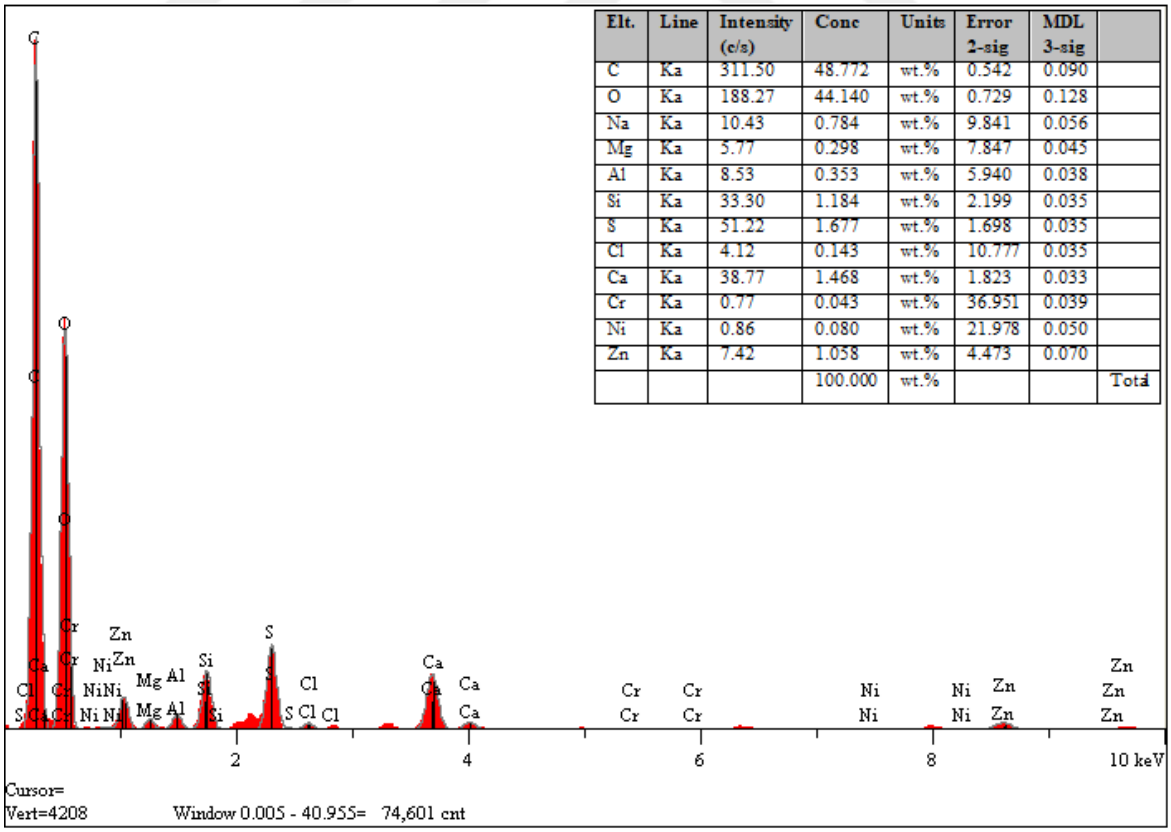


Figure 4.15 SEM-EDS image obtained from non-woven dynamic membrane.

Experimental studies have shown that inorganic elements, such as Mg, Al, Si, Ca, Fe, etc., cause serious clogging that they can form a transition phase through contaminating layers, precipitated cells, and biopolymers. There is a possibility that these substances may cause negligible clogging when passing over the membrane [143][144].

4.1.10 Microbological Results

Before starting the experimental work, the genetic material isolated with the aid of the kit was loaded and run into the gel, without being subjected to PCR treatment. This is the result of the successful extraction of the extraction process. Figure 4.16 represents the gel image of this study.

