**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY**

# FABRICATION OF FORWARD OSMOSIS MEMBRANE AND ITS APPLICATION AFTER MEMBRANE BIOREACTOR

**M.Sc. THESIS**

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

# İLERİ OSMOZ MEMBRANI ÜRETİMİ VE MEMBRAN BİYOREAKTÖR SONRASI UYGULANMASI

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**Date of Submission : 13 March 2017**
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***To my beloved ones,***

**FOREWORD**

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April 2017 Seda Gazioğlu

(Environmental Engineer)

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## ABBREVIATIONS

**CA** : Cellulose Acetate
**CAS** : Conventional Activated Sludge
**COD** : Chemical Oxygen Demand
**CP** : Concentration Polarization
**CTA** : Cellulose Triacetate
**DS** : Draw Solution
**ED** : Electro Dialysis
**EPS** : Extracellular polymeric substances
**FO** : Forward Osmosis
**FOMBR** : Forward Osmosis Bioreactor
**FS** : Feed Solution
**F/M** : Food to Microorganism
**HRT** : Hydraulic Retention Time
**iMBR** : Immersed membrane bioreactor
**MBR** : Membrane bioreactor
**MF** : Microfiltration
**MLSS** : Mixed liquor suspended solids
**MLVSS** : Mixed liquor volatile suspended solids
**MWCO** : Molecular Weight Cut-off
**MPD** : m-Phenylenediamine
**NF** : Nanofiltration
**PA** : Polyamide
**PRO** : Pressure retarded osmosis
**RO** : Reverse Osmosis
**SMP** : Soluble microbial products
**SRT** : Sludge Retention Time
**SS** : Suspended solids
**SVI** : Sludge Volume Index
**TMC** : trimesoyl chloride
**UF** : Ultrafiltration
**VSS** : Volatile suspended solids
**WWTP** : Wastewater treatment plant

**SYMBOLS**

| | |
|---|---|
| **µ** | **:** osmotic pressure |
| **µm** | **:** micrometre |
| **ΔP** | **:** hydrolic pressure difference |
| **Δµ** | **:** osmotic pressure difference |
| **µS** | **:** microSiemens |

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# FABRICATION OF THIN FILM COMPOSITE ELECTROSPUN FORWARD OSMOSIS MEMBRANE AND APPLICATION ON EXTERNAL MEMBRANE BIOREACTOR

## SUMMARY


Water is vital element of life. A secure, sufficient and accessible supply of water is very crucial for the sustainable life for both modern societies. However, due to the population growth and human activities such as irrigation, excessive food production and other industrial activities are causing the environmental footprint on air, water and soil.

In order to provide future investment, it is necessary to limit this environmental footprint on water consumption by treating or reusing the wastewater effluents. Conventional wastewater treatment systems would not handle this treatment phenomenon by sustainable ways. This concept is required more environmental and energy efficient treatment systems for reducing environmental footprint. Methods for treating wastewater by membranes and membrane bioreactors can be the solution for this problem. However, one of the main energy consumption for membrane treatment systems such as UF, NF and RO is pressure. Forward osmosis (FO) is a not pressure driven system and use natural phenomena osmosis for permeate water. High concentration salt solution is used as a draw solution. In FO process, water permeates through the membrane from draw solution to feed solution. During this movement, membrane rejects the salts from draw solution and contaminants from the feed solution. Consequently, mass transfer is bi-directional in this process.

FO is an osmotically driven process that reduces the external pressure, energy input compared the other pressure driven process such as NF, RO. Due to the low hydraulic pressure there is no cake layer compaction in FO, and it reduces the membrane fouling problems.

Fabrication of high performance thin film composite electrospun forward osmosis membrane and assayed its treatment performance on external forward osmosis membrane bioreactor is the main issue of this thesis. In order to obtain high membrane performance, forward osmosis membrane was fabricated by the electrospinning method. Thin film composite (TFC) polyamide coating was applied on the surface of support layer produced by electrospinning. Sulfonated polysulphone solution prepared by dimethylacetamide solvent. In this thesis, a patented membrane that was fabricated in the case of the doctorate studies in the TUBITAK Project with the number 113Y356 is developed. The fabrication method in the electrospinning application was modified. As indicator of membrane forward osmosis performance, membrane characterization was done. In this case, SEM investigation, water and reverse salt flux measurements, fourier transform infrared spectroscopy (FTIR) and contact angle measurements were done.

Considering determining the wastewater treatment performance of TFC FO membrane, membrane bioreactor with ultrafiltration (UF) membrane was operated and

permeating of MBR was performed in FO lab scale system. A commercial UF membrane is used in MBR. MLSS/MLVSS, pH, temperature, and ORP and DO values has been measured for optimizing the activated sludge microorganism's activity.

High strength wastewater was fed to the MBR. The MBR was filled by the activated sludge that was taken from the Paşaköy Biological Treatment Plant. For acclimation of the activated sludge, MBR was started to operation 6 months before from the FO operation and there was not any sludge discharge from the MBR. UF permeate was using as the feed water in external FO system. For UF process each cycle time was 2h in average and then after completing the one cycle UF, samples has been taken from the system and the water characteristic is evaluated. 0,5 M NaCl/water solution with the 42500 µS/cm conductivity has been selected as draw solution. Every cycle in external FO process was started with the volume of 1 L draw solution and 1 L feed solution as UF permeate. The cycle was operated until the draw solution volume reached to the 1,5 L. After the cycle had been completed, sample from FO permeate was collected. Chemical oxygen demand (COD), turbidity, total phosphorus,total nitrogen, total kjehaldahl nitrogen, nitrate, nitrite experiments has done in order to evaluate the UF and FO permeate water quality and treatment performances. At the same time, water and reverse salt fluxes was measured by taken datas of weight from weighing scale and conductivity from the Hach Lange HQ40d conductivity probe.

The results of the present study demonstrate that, 120 L/m2/h pure water flux and 0,3 g/m2/h reverse salt flux was measured. 92 L/m2/h and 0,6 g/m2/h reverse salt flux were measured from the UF permeate operation in the FO system.

Hydrolic cleaning used 3 times in order to prevent fouling of the membrane.Since the first membrane coupon has defect, second membrane coupon installation was applied. Water and reverse salt flux determination also applied for the second coupon.

Organic matter removal was achieved 98% in the UF system. UF permeate COD value was measured 21 mg/L. FO permeate COD values was measured 18 mg/L approximately. COD removal rate was limited around 14%.

Total nitrogen was measured 49 mg/L in the synthetic wastewater. Total nitrogen level in the UF permeate was measured 35 mg/L. The total nitrogen removal rate of UF system was around 30%. In the FO system, TN removal rate was measured 5 mg/L and the removal rate was 85%. Total nitrogen removal rate was %93.

Total kjeldahl nitrogen was measured as 41 mg/L in the synthetic wastewater. In the UF permeate TKN level was 0,2 mg/L. TKN level in the FO permeate was measured as 0,1 mg/L approximately.

Nitrate value was measured as 0.2 m /L in synthetic wastewater. The nitrate value at the permeatet of UF is about 34 mg/L as a result of nitrogen conversion in the bioreactor. The nitrate value measured at the permeate of the FO system is around 4,6 mg/L. The total nitrate removal performance of the system is around 86%.

The nitrite value measured in the feed wastewater is 0,354 mg/L. This value is 0,036 mg/L at the permeate of UF. In FO permeate, nitrite is measured as 0.007 mg / L and the nitrite removal rate of the FO system is about 80%.

Total phosphorus (TP) was measured as 30 mg / L in feed wastewater. The TP value at the UF permeate is 8 mg / L. The UF removal rate of the UF system was determined to be 77%. The TP value is around 0.8 mg/L in the FO permeate. The TP recovery rate of the FO system was 89% and the TP recovery rate of the total system was 97%.

The turbidity value measured in the feed wastewater is around 107 ntu. UF showed a high performance in turbidity removal and the turbidity value at the permeate of the UF is around 2 ntu. The total system has achieved a turbidity value of 99%.

# İLERİ OSMOZ MEMBRANI ÜRETİMİ VE MEMBRAN BİYOREAKTÖR SONRASI UYGULANMASI

## ÖZET

Su hayatın temelidir. Sürdürülebilir bir yaşam için güvenli, yeterli ve ulaşılabilir su temini hem modern şehirler hem de küçük yerleşim birimleri için oldukça önemlidir. Ancak, nüfus artışı and sulama, gıda üretimi ve diğer endüstriyel faaliyetler gibi insan aktiviteleri hava,su ve toprak yapısında etkiler ağırlaşan etkiler bırakmaktadır.

Bir gelecek yatırımı olarak, bu çevresel etki suyun arıtılmasını ve tekrar kullanımını sağlayarak kısıtlanmalıdır.Konvansiyonel atıksu arıtım sistemleri suyun arıtılmasını sürdürülebilir olarak sağlamayabilir. Bu sürdürülebilirlik konsepti, çevresel etkiyi azaltmak için daha gelişmiş ve enerji dostu sistemler gerektirir. Bu problemin çözümünde membran filtrasyon ve membran biyoreaktörler çözüm olabilir. Ancak su NF (nanofiltrasyon), UF (ultrafiltrasyon) ve ters osmoz (RO) gibi membran sistemlerinin temel enerji gideri basınç nedeniyle olmaktadır. İleri osmos uygulaması bir basınç sürücülü system değildir ve doğal bir olay olan osmozu taklit eder. Çekme çözeltisi yüksek konsantrasyona sahip bir tuz çözeltisidir. FO sisteminde su çekme çözeltisinden besleme çözeltisine doğru yani yoğunluğu düşürülmek istenen çözeltiye doğru hareket eder. Bu hareket sırasında, membran çekme çözeltisinden beslemem çözeltisine doğru hareket etmek isteyen tuza ve aynı zamanda besleme çözeltisindeki kirleticilerin çekme çözeltisine doğru hareketine karşı koyar. Sonuç olarak kütle transferi bu sistemde tek yönlüdür.

FO bir osmotik sürücülü sistemdir ve dışardan bir basınç sürücüsü gerektirmez. Bu özelliği ile enerji ihtiyacı diğer NF, RO gibi diğer sistemlere göre daha azdır. Düşük hidrolik basınç nedeniyle MBR içi kullanımında membran kirlenme problemleri azdır.

Bu tez yüksek performanslı ince film kompozit elektrospun ileri osmoz membranı üretilmiş ve harici membran bioreaktör üzerinde arıtma performansı incelenmiştir. Bu tezde, yüksek FO performansı elde etmek amacıyla elektrospin memran üretim yöntemi kullanılmıştır. Sülfonlanmış polisülfon çözeltisi dimetilasetilamid çözücüsüyle hazırlanmıştır İnce film kompozit polyamid kaplama elektrospin yöntemiyle üretilen destek tabakası üzerine kaplanmıştır. İnce film kaplama tekniğinde organic çözücüde çözülmüş trimesoylchloride (TMC) ve inorganic çözücüde çözülmüş m-Phenylenediamine (MPD) çözeltisi kullanılmıştır Bu tezde, 113Y356 numaralı TUBITAK tezi doktora çalışması kapsamında üretilen ve patentlenen bir membranın üretim şartları değiştirilirek geliştirilen bir membran üreilmiştir. Membranın FO performansının belirlenmesi için karakterizasyon çalışması gerçekleştirilmiştir. Üretilen membranın saf su ters tuz akısını belirlemek amacıyla ileri osmoz hücresi içine membrane yerleştirilerek saf su ve 0,5 M NaCl çözeltisi kullanılarak ölçümler yapılmıştır. İleri osmoz performansının belirlenmesinde bir indikatör olarak SEM görüntelemesi, su ve ters tuz akı ölçümleri, fourier dönüşümlü kızılötesi spektroskopisi (FTIR) ve temas açısı ölçümleri yapılmıştır.

TFC FO membranın atıksu arıtma peformansının belirlenmesi amacıyla, membran bioreaktör işletilen ultrafiltrasyon (UF) membran süzüntüsü FO laboraturar ölçekli sisteminde işletilmiştir. UF süzüntüsü besleme çözeltisi olarak kullanılmıştır. MBR'de ticari UF membranı kullanılmıştır Ticari UF membrane modül haline getirilerek dahili olarak işletilmiştir. AKM/UAKM, pH, sıcaklık, ORP ve DO değerleri aktif çamur içerisindeki mikroorganizmaların faaliyetlerinin izlenmesi amacıyla SCADA sistemi ile sürekli takip edilmiş ve kaydedilmiştir. MBR yüksek kirlilikte sentetik atıksu ile beslenmiştir. Çamurun aklimasyonunu sağlamak amacıyla reaktör 6 ay öncesinden işletilmeye başlanmış ve çamur atımı yapılmamıştır. Biyoreaktör sonsuz çamur yaşıyla işletilmiştir.. UF prosesinde her bir döngü ortalama 2 saat sürmüştür. Döngü bitiminde UF çıkışından numuneler alınmıştır.

Uf çıkışından alınan numuneler FO sisteminde besleme çözeltisi olarak işletilmiştir. 42500 µS/cm iletkenliğe sahip 0,5 M NaCl  çözeltisi çekme çözeltisi olarak kullanılmıştr. FO sistemi 20 döngü işletilmiştir FO sisteminde her bir döngü 1L çekme çözeltisi ve 1 L besleme çözeltisi (UF çıkış suyu) ile başlatılmıştır. Her bir döngü çekme çözeltisi 1,5 L hacime gelene kadar işletilmiştir ve döngü sonlarında numuneler alınmıştır. Aynı zamanda su ve ters tuz akılarının grafikleri draw solution ağırlığı ve hem besleme hem de çekme çözeltilerinin iletkenliklerinin anlık olarak ölçülmesiyle oluşturulmuştur.

Bu tez kapsamında sonuç olarak 120 L/m$^2$/h saf su akısı ve 0,3 g/m$^2$/h ters tuz akısına sahip FO membrane UF çıkış suyu ile çalıştırıldığında ise 92 L/m$^2$/h su akısıve 0,6 g/m$^2$/h ters akısına sahip ileri osmoz membrane üretilmiştir.

İleri osmoz sistemine toplamda 3 kez hidrolik yıkama uygulanmıştır. İO hücresinde kullanılan membrane hidrolik yıkamadan zarar gördüğünden dolayı 1 kez değiştirilmiştir. Değişen membranın saf su ve ters tuz akısı tekrar incelenmiştir.

Hem UF hem de FO çıkış sularının kalitelerini belirlemek amacıyla, kimyasal oksijen ihtiyacı (KOİ), bulanıklık, toplam fosfor ve toplan azot değerleri ölçülmüştür.

Organik madde giderimi UF çıkışında %98 olarak başarılmıştır. Çıkış değeri ortalama 21 mg/L civarındadır.  İleri osmoz sistemi çıkışında ise kimyasal oksijen ihtiyacı (KOİ) ortalama 18 mg/L olarak ölçülmüştür. Giderim verimi %14 ile sınırlı kalmıştır. Sistemin toplam KOİ giderim verimi ise %98,6 olarak belirlenmiştir.

Toplam azot değeri besleme atıksuyunda ortalama 49 olarak ölçülmüştür. UF çıkışında ise bu değer 35 mg/L 'ye indirilebilinmiştir. UF sisteminin ortalama toplam azot giderim verimi %30 civarındadır. FO sisteminde ise UF ssiteminden daha yüksek bir azot giderim performansı belirlenmiştir.  FO çıkışında ölçülen toplam azot (TN) değeri 5 mg/L civarındadır. Giderim verimi ise %85' tir. Sistemin toplam azot giderim verimi %93 civarındadır.

Toplam kjeldahl azotu (TKN) değeri besleme atıksuyunda 41 mg/L olarak ölçülmüştür. UF çıkışında TKN değeri 0,2 mg/L 'dir. UF sisteminin TKN giderim performansı %99 civarındadır. FO çıkışında ölçülen TKN değeri ise 0,1 mg/L civarındadır.

Nitrate değeri besleme atıksuyunda 0,2 mg/L olarak ölçülmüştür. Biyoreaktörde azotun nitrata çevirilmesi sonucunda UF çıkışında nitrat değeri 34 mg/L civarındadır. FO sisteminin çıkışında ölçülen nitrat değeri 4,6 mg/L civarındadır. Sistemin toplam nitrate giderim verimi %86 civarındadır.

Besleme atıksuyunda ölçülen nitrit değeri 0,354 mg/L'dir. Bu değer UF çıkışında 0,036 mg/L'dir. FO çıkışında ise nitrit 0,007 mg/L olarak ölçülmüştür ve FO sisteminin nitrit giderim verimi %80 civarındadır.

Toplam fosfor (TP) besleme atıksuyunda 30 mg/L olarak ölçülmüştür. UF çıkışında TP değeri 8 mg/L 'dir. UF sisteminin TP giderim verimi %77 olarak belirlenmiştir. FO çıkışında ise TP değeri 0,8 mg/L civarındadır. FO sisteminin TP giderim verimi %89 olarak , toplam sistemin TP giderimi ise %97 olarak belirlenmiştir.

Besleme atıksuyunda ölçülen bulanıklık değeri 107 ntu civarındadır. UF bulanıklık gideriminde yüksek bir performans göstermiş ve UF çıkışında elde edilen bulaıklık değeri 2 ntu civarındadır. Toplam system bulanıklık değerini %99 verimle gidermeyi başarmıştır.

# 1. INTRODUCTION

Energy efficient water treatment system is one of the most important subject for the local authorities and the scientists due to the high-energy prices andsustainable development concerns. Forward osmosis working principle is the natural phenomena osmosis. Concentration difference between feed and draw solutions caused the osmotic pressure, and the system not required the external pressure.

In competing with conventional MBR processes, the high removal of pollutants with the pressure driven membrane technologies by reducing the pressure requirement has been a one of the most issue researchers. Forward osmosis is one of the most emergent membrane phenomenon. Water flux should be high and the reverse salt flux should be minimum in forward osmosis systems. In order to obtain this situation, membrane characteristic is quite important, however, Forward osmosis membrane fabrication is still an emergent topic in literature.

## 1.1 Purpose of Thesis

The overall objective of this study is to fabricate the electrospun thin film composite forward osmosis membrane and then evaluate its treatment performance. Main goal of the forward osmosis membrane was high water flux and low reverse salt flux.

In this study,high MLSS content MBR with UF membrane module is operated and it permeate was collected daily. UF permeates was used as a feed solution for testing the forward osmosis membrane. In this test, a bench scale forward osmosis system was used. One of the main objective of this study is determining the treatment performance of forward osmosis system. In this case permeate water quality of both UF permeate and FO permeate were determined.

## 1.2 Content of Thesis

In the first part of this thesis importance of the study is emphasized the mission and scope of this thesis are given.

In the second part of this study, literature rewiev is given about membrane technology, membrane fabrication methods and forward osmosis.

At the third part of this thesis, fabrication method of the forward osmosis membrane, characterization of membrane, MBR operation and the analyses is evaluated.

In the fourth part of the study, membrane characterization results and MBR operation results are given. UF MBR and forward osmosis setup results are given comparatively.

In the fifth part, conculusion and the recommendations about this study is evaluated.

# 2. LITERATURE REVIEW

## 2.1 Membrane Technology

Membranes are designed to accomplish separation proses by physical and physicochemical methods. They are generally defined as a selective barrier between two phases. With the identification of the osmose concept, membrane systems were emerged in the end of 18th s and started to examine in the beginnings of 19th and 20th centuries in laboratory scale and then large scale systems were started to operate in 1960s. After 1980s, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and electro dialysis (ED) processes were started use widely in treatment plants. Due to the developments of membrane production methods their usage are progressed in food, chemical, petro chemistry, mining, metal working, biotechnology, electronic etc. industries. In wastewater treatment, membrane is used to reject the pollutants from wastewater. For this purpose, reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) processes are using. In this processes, pressure is applied to membrane and then one form is concentrated as unpermeated and the other form is filtered as permeate. About 75% of the membrane sales consist of the pressure-driven filtration process in the municipal and industrial water treatment processes (Judd, 2003).

### 2.1.1 Membrane structure and materials

Membrane separation performance that is related with the capital and operating cost of membrane process depends on the material and structure. Membrane material should have some characteristics such as:

- Chemical resistance
- Mechanical stability
- Thermal stability
- High permeability
- High selectivity

Chemical resistance is important for drinking water treatment since polymeric membranes react with oxidant and they should not be used with chlorinated water. On the other hand, mechanical strength is considerable since membrane should tolerate the higher transmembrane pressure (TMP) for the operational flexibility (Membrane Filtration Guidance, 2003). For hot wastewaters such as textile wastewaters, thermal stability must be considered. Otherwise, high permeability, high selectivity and stability have importance due to the economical and operational aspects.

Material of isotropic membrane may be categorized according to separation size of molecules as dense and porous. Schematic diagrams of structure of membranes are given in the Figure 1. The Dense membranes has highest selectivity and some profits on physicochemical interactions between permeate and membrane. Permeate transportation is occurred under the force of pressure, concentration or electrical potential gradient; moreover, related directly diffusion and solubility in the membrane material (Baker, 2013). Beside, separation is related to the rejected material size and membrane pore size for porous membranes (Judd, 2003). Porous membranes are used in microfiltration, ultrafiltration, forward osmosis and nonporous membranes are used in pervaporation, vapor permeation, gas separation, dialysis and reverse osmosis (Mulder, 1998). Anisotropic membranes have thin surface layer and thicker porous support layer. Membranes should be thin as much as possible for achieving the high transport rates that is important for economic reasons. Anisotropic membranes use widely for commercial processes since they provide high water fluxes (Figure 2.1) (Baker, 2013).

Membrane classification can be done by water interactivity also. In this categorization hydrophilic and hydrophobic terms are used. Hydrophilic refers to affinity for water and hydrophobic refers to water repelling. These properties indicate the whether the membrane can be wetted or not, moreover material resistance to fouling for some degree (Membrane Filtration Guidance, 2003).

Membranes can be categorized through the material composition as well; organic (polymeric) or inorganic (ceramic, metallic). Morphology of the membrane is related with the formation of the material and the method of the processes during production (Judd, 2003).

Membranes can be produced from three types of materials as synthetic polymers, modified natural products and miscellaneous materials for instance inorganic, ceramic, metals, dynamic and liquid membranes (Scott and Hughes, 1996). Generally, polymeric substances are used for membrane manufacturing for water treatment whereas the economic reasons. Metallic, ceramic, dynamic, and liquid membranes have sophisticated usage areas.

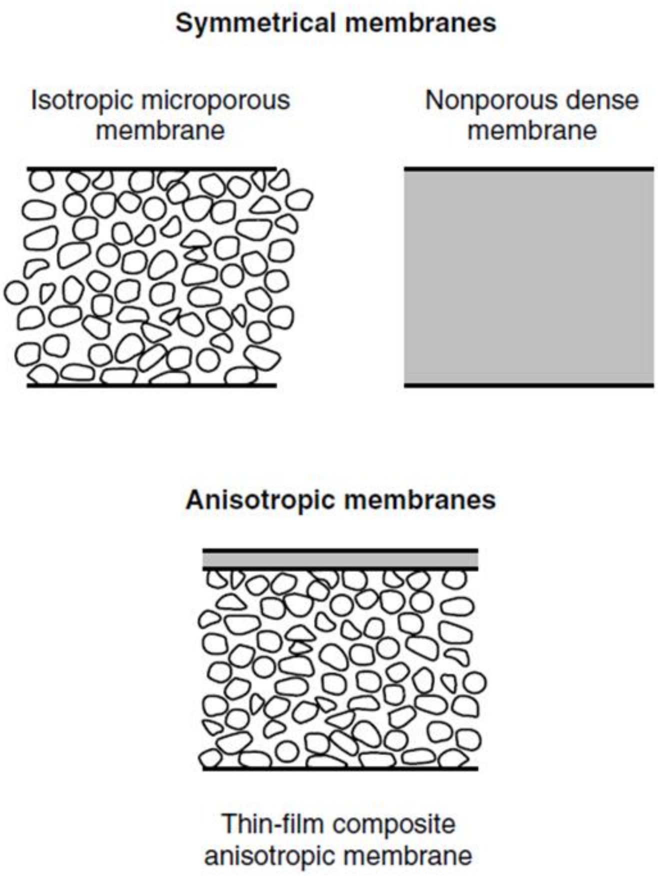


**Figure 2.1 :** Structure of membranes schematic diagrams.

### 2.1.2 Membrane classification

Membranes that are used for wastewater treatment can be classified in five categories according to their pore size:

- Microfiltration (MF)
- Ultrafiltration (UF)
- Nanofiltration (NF)
- Reverse Osmosis (RO)
- Electro dialysis and electro dialysis reversal (ED/EDR).

Figure 2.2 depicts various membrane classifications according to their pore size and separation property. Classification of the membranes can be done by either the membrane filtrate the dissolved particles or suspended or colloidal particulates. Reverse osmosis, nanofiltration and ED/EDR membranes remove solutes and microfiltration membranes remove particles.

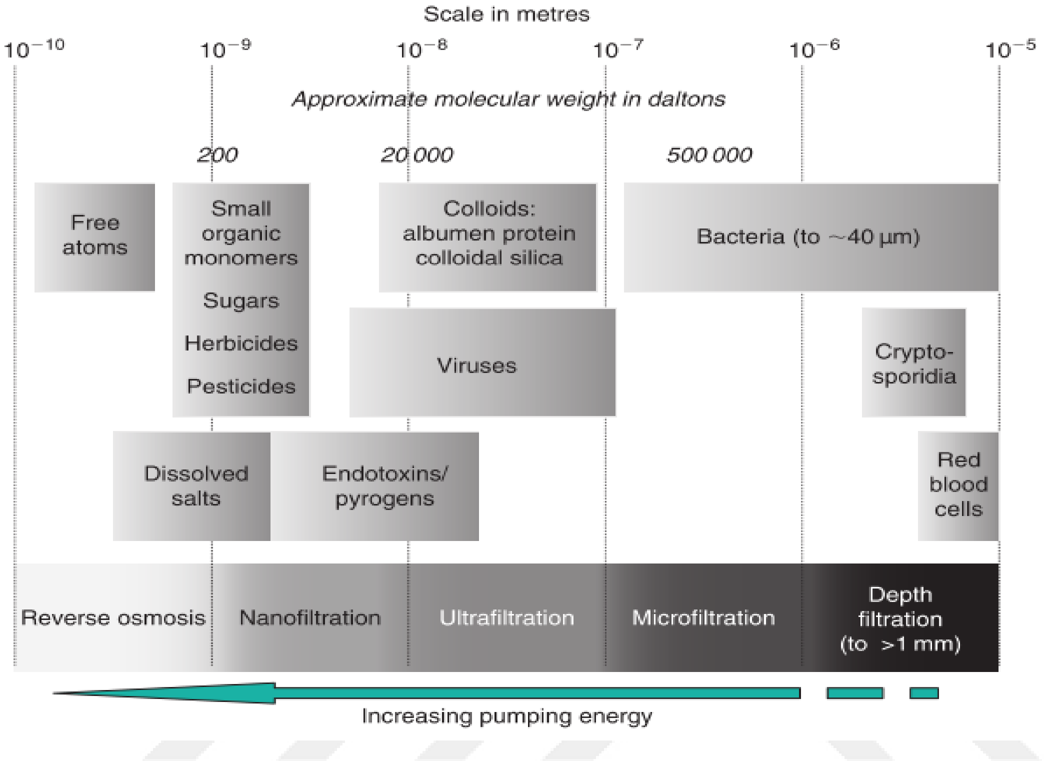


**Figure 2.2 :** Membrane size spectrum (Judd and Judd 2008)

#### 2.1.2.1 Microfiltration

Microfiltration is oldest membrane prosess and removes particulates, bacterias and protozoan cysts (WEF, 2011). The pore size of MF is in the range of 0 05-10 µm. Particles larger than this pore size cannot transfer from MF membrane; however, generally they adsorbed on the pore and cause size reduction. Secondary filter layer from these particles is formed and membrane separate smaller particles than its pore size. This situation is also resulted by the flux reduction (R. Singh, 2005).

