ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

FABRICATION AND CHARACTERIZATION OF HOLLOW FIBER MEMBRANE WITH BISBAL ADDITIVE: MEMBRANE BIOREACTOR (MBR) APPLICATION

M.Sc. THESIS

Fatma Nur Şeyma YAVUZ

Department of Environmental Engineering

Environmental Biotechnology Programme

JANUARY 2015

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

FABRICATION AND CHARACTERIZATION OF HOLLOW FIBER MEMBRANE WITH BISBAL ADDITIVE: MEMBRANE BIOREACTOR (MBR) APPLICATION

Fatma Nur Şeyma YAVUZ
(501121809)

Department of Environmental Engineering

Environmental Biotechnology Programme

Thesis Advisor: Prof. Dr. İsmail KOYUNCU

JANUARY 2015

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

BISBAL İLAVELİ HOLLOW FİBER MEMBRAN ÜRETİMİ VE KARAKTERİZASYONU: MEMBRAN BİYOREAKTÖR (MBR) UYGULAMASI

YÜKSEK LİSANS TEZİ

Fatma Nur Şeyma YAVUZ
(501121809)

Çevre Mühendisliği Anabilim Dalı

Çevre Biyoteknolojisi Programı

Tez Danışmanı: Prof. Dr. İsmail KOYUNCU

OCAK 2015

Fatma Nur Şeyma YAVUZ, a **M.Sc.** student of ITU **Graduate School of Science, Engineering and Technology** student ID **501121809**, successfully defended the **thesis** entitled "**FABRICATION AND CHARACTERIZATION OF HOLLOW FIBER MEMBRANE WITH BISBAL ADDITIVE: MEMBRANE BIOREACTOR (MBR) APPLICATION**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. İsmail KOYUNCU** İstanbul Technical University	.....
Jury Members :	**Prof. Dr. Süleyman ÖVEZ** İstanbul Technical University	.....
	Prof. Dr. Halil HASAR Fırat University	.....

Date of Submission : 13 December 2014
Date of Defense : 23 January 2015

To my beloved ones,

FOREWORD

First of all, I would like to thank my thesis supervisor Prof. Dr. İsmail KOYUNCU for his guidance and supportance during every moment of my thesis and also appreciated for giving me the chance of working at MEM-TEK as a member of his scientific research group.

I would like to express my sincere thanks to Doç. Dr. Derya İMER YÜKSEL for her great support, valuable suggestions, encouragements and understanding throughout my studies. Also, I am deeply grateful to my co-worker Res. Assis. Reyhan ŞENGÜR who shared all her knowledge and laboratory experience with me. Everytime when I was in need of any help, they were at there with all their supports and friendships.

And, I want to thank all other MEM-TEK researchers who are not only great colleagues but also dearest friends.

Finally, I especially grateful for love, support and patience of my family (Ali&Selma-Büşra YAVUZ) who are always with me.

December 2014

Fatma Nur Şeyma YAVUZ
(Chemical Engineer)

TABLE OF CONTENTS

Page

ABBREVIATIONS

BisBAL	**:** Bismuth dimercaptopropanol
BSA	**:** Bovine Serum Albumin
BT	**:** Bismuth Thiole
CA	**:** Cellulose acetate
COD	**:** Chemical Oxygen Demand
E. coli	**:** *Escherichia coli*
EPS	**:** Extracellular polymeric substances
Ɛ	**:** Porosity
F/M	**:** Food to Microorganism
HF	**:** Hollow Fiber
HRT	**:** Hydraulic Retention Time
iMBR	**:** Immersed membrane bioreactor
MBR	**:** Membrane bioreactor
MF	**:** Microfiltration
MLSS	**:** Mixed Liquor suspended solids
MWCO	**:** Molecular Weight Cut-off
NaOCl	**:** Sodium Hypochloride
NF	**:** Nanofiltration
NMP	**:** 1-methyl-2-pyrrolidone
PAN	**:** Polyacrylonitrile
PES	**:** Polyethersulfone
PS	**:** Polysulphone
PVDF	**:** Polyvinylidenediflouride
PVP	**:** Immersed membrane bioreactor
RO	**:** Reverse Osmosis
SEM	**:** Scanning Electron Microscopy
SMP	**:** Soluble microbial products
SRT	**:** Sludge Retention Time
SS	**:** Suspended solids
SVI	**:** Sludge Volume Index
UF	**:** Ultrafiltration
VSS	**:** Volatile suspended solids

LIST OF TABLES

Page

LIST OF FIGURES

Page

FABRICATION AND CHARACTERIZATION OF HOLLOW FIBER MEMBRANE WITH BISBAL ADDITIVE: MEMBRANE BIOREACTOR (MBR) APPLICATION

SUMMARY

Water scarcity is one of the most important problems of our world. In 21st century, demand of water is getting higher day by day because of increasing population and limited supplies. Treatment and reuse of available water is an important issue for providing water.