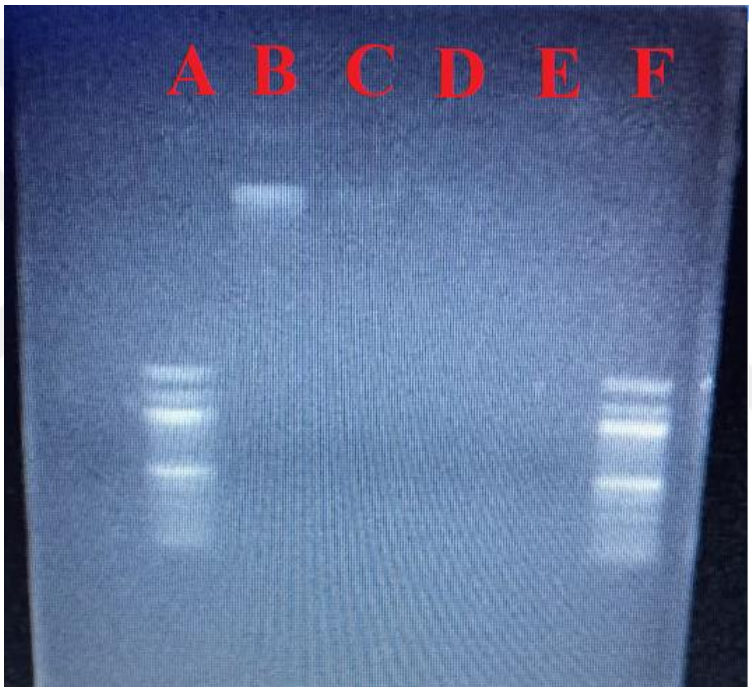


Figure 4. 16 Line A and F represents the 100 kb ladder and B, C, D and E represents the extracted DNA sample with dilution rate 1, 0.2, 0.1 and 0.02.

In the first step of the experimental study, isolated 16S rRNA genetic material was subjected to PCR1 using 27F and 1492R universal primers. As a result of the work, the genetic material of bacterial cultures was cut with restriction enzymes and specific regions were multiplied. PCR1 product was stored at -20ºC. The result of the PCR1 demonstrated at Figure 4.17.

In the second step of the experimental study, the PCR1 product was subjected to PCR2 using 357F-GC and R518 primers. After the PCR2 process, genetic material was loaded to the 1% agarose gel and run. The result of the PCR2 represented at Figure 4.18.

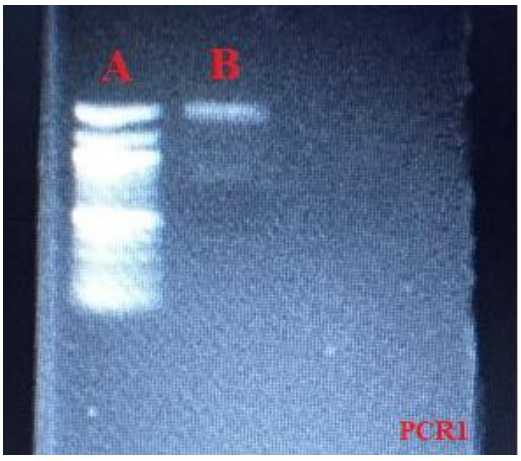


Figure 4.17 PCR1 experimental study result. Line a is the 100 kb ladder and the line B is the amplified products.

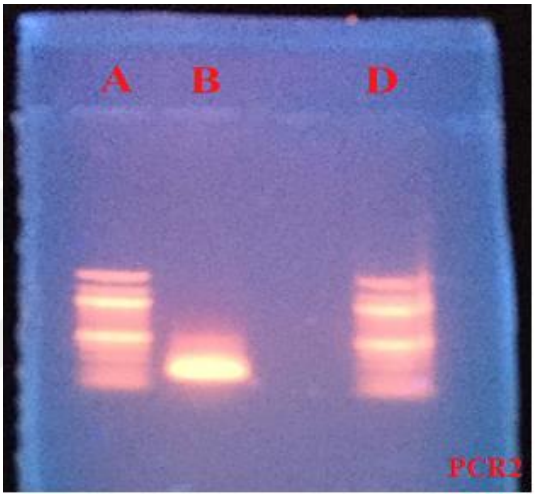


Figure 4.18 PCR2 experimental study result. Line A and D represet the 100 bp ladder and line B represents the amplification of the PCR2 products.

Until this stage of the study, in the PCR operations carried out, the bacterial genomes, which constitute a very large length, were shortened and amplified. After the PCR2 run, the bacterial genetic material, which became a shorter fragment, was finally subjected to a re-run with a different operation (DGGE) consisting of two different gel constituents. In the PCR1 and PCR2 studies, the amplified regions were found in the 100 kb ladder band which was at the top of the gel. In the DGGE study, these bands are separated from each other and represent individual bacterial species in an individual sense. The results obtained in the DGGE study are shown in Figure 4.19.