Figure 2.3 are shows the process modes. MF membrane processes are commonly operated in dead-end filtration mode. In this mode, feed flow is forced perpendicularly through to the membrane surface under pressure. Water and smaller molecules than MF pore size filter through the membrane and there is no reject stream generation. In cross-flow membrane processes, feed flow is circulated across the membrane surface and unlike dead-end mode, there is two-stream production as permeate and retentate contains particles. In this mode, membrane lifetime is longer than dead-end mode. In semi-dead-end filtration system is operated both with the dead-end and cross-flow mode (Baker, 2004)

Ultrafiltration membranes have pore diameters in the range of 0.001 to 0.02 microns. UF and MF membranes are typically used in membrane bioreactors (MBRs) and can be used as pretreatment to NF and RO applications. Proteins, dyes and other macromolecules can be concentrating or purified by UF. For sustainability concerns, recycling or raw materials, products and by products is an important concern in wastewater treatment plants (WWTPs). In this concept, paint recovery in electrophoretic painting industries, and lignin and lignosulforates from black liquor in the pulp and paper industry can achieved by UF systems (Schafer, 2001).

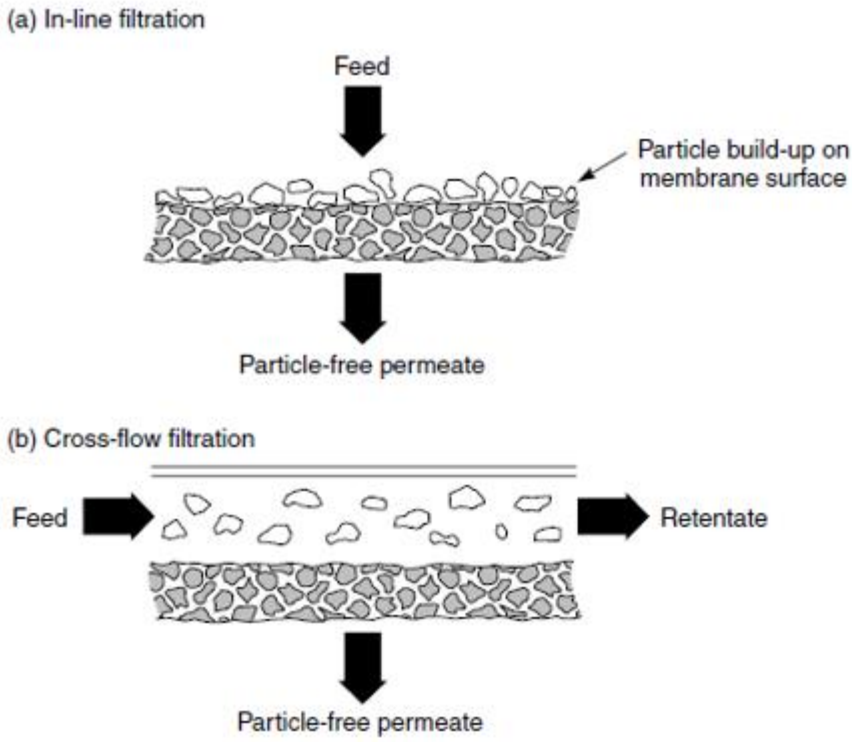


**Figure 2.3 :** Process modes of filtration (a) in line and (b) cross-flow filtration (Baker, 2004).

UF membranes fabricate generally in two forms: tubular and flat sheet, moreover, are produced from cellulose acetate or noncellulosic plastics (synthetic polymers) as acrylates or polysulfones and ceramic. Structure of UF membrane is porous and more asymmetric compared to the MF membranes. UF membranes are operated under low transmembrane pressures such as 0,5 to 5 bars (Jacangelo, 1996). The characteristics of the MF and UF membranes are summarized in table 2.1.

**Table 2.1 :** Characteristic features of Microfiltration and Ultrafiltration (Institut für Siedlungswasserwirtschaft 2006).

| | Microfiltration | Ultrafiltration |
|---|---|---|
| Operation Mode | Cross-flow and dead-end-operation | Cross-flow and dead-end |
| Operationg Pressure | 0,1-3 bar (transmembrane) | 0,5-10 bar (transmembrane) |
| Separating mechanism | Screening controlled by covering | Screening controlled by covering layer |
| Moldecular separation size | Solids> 0,1 µm | Colloids:20.000-200.000 Dalton<br>Solids> 0,005 µm |
| Membrane type | Symmetric polymer or ceramis membranes | Asymmetric polymer composit or ceramic |
| Module type | Spiral-wound,hollow-fibre and tubuler,flat sheet | Spiral wound,hollow fibre and tubular and flat sheet |

#### 2.1.2.2 Nanofiltration

Nanofiltration (NF) is a pressure driven process and can remove soluble matters. At first, NF was developed for the purpose of membrane softening. NF can remove 60 to 80 percent of the total hardness, more than 90 percent of the color, and virtually all the turbidity. But NF is less effective for removing monovalent ions. These single charged species are removed by diffusion and sieving mechanism through the reverse osmosis.

NF membranes pore size is larger than reverse osmosis membranes and smaller than ultrafiltration membranes and their pore size is 0.002 µm. The molecular weight cutoff (MWCO) typically ranges from 200 to 1000 Daltons. The characteristics of the NF membranes are summarized in table 2.2.

Up to now nanofiltration has not been used in municipal waste water treatment. In industrial waste water treatment, NF is used as relief of ion exchangers or downstream reverse osmosis units, removal of color in the waste water of the textile and the pulp and paper industry, demineralization of the waste water containing surfactants (Institut für Siedlungswasserwirtschaft, 2006).

**Table 2.2 :** Characteristic features of nanofiltration (Institut für Siedlungswasserwirtschaft, 2006).

| | Nanofiltration |
|---|---|
| Operation Mode | Cross-flow operaion |
| Operationg Pressure | 2-40 bar (transmembrane) |
| Separation mechanism | Solubility/diffusion/charge (ion selectivity) |
| Moldecular separation size | Dissolved matter: 200 – 20.000 Dalton<br>Solids > 0.001 μm |
| Membrane type | asymmetric polymer or composite membrane |
| Module type | spiral-wound, tube, and cushion modules |

## 2.2 Membrane Fabrication Methods

According to polymer and preferred membrane structure, fabrication techniques are chosen such as phase inversion, solution coating, interfacial polymerization, stretching, track etching and electrospinning.

### 2.2.1 Phase inversion

Phase inversion method or phase separation method means transform one phase casting solution into two separate phases; solid polymer rich phase and liquid polymer poor phase which forms the membrane pores (Baker, 2004). There is various ways for achieve this transformation:

Immersion precipitation: Water is used as non-solvent in coagulation bath and the polymer solution is immersed in it. The solvent surrounding the polymer moves into the water and causes phase separation. According to exchange of solvent and non-solvent, demixing and precipitation is occured.

Thermally induced phase separation, polymer sets by temperature decreasing. The solvent is removed by extraction, evoporation or freezing.

Evaporation-induced phase separation: This method is also called as solution casting method. Polymer concentration is increased by evaporation and phae separation is occured. Precipitation or demixing/precipitation result.

Vapor-induced phase separation: Polymer solution is exposed to athmosphere containing a non-solvent (generally water); absorption of non-solvent causes demixing/precipitation (Singh et al, 2013).

### 2.2.2 Solution casting

Solution casting method is generally used at laboratory scale and applied as phase inversion method. Polymer is spread onto the glass plate as a thin film by the help of casting knife. Then glass plate is immersed into the water for the forming of the polymer film layer.

### 2.2.3 Interfacial polymerization

Interfacial polymerization method is generally used for fabrication of anisotropic membranes such as thin film composite (TFC) RO and NF membranes. Thin film is produced by the reaction of two monomers. In this method microporous, support membrane is soaked into the aqueous of polymerica amin and then solvent solution acting as reactant such as diacid chloride. The process is illustrated in figure 2.4.

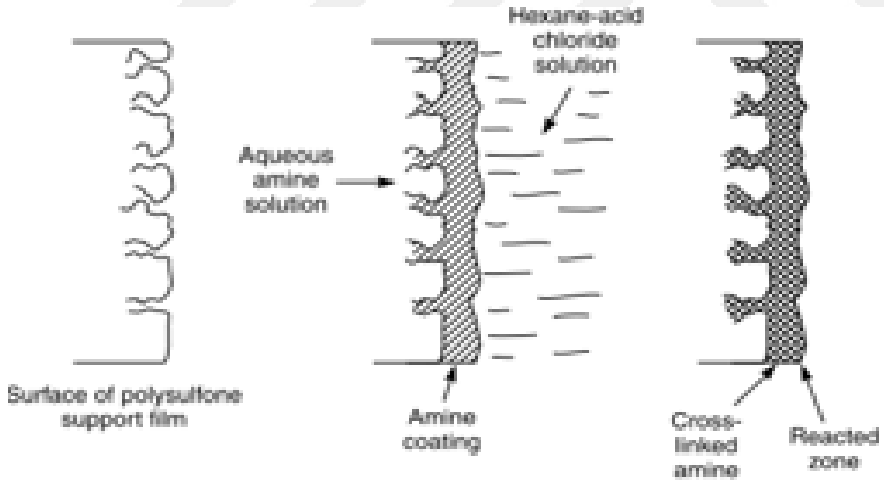


**Figure 2.4 :** Illustration of interfacial polymerization process ( Laila et al, 2013).

By interfacial polymerization method, most of the NF and RO membranes are produced which have polyamid (PA) thin TFC layer on the surface (figure. 2.5). Generally, m-phenylenediamine (MPD) and trimesoyl chloride (TMC) monomers are used for TFC. Other amine monomers for fabrication of TFC PA membranes include p-phenylenediamine, piperazine, triethylenetetramine, N-N′-diaminopiperazine, N-(2-aminoethyl)-piperazine, and poly (ethyleneimine).

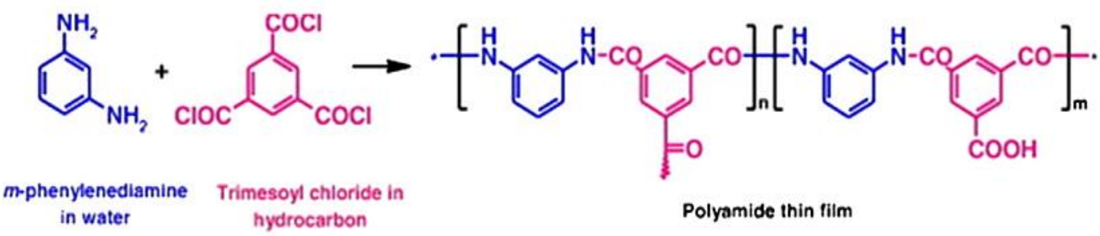


**Figure 2.5 :** Formation of thin film PA membrane from m-phenylenediamine (MPD) and trimesoyl chloride (TMC) via interfacial polymerization (Singh et al, 2013).

Dense, highly cross linked polymer layer that is about 0,1 µm or less, appeared on the support layer bu interfacial polymerization. Since the polymer is highly crosslinked, selectivity of membrane can be also high. PA layer film affects water flux importantly. The film should have high surface porosity that is not decreased the water flux (Baker, 2004).

### 2.2.4 Stretching

Expanded film membranes are produced by stretching method by crystalized polymers. At the first step, stretching is apply by elongating the polypropilen fastly around the melting point of polymer. Then, cyristalits inside the semi cyristalized polymer accelerate towards to stretching direction. The result is that crystalline regions are located parallel to the extrusion direction. As long as obtaining porous structure, mechanical stress is apply.Pore sizes are in the range between 0.1 and 3 µm (Nne, 2004).

### 2.2.5 Track etching

Tracking the sheet of polymeric material and then etching away the polymeric material along the tracks in an alkaline or hydrogen bath (according to the material). In this process, the radiation source bombard the polymeric sheet for the formation of pores. The polymer bonds are broke onto the polymeric sheet by the radiation perforation; moreover, they set back ways consist of fragile damaged polymeric molecules. After etching solution these ways are etched and pores are occurred (Khulbe et al, 2008).

### 2.2.6 Electrospinning

The term “electrospinning” came from “electrostatic spinning” Electrospinnig is a technique for smooth nanofiber fabrication from different polymers. In this technique, high electric field is used to nanofiber fabrication from charged polymer solution (Ahmed et al.,2015).

The first patent of this technique obtained by J. F. Gooley in 1900 and further improvement in the commercial area was about textile production. By further developments about generation of one dimensional polmer structures paved the way of usage of electrospinning technique in wide area research after 1990s. Theories about electrospinning such as Taylor Cone theory, Bending Instability theory, Electrically Forced Jet-Stability theory ensure better designed setups and understanding for researches. In the light of these theories, electrospun nanostructures derived from single solidified polymer nanofibers to polymer/inorganic hybrid nanofibers, inorganic and hollow nanotubes etc. Today, electrospinning technique is used tissue engineering, drug delivery, optoelectronics, chemiresistors, catalysis, filters, fiber reinforcement, wounding healing, photoelectronics, FET, magnetic devices (Li & Wang, 2013).

### 2.2.7 Electrospinning setups

In electrospinning technique, high voltage supply, syringe for polymer dosage and a collector are fundamental components (Figure 2.6).

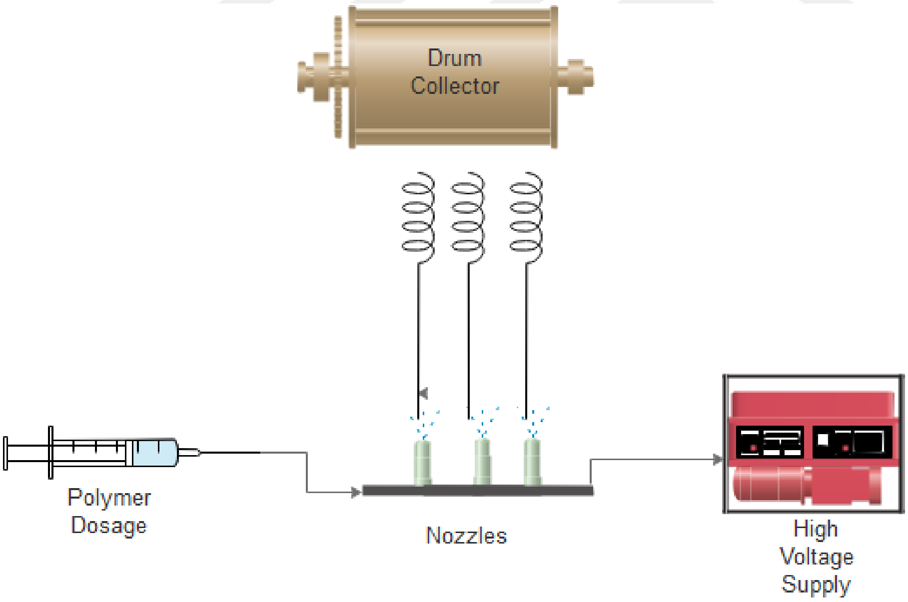


**Figure 2.6 :** Shematic of electrospinning process.

When high voltage is applied, the polymer drop dosed from syringe is polarized and the induced charges distribute the fibers on the surface. By continue of this process, fibers roll up on the collector and the surface from fibers is produced (Li & Wang, 2013).

## 2.3 Forward Osmosis and Reverse Osmosis

### 2.3.1 Forward osmosis

Osmosis is a physical phenomenon that is conventionally defined as the transition of the water through the selective membrane. Driving force in this phenomenon is osmotic pressure that is defined as the pressure that must be applied to the solution to stop the net flow from a pure diffusion solvent across the membrane into the solution (Figure 2.7). Osmotic pressure has a relation with the chemical potential such as concentration and boiling point elevation and freezing point depression. The osmotic pressure increases with the concentration of the solution increases. Osmotic pressure (represented by π (pi) is a function of the dissolved solids concentration where n is sum of all ions (2.1). For every 100 ppm total dissolved solids (TDS) it ranges 0.6 to 1.1 psi. Brackish water (1,500 ppm TDS) has 15 psi osmotic pressure (Kucera, 2010).

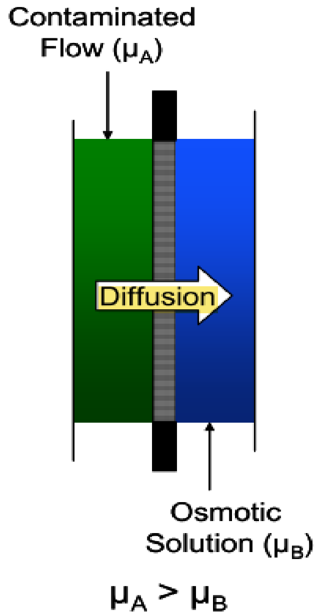


**Figure 2.7 :** Flow of water through the low concentration to low chemical potential (high salt concentration) (Miller and Evans 2006).

Forward osmosis (FO) is technical term for describe osmosis; FO has same principles with osmosis but there is further engineering applications in it. As the same, osmotic pressure plays the essential role in FO. FO has two main advantages such as low energy consumption and low fouling property in both desalination process and membrane bioreactors.

$$\pi = nRT \quad (2.1)$$

Batchelder patented in 1965 a method of FO-desalination suggesting a draw solution with sulfur dioxide (Alsvik & Hägg, 2013). There is more than 1000 publications about FO since 18th century, however, there is much more interest since 2005 (Figure 2.8).

Usage areas of FO's are industrial wastewater treatment (at bench-scale), landfill leachate concentration (pilot and bench-scale) and liquid food treatment in food industry. There is also studies of FO about reclaiming waste water for potable reuse in life support systems, desalination of seawater and purifying water in emergency situations (T. Cath, Childress, & Elimelech, 2006).

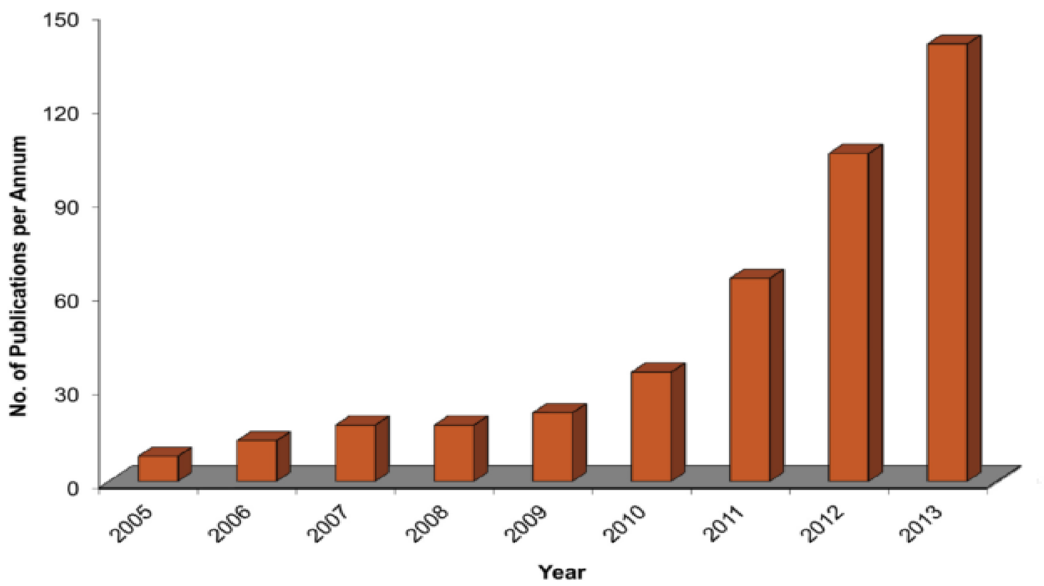


**Figure 2.8 :** FO publication growth (Lutchmiah et al. 2014a).

### 2.3.1.1 Forward osmosis process

In FO process, water permeates through the membrane from draw solution to feed solution. During this movement, membrane rejects the salt and contaminants in the feed solution. Because of this, mass transfer is bi-directional in this process. FO is an osmotically driven process that reduces the external pressure and energy input compared the other pressure driven process such as NF and RO. Due to the low hydraulic pressure there is no cake layer compaction in FO and it reduces the membrane fouling problems (Xie, 2014). Draw solution is a high concentration solution. By the time, due to the water movement to the draw solution osmotic pressure is decreased and must be concentrated for reuse. Although it is not necessary for all FO applications, draw solution concentration is usually applied for desalination and water/wastewater treatment applications. FO process scheme is given in figure 2.9.

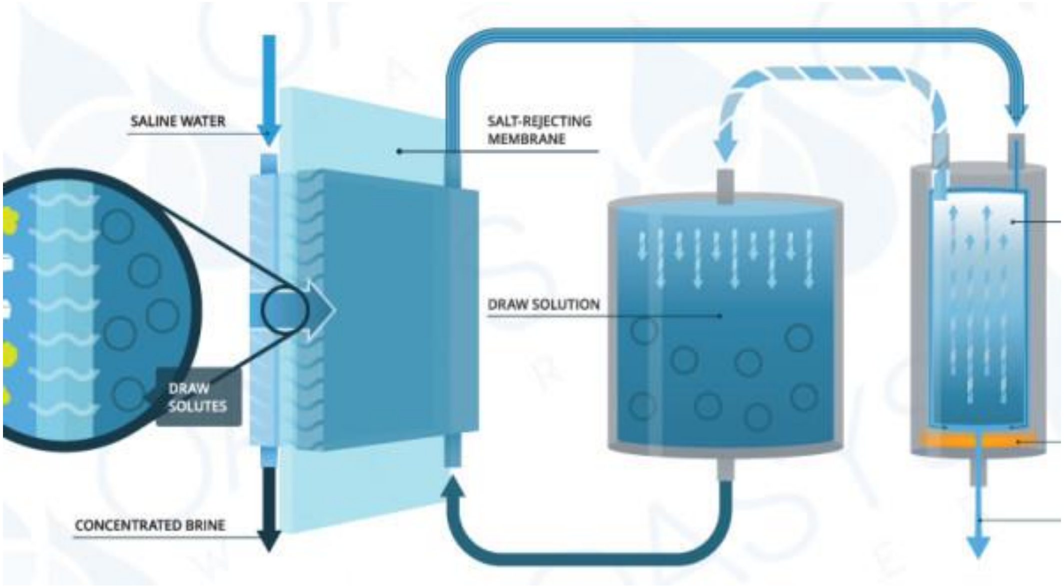


**Figure 2.9 :** Forward Osmosis Process (oasyswater.com).

#### 2.3.1.2 Previous FO studies for wastewater treatment

Rejection of salt and other contaminants in feed solution can be achieved by FO membrane since mass transfer in FO is bi-directional. While reverse diffusion of draw solution, forward diffusion of water and feed solute is ensured.

Direct FO applications has a promising attention in consideration of low energy requirement (Ding et al, 2014) Landfill leachate, anaerobic digester concentrate, activated sludge solution and domestic wastewater examined the rejection mechanism for 40 trace organic polutants.(Cartinella et al., 2006), studied of the rejection of hormones by FO process. Cath et al, 2010 studied for the investigation the treatment performance of FO system both with secondary and tertiary treated effluents from a domestic wastewater treatment plant and impaired surface water were used as feed water to the process in bench scale and pilot scale. They achieved 74% ammonia rejection and 85% nitrate rejection.They also reported the rejection of six pharmaceutical compounds 72% (salicylic acid) and more than 99% diclofenac (Xie, 2014).

#### 2.3.1.3 Membrane properties of forward osmosis process

Ideal FO membrane should have a high rate of water flux. During water permeation, membrane should not allow to cross contamination of salts. High permeate water flux and low reverse flux are important for replacement costs and potential environmental impacts. On the other hand, salt rejection is significant during membrane bioreactor operation since salt has an inhibition effect on biological activity of the activated sludge.

Ideally, FO membrane should has some important characteristics for wastewater treatment applications:

- a dense, ultra-thin, active-separating layer for high solute rejection;
- an open, thin (as possible), hydrophilic SL, with high me- chanical stability, sustaining long-term operation and reducing ICP;
- a high affinity for water (hydrophilicity) for enhanced flux and reduced fouling propensity (Lutchmiah et all., 2014)

Commercial FO membranes are fabricated by cellulose triacetate (CTA). CTA membranes are resistant to chlorine, thermal, chemical and biological degradation (Mulder, 1998). Thin-film composite (TFC) membranes is also used for FO process and it is reported that they are superior than CTA membranes in terms of permeability and stability (Lutchmiah, Verliefde, et al., 2014b).

Forward osmosis membranes are selling commercially by HTI, Oasys Water, Porifera and Aquaporin companies (www.filtsep.com 01.03.2015). "Hydration Technology Innovations (HTI)" produces cellulose triacetate, "Oasyse Water", "Porifera" produces TFC, and "Aquaporin" produces biomimetic FO membranes.

#### 2.3.1.4 Membrane orientation

FO membranes are asymmetrical membranes that have two different layer as active and support. Active side is dense and selective and porous support layer provides mechanical strength.