At the last years, membrane filtration systems have been a popular alternative as advance treatment processes because of their advantages such as low space requirement, easy application and no need for chemical additives when comparing with the conventional systems. With the improvement of advanced treatment technologies, managing and solving emerging water crisis of the world can achieved practically.

There are some challenges for the application of membrane filtration systems such as fouling which is the major problem for the operation of membrane processes. Especially, biofouling is the most challenging problem in membrane bioreactors. For solving this problem, some approaches were improved and experienced. The better and more effective way is modification of the membranes before the occurrence of fouling by an enhancement of its structure with antibacterial additives. Improvement of membrane properties at fabrication can be effective and useful for solving the problem.

In this study; fabrication and characterization of polyethersulfone (PES) ultrafiltration hollow fiber membranes with an antibacterial additive and investigating its anti-biofouling effects with an application of submerged membrane bioreactor were objected.

To achieve our aim, BisBAL which is one of the bismuth thioles, known as its antibacterial features, was used as an additive. Ultrafiltration hollow fiber membranes were spun by using phase inversion method.

After choosing the optimum recipe (18 % PES, 7 % PVP K90, 75 % NMP), membranes were fabricated with and without additive (called as enhanced and pristine in order of term) for different spinning parameters. Air gap, take-up speed were changed in these spinning parameters. After spinning, post treatment process applied for all membranes with NaOCl for 2 days. Then, they were prepared as modules. All characterization experiments were done by these modules. Permeability, porosity, contact angle, water flux recovery, total fouling ratio, BSA rejection rate, mechanical stability and surface morphology assessment (by scanning electron microscopy (SEM), optic profilometer and stereo microscopy) of the membranes were measured and calculated. Then, the membranes (pristine and enhanced with BisBAL additive) were fabricated again with the selected spinning condition (air gap: 0 cm, take-up speed: 7.1 m/s, coagulation bath temperature: 35 ^{o}C) which had the best results.

According to characterization results, membranes were fabricated properly which had circular shapes as expected. Effects of BisBAL observed with images of membranes clearly. It was monitoring that pristine membrane had structure as finger-like that was changed to sponge-like with BisBAL additive. Also enhanced membrane with (30 μm.) BisBAL addition had better permeability, mechanical stability and less fouling properties, contact angle degree (more hydrophilic).
Antibacterial properties of the membranes were found using with *Escherichia coli* which was taken from "Microorganism Culture Collection Research and Application Center (KÜKENS) of Turkey". Pure culture bacteria species were growth on membranes during 6 days at 37 °C in Standard Plate Agar. After incubation, the growth degree of *E. coli* was observed visually. Less growth found on enhanced (with BisBAL) membranes. According to the results, enhanced with BisBAL additive membranes showed more antibacterial properties than pristine membranes.

Hollow fiber (dead end) filtration modules were immersed into an aerated batch bioreactor (6 lt.) that fed with synthetic wastewater. To investigate antibiofouling effects of the enhanced membrane with BisBAL additive, system has been operated for 30 days. Throughout the MBR application; flux, COD, VSS and SS were measured and calculated on daily basis.
Average suspended solid amounts of mixed liquor was 16000 mg/l. COD removal percentages and flux rates were higher for enhanced membrane than pristine. Because

of the parallel correlation between biofouling and EPS-SMP amounts, that was explained at the literature review section, EPS-SMP experiments were done on pristine and enhanced membranes at the end of the MBR operation. EPS-SMP values of enhanced HF membrane were lower than pristine as expected. These results proved the antibiofouling effect of BisBAL. Also, confocal scanning laser microscopy images were taken for observing the deposition of organic matter and fouling rates on the surfaces at 25^{th}, 27^{th} and 29^{th} days of membrane bioreactor operation. Formation of biofilm layer was observed on surfaces of both membranes but biofilm layer thickness of pristine was more than enhanced membrane. All results demonstrated that antibiofouling features of BisBAL.