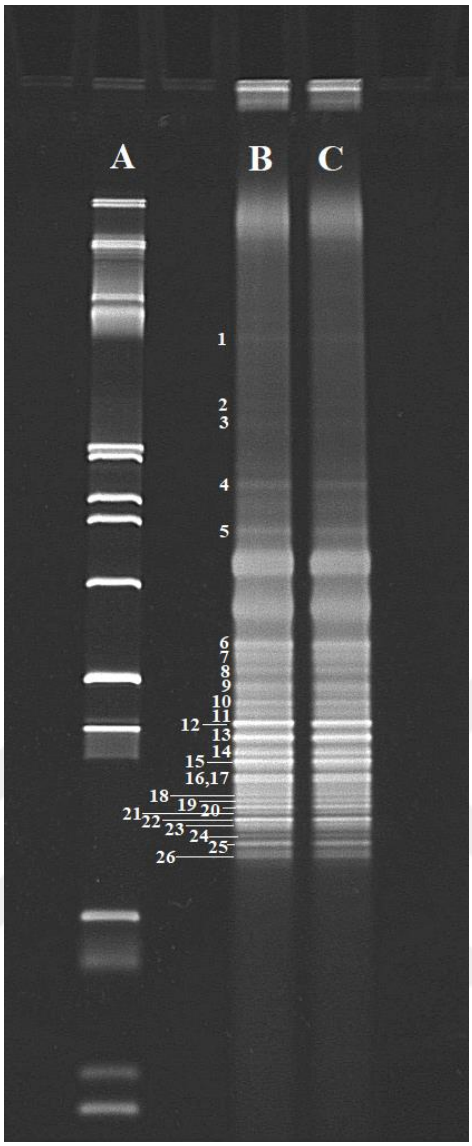


Figure 4.19 First experimental period, DGGE study result. Line A represents the 100 kb ladder. Line B and C represents the PCR2 product. Numbers from 1-26 represents the amount of bacterial species exist inside of the AeMBR.

At the final stage of the experiment (30-35 days), another DGGE work was done to see the number of the bacterias which were still living inside of the reactor and which were eliminated. So, basically MBR is a life chamber for all bacteria species living inside of it and through the time some of them increase in amount and some of them die. Figure 4.20 represents the second DGGE work done at the final stage of the experiment. At the middle part of the sample, some of the new species became identical, if it is compared with the previous DGGE analysis. However, some of the bacterial species eliminated at the down part of the experiment. In the first experiment, there were 26 species. However, second experiment shows that 24 bacterial species left in the reactor. In this context, some of the bacterial species causing flocking were eliminated and new

bacterial species arose in the bioreactor. It has been reported in the literature that the bacterial population changes depending on the temperature [129].

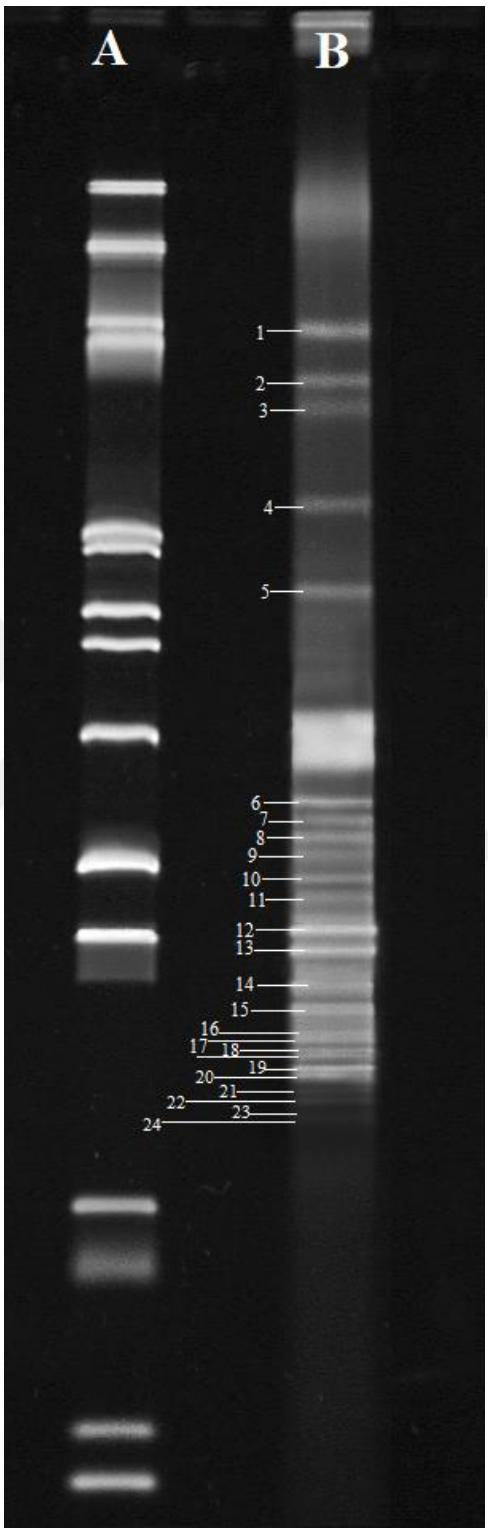


Figure 4.20 Final experimental period, DGGE study result. Line A represents the 100 kb ladder and Line B PCR2 product. Numbers from 1-24 represents the amount of bacterial species exist inside of the AeMBR.