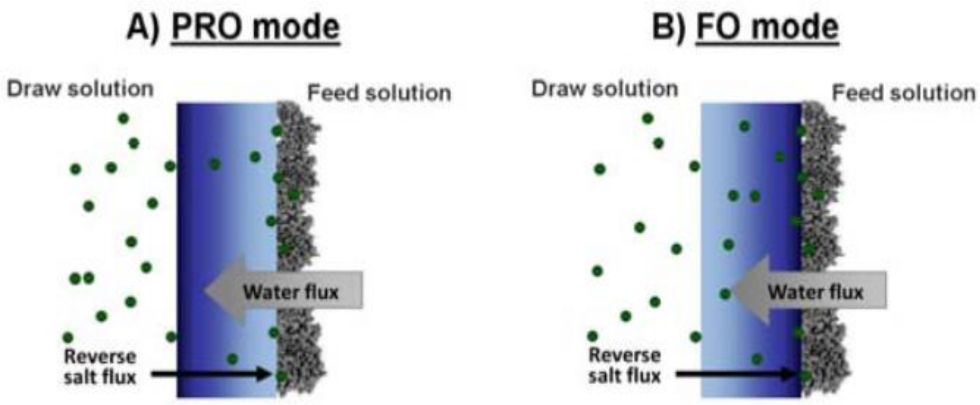


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**Figure 2.1 :** A) Pressure retarded osmosis (PRO) and forward osmosis (FO) modes (Alsvik et al., 2013)

FO and PRO modes are two different configurations for FO membrane operation. In FO mode, active side of membrane contact with the feed water and in PRO mode, feed solution is contact with the support layer (Figure 2.10).

Membrane orientation plays a role on the fouling. Stability can be observed against the draw solution and membrane fouling in FO mode, however, PRO mode; due to the internal concentration polarization (ICP) water flux is reduced (Zhao et all., 2011).

#### 2.3.1.5 Module configuration

Membrane module term is referred to packing of membranes into the single operational unit. Pressure support structures, feed inlet and concentrate outlet ports and permeate draw-off points are taken places on the membrane module. There is three important cosiderations for designing modules:

- Achieving sufficient circulation of the feed water for prevent the ICP
- Maximizing the membrane surface area in certain volume
- Prevent the mixing of feed and permeate flows (Jacangelo, 1996).

Configurations that are used for forward osmosis wastewater applications is given in table 2.3.

**Table 2.3 :** FO module configurations for wastewater treatment (Lutchmiah, et al. 2014a).

| Configuration | Advantages | Disadvantages |
|---|---|---|
| Spiral Wound (SW) | High packing density<br>Easy cleaning of fouling deposits | Limited pressures in membrane envelop<br>Clogging of spacers |
| Hollow Fibre (HF) | Self supported characteristics<br>Appropriate flow patterns<br>Simplicity of fabrication<br>High packing density | Limited mixing at membrane surface<br>In open channels the CP film grows undisturbed in the channel |
| Plates and frame (PNF) | Well-suited to wastewater applications<br>Less complicated in design<br>Higher cross-flow velocities | More expensive per m2 of the membrane area |

#### 2.3.1.6 Concentration polarization

Concentration polarizastion (CP) is a result of the concentration difference between draw solution and feed solution in osmotically driven membrane process. In the both PRO and FO mode, external concentration polarization exist on the surface of the active layer (figure 2.1). External concentration polarization scales down the net driven force owing to increase of the osmotic pressure on the active layer on the feed flow side and decrease of the osmotic pressure on the active layer on the draw solution. Destructive effect of the draw side external concentration polarization can be a limiting factor when the water flux is high (Chanukya et al.,2013).

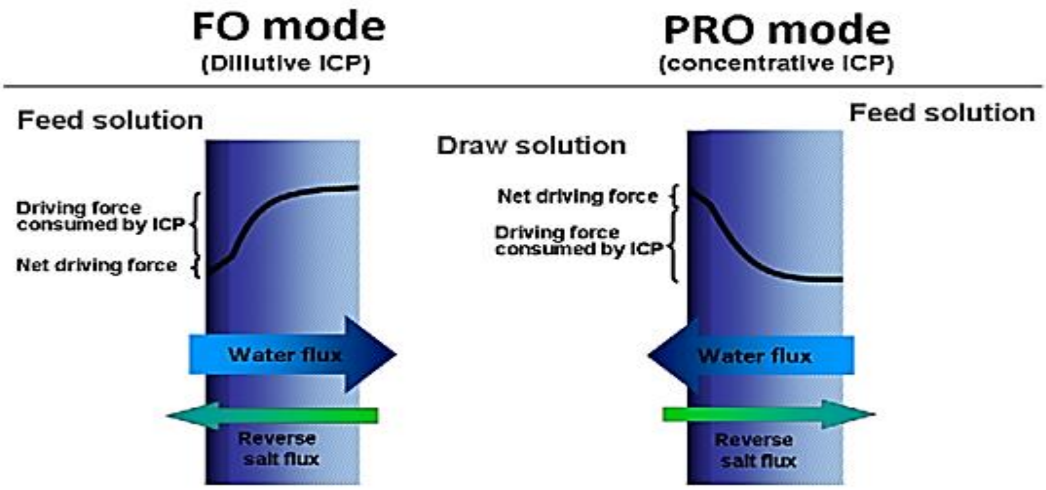


**Figure 2.1 :** Dilutive and concentrative ICP illustrations.

Internal concentration polarization (ICP) takes place only osmotically driven membrane process such as FO and PRO. Concentrative ICP appears when the active layer contacts the draw solution. Efficient driving force decreases by the draw solution accumulation between active and support layer. Dilutive ICP befalls if the active layer contacts with the feed solution. In the porous support, water flux from the feed to draw solution ends up with the transmembrane osmotic pressure reduction (Alsvik & Hägg, 2013).

#### 2.3.1.7 Reverse salt leakage

Although draw solution serves a prime power to FO process, can limit the process also since the reverse solute leakage. Leakage of the solutes in draw solution through the membrane to feed flow side is called as reverse salt leakage. This leakage has negative effect on the process performance by the osmotic pressure declination (Lutchmiah et al. 2014). In FO membrane bioreactor systems reverse salt leakage may has negative effects that are related with the process sustainability but some recent researchs has been linked that there is not highly affect on the biological activity because of the low salt concentrations reached at steady state (Lefebvre & Moletta, 2006). FO membranes do not enable to 100% salt rejection (Hancock & Cath, 2009),however, it can be limited.

### 2.3.2 Reverse osmosis process

Reverse osmosis (RO) process has been using in 80% of the total number of desalination plants installed worldwide since 1960s. (Greenlee, Lawler, Freeman, Marrot, & Moulin, 2009).In this process, hydraulic pressure is given to the feed flow side and water permeate from the semipermeable membrane. Hydraulic pressure reverse the osmotic pressure direction and membrane acts as a barrier and keeps minerals and other contaminants in the feed side (Figure 2.12). As a result, concentrated salt solution remains in the feed side and pure solution on the other side of the membrane. Contaminant particles as small as 0.00001 μm can be removed by reverse osmosis process such as hardness, color, many kinds of bacteria and viruses, organic contaminants. The basic water flow equation through the membrane is given as follows (R. Singh, 2005):

$$J_w = A\ (\Delta P - \Delta \pi) \qquad (2.2)$$

In the equation given below; $J_w$ is the membrane water flux, A is the membrane permeability coefficient for water, $\Delta P$ the hydraulic pressure differential across the membrane and $\Delta \pi$ the osmotic pressure differential across the membrane. Water flux is important in terms of system design, it should be arranged according to influent water quality since higher flux causes the rapid fouling on the membrane. Water transport coefficient is related with the membrane characteristic and changes directly with the temperature (Kucera, 2010). It can be concluded that, RO process efficiency is highly correlated with the RO membrane properties.

RO membranes should have high mechanical strength due to the high hydraulic pressure. For instance RO membranes that are used in seawater desalination are exposed to 2400 kPa (24,5) atm pressure, however, they typically operating under 7-10 bars. RO membranes are generally used in crossflow mode that decreases the fouling of the membrane since parallel flow to membrane. It helps to clean off the membrane surface. Materials that are using in RO membrane active surface production are cellulose acetate (CA), polyamide (PA) and composite, and the other combinations of the organic polymers. CA membranes not have highly mechanical durability and resistant to fouling and also can only be use in a 4.5-7.9 pH range. On the other hand, polyamid membranes have higher mechanical strength and pH-temperature resistant (Xu et al., 2013).

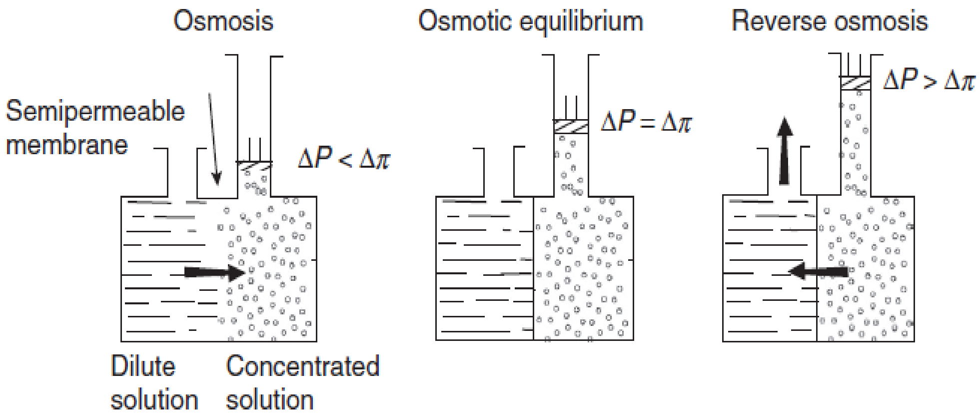


**Figure 2.2 :** At osmotic equilibrium, the osmotic pressure (ΔP) across the membrane is balanced by the hydrostatic pressure (ΔP) applied to the concentrated solution (Singh, 2005).

### 2.3.3 FO process versus RO process in membrane technology

RO is one of the most common desalination and wastewater reuse process. Although RO effluent quality is cost-competitive and has higher quality than conventional biological and thermal processes RO is not a best efficient and sustainable process because of the high energy consumption and fouling problem. Making a desalination and wastewater reuse process more sustainable requires some steps: decreasing the energy consumption, chemical cleaning agents to mitigate fouling and environmental impacts due to the brine discharge (Boo, Lee, Elimelech, Meng, & Hong, 2012). In the case, forward osmosis process can be an option of low fouling propensity expectations since FO is not a pressure- driven process (Figure 2.13).

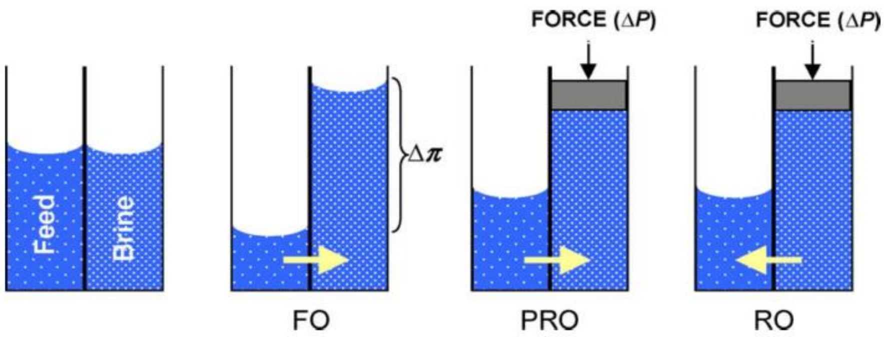


**Figure 2.1 :** For FO, no hydraulic pressure is applied and water diffuses to draw side. For PRO water moves to draw side under positive pressure. For RO, due to the hydraulic pressure water diffuses to less saline side (Cath, et al.,2006).

In addition, FO draw solution can be reuse after DS reuse process and it results with the brine discharge minimization such as RO, heating , electro dialysis, NF, UF and membrane distillation (Luo et al., 2014). However; McGovern et al. reported that forward osmosis needs more research about draw solution and fouling tendency optimization for making forward osmosis more energy efficient than reverse osmosis.

However; McGovern et al. reported that forward osmosis needs more research about draw solution and fouling tendency optimization for making forward osmosis more energy efficient than reverse osmosis.

### 2.4 Membrane Bioreactor

Conventional activated sludge systems consist of aeration and sedimentation tank. In aeration tank microorganisms accumulate and oxidize organics (chemical oxygen demand, COD) and minerals as electron donors and by using oxygen or nitrate as electron acceptors. For maintain the desired water discharge quality, suspended materials are settled with the gravity in settlement tank. In membrane bioreactor technology, filtration is used instead of settlement tank (Figure 2.14). Ultrafiltration and microfiltration membranes (pore size in the range of 0, 05 and 0, 4 µm) are used in an attempt to bacterial flocs and suspended solids removal.

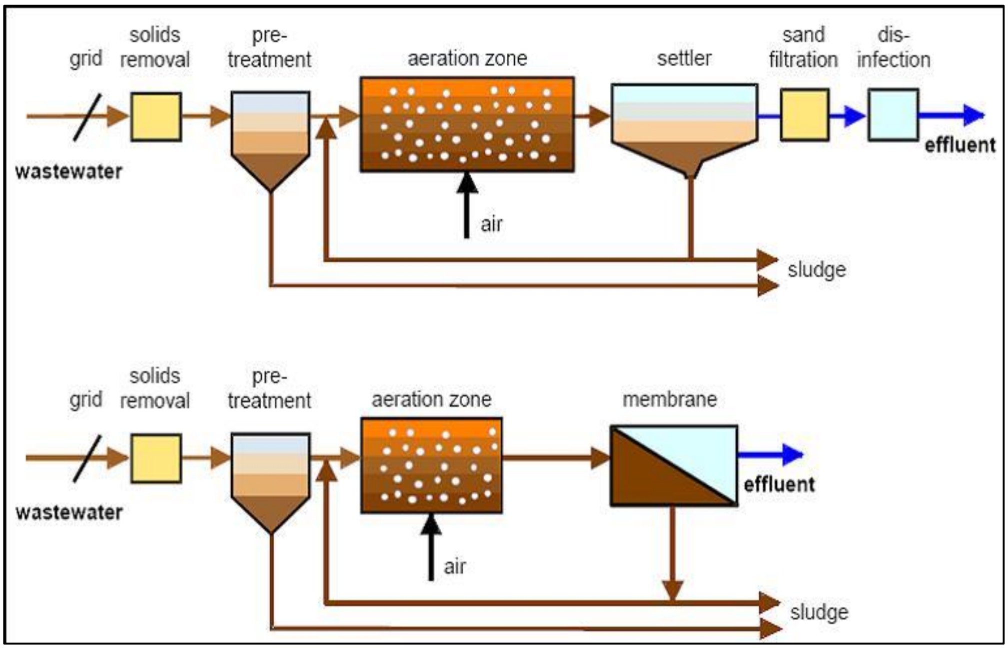


**Figure 2.2 :** Schematic of CAS process (top) and membrane bioreactor(bottom)https://upload.wikimedia.org/wikipedia/commons/d/da/MBRvsASP_Schematic.png

The idea to combine the activated sludge and the membrane filtration systems was emerged in the research in the Rensselaer Polytechnic Institution and Dorr-Oliver, Inc. Milford in United States firstly. In first MBR system (Membrane Sewage System-MST), ultrafiltration membrane was used. In 1970-1980 years MBR systems were developed in Japan (Radjenović et al., 2008). These systems were using as large scales world widely.

Main advantages over the conventional activated sludge systems are:

- Lower energy consumption for fabrication and maintenance for submerged systems,
- Smaller aeration tank volumes due to the higher concentration of MLSS/MLVSS,
- Effluent quality is not depending on the sludge settling characteristics since secondary clarifier is replaced by membrane module. Effluent quality is improved.
- Biomass concentrations can be higher as 10-30 g $L^{-1}$ whereas conventional process utilizes biomass concentration less than 5 g $L^{-1}$.
- MBR process are operated with high solids retention times that makes system more efficient in organic matter removal and durable to the load variations and toxic shocks (Gupta et al., 2008).

Main disadvantages of MBR systems can be summarized as follows:

- More extensive pretreatment requirement
- More chemical cleaning requirement
- Inevitable membrane fouling formation
- Lower effluent production capacity
- Low oxygen transfer efficiency
- Pilo scale often needed for full-scale design
- Membrane replacement is relatively expensive
- Complicated control systems
- No standard configuration is available (Sadr and Saroj,2015).

### 2.4.1 Overview of membrane bioreactor capabilities

MBRs can be operated higher sludge retention times (SRT) and also higher mixed liquor concentrations (MLSS) than the conventional activated sludge (CAS) systems. Thereby, soluble COD can be removed better by MBR systems ((Judd et al, 2008). COD removal can be achieve 90% by activated sludge systems, however, MBR's COD removal rates can be higher as 96-99%. Discharge quality of MBR systems include SS< 1 mg/L, turbidity <0,2 NTU and up to the 4 log virus (depending of the membrane pore size) (Hai et al, 2014). This higher quality of the discharge water enables to reuse wastewater.

On the other hand, MBR systems requires less clarifier spaces and higher SRTs provides the smaller aeration basin thus MBR systems can be establish smaller areas and it minimize the footprint compared to the conventional activated sludge systems (WEF, 2012). Judd et al reported that; lower sludge production is another advantage for MBR systems due to the higher efficiency such as long SRTs, high MLSS and low F/M ratios. In addition, salty wastewaters that cannot be treated by the CAS, can be treated by the MBRS (Haandel and Lubbe, 2011).

There is some disadvantages of MBR such as membrane fouling according to the wastewater organic and inorganic material content. In addition, membranes have a lifetime and it is related with the system operation parameters such as pH, temperature, pressure ((Radjenović et al., 2008).

Cost comparison of MBR vs. CAS is a difficult process. Nevertheless, it must be considered that even energy and equipment costs are higher than CAS in MBR systems; total water costs are competitive due to the smaller footprint and lower installation costs (Hai et al, 2014).

### 2.4.2 Nitrogen and phosphorus removal

Regulations restrict nutrient concentration in treated discharged water for avoiding eutrophication phenomena. In this case, MBR should has the nutrient removal capability. For biological nitrogen removal, two-stage configuration is required which are the aerobic environment for nitrification and anoxic environment denitrification. High biomass concentration and accumulation of slowly growing microorganisms in MBRs provide better nutrient removal than CAS. MBR can remove efficiency higher than 90% ammonium ($NH_3$-N). TN removal needs different aeration configurations for nitrification and denitrification. Post denitrification is used for enhance N removal in MBRs and possible even without any additional carbon source. On the other hand, anoxic/oxic-MBR ($A_2O$-MBR), alternating nitrification/denitrification and Anammox are the configurations for TN removal. In the other process such as up-flow anaerobic sludge blanket (UASB) and aerobic MBRs, TN removal can be %80 efficiency. On the other hand, TN removal can be done without different aeration conditions; in a single tank by means of the sludge floc structure (Figure 2.15).

Generally, phosphorus removal is carried out by chemical precipitation by metal coagulants or lime; however, without this chemical addition, phosphorus removal can be done by biological technologies. In MBRs phosphorus removal can be done by chemical precipitation in elevated sludge ages  Even membrane rejection has not a higher effect on P removal some improvements can be done for biological phosphorus removal in MBR systems. In spite of, enhance biological phosphorus removal (EBPR) perform in MBRs at sludge ages up to 30 days. For phosprous removal, MBR system is combined with the anaerobic biological reactor and phosphorus recovery process. In this system, phosphorus rich sludge is transferred to the anaerobic zone for cycling to achieve phosphorus release and recycled by the chemical precipitation or crystallization (Wen et al. 2010).

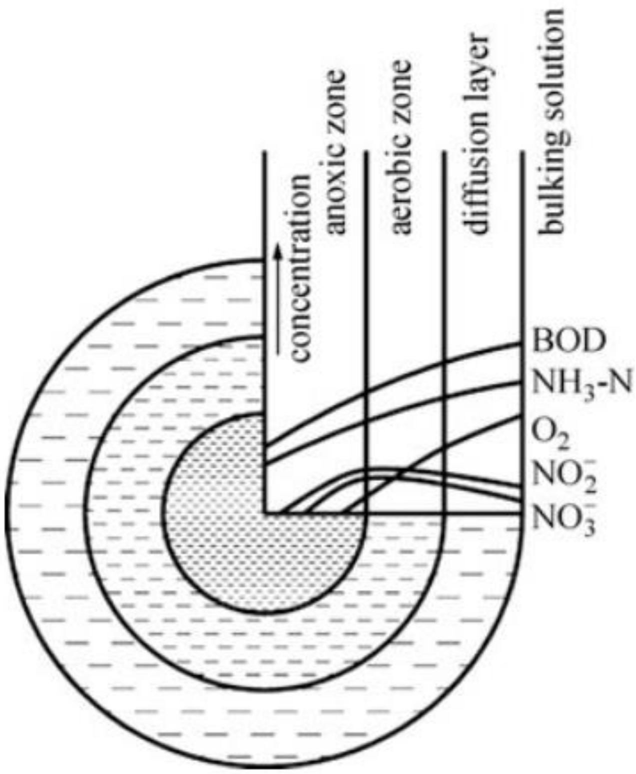


**Figure 2.3 :** Heterogenous environment in a sludge floc (Huang et al.,2010).

#### 2.4.2.1 Organic Matter and Suspended Solid Removal

In MBR systems, organic matter is oxidized by microorganism and removal is improved by membrane rejection. COD (Chemical Oxygen Demand) and suspended solids (SS) can be treated with more than 90% efficiency. Due to the higher resilience time in MBR than CAS, biodegradation of these parameters are higher. Almost all of the SS is removed by MBRs. Bacteria removal efficiency is higher in MBR systems (Wen et al., 2010).

Output quality of MBRs can be suspended solids <1 mg/L, turbidity < 0,2 nephelometric turbidity unit (NTU). With high effluent quality water, MBR system effluent can be used for reuse applications or feed water source for RO treatment.

Higher sludge retention times ensure longer mineralization times for biodegradable organics at the same time adaption time to microorganisms. For this reason, microorganism can adapt wastewater without higher growth rates and floc formation (Radjenović et al., 2008).

### 2.4.3 Fouling in membrane bioreactors

Bacteria, suspended solids, colloids, inorganic and organic compounds form a gel layer on the surface of the membrane and it is called as membrane fouling. Fouling on the membrane occurs as (Figure 2.16):

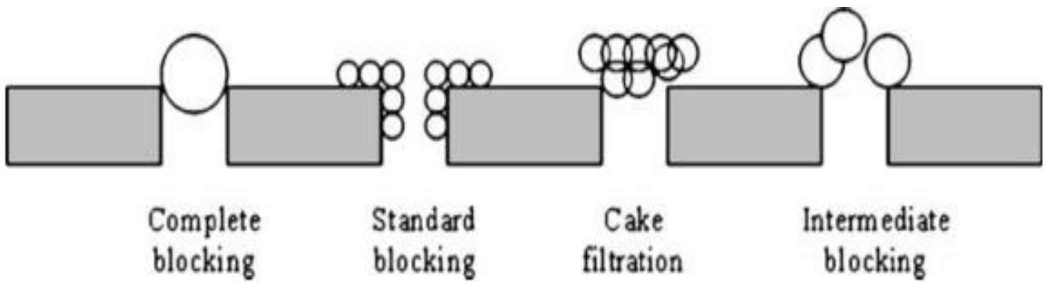


**Figure 2.4 :** Fouling mechanism (Radjenović et al., 2008).

Complete blocking caused by occlusion of pores by the particles with no particle superimposition, İntermediate blocking caused by occlusion of pores by particles with par- ticle superimposition, Standard blocking where particles smaller than the membrane pore size deposit onto the pore walls thus reducing the pore size. Cake filtration where particles larger than the membrane pore size deposit onto the membrane surface (Radjenović et al., 2008).

Fouling causes permeate flux decreasing or increase in TMP during process. Fouling in MBRs causes pore blocking or cake layer formation on the surface. SMP (Soluble microbial products) can cause pore blocking and this situation called irreversible fouling (Deowan, Bouhadjar, & Hoinkis, 2015). Membrane fouling can be classified as reversible and irreversible. If the reversible fouling is occurred membrane can be restored with backwashing or hydrodynamic scouring (surface washing). Non-back washable reversible fouling can be removed by chemical cleaning. Irreversible fouling is consisted with the chemisorption and pore plugging mechanisms and transmembrane flux cannot be recovered neither backwashing nor chemical cleaning (Guo, Ngo, & Li, 2012).There is some concepts for describing the operation flux for fouling control such as critical flux and sustainable flux. Critical flux is described as the flux rate which no particulate fouling occur. However, this flux concept has some problems since membranes are not operated under steady state conditions and fouling is affected by variable parameters. Thus, there are some confusions this concept is not recommended for MBR technologies and applications. Another concept “sustainable flux” describes the flux rate which fouling can be prevented by fouling control mechanisms economically. MBR that is operated with the sustainable flux rate would not exceed the capacity of fouling control mechanism and membrane permeability would not decreased (WEF et al.,2011).

Feed water characteristic, membrane properties (pore size, hydrophobicity etc.) and module/system design and hydrodynamic conditions on the membrane surface can affect the membrane fouling. Pore size effect is related with the feed water characteristics. If particle size is smaller than the pore size, pore blocking is observed more. On the other hand, it is expected that hydrophobic membranes is more skillful against the hydrophilic membranes; however, hydrophobicity often occur with the other membrane modifications such as pore size and morphology so there is no direct correlation between hydrophobicity and fouling.(Le-Clech, Chen, & Fane, 2006).

Good system design improves mass transfer over the membrane surface. Feed solution property such as pH and ionic composition can affect the fouling. High ionic strength and hardness lead to membrane-foulant and foulant-foulant interaction that can cause organic or inorganic fouling. For avoiding this phenomenon, pretreatment can be applied to the feed water. In addition, hydrodynamic conditions such as increased crossflow enhance the mass transfer (Fane, Tang, & Wang, 2011).

#### 2.4.3.1 Fouling control

There are physical and chemical methods for reduce or control the membrane fouling.

**Air Scour**

This method is generally used in submerged MBRS by making a shear stress on the membrane surface by aeration. Aeration provides a scouring action and reduces membrane cake fouling. On the other hand, excessive aeration may cause the sludge floc breakage and also production of SMP (soluble microbial products) thus the aeration rate should be arranged properly.

**Relaxation**

Relaxation means the operation of MBR intermittently.

**Absorbent and Coagulant Addition**

Absorbent and coagulant addition is used for reducing fouling in MBR by adding ferric chloride, alum and powdered activated carbon. They reduce the SMP rate in the mixed liquor with proper dosage. They reduce fouling and increase the membrane performance. Main advantage is reducing air scour and energy saving and main disadvantage is operational costs by chemical adding.

**Backwash Cleaning**

This physical method is applied by feeding permeate by opposite direction may include the chemical addition.

**Chemical Cleaning**

In chemical cleaning, sodium hypochlorite for organic foulant removal, citric acid for inorganic foulant removal, other mineral acid or caustic is used. There are variable chemical cleaning techniques such as chemically enhanced backwash and recovery cleaning. In chemically enhanced backwash, cleaning solution is passed through the membrane in reverse direction during the membrane in the mixed liquor. Recovery cleaning is applied in stiu or ex situ by feeding the cleaning solution by either direction.

**Mechanical Cleaning**

When chemical cleaning is not seem as a solution, membranes is cleaned by physically by hand or water spraying. It is generally required when the cake on the membrane is difficult to remove (WEF et al., 2011). In the case of membrane chemical sensivity, mechanical cleaning can be applied by washing membrane surface carefully even it is not efficient as chemical cleaning.

#### 2.4.3.2 Biofouling

Biofouling is the formation of the microorganisms on the membrane surface. It can be occur by deposition, growth and metabolism of the bacteria cells or flocs on the membrane (Guo et al.,2012). Indicators of the membrane fouling are:

- water flux decrease due to the biofilm formation on the membrane,
- concentration polarization increase due to the lowered solute rejection (in RO and NF membranes),
- module differential potential increase,
- biodegradation of the membrane and module material,
- formation of the concentrated human pathogens on the membrane surface (Ridgway et al., 1999).

Parameters that influence MBR fouling can be categorized into the three main groups: membrane and module characteristics, feed and biomass parameters and operating conditions that summarized in table 2.4.

**Table 2.4 :** Membrane fouling parameters (Hai, 2011).

| Configuration | Advantages | Disadvantages |
|---|---|---|
| Membrane Characteristics | Feed-biomass characteristics | Operating Conditions |
| Physical parameters<br>-Pore size and distribution<br>-Porosity/roughness<br>-Membrane configuration | Nature of feed and concentration<br>Biomass fractionation | Aeration, cross-flow velocity |
| Chemical parameters<br>-Hydrophobicity<br>-Materials | Biomass (bulk) parameters<br>-MLSS<br>-Viscosity<br>-Temperature and DO | Sludge Retention Time (SRT) |
| | Floc Characteristics<br>-Hydrophobicity/surface charge<br>Soluble microbial products (SMP) | Unsteady state operation |

### 2.4.4 MBR design parameters

In MBR design, there are some main factors such as pre-treatment, membrane maintenance, membrane selection, flux, SRT, and MLSS concentration. Fine screening must be done for feed water for large particles and hairy matters removal that are harmful for membranes. Membranes that are using in MBR must mechanically and chemically durable since intense chemicals are using during cleaning. Another main consideration must be the flux since they are directly affect the capital costs due to the effect on membrane area and footprint. Operating costs are also affected by flux due to the fouling and on chemical and air use for cleaning (Faisal et al., 2014).

Membranes in wastewater bioreactors can be operated as submerged and external (Figure 2.17). In submerged design, membranes are took place in the mixed liquor reactor and permeate is removed by the suction where the TMP is <1 atmosphere. In submerged bioreactor, bubbling is used for avoiding deposition and fouling. In external design, the feed is draw by the TMP that is generated by the pump. There is two operation mode; constant TMP and constant flux. During constant TMP operation, deposition and fouling cause the flux decline that is initially rapid but becomes more gradual. In constant flux operation, deposition and flux cause a increase in TMP, that is initially gradual. Generally, constant flux is used widely for MBR operation since it provides a steady output.

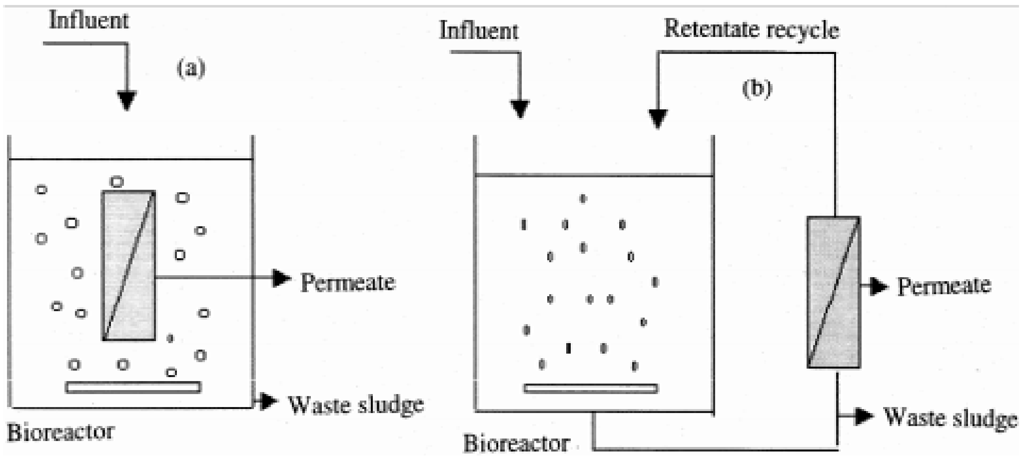


**Figure 2.5 :** Bioreactor system (a) submerged and (b) external (Gupta et al., 2008)**.**

These two configuration have different advantages and configuration choose is applied by considering different factors such as energy and membrane area. Submerged MBR has lower energy reqirement than external MBR; however, external MBR consumes higher energy but lower membrane area. Comparison of these configurations for selection is given in table 2.5. Membrane area requirement can affect the module number and directly affects the economics. Capacity extension is one of the main factor for system selection for growing cities and holiday destinations.

**Table 2.5 :** Comparison of submerged and external MBR (Vigneswaran,2009).

| | Submerged MBR | External MBR |
|---|---|---|
| Suitability | Low strength wastewater with good filterability | High strength wastewater with poor filterability |
| Membrane Flux | Lower membrane flux or lower permeate per unit area of membrane | Higher membrane flux or higher permeate per unit area of membrane |
| Transmembrane Pressure | Lower TMP is required | Higher TMP is required |
| Power Requirement | Less power is required per $m^3$ of wastewater treated | More power is required per $m^3$ of wastewater treated |
| Sensitivity | Less sensitive to variations in wastewater characteristics and flow fluctuations | More sensitive to variations in wastewater characteristics and flow fluctuations |
| Membrane area requirement | More area is required | Less area is required |
| Economics | Generally less expensive at lower wastewater influent rate | Generally more expensive at lower wastewater influent rate |
| Membrane backwashing & cleaning | More frequent backwashing and cleaning reqired | Less frequent backwashing and cleaning reqired |
| Operation | Less operational flexibility | More operational flexibility with control parameters like |
| Extension of WWTP Capacity | Difficult to extend | Easier to extend |

## 2.5 Forward Osmosis Membrane Bioreactor (FO-MBR)

Forward osmosis membrane bioreactor (FOMBR) is the combination of FO membrane and bioreactor. First FOMBR idea was came up by the Cornelissen et al in 2008. In this research, salty draw solution is used and no external pressure is applied.

In conventional bioreactors, for drawing water from the mixed liquored, external pressure is applied. Water molecules moves through the membrane pores and collected separately. Differently, in FOMBR, osmotic pressure difference is used for draw water. Concentrated salt solution is circulated across the FO membrane and water molecules moves from the lower water concentration to concentrated salt solution and dilutes it. During this process, FO membrane rejects the solute molecules or ions. Osmotic pressure is used as a driving force rather than the hydraulic pressure thus this process does not require any energy input. Draw water circulated until the flux is decreased. This diluted draw water can be recovered by reverse osmosis as reject and permeate can be reused (Faisal et al., 2014). Fouling is one of the largest problem to the application of membrane bioreactors (Siddiqui et al, 2015). Biofouling is a limit for MBR operation cause is a reason for membrane module lifetime shortening and increased energy production due to the high aeration requirement (Zhang et al, 2014). Since FOMBR is not a pressure driven system, membranes that used in FOMBR have low tendency to the fouling (Cath et al.,2006).

### 2.5.1 Development of FOMBR

Cornelissen et al. proposed first FOMBR reactor in 2008. The figure 2.18 shows the publication growth of the FOMBR by years.

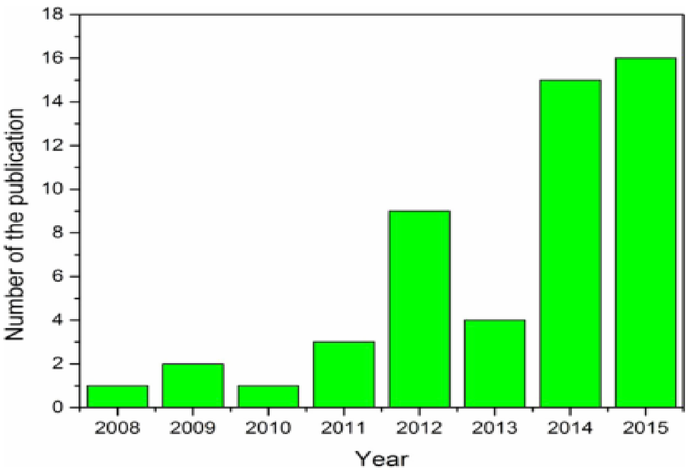


**Figure 2.6 :** Publication number increase on FOMBRs between 2008 and 2015 (Wang, Chang, & Tang, 2016).

First review article was published in 2012 and there had been 51 academic papers up to date. After 2011, new research areas started to investigate such as energy harvesting and resource recovery.

### 2.5.2 Overview of FOMBR capabilities

#### 2.5.2.1 Organic matter removal

Organic matter removal is occurred by both biological degradation by activated sludge and FO rejection. COD or TOC removal efficiency can be more than 90% in FOMBRs.

Since their porous structure, conventional MBR system's microporous membranes cannot reject the soluble materials. However, cake layer formation on the membrane provides a contribution to soluble organic matter removal by 28-78% removal efficiency. On the pther hand, non-porous composition of the FO membranes implements the TOC removal. On the other hand, due to the high retention times in bioreactors, organic matter removal can be enhanced

#### 2.5.2.2 Nutrient removal

$NH_4^+$-N removal was enhanced by the biological process and rejection of the FO membrane. $NH_4^+$-N rejection by CTA-FO membrans is about 80%. $NH_4^+$-N removal could be achieved by 98% efficiency with the active layer (AS)-feed solution (FS) orientation with 10 days SRT. Besides, $NH_4^+$-N removal may be inhibited by increase of salinity. As a result of the salinity inhibiton, $NH_4^+$-N can be accumulated in the bioreactor and the effluent may contain $NH_4^+$-N.

The removal rate of nitrite and nitrate is about 70% for FO membranes. Futhermore, nitrogen removal rates can be enchanced by the post-treatments.

Phosphorus removal can be more than 99% for TP due to the high rejection of FO membrane for phosphates. By the help of the membrane selectivity, inorganic kations such as $Ca^{2+}$ and $Mg^{2+}$ accumulate in the bioreactor and $Ca_3(PO_4)_2$ phosphate sediments can be formed (Wang et al., 2016).

### 2.5.3 Draw solution

Draw solution selection is an important decision since the type of draw solution affects forward osmosis, bioreactor and draw solution recovery performance. Ideal draw solution has high osmotic pressure, reverse flux of the draw solute must be minimum and able to recovery and has a small molecular weight and low viscosity favorably (Ge, Ling, and Chung 2013). In addition, ideal draw solution should not be toxic and has high costs.

Osmotic pressure is alterable according to the draw solution and this can affect the water flux. Van't Hoff equation as shown below can define the osmotic pressure ($\pi$) for ideal dilute solute.

$$\pi = n\left(\frac{c}{MW}\right)RT \tag{2.3}$$

In equation n defined as the number of moles of species formed by the dissociation of solutes in the solution, c is the solute concentration in g/L of solution, MW is the molecular weight of the solute, R is the gas constant (R=0,0821) and T is the absolute temperature of the solution. Since the equation is limited for large MW, there is another equation for osmotic pressure definition which is shown below.

$$\frac{\pi}{cRT} = 1 + Bc + Cc^2 + Dc^3 + \cdots \tag{2.4}$$

In equation; B, C and D are the osmotic virial coefficients that can be determined by experimental osmotic pressure datas. From the both equation, it can be said that osmotic pressure is determined from solute concentration substantially (Chekli et al., 2012).

Draw solution can be classified into the three group; inorganic DS, organic DS and other compounds. Draw solution's characteristics impacts on the system performance of FO is summarized in table 2.6.

**Table 2.6 :** Characteristics of draw solution that affects FO process and their impacts (Chekli et al. 2012).

| DS Characteristics | Impact on FO process performance |
|---|---|
| Osmotic pressure | A high DS osmotic pressure and low feed solution osmotic pressure induce high water fluxes across the membrane |
| Water solubility | High solubility induces high osmotic pressure and therefore can achieve high water flux and high recovery rates |
| Viscosity/diffusivity | A low viscosity combined with high diffusivity leads to high water fluxes |

**Table 2.6 (continued) :**Characteristics of draw solution that affects FO process and their impacts (Chekli et al. 2012).

| | |
|---|---|
| Molecular Weight (MW) | Small MW solutes produce higher osmotic pressure than larger MW for equal mass of DS but induce higher reverse draw solute flux than larger MW DS |
| Concentration | Less sensitive to variations in wastewater characteristics and flow fluctuations |

In addition, specific characteristics of a particular draw solute may also influence the FO process performance. For example, a new class of DS can display unique properties. Such properties can be particle sizes or particle agglomeration due to special magnetic properties when using magnetic nanoparticles (MNPs). Some DS can also act as precursor to scaling and membrane fouling during reverse diffusion when DS containing SO42+ and Mg2+ are used, respectively.

**Inorganic Draw Solution**

Generally inorganic draw solutions are used for FO process. Sodium chloride, magnesium chloride, ammonium bicarbonate are the common used inorganic draw solutions. Most widely, sodium chloride is used, especially for food production and wastewater treatment. NaCl is a cheap and natural salt for draw solution. Also, it is appropriate for reconcentration by RO process and has high solubility beside high osmotic pressure .NaCl is the most commonly used draw solution with 40% (Figure 2.19).

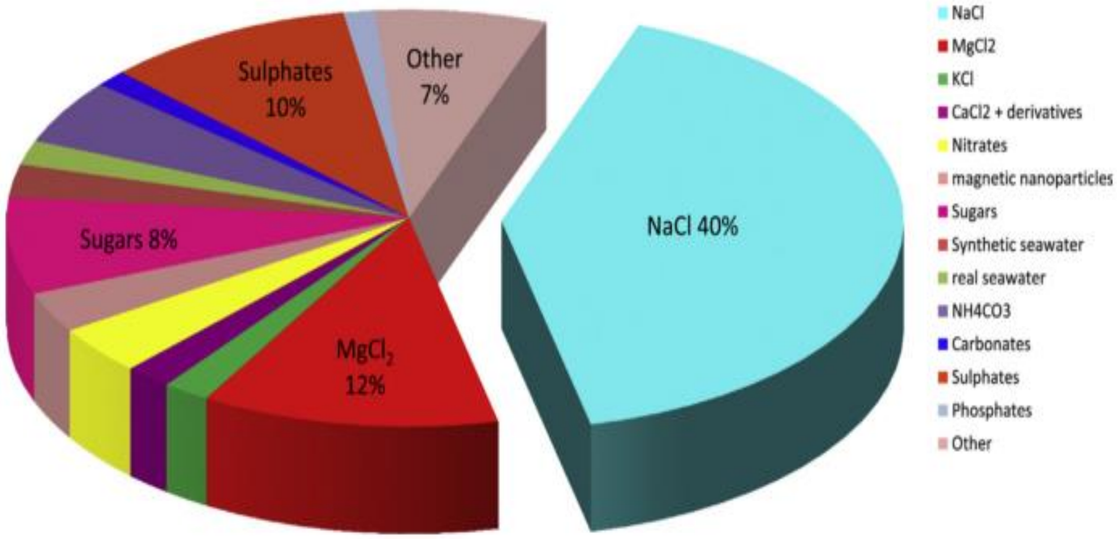


**Figure 2.7 :** Draw solutions variety's rates used in the FO researches (Lutchmiah, et al. 2014b).

Forward osmosis membranes cannot reject salt by 100% efficiency and reverse salt flux can be occurred. The major limitation for FOMBR is the accumulation of total dissolved solids (TDS) concentration within the reactor because of the reverse salt flux which can inhibit the mixed liquor activity. MBRs are usually operates in 5 to 50 days SRT therefore these high SRTs may lead the higher TDS accumulation in reactor. It is reported that the salinity concentration should not exceed 2 g L-1 for prevent the inhibition of the microbial community (Holloway et al., 2014) Another negative effect of TDS accumulation may be the reducing flux by virtue of decreasing osmotic pressure difference between the reactor and draw solution (Faisal et al.,2014). All of the FOMBR published researches used inorganic salt draw solution (Bowden, Achilli, & Childress, 2012).

On the other hand, flow diagram given in figure 2.20 shows the basic steps for the draw solution selection.

### 2.5.4 Transition velocity

Flow velocities is highly effective on mass transfer. Higher cross flow velocities would be the reason of external concentration polarization which is affected by both DS and FS flows (Lutchmiah, et al. 2014a). On the other hand, Klaysom et al (2013) reported that high flow rate lower possible ECP effects due to the better hydraulic conditions and might thus increase fluxes.

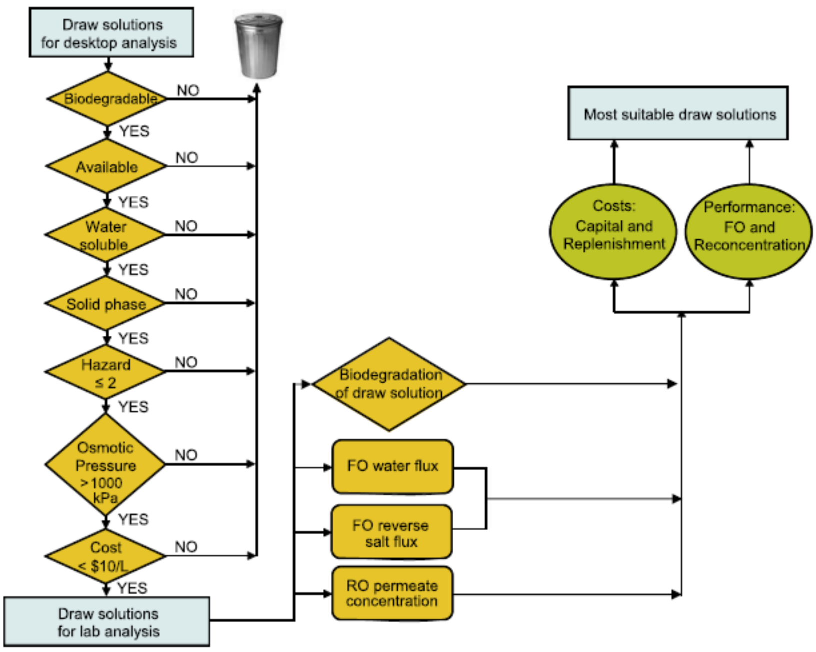


**Figure 2.8 :** Flow diagram for draw solution selection (Achilli, Cath, and Childress 2010).

# 3. MATERIALS AND METHODS

## 3.1 Introduction

This study was performed in a National Research Center of Membrane Technology (MEMTEK) located in ITU. In the case of this thesis, thin film composite electrospun forward osmosis membrane is fabricated by developing the fabrication conditions of patented electrospinning membrane.

The MBR system consist of five containers which are called (1) W.W. tank by effective volume of 10 L. (2) Bioreactor tank, which is contain the module of UF membrane, activated sludge, also consisted of a completely mixed aeration. The activated sludge tank height is 25 cm,radius is 27 cm and effective volume of 10 L, (3) UF permeate collector tank. The Lab Scale MBR was fed from synthetic domestic W.W. The W.W is made with following compounds by dissolving them in tap water: glucose ($C_6H_{12}O_6$), urea($CH_4N_2O$), dipotassium phosphate ($K_2HPO_4$), ammonium sulfate $(NH_4)_2SO_4$ ), sodium carbonate ($Na_2CO_3$ ).

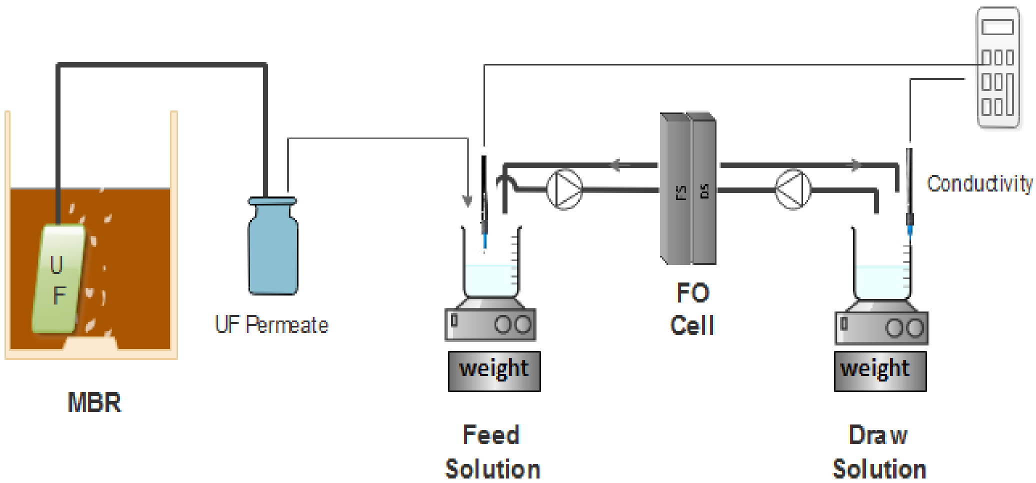


**Figure 3.1 :** Schematic of the MBR and bench scale FO system.

Bioreactor filled with activated sludge a wastewater treatment plant from sludge recycling unit (taken from Pasakoy, one of the W.W treatment plants in Istanbul). There was not any sludge discharge therefore; the sludge retention time (SRT) was infinite. For reaching the MLSS concentration to 9-12g/L, the activated sludge was feed with nutrient material of synthetic WW. An air diffuser beneath the membrane module was used for aeration and mixing the liquor. UF permeate is treated externally by the forward osmosis sysyem. In UF system, the membrane-filtered effluent was continuously removed with a pump to transfer the effluent. 1L UF permeate is transferred to the FO system and examined with the FO bench scale system

In FO bench scale system; 40,5 $cm^2$ electrospun TFC-FO membrane is inserted to FO cell and draw solution weight and conductivity moreover feed solution conductivity datas has been monitored continuously with the PC system (Figure 3.1)

UF permeate is used as feed solution and 0,5 M NaCl solution is used as draw solution. By reaching the draw solution volume to 1,5 Lsystem is stopped and the sample from draw side is taken and removal of COD, TN, TKN, TP, $NO_2$, $NO_3$ and turbidity is evaluated from the draw solution sample.

### 3.2 Materials and Method

### 3.2.1 Preparation of nanofiber forward osmosis membrane substrate

40% sulfonated polysulphone (SPSU, Udell® P-1700) was dissolved in solvent dimetilasetamid (DMAc,>99.5%, Akkim) for obtain concentration 30% w/w. Before adding polymer into the solvent, SPSU was dried in the oven at 105ºC for 1 hour in order to removing all of the moisture content. After adding SPSU into solvent, they were mixed at 300 rpm for 24 hours. Polymer mixture was vacuumed so that air bubbles is removed. Electrospinning machine NE100, Inovenso Co. Ltd, Turkey was used for fabrication of support layer. (Figure 3.2). In this machine, there is a drum collector with 20 cm diameter and the nanofibers collect on the surface of drum. This collector drum moves toward two direction for obtaining a uniform nanofiber structure. There is a three tips on the metal stick that feeds the polymer and the distance between collector drum and the metal stick can be arrange 0 to 19 cm. A high voltage supply connects with the metal stick with 3 tips.High voltage serves polymer in order to increase the surface potential. High surface potential maintains the web-like structure from the polymer drops on the tips. This web-like structure adhere to the metal drum instantly.New Era branded syringe pump was used for feeding polymer to the machine.

**Figure 3.2 :** Electrospinning machine NE100 Inovenso located in MEMTEK.

Fabrication conditions is given in the table 3.1. In order to improve the structural integrity of the membranes post heat treatment was applied at 180 ºC for 3 hours. Heat is applied above the glass transition temperature and below the melting point. When heat is applied, fibers accomplished the crystalline structure and their mechanical strength is improved (Gopal et al., 2006).

**Table 3.1 :** Electrospinning conditions.

| Polymer | Spinning Time (h) | Polymer Dosage (mL/h) | kV | Distance tip and collector (cm) | Drum rotation speed (rpm) |
|---|---|---|---|---|---|
| **30% w/w SPSU** | 6 | 0,5 | 28-30 | 15 | 350 |

### 3.2.2 Preparation of polyamide selective layer

Polyamide selective layer on the nanofiber substrate via interfacial polymerization formed by MPD and TMC solutions. MPD and TMC were prepared as organic and inorganic solutions. Schematic diagram of preparation of electrospun nanofiber supported TFC membrane is given in figure 3.3.