4.2 Discussion

In the study, it was observed that the reactor was operated at stable condition about 30 days. Daily COD, turbidity, TMP, pH, electrical conductivity, temperature and ORP values were measured over a period of 15 days immediately after 30 days of stable reactor circumstance. However, the membrane and membrane filtration performances of the two membrane modules operated at 10 LMH flow were compared during the operation. During the first period of the experimental run, 0.45 μm membrane and non-woven dynamic membrane COD removal efficiencies were noted as 98% and 94%, respectively. In addition, 0.45 μm membrane and non-woven support layer mean permeate COD values were found to be 9 mg/L and 31 mg/L. Since some dissolved organics in the reactors are filtrated by the developing cake layer on the membrane surface, very low permeate COD values were detected in the membrane effluent compared to the input COD values. In the reactor operated at 10 LMH flow, there was almost no need for chemical washing. Small quantitative changes in the results of SRF / SF, SMP / EPS, CST and viscosity analyzes were observed due to the increase in the amount of protein and carbohydrate present in the slurry.

In the second period of the experimen, the flux was increased to 15 LMH and the physical and chemical washings were regularly maintained for 0.45 μm and non-woven dynamic membranes. The average COD removal efficiencies were measured as 97% and 90%, respectively, for the real membrane and non-woven support layer. Besides, it was mentioned that regular chemical washing is more advantageous than physical washing in congestion relief. After chemical washing, the cake layer formed over the surface of both membranes was eliminated. 0.45 μm membrane turbidity values are almost unchanged, while non-woven dynamic membrane turbidity values are increasing significantly after washing. This increase continues until the cake layer is formed. After the cake layer is formed, the turbidity values give similar results to the 0.45 μm membrane turbidity values. For both types of membranes, it has been determined that the chemical wash effectively removes irreversible plugging and the chemically cleaned membrane resistance is very close to the resistance of the new membrane. This study was confirmed in the TMP measurements made.

SMP and EPS formed in both membranes were also measured and it was observed that high molecular weight SMPs on the membrane surface were retained in the cake or gel layer. This increases the filtration resistance and leads to the formation of high TMP

values. Although periodical physical washing was performed to reduce high TMP values, chemical washing applications were carried out during the experimental study in order to remove membrane fouling. After chemical washing, similar to the previous work, the pollutants on the membrane surface and in the pores were removed almost completely and the resistance of the chemically washed membrane became very close to that of a new membrane.

In the third period of the study, the flux was increased from 15 LMH to 20 LMH and the membrane resistance rapidly increased. Nevertheless, it was observed that daily physical washing of the 0.45 μm membrane resulted in very rapid fouling. The average COD removal efficiencies were measured as 95% and 80%, respectively, for the real membrane and non-woven support layer. The non-woven dynamic membrane was blocked during the day and chemical washing was applied to prevent this fouling. Thus, the frequency of membrane fouling increases with the increase of influx. The turbidity values of 0.45 μm membrane averaged around 0.2 NTU while the non-woven support layer turbidity values were measured as approximately 7.5 NTU.

In the SEM images taken from the membrane samples, real and non-woven membranes showed cake thicknesses of 121 μm and 316 μm, respectively. During operation, both membranes encounter micro-contaminants and precipitates. Therefore, it can be said that these molecules are trapped by the membrane, cause fouling and increase the resistance of the cake. It is also known that there are smaller molecules in the cake layer than micro-contaminants. These molecules are removed by the cake layer or by the active microorganism in the cake layer during filtration. With the resulting sulfur compounds, the metals can easily form metal sulfide compounds. DGGE analysis, however, identified 26 different bacterial species that produce cake on the membrane and cause high-flux fouling in the first period of the experimental work. In the last period, another DGGE analysis was made to identify the number of the bacterial species inside of the bioreactor. This second DGGE analysis showed 24 bacterial species. In the context, it was determined that two bacterial species causing the fouling were missing as compared to the first DGGE analysis.

As a conclusion, performance of 0.45 μm and non-woven dynamic membrane was investigated. Remarkable amount of COD was treated (averagely) by 0.45 μm and non-woven dynamic membrane around 97% and 86%, respectively. MBR was efficiently operated at 10 LMH for each membrane type and relatively sustainable at 20 LMH flux.

Offline chemical cleaning eliminated almost complete irreversible fouling that were close to those of new membranes. In fact, at modest fluxes, it was also possible to operate without chemical cleaning. In the price-performance parity, dynamic membrane performance was fair enough to employ.

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Papers

Veral, M.A., Kizilet, A., Cinar, O., (2016). “Comparison of performance of membrane bioreactor with dynamic membrane bioreactor”, ICOEST.
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AWARDS

International University of Sarajevo, Success scholarship (2008-2012)
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