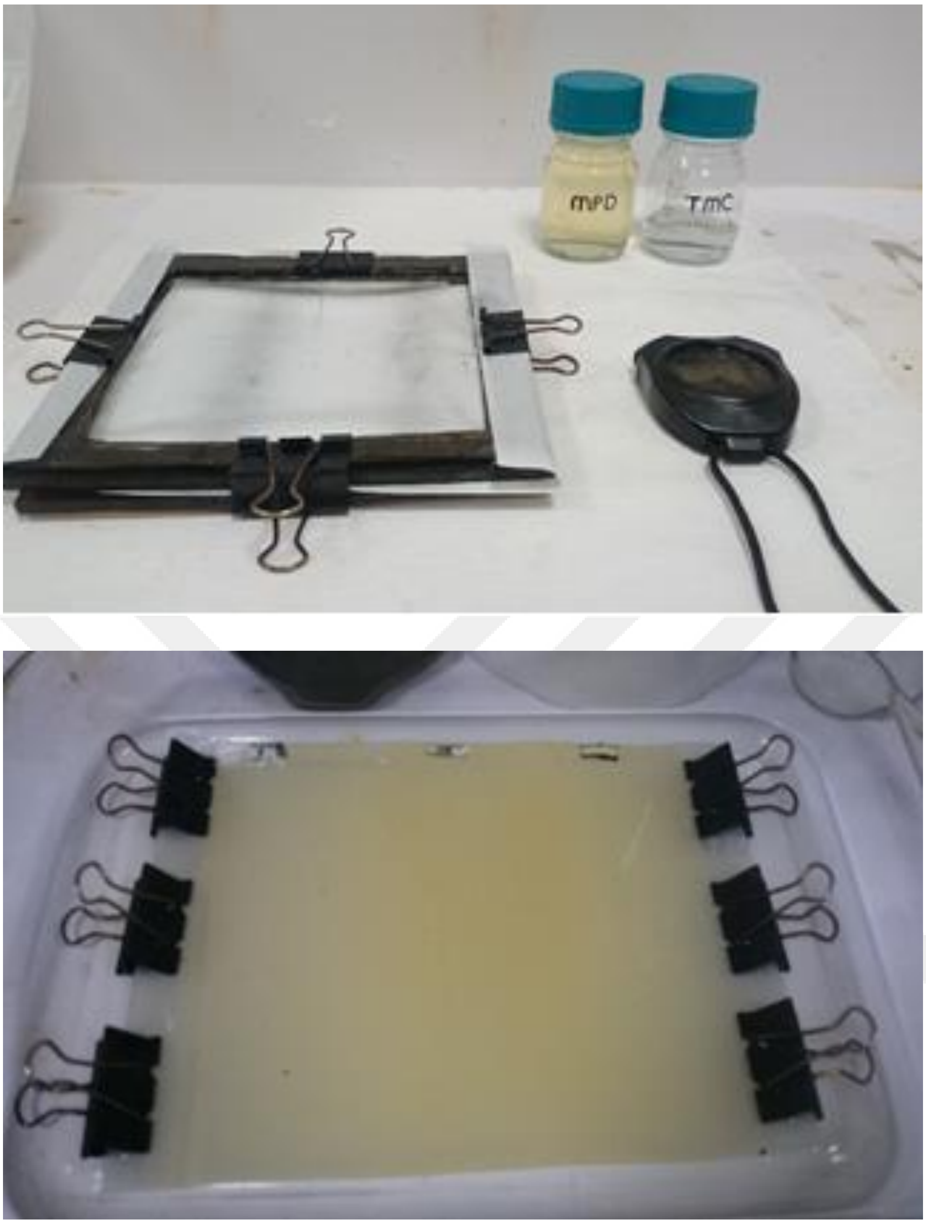


**Figure 3.3 :** TFC equipments for flat sheet membrane and membrane with PA layer.

The nanofiber substrate was first fixed up into a leakproof rubber frame (fig. 3.3). 2 % w/w MPD aqueous solution with 2 % w/w CSA, 2,75 % w/w TEA and %0,1 w/w SDS was prepared and pH was controlled at 7-8. The MPD solution were spilled onto the substrate and removed after 10 min. Next, the frame was cleaned by towel and the substrate was fixed again into the frame and then 0, 1 % w/w TMC n-hexane solution was spilled and removed after 30 s to allow polymerization reaction. The composite membranes were cured in the oven at 70 ºC for 7, 5 min. The synthesized TFC membranes was stored in the DI water at the cold room. Care was taken against fold the membranes.

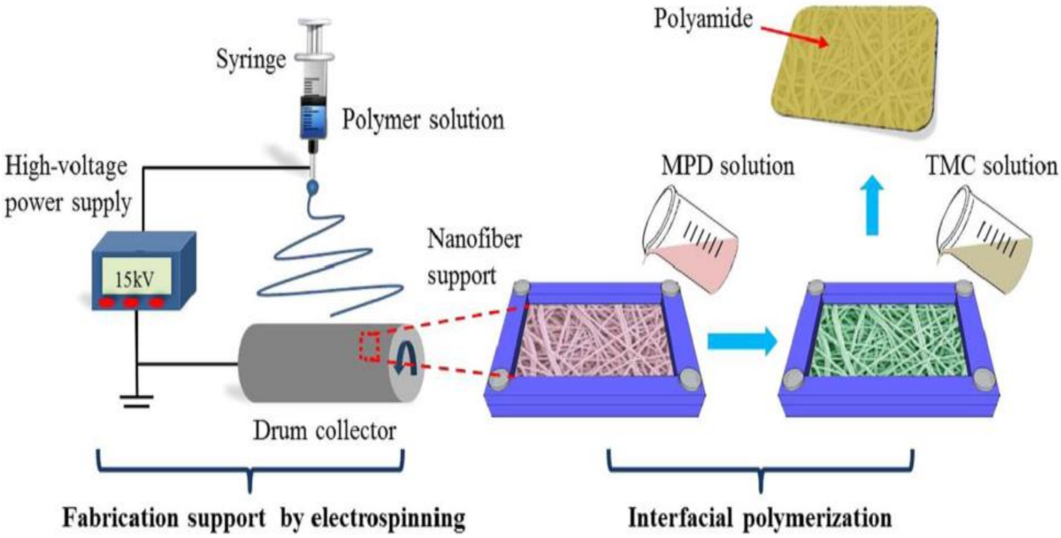


**Figure 3.4 :** Fabrication steps of electrospun TFC-FO membrane (Pan et al, 2017).

### 3.2.3 Characterization of forward osmosis membrane

#### 3.2.3.1 Testing membrane performance in fo mode

Pure water flux and reverse salt flux of the TFC membrane were evaluated in a laboratory scale FO test unit. Figure 3.7 depicts the laboratory scale FO test unit. The dimensions of the cell is 10x13x7 cm for cell height, length and width. There is an internal niche inside the cell for the insertion of the membrane coupon. Two black rubber was used for compaction around the membrane coupon. Internal niche allows to 40,5 $cm^2$ rectangular membrane coupon insertion.

The FO membrane cell unit has four channels; two of them on the feed solution side and the others on the draw solution side for both feed and draw solution currents. The channels were circular with 7 mm diameter and conducted to the DS and FS as closed loop. Mesh spacers were placed into the cell for obtaining support to the membrane. In FO mode, active layer of TFC membrane is placed against to the feed solution and the support layer is place against to draw solution. 0,5 M NaCl was used as a draw solution and the pure water is used as a feed solution.

A 1 L feed solution (FS) and 1 L draw solution (DS) was circulated by gear pumps (Cole Palmer, Vernon Hills, IL) Temperatures of both DS and FS were set as 25° ± 1 °C. Conductivity was measured by Hach Lange HQ40d conductivity probe. The crossflow velocity during the experiment was 0,354 cm/s and 0,68 cm/s. Weight change of draw solution were recorded by time to determine water flux. Reverse salt flux through the feed solution was recorded by conductivity meter by time. The water flux (Jw) was calculated by dividing the produced water at draw solution by the time with the membrane area in the FO cell as given by the formula;

Reverse salt flux was calculated by the reverse salt flux mass balance in the equation 3.1.

$$c_f(V_{FO} - J_w \times t) = J_s \times A_m \times t \tag{3.1}$$

Where;

$c_f$ is the NaCl concentration of the FS (g/L),

$V_{FO}$ is the initial volume of the FS (L),

Jw is the water flux ($Lm^{-1}h^{-1}$),

$A_m$ is the membrane area ($m^2$)

$J_s$ is the reverse salt flux ($gm^{-1}h^{-1}$).

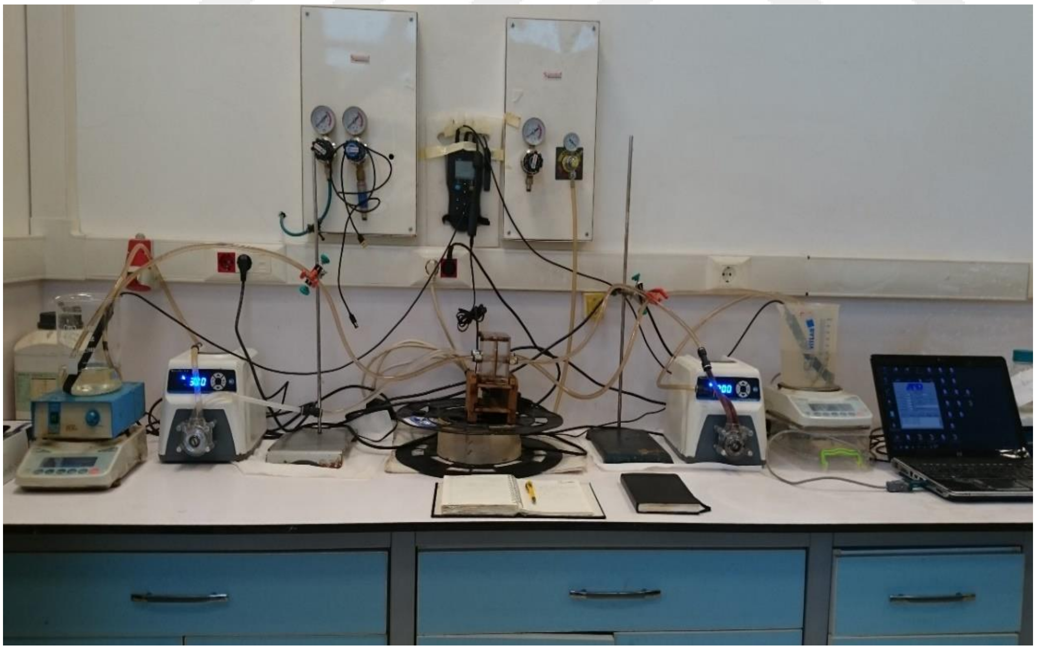

**Figure 3.5 :** Lab scale FO testing unit

The equation for salt rejection calculation,

$$x = 1 - \frac{Reverse\ salt\ amount\ (mol)}{Produced\ water\ (L\ )/(0{,}5\ M)} \tag{3.2}$$

#### 3.2.3.2 Scanning electron microscopy (SEM)

SEM (FEI Quanta FEG 200) (Figure 3.6) was used to examine the surface morphology of electro spun TFC-FO membranes. After the preparation of membranes (dried by liquid nitrogen and cut for clean view), they were coated with 3-4 nm with Palladium and Gold (Pd-Au) by using Quorum SC7620 ion sputtering equipment (Momen, 2015) Both of the support layer morphology and polyamide TFC layer morphology were investigated

**Figure 3.6 :** SEM Device

#### 3.2.3.3 Contact angle

Contact angle measured the hydrophobicity of a solid surface by liquid by Young equation (Liao, Wang, & Fane, 2013) . Attension T200 Theta (Figure 3.7) measures contact angle.

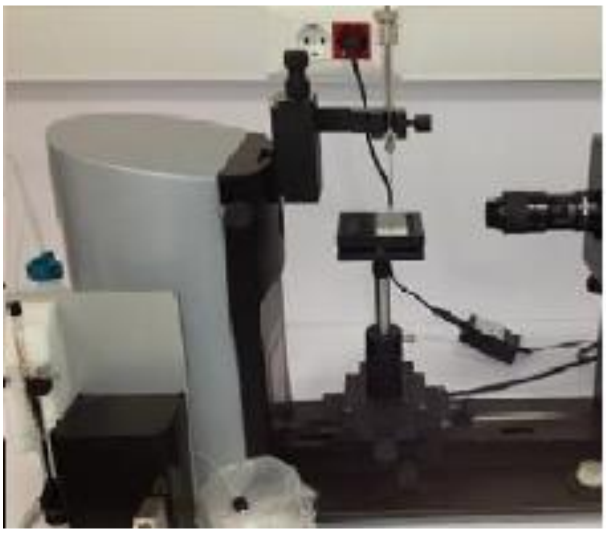

**Figure 3.7 :** Contact angle device.

The static sessile drop method and dry membranes was used. . A small drop of distilled water was dropped on the membrane surfaces, and then the images were taken 10 times in 1 interval. The angle that is occured between the water- membrane interfaces is the contact angle. Analyses were performed 4 different area of the membrane in order to obtain precision.

#### 3.2.3.4 Fourier transformation infrared spectroscopy (FTIR)

Information about the presence of specific functional groups on the membrane surfaces was obtained by Fourier Transform Infrared Spectroscopy (FT-IR) (Spectrum 100, PerkinElmer, USA) technique (Figure 3.8).

**Figure 3.8 :** FTIR device.

### 3.2.4 UF- MBR

An external membrane bioreactor (MBR) has been operated with high strength synthetic wastewater in the case of this thesis (figure 3.9) The MBR was filled by the activated sludge which was taken from the Paşaköy Biological Treatment Plant. Sludge was taken from the aeration tank recycle unit. The MLSS and MLVSS value of the activated sludge during the reactor installation was 11920 mg/L and 6120 mg/L

A commercial UF membrane (Philos,PES) module was submerged to the 10 L reactor and its permeate was used as a feed water in the FO bench scale system. The sludge age of the reactor could considered to be as infinite since excess sludge has not been taken out of the system systematically.

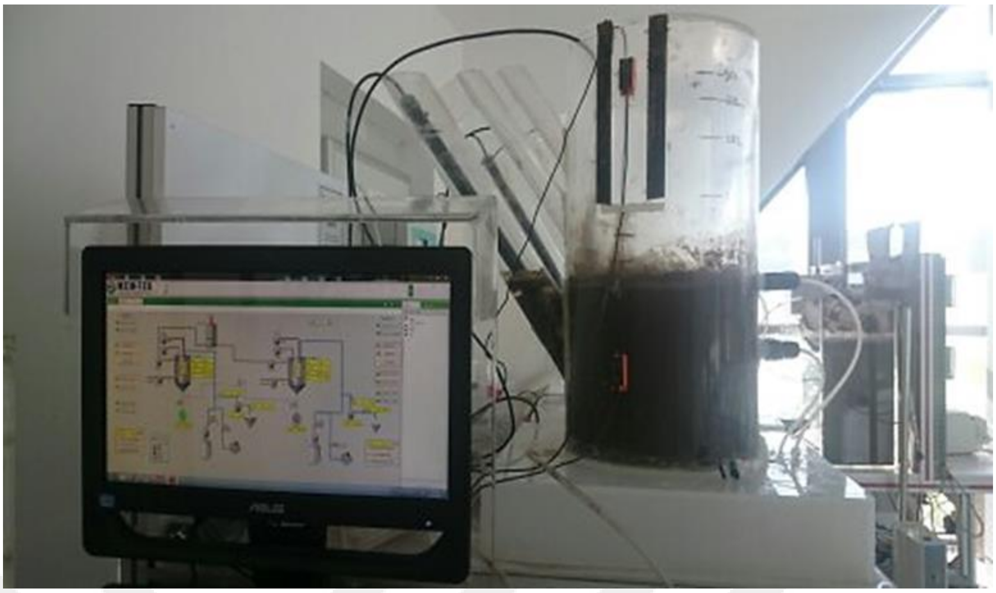

**Figure 3.9 :** Overall layout of membrane bioreactor.

Membrane bioreactor has its own SCADA (Supervisory Control and Data Acquisition) system for control and collecting datas. It has probes for collecting data of pH, ORP, temperature and dissolved oxygen (DO) continuously. The probe datas was monitored from the control panel simultaneously (Figure. 3.10).


**Figure 3.10 :** pH, ORP, DO and temperature control panel of MBR.

### 3.2.4.1 Wastewater source and its characterization

As the feed water for MBR, synthetic domestic wastewater is used. The COD value of synthetic wastewater was arraneged to 1000 mg/L COD approximately. Synthetic wastewater was prepared one time in the range of 3 days. Glycose was used as a carbon source and $KH_2PO_4$ was used as phosphorus source. Reference wastewater characterization is given in table 3.2.

**Table 3.2 :** Synthetic domestic wastewater compounds

| Chemical | Concentration (mg/L) |
|---|---|
| Glycose ($C_6H_{12}O_6$) | 1430 |
| Urea ($CH_4N_2O$) | 85 |
| $KH_2PO_4$ | 70 |
| $(NH_4)_2SO_4$ | 70 |
| $MgSO_4.7H_2O$ | 70 |
| $Na_2CO_3$ | 450 |
| NaCl | 70 |
| $CaCl_2.2H_2O$ | 15 |

Characterization of synthetic wastewater which is prepared by dissolving the chemicals (table 3.2) by the tap water in is given in table 3.3.

**Table 3.3 :** Synthetic WW Characterization

| Parameter | Values |
|---|---|
| Total COD (mg/L) | 1009±98 |
| Soluble COD(mg/L) | 855±91 |
| Conductivity (µS/cm) | 1348±52 |
| pH | 7.36±0.64 |
| Turbidity (NTU) | 99±11 |
| $BOD_5$ (mg/L) | 630±42 |
| $NO_3$-N (mg/L) | 0.39±0.25 |
| $NO_2$-N (mg/L) | 0.06±0.03 |
| Total Phosphorus (mg/L) | 14.82±1.38 |
| Total Nitrogen (mg/L) | 55±4 |
| Ammonium Nitrogen (mg/L) | 15±2 |

#### 3.2.4.2 MLSS and MLVSS concentrations

Before the feeding, activated sludge sample was taken (10 ml) from the aerated batch reactor on daily basis. A filter placed into the set for filtering under vacuum. After the filtration was over, it was dried in oven at 105°C for one hour. Then, waited in desiccator for one hour and weighted for MLSS measurement. Dried sample ignited at 550 °C for 30 minutes in oven. The weighted lost on ignition of the solids represents the MLVSS.

MLSS and MLVSS were calculated by the equations (3.3) and (3.4).

$$MLSS\left(\frac{mg}{L}\right) = \left((A - B)xV\right)x1000 \tag{3.3}$$

$$MLVSS\left(\frac{mg}{L}\right) = \left((C - A)xV\right)x1000 \tag{3.4}$$

where;
A = Weight (mg) of filter with residue,

B = Weight (mg) of filter,

C = Weight (mg) of filter with residue after ignition,

V = Volume (ml) of the sample.

#### 3.2.4.3 Temperature and dissolved oxygen observations in bioreactors

Temperature and dissolved oxygen (DO) probe was measuring the temperature continuously. Temperature is important for activated sludge activity in the system. DO was controlled for optimizing the aeration system.

#### 3.2.4.4 pH changes during operation

pH probe in the reactor measuring and collecting pH datas from reactor continuously. pH is vital for microorganism in the system since their activities can be inhibit by the pH changes.

#### 3.2.4.5 ORP observations

ORP, oxidation reduction potential or redox potential is measuring the potential of oxidation reduction. Its unit is mV. ORP value is indicator of degradation potential of microorganisms in the reactor. ORP value was measured and saved continuously by the SCADA system.

### 3.2.5 Organic matter removal

Permeate that is collected from both UF module and FO system is collected and measured on daily basis. COD analyses will done with closed-reflux method as defined in Standard Methods.. 2,5 mL water sample is added to the COD tubes. Synthetic waste water samples diluted with distilled water (1:5) as 2.5 ml due to the their high COD levels. And were filtered by microfilters (0.45 μm) and pour into the COD digestion tubes for soluble COD concentration Added with 1.5 ml standard potassium dichromate digestion and 3.5 ml sulfuric acid reagents into the tubes and transferred to the pre-heated COD digester at 150ºC for 2 hours.

Experiments of COD was carried out with blank sample by using distilled water. After the tubes were cooled to room temperature, titration was applied. After transferred the contents of the COD digestion tube in 100 ml beaker. Adding 3 drops of ferroin indicator and titrate against 0.025 N FAS (Ferrous Ammonium Sulfate) solution till the colour change (from blue-green to brownish red). CODs were calculated according to the equation 3.5.

$$COD = \frac{(A - B) * N * 1000}{V_{Sample}} \qquad (3.5)$$

where;

A: Used volume of FAS for blank (ml),

B: Used volume of FAS for sample (ml),

N: Normality of FAS solution.

### 3.2.6 Nitrogen removal

Nitrogen removal was evaluated by total nitrogen, total kjeldahl nitrogen, nitrate and nitrite measurements. As indicators of nitrification process, nitrite ($NO2^-$) and nitrate ($NO3^-$) measurements were done. Nitrification is a biological process which oxidizing the ammonia to nitrate via nitrite by nitrifying bacterias under aerobic conditions. Formulas of these cycles is given in equation 4.1.

$$2\ NH_4^+ + 3\ O_2 + \rightarrow 2\ NO_2^- + 2\ H_2O + 4\ H^+ \qquad \textit{( Nitrification)} \qquad (4.1)$$

$$2\ NO_3^+ + 12\ H^+ \rightarrow N_2 + 6\ H_2O \qquad \textit{(Denitrification)}$$

In nitrification process, ammonia ($NH_4$) is oxidized to nitrite ($NO_2^-$) and then nitrate ($NO_3^-$). Due to the nitrification bacterias (*Nitrosomonas, nitrobacter*) have low growth rate and sensitive, in nitrification process dissolved oxygen level should be higher than 1 mg/L and temperature should be 12 C minimum. An favorable C:N:P ratio must be provided.

In denitrification process, nitrate and nitrite are converted to the $N_2$ by anoxic denitrification bacterias. Carbon source existence is required for denitrification process.

### 3.2.6.1 TN removal

TN is the sum of organic, ammonium, nitrate and nitrite.Nitrate and nitrite are inorganic nitrogen. Since ammonium is the type of the kjehaldl nitrogen, TN is the sum of TKN and inorganic nitrogen (figure 3.9).

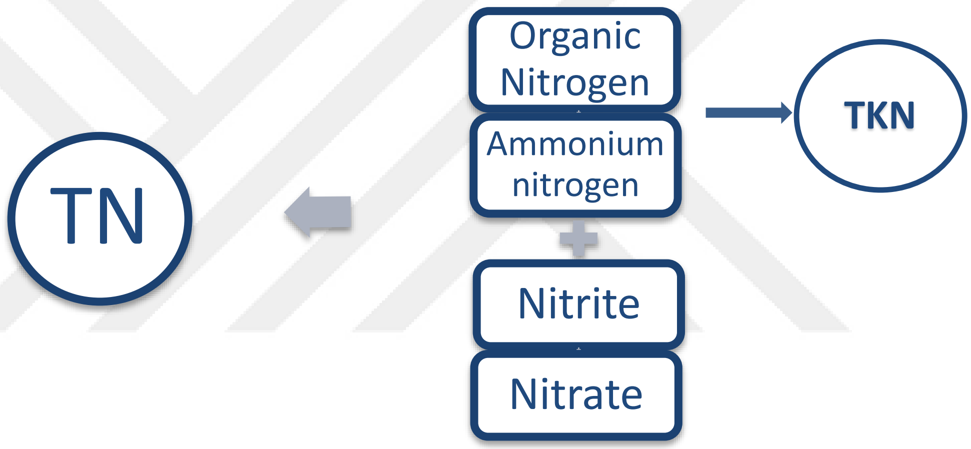


**Figure 3.11 :** TN components.

TN was measured by Laton Total Nitrogen cuvette test.The measurement range of Laton TN kits is between 5-40 mg/L and 20-100 mg/L.

### 3.2.6.2 TKN removal

FOSS ASN 3503 Kjeltec™ System was used for the determination of kjeldahl nitrogen in water samples.

Sample Preparation: Sample volume is choosen according to expecting nitrogen concentration. 50 mL sample volume is choosen for FO and UF permate, 25 mL sample volume for wastewater.

Digestion: 250 mL digestion tube used for samples. two kjeltabs are added. 12 mL $H_sSO_4$ is added to tubes. Putted boiling rod with open and downwars or boiling stones in place, position the exhaust and turn on the aspirator. Samples are digested for 70 minutes in a preheated block digester at 420ºC. Depending on sample content, foaming can occur. If this is the case, the samples have to be heated slowly.

Distillation: Distillation is performed automatically. Dilute cool digestion tube is inserted to the distillation unit. 75 mL pure water is added. 25 mL receiver solution is added to receiver flask. 50 mL 40% NaOH is added to the tube. Distil for the prescribed time and distillate is titrated with standardized boric acid titrant.

. TKN in this study is calculated by following equation:3.6.

$$TKN = \frac{amount\ of\ titrationx\ 0{,}02x14x1000}{Volume\ of\ Sample} \quad (3.6)$$

#### 3.2.6.3 $NO_3^-$ and $NO_2^-$ removal

Nitrate ($NO_3$) removal was measured by Hach Lange LCK 340 (5-35 mg/L $NO_3$-N; 22- 155 mg/L $NO_3$) and Hach Lange LCK 339 (0.23-13.50 mg/L $NO_3$- N; 1-60 mg/L $NO_3$) analyse kit.

**Figure 3.12 :** Hach Lange DR 500 UC spectrophotometer.

Nitrite ($NO_2$) Hach Lange LCK 342 (0.6-6.0 mg/L $NO_2$-N; 2-20 mg/L $NO_2$) and Hach Lange LCK 341 (0.015-0.6 mg/L $NO_2$- N; 0.05-2.0 mg/L $NO_2$) analyse kits were used. Results was measured by the Hach Lange DR 500 UC spectrophotometer (figure. 3.10).

#### 3.2.6.4 Phosphorus removal

Hach lange spectrophotometric kits were used for TP analyse. Hach Lange LCK 350 (2- 20 mg/L $PO_4$-P; 6-60 mg/L $PO_4$) ,Hach Lange LCK 349 (0.05-1.5 mg/L $PO_4$-P;

0.15-4.5 mg/L $PO_4$) , Hach Lange LCK 341 (0.5-5 mg/L $PO_4$-P; 1.5 - 15 mg/L $PO_4$) analyse kits were used.

#### 3.2.6.5 Turbidity removal

Turbidity was measured by using the nephelometric turbidity unit (ntu). Turbidity is the amount of cloudiness in water samples.  The factors that is the reason for turbidity are silt, bacterias, organic and inorganic matter, soluble colorful organic matters. Sample was taken from synthetic WW, UF permeate and FO permeate (figure 3.11).

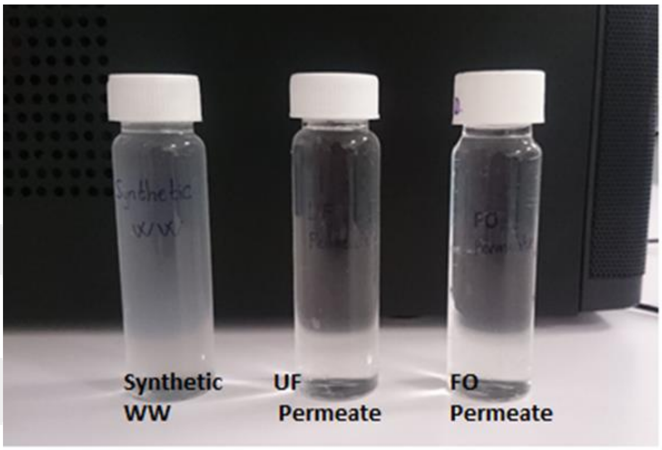


**Figure 3.13 :** Samples for turbidity measurement (Synthetic WW, UF and FO Permeates).

Turbidity measurements have done by using the Hach 2100 P device that can be seen in the figure 3.12.


**Figure 3.14 :** Hach 2100P turbiditymeter.

### 3.2.7 FO Bench Scale System Operation, UF Permeate as Feed Water

FO membrane performance that was developed in the case of this thesis has been investigated in FO bench scale system. FO experiments was performed by using UF permeate as feed solution and 0,5 M NaCl solution was used as draw solution. Water flux, reverse salt flux and the FO permeate quality were monitored during the experiments.

#### 3.2.7.1 FO Cell

The FO experiments were carried out by use of dual channel cross-flow FO cell. In FO cell, there is 4 channels for water input and output for draw and feed solution flow. FO cell can be seen from the figure 3.13.

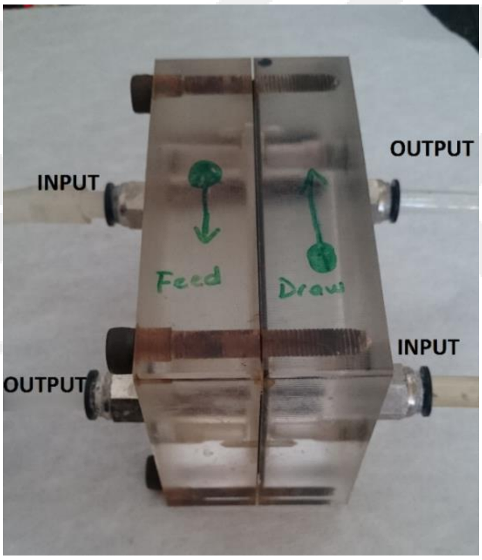


**Figure 3.15 :** FO Cell

#### 3.2.7.2 Feed solution

Philos (PES) flat sheet UF membrane module was operated internally in MBR. 1L permeate was collected from the MBR and then used as a feed water in FO system. UF water samples has been taken and stored before the FO system operation.

#### 3.2.7.3 Draw Solution

Higher osmotic pressure is one of the key parameter for DS selection. Due to the high solubility, easily accessibility and one of the most preferred salt in literature, sodium chloride 0,5 M was choosen as draw solution. In FO mode active layer was faced through the feed solution.

# 4. RESULTS AND DISCUSSION

In the case of this thesis, forward osmosis electrospun thin film composite membrane was produced and characterizated. In order to evaluate the wastewater treatment performance of this TFC-FO membrane, a bench scale FO system was used and TFC-FO membrane was installed in a cell as a 40,5 $cm^2$ coupon. On the other hand, UF membrane module in MBR has been operated and UF permeate has been used as feed solution in bench scale FO system. 0,5 M NaCl solution was used as a draw solution. System had been started with 1L draw and 1L feed solution volumes feed and draw solutions has been circulated from symmetric channels on both side of FO cell. System has been operated until the draw soluton volume reached to 1, 5 L. Active layer was faced to the feed solution (UF permeate). Conductivity and weight of feed and draw solutions has been measured continuously for water flux and reverse salt diffusion calculation. Due to evaluating the pollutant removal performance of FO membrane, COD, total nitrogen, total phosphorus measurements were examined for both UF and FO permeates.

FO membrane characterization, MBR operation and bench scale FO system results are given in results and discussion part.

## 4.1 Characterization of Forward Osmosis Membrane

Two pieces of TFC-FO membrane was used in the FO system that produced at the same time with the fabrication conditions. First membrane has been defect after 14 cycle. Defect had been realized by the extreme increase of feed water conductivity since the draw solution was rejecting to the feed side. Water and salt fluxes was measured for both membranes and the other characterization studies was done for only first membrane.

### 4.1.1 Forward osmosis water and salt fluxes (Pure water as feed solution)

Forward osmosis pure water and reverse salt flux datas for first operation is given in figure.4.1. Different pump velocities was examined first 300-300 rpm and 250-600 rpm.

Two different membrane that was produced in the same conditions was used for FO operation. They showed different pure water and salt fluxes. Forward osmosis

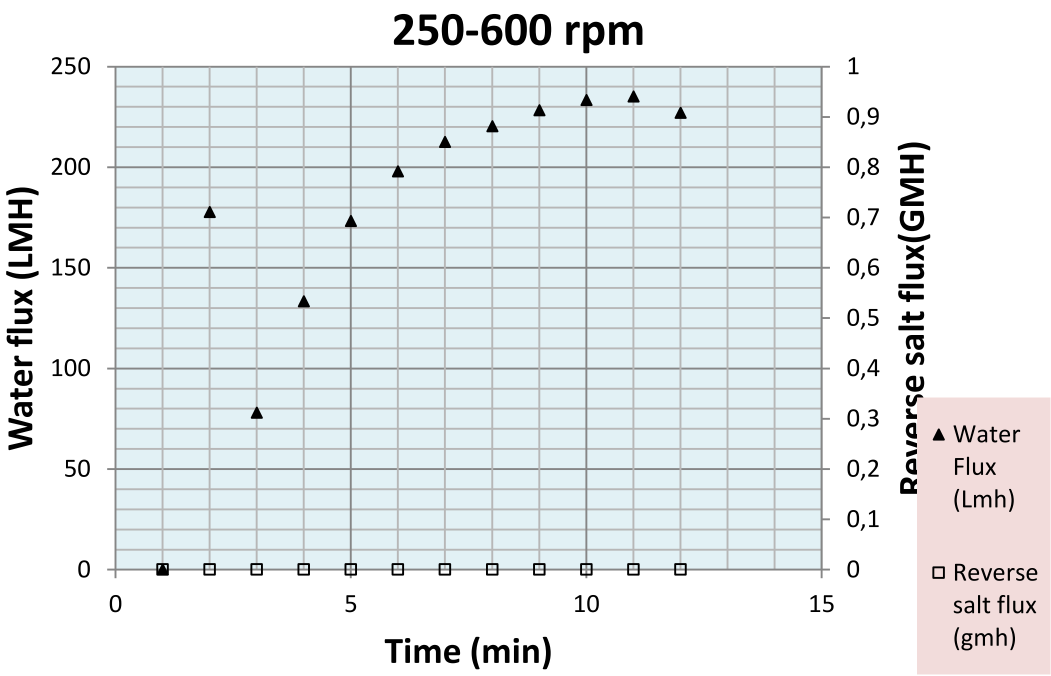


**Figure 4.1 :** Pure water and reverse salt fluxes at 250-600 rpm

Pure water and reverse salt flux datas is given in figure.4.1 and 4.2. Pure water and reverse salt fluxes at the same rpm for first membrane coupon.

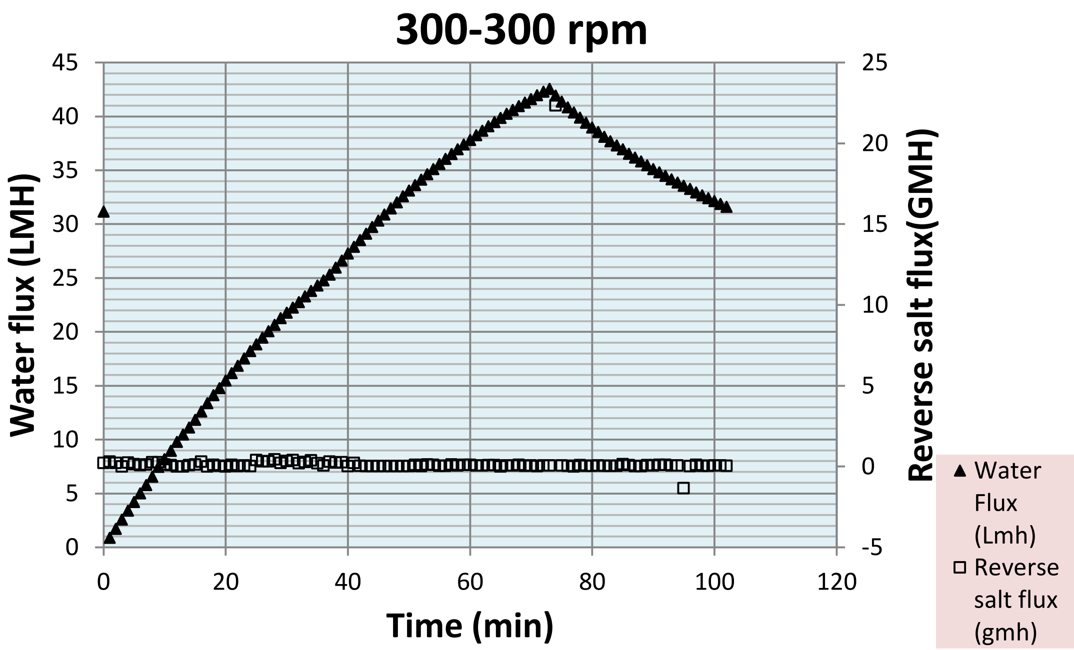


**Figure 4.2 :** Pure water and reverse salt flux at 300-300 rpm.

It can be said that by increasing the draw solution transition velocity, water flux was increased extremely high.On the other hand, salt rejection is not changed. In figure 4.3, it can be seen that water and salt fluxes is higher that the first membrane. The reson for this situation can be the defect on the membrane due to the increase on the reverse salt flux. However, this defect might be healed up because reverse salt flux was decreased by the time.

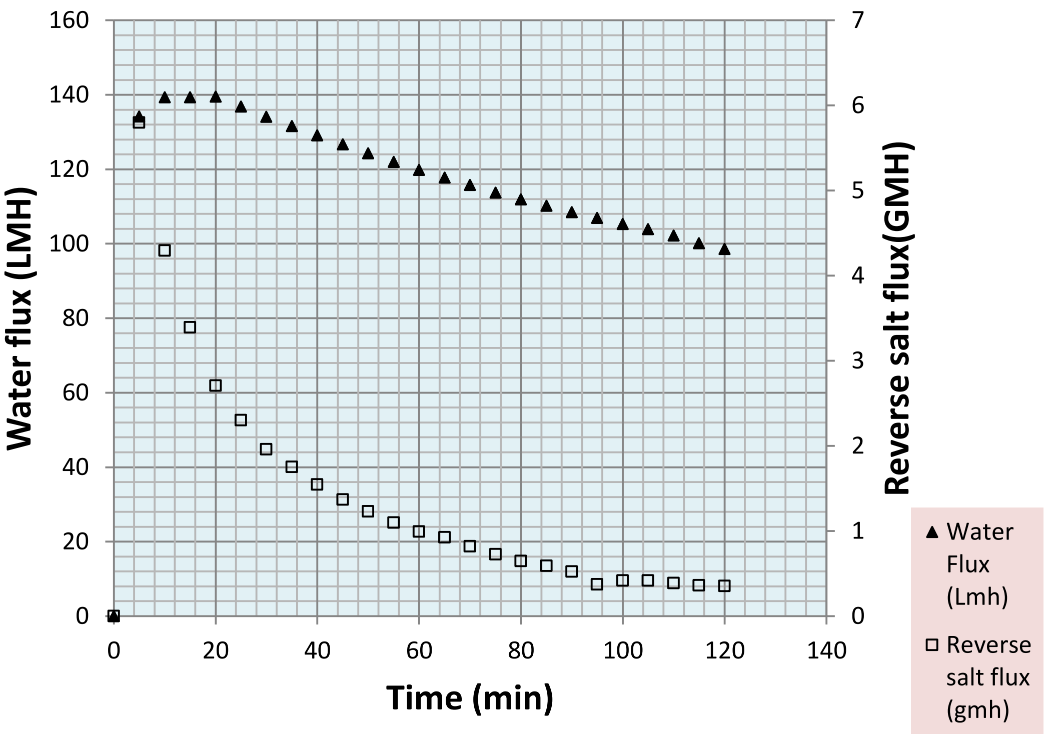


**Figure 4.3 :** Pure water and reverse salt fluxes for 2nd membrane.

### 4.1.2 SEM Images

SEM images of both support layer of electrospun and TFC layer of FO membrane with different magnitutes are given in figures 4.4 and 4.5. In figure 4.4, it can be seen that the fibrous structure was obtained after electrospinning. The reticulum structure that is obtained by the post heat treatment process. The minimum fiber thickness is 247 nm, and maximum 1235 µm. The average fiber thickness is 570 nm.The wet polymer structures has not be seen in the SEM images.

In figure 4.5 represents TFC layered FO membrane is shown. Within the SEM image,closed cavitiy morphologies as an indicator for interfacial polymerization .

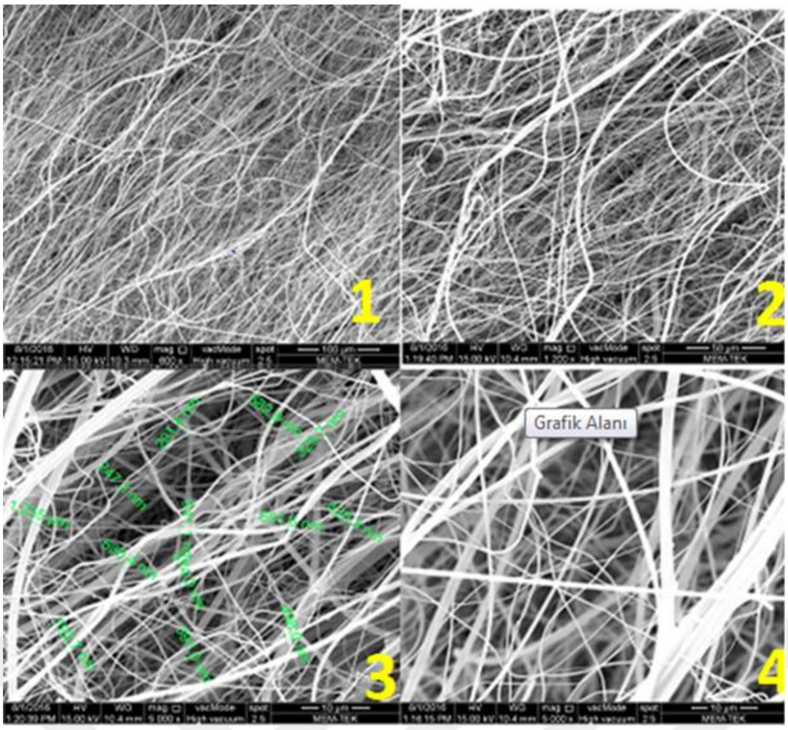


**Figure 4.4 :** SEM Images of support layer of electrospun FO membrane (1); 600x (2) 1200 x,(3);600x, (4);500x magnitutes.

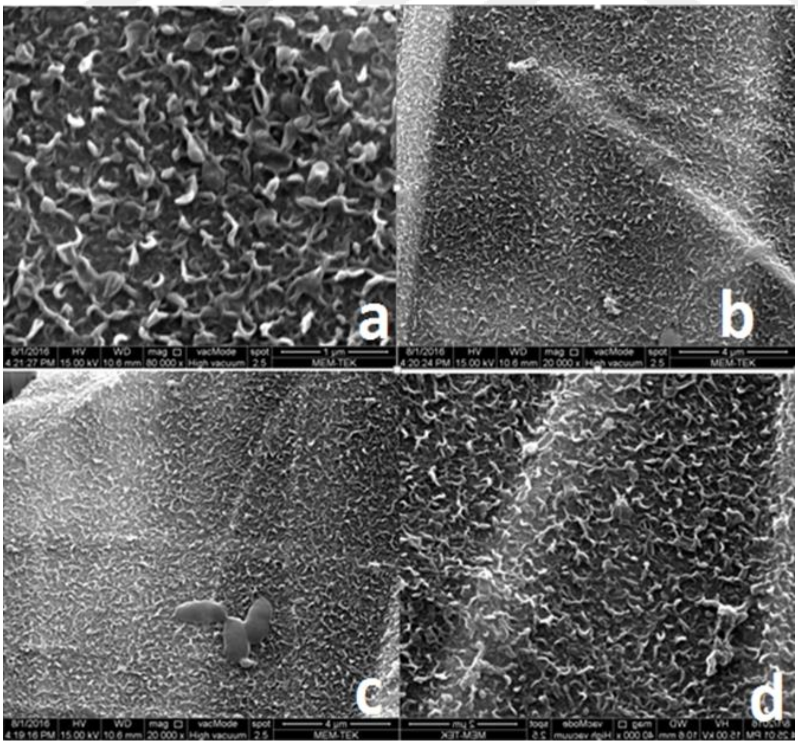


**Figure 4.5 :** SEM images of TFC FO membrane surface (a); 80000x,(b); 20000x,(c); 20000x,(d) 40000x magnitutes.

### 4.1.3 Contact Angle Measurement

Hydrophobicity of membrane is understoodd by contact angle measurements. These measurements were done by using two sample. Pure water was used for the drops and 5 drops were used for each samples. Mean contact angle result of electrospun support layer is measured as 113 º and the standard deviation is 2, 3. Mean contact angle result of TFC-FO membrane before FO operation is 59 º and the standard deviation is 10 (table 3.4).

**Table 3.4 :** Contact angle results of FO membrane

| | Support Layer | TFC FO membrane before FO application | TFC FO membrane after FO application |
|---|---|---|---|
| Contact Angle | 113 | 59 | 42 |
| Standard Deviation | 2,3 | 10 | 7 |

Mean contact angle results of TFC-FO membrane after FO operation is 42 º and the standard deviation is 7. Hydrophobicity characteristic is significantly change after TFC polyamide coating. There is not a significantly change between the hydrophobicity characteristic between before FO application and after application. This means that organic foulants was not highly decreased the hydrophobicity characteristic of TFC FO membrane.

### 4.1.4 FTIR

A used TFC FO membrane that is operated in the system and the unused TFC FO membrane FTIR graphs is given in figure 4.6 and 4.7.

There is typical absorption peak in 1013 cm-1. It is the indicator of sulfonic acid groups around 1025 $cm^{-1}$. Peaks around 1668 $cm^{-1}$ is increased for used membrane FTIR graphic. Tang et al, (2014) claimed that the intensity of the peaks at 1668 $cm^{-1}$ increases when the amount of substituted polar groups ($HSO_3$) or the polarity of substituted groups on the benzene rings increases (p.1166). Peaks at 1238 and 1166 $cm^{-1}$, is the indicator of stretching vibrations of O-S-O (Song et al, 2016).

Two FTIR graphs (fig. 4.6 and 4.7) hare highly similar to each other. It can be said that it is the result of low fouling rate.

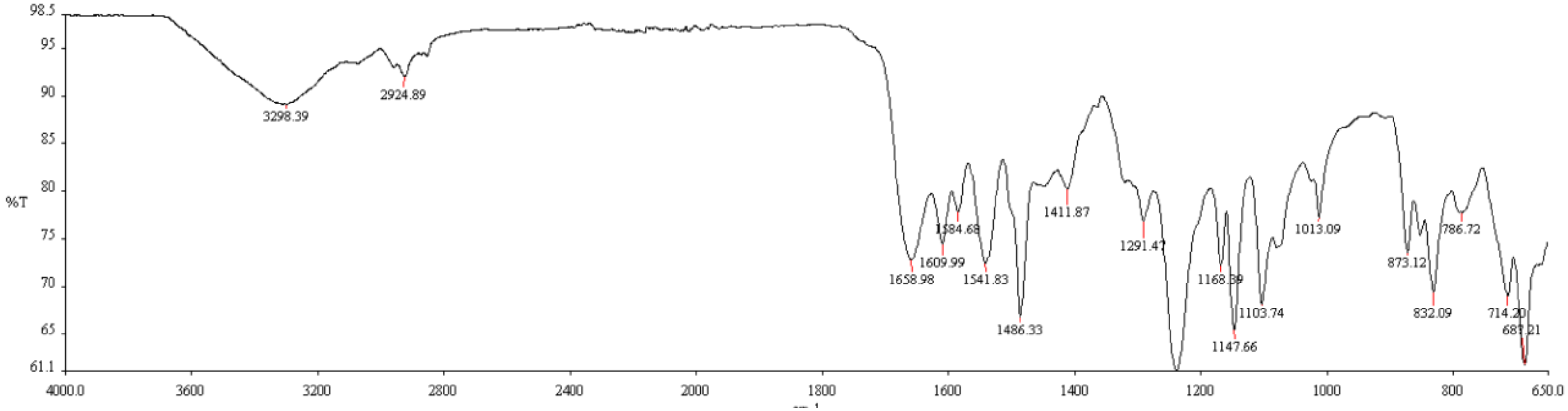


**Figure 4.6 :** Unused TFC FO membrane FTIR graph.

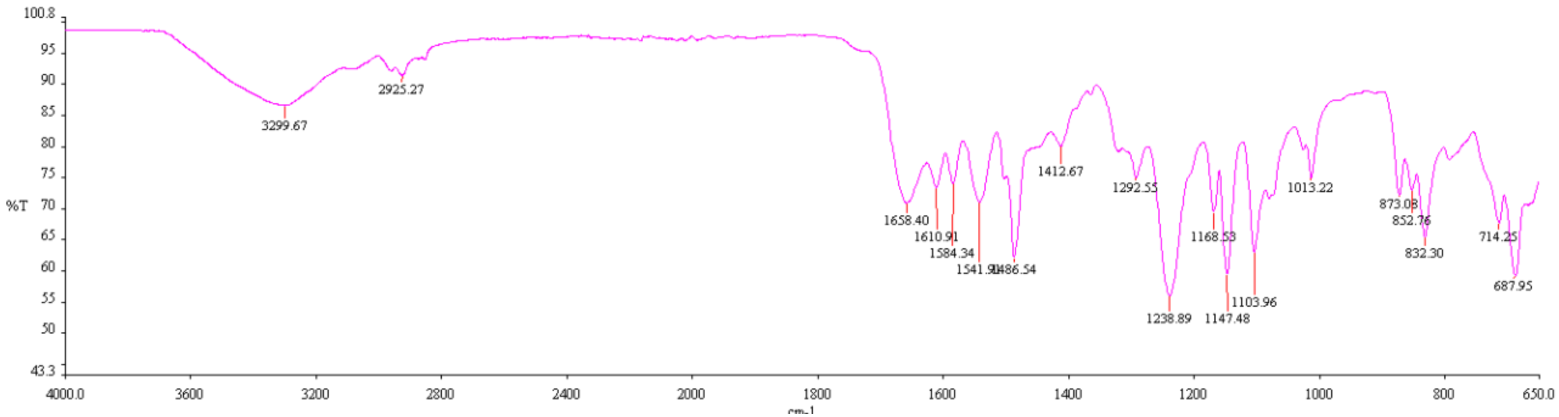


**Figure 4.7 :** FTIR graph after FO operation.

### 4.2 MBR Studies

#### 4.2.1 MLSS/ MLVSS Changes of reactor

MLSS and MLVSS values is given in figure 4.8. Reactor was started to operation with UF for acclimation before the study. MLSS value is 11675 mg/L and MLVSS value is 6600 mg/L approximately. The MLVSS/MLSS value is 0,57. This value is appropriate for MBR operations according the literature. There is a high fluctuation in MLSS values however; MLVSS values are more stabile than MLSS.

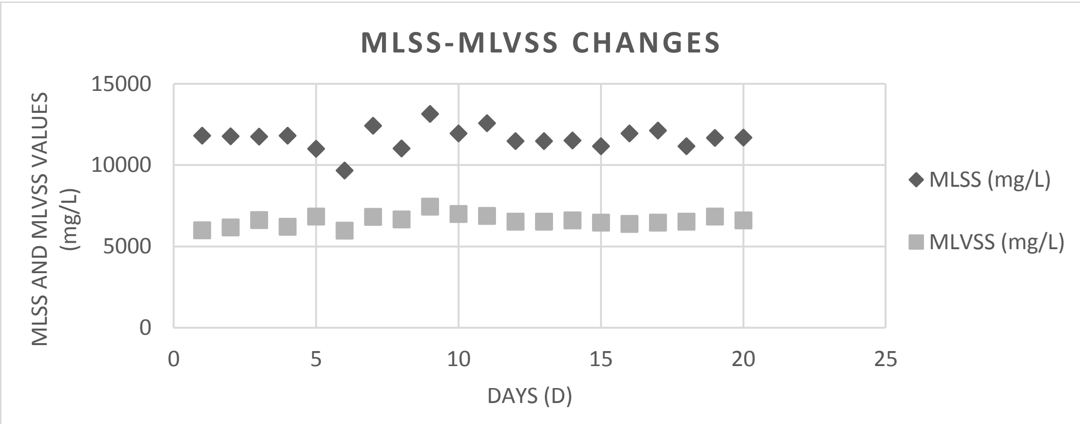


**Figure 4.8 :** MLSS and MLVSS changes during operation.

#### 4.2.2 Temperature Profile

Temperature profile is given in figure 4.9. Mean value of the temperature is 15,4 ºC. It can be seen that temperature was higher in the beginning of the operation and then it decreased 3-4 °C. However this temperature values was appropriate for the membrane bioreactor operation.

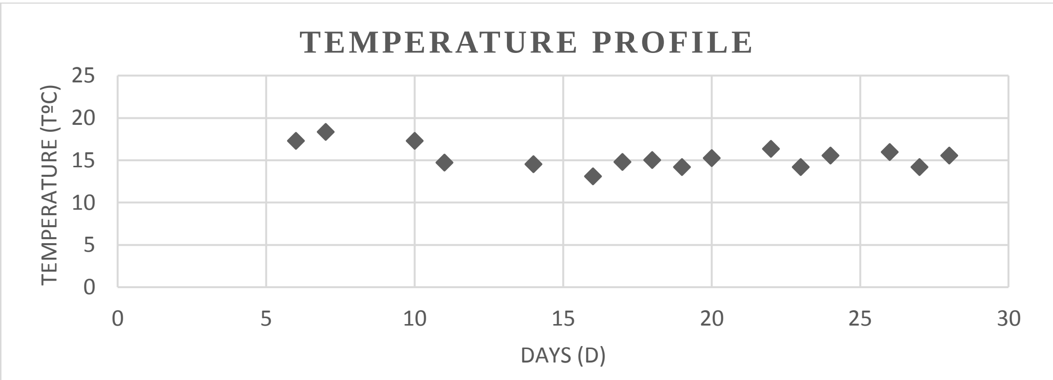


**Figure 4.9 :** Temperature profile of MBR during operation

### 4.2.3 DO Profile

Mean DO values was measured as 9,5 mg/L (figure. 4.10). This value is about 1-2 mg/L in common MBR applications. Compared to the common applications, 9,5 mg/L is quite higher. Even air diffusor capacity adjusted to minimum tune DO could not be decrased.

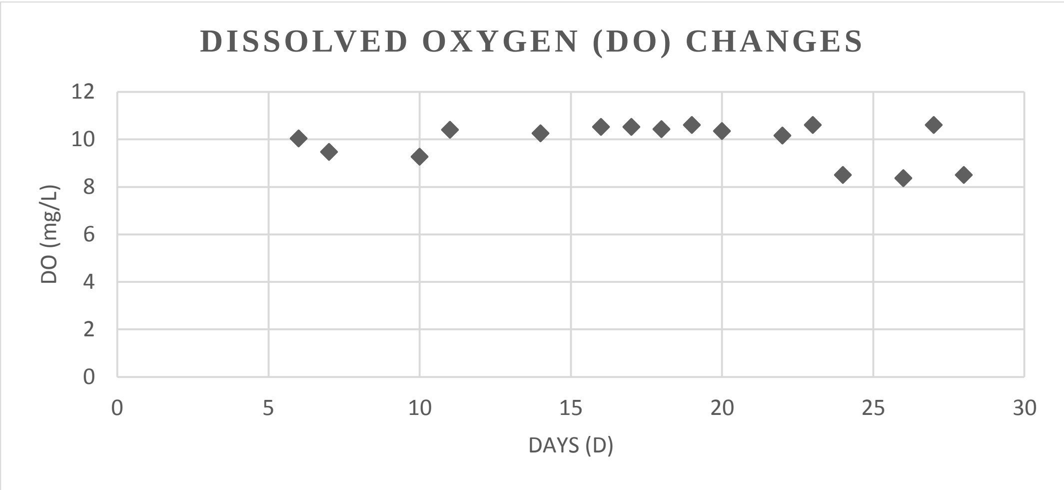


**Figure 4.10 :** DO Profile of MBR.

### 4.2.4 pH Profile

pH changes during the MBR operation is given in figure 4.11. There is no any fluctuation in the profile. General pH value is about notral values. This pH stabilization is one of the outcome of long acclimation period of the activated sludge in the MBR reactor.

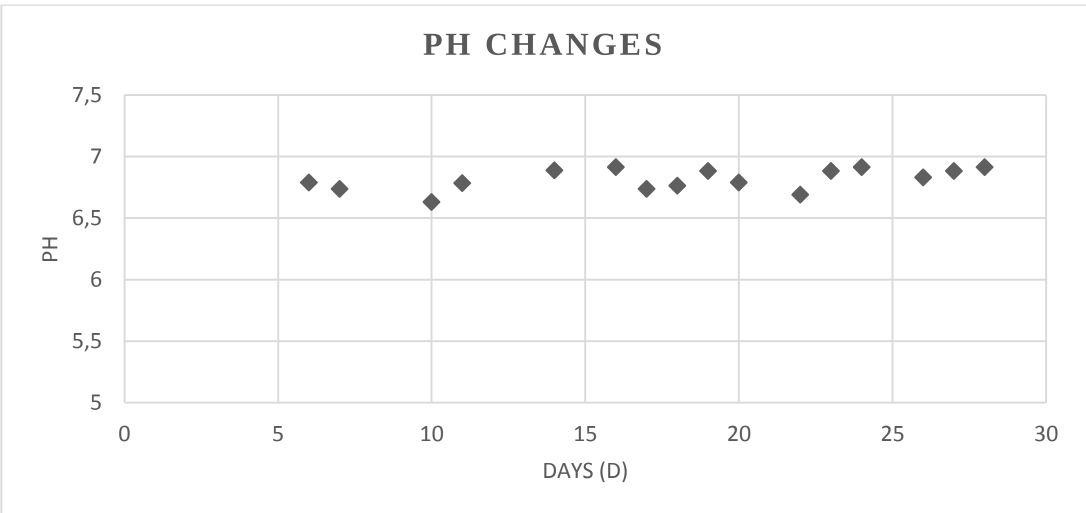


**Figure 4.11 :** pH profile of MBR.

### 4.2.5 ORP Profile

ORP (organic retention potential) profile is given in figure 4.12.ORP values is between 179 and 225 mV. The help of high oxygen reduction potential operates an efficient aerobic treatment.

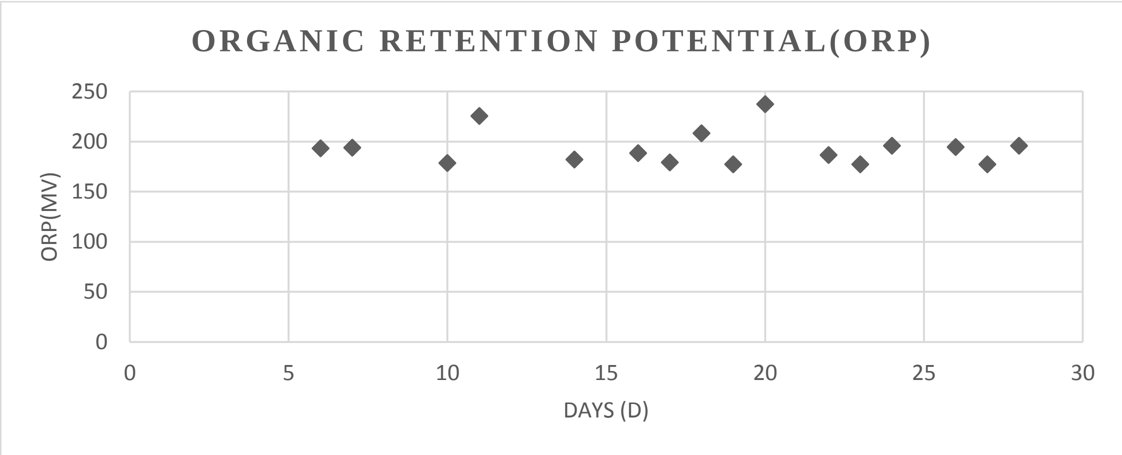


**Figure 4.12 :** ORP profile.

### 4.2.6 TMP Profile

TMP profile is given in figure 4.13. It can be said that the transmembrane pressure is lower than the other UF-MBR applications in the literature.

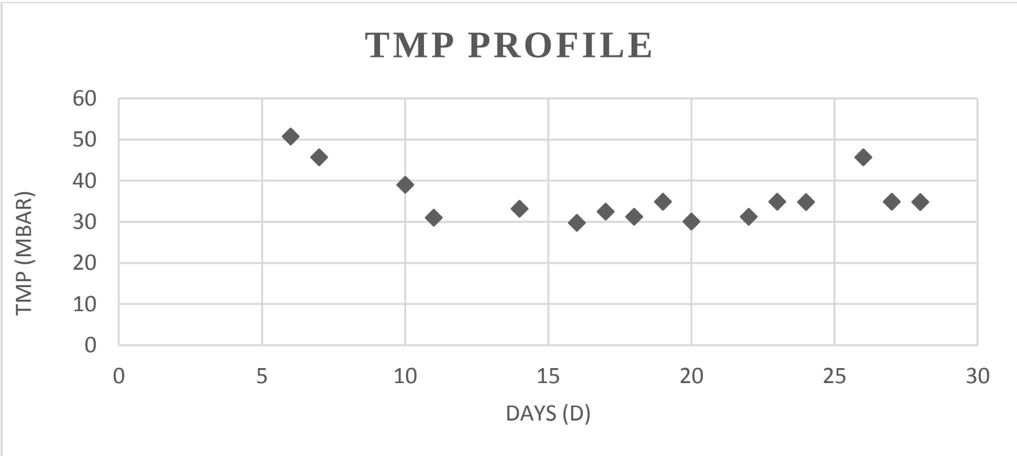


**Figure 4.13 :** TMP Profile.

### 4.2.7 UF-MBR Performance

UF membrane module has been operated at steady-state aerobic MBR system at infinite sludge age.There was not any excess sludge discharge System performance was evaluated by the sample measurements for both feed water as synthetic high strength domestic wastewater and UF permeate. Organic matter removal was determined in terms of COD. Nutrient removal was measured in terms of nitrogen and total phosphorus analyses. Turbidty removal was also evaluated.

#### 4.2.7.1 COD Removal

Steady state UF-MBR COD removal results has been reported in figure 4.14. Synthetic high strength domestic feed water average COD value is 1313 mg/L. On the other hand, mean value of the UF permeate is about 21 mg/L. In conclusion, UF-MBR COD removal efficiency is 98%.

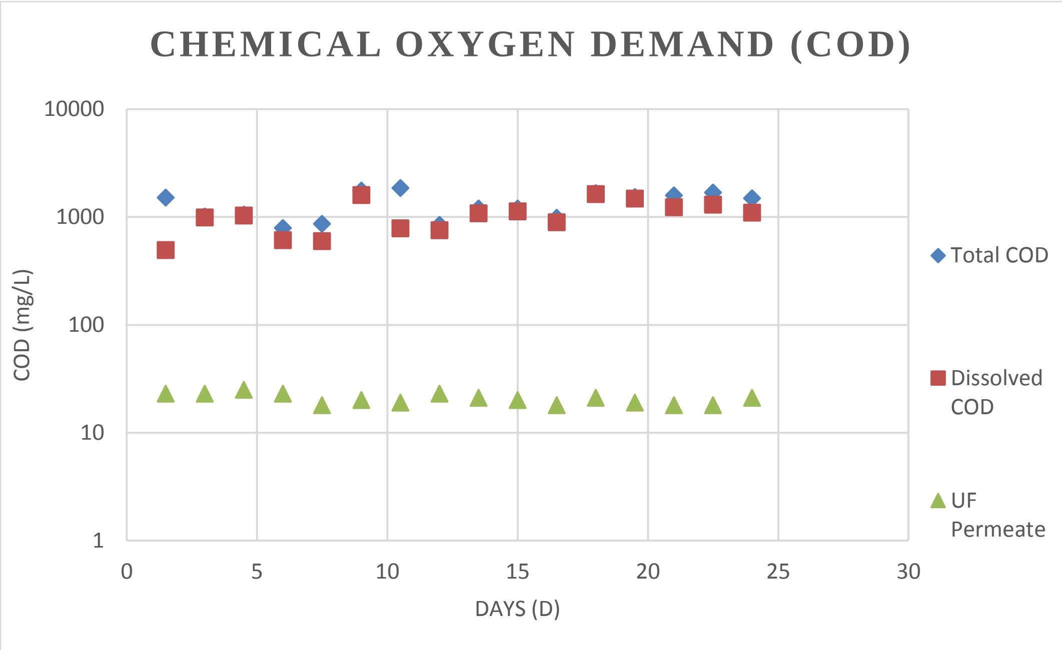


**Figure 4.14 :** UF permeates COD values (Logarithmic scale)

#### 4.2.7.2 Nitrogen Removal

Ammonium nitrate and urea were used as a nitrogen source for the preparation of synthetic wastewater.

Nitrate and nitrite as a byproduct of the nitrification was expecting in the UF permeate.

#### TN Removal

The spectrophotometric measurement kits was used for TN measurement. TN measurements were done by weekly.

TN value is fluctuating between 53 and 45 mg/L the synthetic wastewater (fig.4.15). UF permate TN value is between 29 and 40 mg/L. UF-MBR TN removal efficiency is

53%. TN value discharge limit is 15 mg/L according to municipal wastewater discharge standards. UF permeate TN value should be decreased with secondary process.

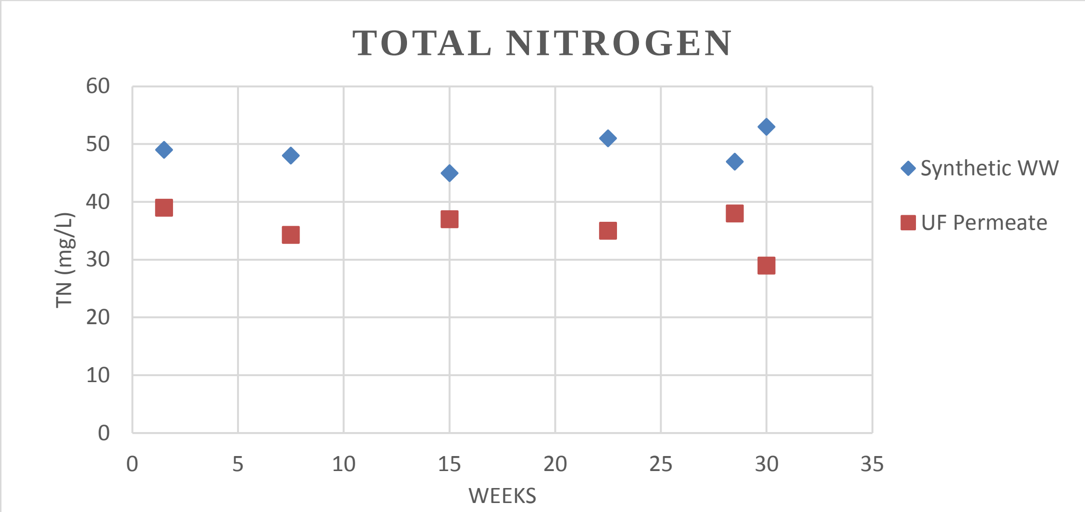


**Figure 4.15 :** Total nitrogen concentrations of UF permeate.

**TKN Removal**

Total kjeldahl nitrogen is the indicator of the ammonia concentration in water samples. Ammonia nitrogen concentration in synthetic wastewater is between 45-51 mg/L (fig. 4.16) In UF permeate; ammonia nitrogen concentration is saliently low. The nitrate concentration was relatively high and the TKN concentration was low in the reactor. Low TKN or ammonia concentration and high nitrate concentration are indicator of ammonia oxidation (nitrification).

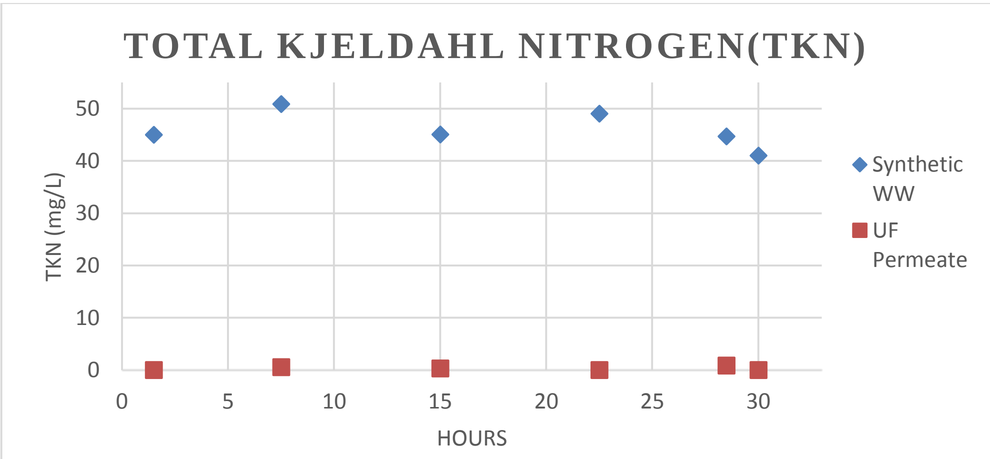


**Figure 4.16 :** Total kjeldahl nitrogen concentration of synthetic wastewater and UF permeate

**Nitrate Removal**

Mean nitrate concentration in the synthetic wastewater was measured as 0,6 mg/L. Mean nitrate concentration in UF permeate was measured as 34 mg/L (figure. 4.17). Higher values of nitrate concentrations links to be nitrification in well mixed aerated membrane bioreactor.

High nitrate concentration in the effluent refers that UF membrane is not highly selective for nitrate ions.

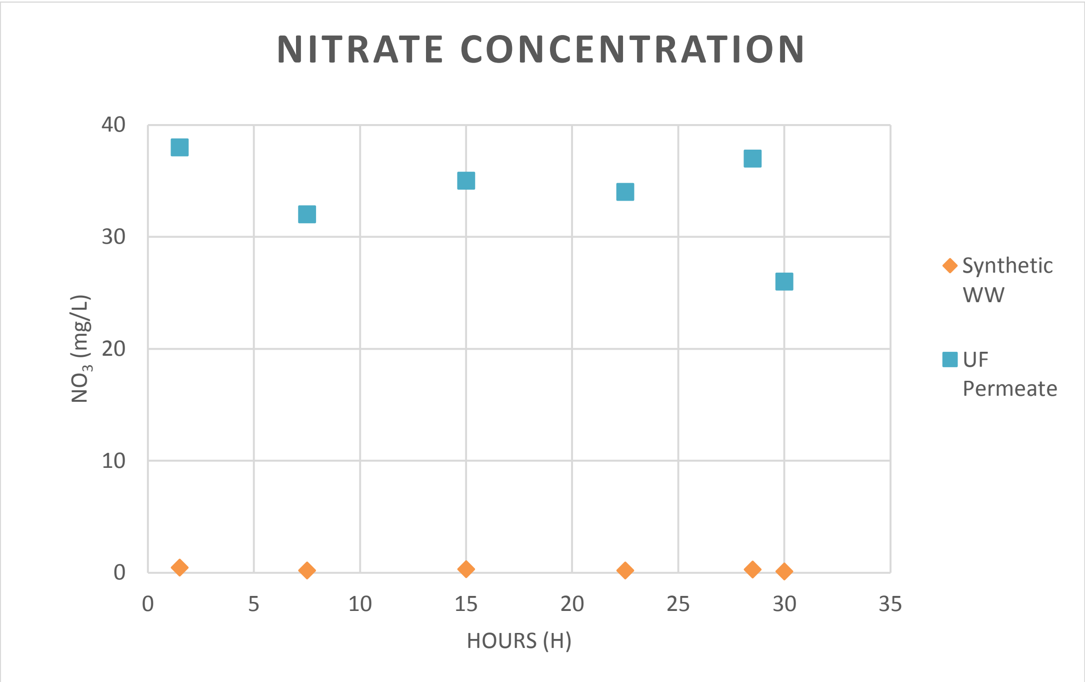


**Figure 4.17 :** Nitrate values of UF permeate.

**Nitrite Removal**

Nitrite analyses were done weekly by using spectrophotometric kits. Figure 4.18 is examined the nitrite concentration, that is between 0-1 mg/L in the synthetic wastewater. Low concentrations nitrite in UF permeate (0,007-0,1 mg/L) was observed in the UF-MBR effluent.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO + N_2O \rightarrow N_2 \qquad \textit{Denitrification} \qquad (4.1)$$

Nitrite is highly toxic to the organisms in the environment and also a by-product of denitrification process (4.1). Denitrification process requires anaerobic conditions and alkalinity. Since the reactor has been operated aerobic conditions, no nitrite concentration is expecting in the effluent.

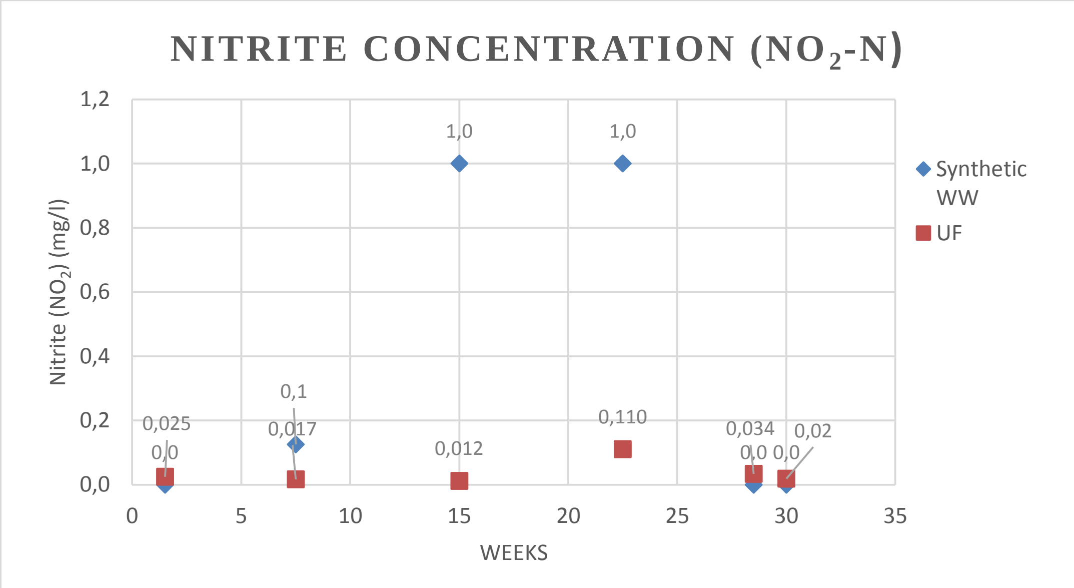


**Figure 4.18 :** Nitrite concentrations of UF Permeate.

#### 4.2.7.3 Phosphorus Removal

$KH_2PO_4$ was used as phosphorus source for the synthetic wastewater preparation and phosphorus average concentration was measured as 40 mg/L. The influent phosphorus average concentration of UF is 4 mg/L approximately. The minimum value is 2 mg/L and the maximum measured concentration is 10 mg/L (figure. 4.19).

The phosphorus consumption amount during the cell growth and metabolism is about 1-2% of the total suspended solids (Radjenović et al., 2008). On the other hand, phosphorus accumulating organism (PAOs) absorb phosphorus for their normal metabolic requirements and accumulate phosphorus as the intracellular storage of polyphosphate (poly-P). PAOs release Poly-P from their metabolism under anaerobic conditions and then it is consumed during the next aerobic phase. In order to achieve phosphorus removal, anaerobic and aerobic zone is required for activated sludge systems.The phosphorus consumption amount during the cell growth and metabolism is about 1-2% of the total suspended solids (Radjenović et al., 2008). On the other hand, phosphorus accumulating organism (PAOs) absorb phosphorus for their normal metabolic requirements and accumulate phosphorus as the intracellular storage of polyphosphate (poly-P). PAOs release Poly-P from their metabolism under anaerobic conditions and then it is consumed during the next aerobic phase. In order to achieve phosphorus removal, anaerobic and aerobic zone is required for activated sludge systems.

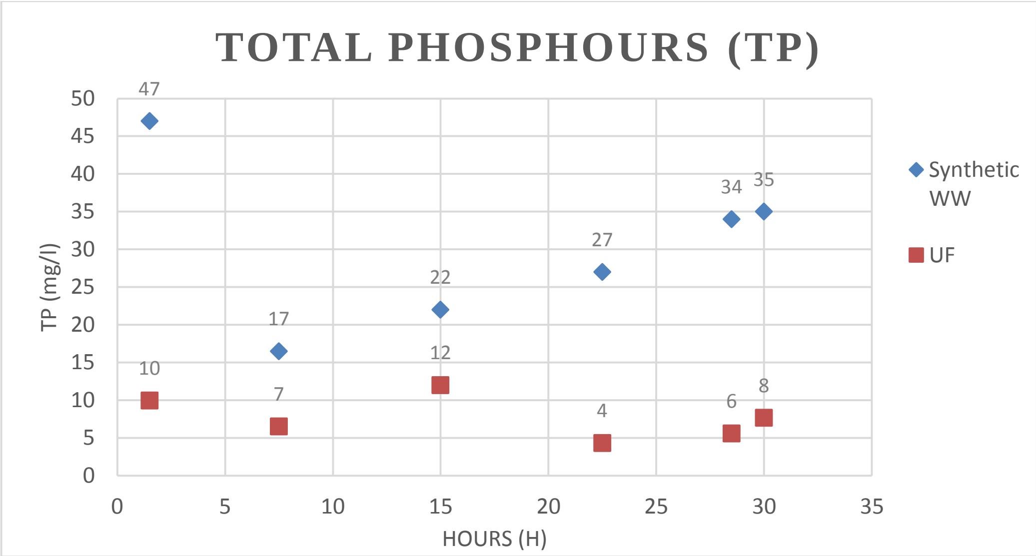


**Figure 4.19 :** TP values of UF permeate and synthetic wastewater.

Although the MBR was operated under aerobic conditions, there is a significant phosphorus removal in the system. Formation of anaerobic zones around the diffusor can be the reason for this phosphorus removal. Setting the both anaerobic and aerobic zones in the same reactor could accelerated the phosphorus removal.

### 4.2.7.4 Turbidity Removal

Turbidity was measured twice for eash UF and synthetic WW samples and their mean values is given in the figure 4.20.

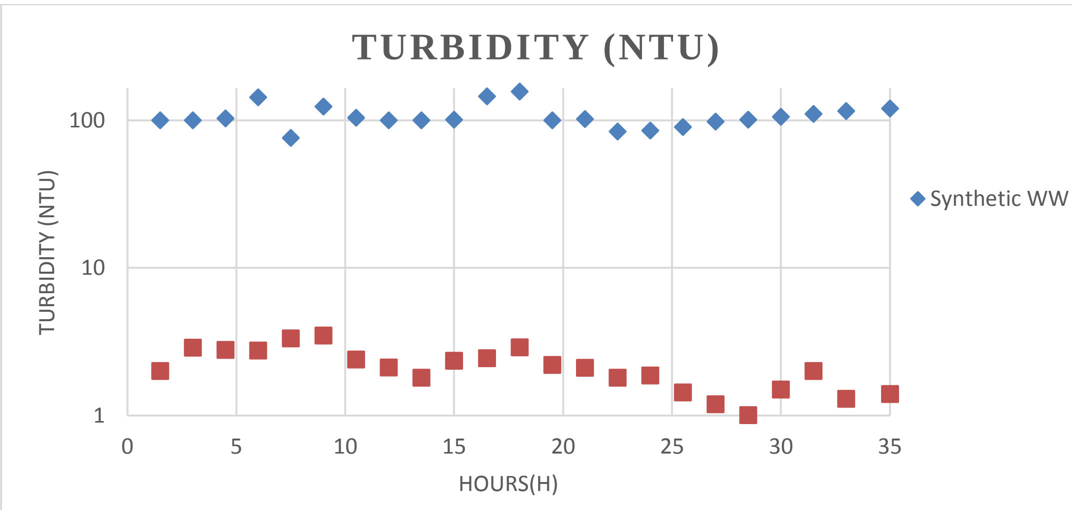


**Figure 4.20 :** Turbidity values of synthetic WW and UF permeate (logarithmic scale).

Average turbidity of synthetic WW is 100 ntu approximately. UF is highly efficient on turbidty removal with 98% removal. Turbidity level in the UF effluent is 3 ntu meanly.

## 4.3 FO Studies after UF-MBR

### 4.3.1 FO Setup Water and Salt Fluxes (UF permeate as feed solution)

A bench scale FO setup were conducted in the FO mode and with 0,5 M NaCl solution that calibrate to 42500µS conductivity as the draw solution.A FO cell for membrane arrangement was used and one 40,5 $cm^2$ membrane coupon was inserted to FO cell.

UF permate, which has been filtrered by UF module from the operated MBR, was used as feed solution; moreover, its water and reverse salt flux is investigated. Active layer was faced to UF permeate as feed water in the FO cell and cross water velocities was fixed to same as 0,26 cm/S.

System is operated 15 days, feed, and draw solutions renewed in daily basis. Only hydrolic cleaning was used against to fouling. Hydrolic cleaning was applied by passing distilled water from the pipes. Since the extreme water flux decline (below 2 LMH), first hydrolic cleaning was applied after 8 h (can be seen from the figure. 4.21 (i)). Water flux was only increased to 3 LMH and the reverse salt flux was remained stable.After 16 h (can be seen from figure 4.21;(ii) point), a new FO membrane coupon from the same membrane sheet was inserted to the FO cell since water flux was not satisfactory. After new membrane insertion, water flux was increased to 49 LMH and then decreased to 16 LMH. However, reverse salt flux was increased to 10 GMH and then decreased to 2,8 GMH. Both water and reverse salt fluxes were decreased approximately with the same ratio.

According to the diagram, the water flux is sharply declined from 48 LMH to 5 LMH after 27 h operation and 82% flux reduction was observed. After 30 h flux was rised to the 110 LMH (fig. 4.14 (iv) point). This salient increased was due to new membrane insertion. FO membrane was changed by the new one that was produced with conditions with the other tested FO membranes. Average water and reverse salt flux was 82 LMH and 0,6 GMH for the new FO coupon. Dong et al (2014) examined the FO bench scale system as post treatment by using MBR effluent that was fed with the landfill leachate as feed solution and 0,5 M NaCl solution as draw solution. They used

CTA-HTI commercial FO membrane in FO cell both in AL-DS mode and in AL-FS mode. Their AL-FS water flux was 18 LMH. In the case of this thesis, first membrane initial fluxes are 2,5 times higher than CTA-HTI membrane values. Second membrane water fluxes are 5,5 times higher.

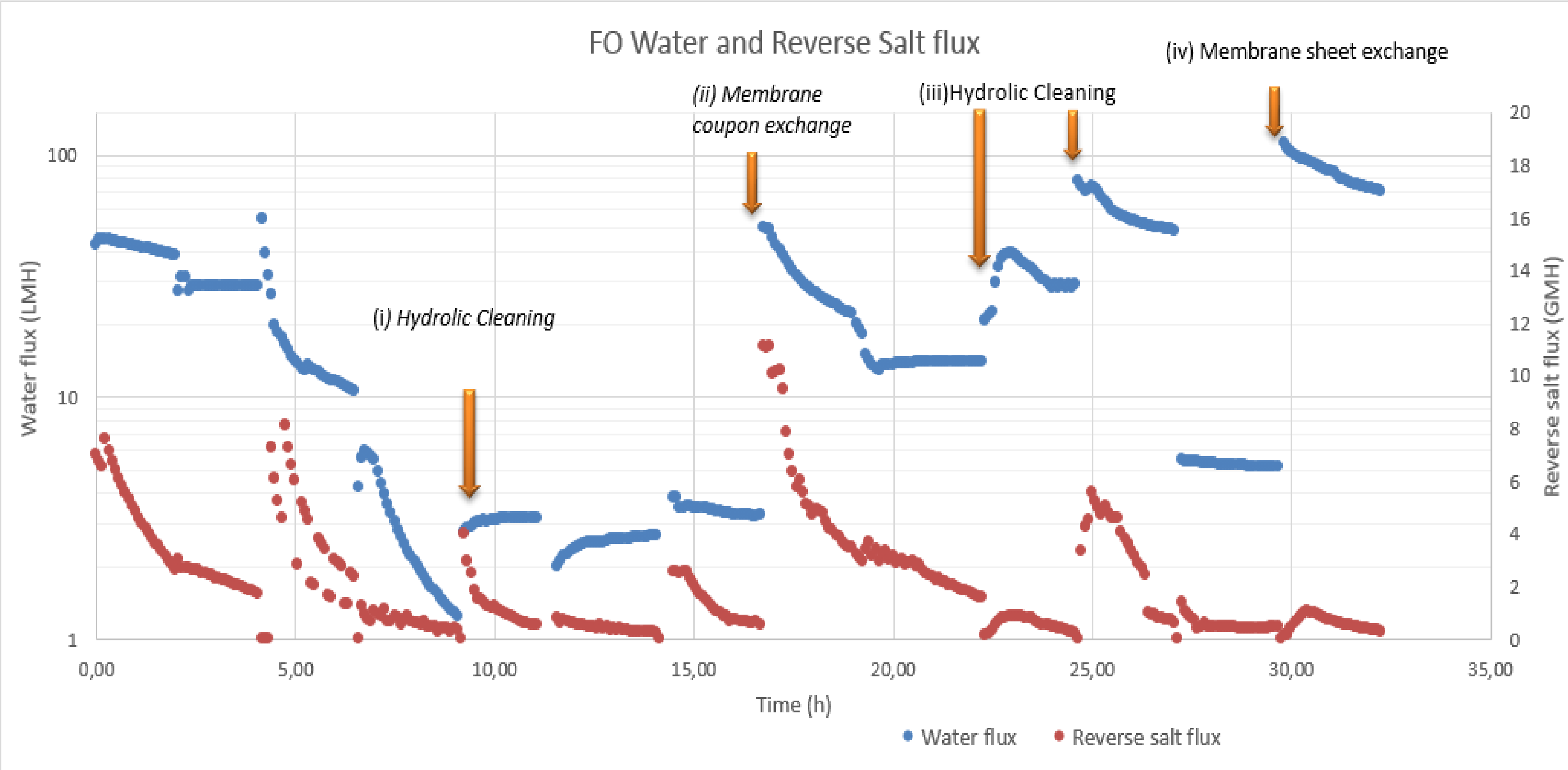


**Figure 4.21 :** Water and reverse salt fluxes of FO system (UF permeate was used as FO feed water).

### 4.3.2 COD Removal

FO permeates were collected daily and their COD values were measured daily. FO samples was contain 12 g/L NaCl meanly. When NaCl salt dissolves, chloride ($Cl^{-}$) ions are formed. Chloride is one of the most commonly use disinfectant in water treatment. $Cl^{-2}$ ions are strong oxidizants. Chloride and silver sulfate react with each other and silver chloride (AgCl) is formed as the end product. Silver chloride makes cloudiness in the samples, makes positive absorbance, moreover, causes positive interference in colorimetric method.

In order to prevent chlorine interference in the measurement, mercury sulfate ($HgSO_4$) precipitation was used. 4,5 g $HgSO_4$ is added to the COD bottles before adding the COD chemicals and wait until $HgSO_4$ is precipitate. Sample for the COD measurement was taken from the supernate according to prevent $HgSO_4$ cloudiness. Despite samples were taken from the supernate, $HgSO_4$ cloudiness cannot be totally prevented.

COD experiments results are given in figure 4.22 for both UF and FO system permeates .

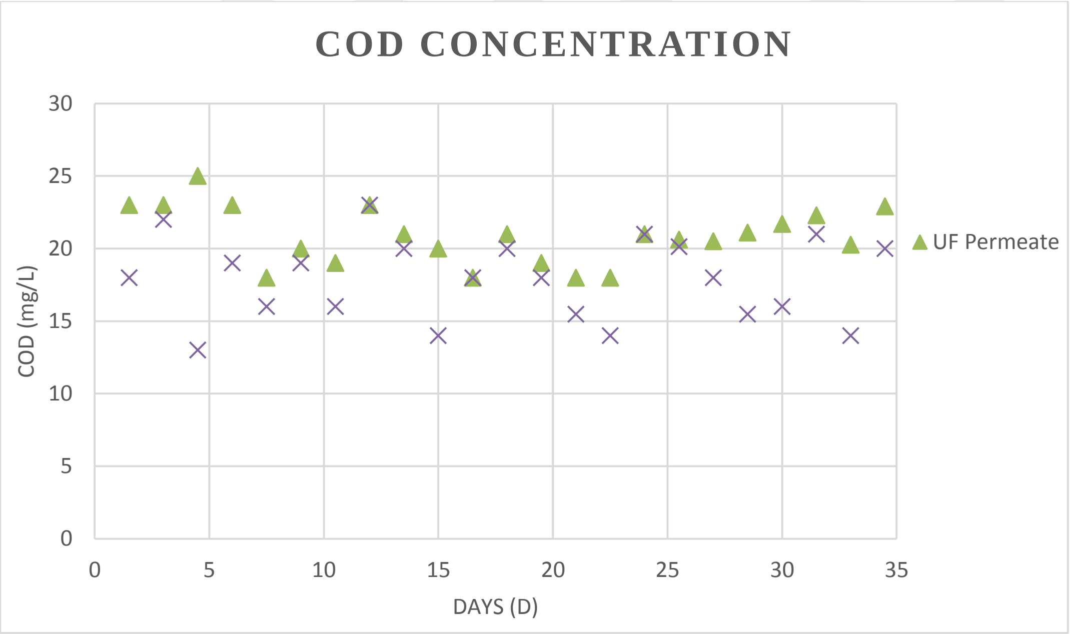


**Figure 4.22 :** COD values of UF and FO Permeates.

UF-MBR has higher COD removal efficiency than 90%. After UF-MBR treatment, only dissolved COD is remained in the permate. As can be seen in the figure 4.22, COD concentrations are very similar between UF and FO permeates. COD removal rate reach to 48% as maximum however, it could be decreased to the 2%. Mean COD removal rate is 12%  for FO system. FO membrane has not high retention capacity against to dissolved matters. FO membrane could permeate the the dissolved COD from its structure hence low COD removal rates can be the indicator of this situation.

Although mercury sulfate precipitation was applied against the chloride interference, unprobable high COD levels in the FO effluent can be the result of the interference likewise.

### 4.3.3 Nitrogen Removal

Total nitrogen, total kjeldahl nitrogen, nitrate ($NO_3^-$) and nitrite ($NO_2^-$) experiments were examined for nitrogen removal determination.

#### 4.3.3.1 TN Removal

For preventing the degradation, samples were taken daily basis and stored at cold room at +4°C. TN measurements were done weekly for FO permeates.

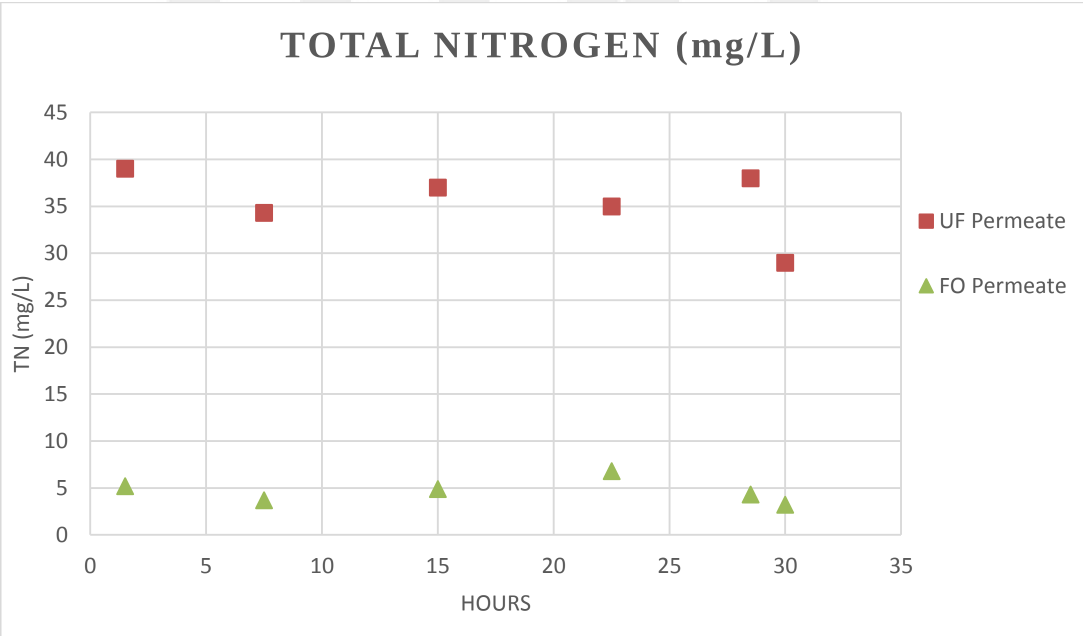


**Figure 4.23 :** TN Values of UF and FO Permeates

Total TN removal efficiency of the system is 94% as it can be seen in figure 4.23. There is not a highly efficient TN removal for UF-MBR. FO system TN removal is higher than UF-MBR. FO total nitrogen removal with 87% efficiency is higher than the UF-MBR efficiency (53%).

#### 4.3.3.2 Total Kjeldahl Nitrogen (TKN) Removal

TKN was measured by direct distillation method in the UF permeate and the FO permeate. Experiments were done for one sample per week. Organic nitrogen and ammonia nitrogen is measured by TKN (Total Kjeldahl Nitrogen) experiment. Organic nitrogen is digested to the ammonia nitrogen ($NH_3$-N) by the digestion method. As a result, ammonia and organic nitrogen was measured together in titration.

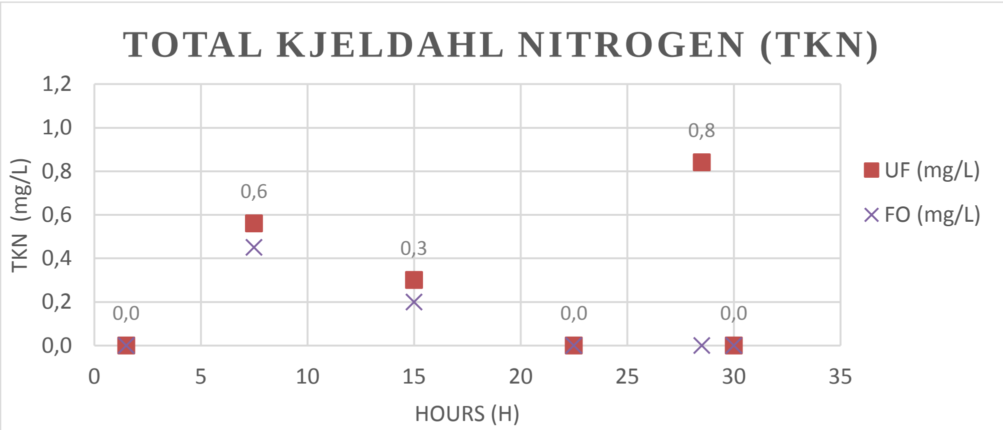


**Figure 4.24 :** Total Kjeldahl Nitrogen (TKN)

Ammonia nitrogen concentration was measured between 0-1 mg/L in the UF permeate. It can be said that UF-MBR is highly efficient for ammonia nitrogen removal. FO permeate,TKN value is 0-0,5 mg/L (figure 4.24).

Holloway et al. (2007) was investigated the treatment feasibility of the anaerobic concentrate centrate in the bench scale FO system.Centrate was used as feed solution and 1,2 M NaCl was used as draw solution. They achieved 91% TKN removal. Since the TKN value of UF permeate is negligible, the rejection performance could not be calculated.

#### 4.3.3.3 Nitrate Removal

Nitrate is the product of the nitrification process. UF-MBR was operated under conditions suitable for nitrification. Therefore nitrate concentration is expecting in the UF permeate. Nitrate concentration is UF effluent was measured 37 mg/L in average.

Xue et al. 2015 outlined the seawater-driven forward osmosis process with treated municipal wastewater in order to observe nutrient rejection. They used three flat sheet membrane ; polyamide coated polysulfone membrane and CTA1 and CTA2 membranes.  CTA membranes achieved 60% and 85% nitrate rejection. Over 90% nitrate rejection was achived by TFC-PSU support membrane. Similar results; 10% lower, are obtained with the TFC-PSU membrane in this study.

In this study, 4,6 mg/L $NO_3$ –N average concentration was determined in FO permeate (Figure 4.25). The nitrate removal efficiency was measured as 89,3 % in average in forward osmosis system. This removal rate coheres with the previous study (Xue et al.,2015).

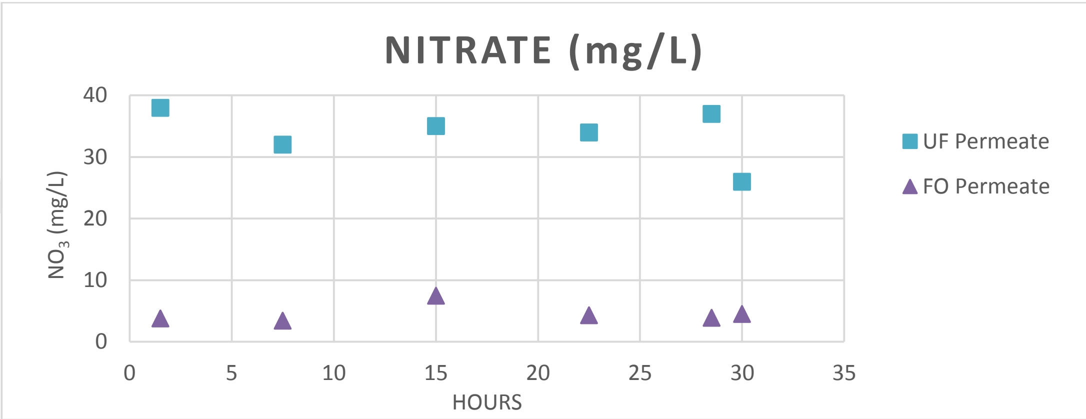


**Figure 4.25 :** Nitrate measurements

#### 4.3.3.4 Nitrite ($NO_2$) Removal

Nitrite concentration of UF is between 0,11-0,017 mg/L. In FO permeate, nitrite concentrations are between 0,003-0,021 mg/L (Figure 4.26). Nitrite removal rate for FO system was calculated as 81% meanly.

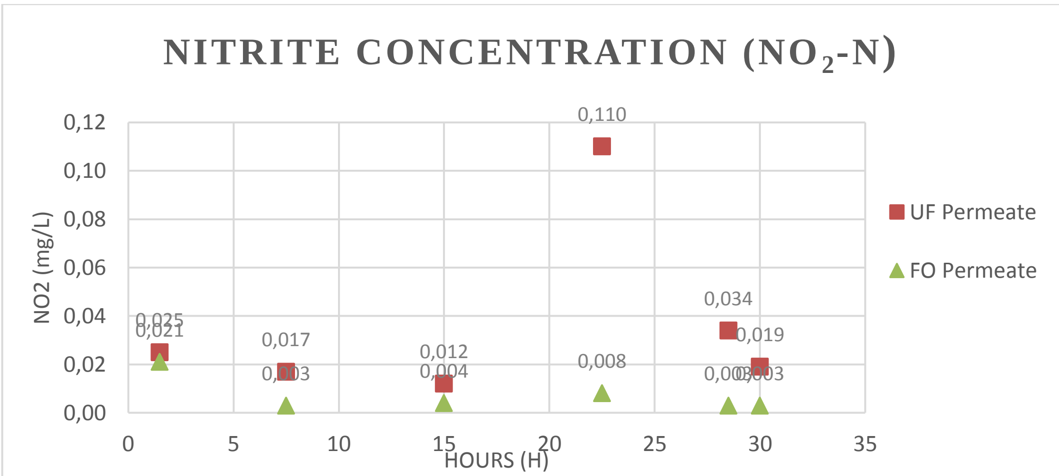


**Figure 4.26 :** Nitrite concentration in synthetic UF and FO permeates.

### 4.3.4 Total Phosphorus (TP) Removal

Phosphorus concentration in surface waters is the main reason of eutrophication and excessive growth of weedy spaces phosphorus removal is an important subject according to this situation. Phosphorus concentration for discharge water should be under the 1 mg/L according to regulations.

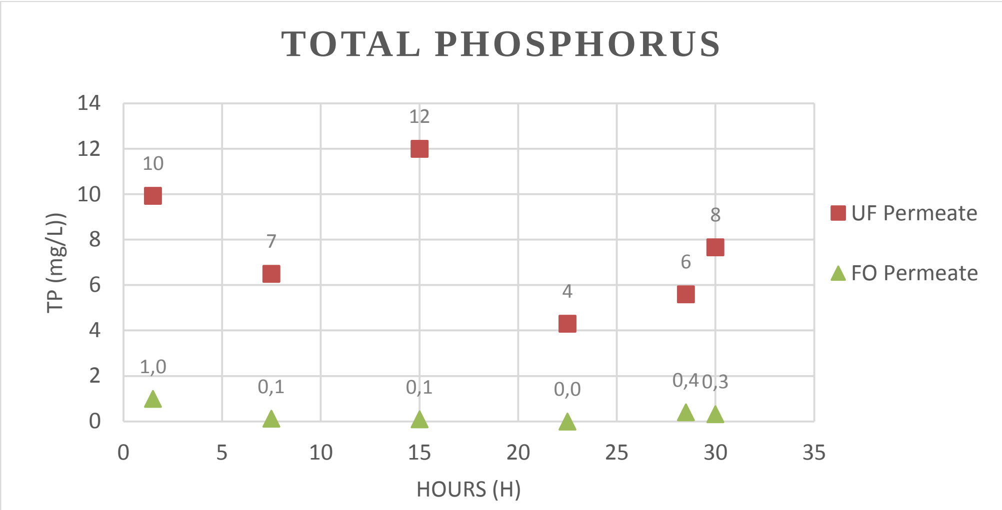


**Figure 4.27 :** TP Values

TP measurement results are given in figure 4.27. It can be seen that UF-MBR system is more efficient than the FO system for total phosphorous removal. TP concentration could be eliminated in one cycle. On the other hand it was fluctuate around 0-2 mg/L. TP maximum removal efficiency of FO system is 100% and the minimum is 86%. The average value of the FO system removal performance is 90% approximately which is very similar with the 90-100% reported in previous studies (Sun et al., 2016, Dong et al., 2014). Consistent with findings, phosphorus removal by forward osmosis membrane can be achieved.

### 4.3.5 Turbidity Removal

In figure 4.28, turbidity values of the synthetic wastewater, UF and FO permeates are given. Since the UF module is highly efficient for turbidity removal there is no high removal rate observations for FO system. However, FO turbidity removal is 53% in average. 99% removal efficiency is observed for total system (figure 4.28). There is a clearly defined pattern to the graph, and this can be taken to mean that both UF and FO system is highly efficient for turbidity removal from wastewater.

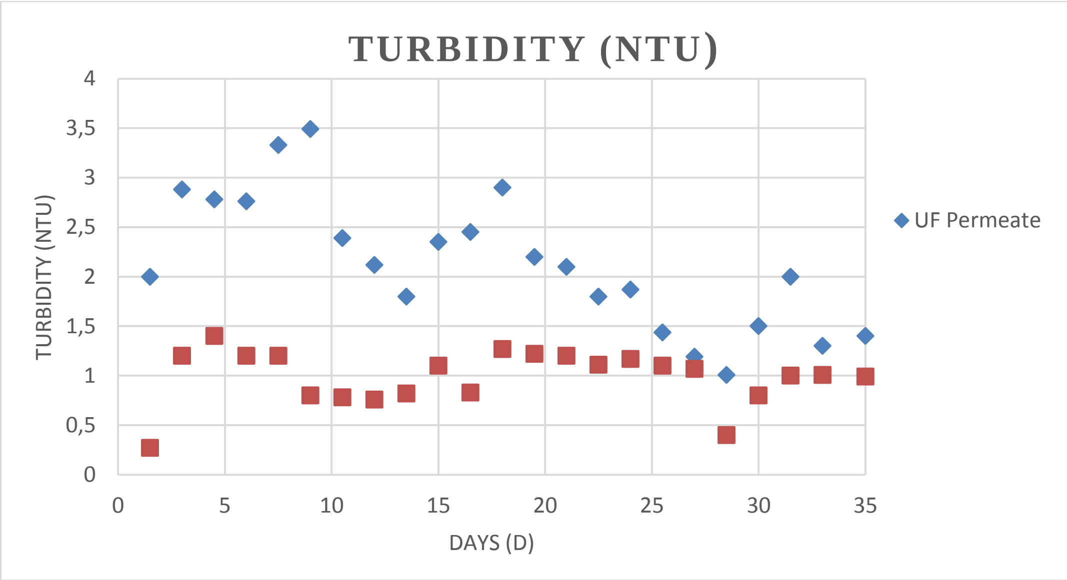


**Figure 4.28 :** Turbidity changes of UF and FO permeates.

# 5. CONCLUSION AND RECOMMENDATIONS

A membrane bioreactor with UF membrane module was operated and fed with high strength synthetic wastewater. UF effluent water characteristic was investigated.

An electrospun sPsf FO membrane was fabricated via using electrospinning technique and it was coated with PA layer by using TFC technigue. FO membrane water flux, surface morphology and propert analyses was examined. Water flux and reverse salt flux analyses was performed in AL-FS mode.40 LMH water and 0,3 GMH reverse salt flux is obtained for the first membrane. 140 LMH water and 2 GMH (in average) reverse salt flux was determined Bench scale FO system was used for electrospun TFC-FO membrane performance investigation. UF permeate was used as feed water in FO system.

MBR was operated with high strength municipal wastewater high MLSS-MLVSS concentrations such as 11675 mg/L and 6600 mg/L in average.UF module in MBR was commercial Philos membrane. MBR COD removal efficiency was quite high. 98% COD removal efficieny was recorded. TN removal efficiency was 53,3%. Total phosphorus minimum value is 2 mg/L, the maximum measured concentration is 10 mg/L for UF permate, and it was 40 mg/L for synthetic wastewater. This high TP removal efficiency was related with the anaerobic zones in the MBR.

Fabricated forward osmosis membrane could not be operated in the forward osmosis membrane bioreactor directly. FO membrane module could not be made due to the problems during the module production. Low durability of the membrane was the obstacle against the module production.. FO membrane has been directly used in the FO cell in the bench scale system.

Permeate that is collected from MBR was used as feed solution in FO bench scale system. FO system organic matter removal was not high. It was about 14,3% COD removal (Table 5.1). The nutrient removal effiency was relatively higher.Nitrogen removal was evaluated in terms of TN, TKN,nitrate and nitrite. Total kjeldahl nitrogen removal was 52% for the FO setup.Nitrate removal was 86% and the nitrite removal was calculated 98% for the hole system. Total phosphorus removal was relatively high, 89% removal performance was obtained. Total phosphorus removal for the hole system is 97,3%. Total turbidity removal efficiency of the MBR+UF system was 98% and the FO system was 53%. Turbidity was removed approximately totally for the hole system.

**Table 5.1 :** Average values of the parameters and removal rates.

| | Average Value | | | Removal Rate (%) | | |
|---|---|---|---|---|---|---|
| | Synthetic WW | UF Permeate | FO Permeate | UF-MBR | FO System | Total System |
| COD (mg/L) | 1331 | 21 | 18 | 98,4 | 14,3 | 98,6 |
| TN (mg/L) | 49 | 35 | 5,2 | 30 | 85,1 | 93,1 |
| TKN (mg/L) | 41 | 0,2 | 0,1 | 99,5 | 50,0 | 99,8 |
| Nitrate (mg/L) | 0,2 | 34,0 | 4,6 | - | 86,5 | 86,5 |
| Nitrite (mg/L) | 0,354 | 0,036 | 0,007 | - | 80,6 | 98,0 |
| TP ( mg/L) | 30 | 8 | 0,8 | 77,0 | 89,0 | 97,3 |
| Turbidity (ntu) | 107,1 | 2,1 | 1,0 | 98,0 | 53,7 | 99,1 |

FO bench scale system was operated 33 hours totally. Membrane has changed 3 times and hydrolic cleaning was applied 3 times. There was no chemical cleanining requirement. Third membrane was changed after the hydrolic cleaning since hydrolic cleaning was damaged the membrane in the FO cell.

In order to increase the stability, FO membrane fabrication methods can be developed or new membrane configurations can be studied. Fabricated modules would be operated aerobically or anaerobically in the forward osmosis membrane bioreactor. In order to overcome the diffuculity of the electrospun membrane module production, new module configurations can be developed

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