BISBAL ILAVELI INCE BOSLUKLU (HOLLOW FIBER) MEMBRAN URETIMI VE KARAKTERIZASYONU: MEMBRAN BIYOREAKTOR (MBR) UYGULAMASI

ÖZET

Dünyanın en önemli problemlerinden birisi su kıtlığı sorunudur. 21. yüzyıl itibariyle, kısıtlı su kaynakları ve nüfus artışı sebebiyle su ihtiyacı da her geçen gün artmaktadır. Bu ihtiyacı karşılayabilmek için suyun yeniden kullanılması ve arıtılması oldukça önem teşkil etmektedir. Son yıllarda membran filtrasyon sistemleri ileri arıtma teknolojisi olarak, geleneksel ileri arıtma sistemlerine göre daha az alan gereksinimi duyması, kolay uygulanabilirliği ve kimyasal ilaveler gerektirmemesi gibi avantajlarıyla oldukça revaçta bir alternatif haline gelmiştir. İleri arıtma sistemlerinin gelişmesiyle, halihazırdaki kaynakların yönetilmesi ve ortaya çıkmakta olan su krizinin çözülebilmesi pratik olarak mümkün görünmektedir.

Membran filtrasyon sistemlerinde, etkin bir sonuç alabilmek için çözülmesi gereken bazı konular bulunmaktadır. Bunlardan birisi ve en önemlisi olan tıkanma problemleri, membran filtrasyon sistemlerinin işletilmesi esnasında sorun teşkil etmektedir. Bu problemi çözebilmek için çeşitli yollar ve yaklaşımlar geliştilmekte ve denenmektedir. Tıkanma oluşmadan evvel müdahale etmenin en etkili ve iyi yol olduğu düşünülmektedir. Bu müdahale membranların yapıları geliştirerek yapılmaktadır. Membran üretimi esnasında, üretim materyallerine antibakteriyel maddeler ilave edilerek, membran filtrelerin daha dayanıklı ve biyotıkanmaya dirençli olmaları sağlanmakta, böylece kirlenme ve tıkanma oluşumunu en aza indirgemek amaçlanmaktadır. Membranların özelliklerinin geliştirilmesiyle, daha etkin ve faydalı bir sonuç elde etmek ve ilgili sorunları çözebilmek mümkündür.

Bu çalışma kapsamında; polietersülfon (PES) kullanılarak ultrafiltrasyon düzeyinde ince boşluklu (hollow fiber) membran üretimi gerçekleştirilmiştir. Üretilen bu membranlara antibakteriyel madde ilavesi yapılarak, anti-biyotıkanma özelliği edinmesi amaçlanmış ve batık membrane biyoreaktörde işletilmesi ile üretilen membranların anti-biyotıkanma özelliğinin araştırılması hedeflenmiştir.

Bu amacı gerçekleştirebilmek için, antibakteriyal madde ilavesi olarak bizmut tiyollerden biri olan ve güçlü antibakteriyel özelliğiyle bilinen BisBAL maddesi kullanılmıştır. Ultrafiltrasyon mertebesindeki ince boşluklu membranlar, faz ayrımı yöntemi kullanılarak üretilmiştir. BisBAL ilavesi miktarı, daha evvelki çalışmalar (Durmaz, 2014) baz alınarak 30 μm. olarak belirlenmiştir. En uygun çözelti reçetesini bulabilmek için, bir birçok farklı konsantrasyon ve farklı malzemeler kullanılarak membran üretimleri gerçekleştirilmiştir. Bunların sonucunda %18 PES, %7 PVP K90 ve %73 NMP kullanılmasına karar verilmiştir. Bu reçete kullanılarak BisBAL ilaveli ve ilavesiz (saf) membranlar üretilmiş ve farklı işletim parametreleri kullanılarak en uygun döküm şartları bulunmuştur. Parametrelerdeki değişkenler çekme hızı, hava boşluğu ve koagülasyon banyosu sıcaklığı olmuştur. Üretilen membranlar, üretim sonrasında sodyum hipoklorit çözeltisinde 2 gün boyunca bekletilerek bir ön işleme tabi tutulduktan sonra modüller halinde hazırlanıp, karakterizasyon testlerine geçilmiştir.

Membranlara; geçirgenlik, porozite, temas açısı, geri kazanım, toplam kirlenme derecesi, BSA giderimi, mekanik dayanıklılık testleri uygulanmış ve taramalı elektron mikroskobu, stereo mikroskop ve optik profilometre kullanılarak yüzey morfolojileri tanımlanmıştır. Elde edilen sonuçlar göz önünde bulundurularak en iyi sonucun alındığı üretim parametreleri (hava boşluğu: 0 cm, çekme hızı: 7,1 m/s ve koagülasyon banyosu sıcaklığı: 35 ^{o}C) en uygun olarak belirlenmiş ve membran biyoreaktör uygulamasında kullanılmak üzere bu koşullarda, BisBAL ilaveli ve ilavesiz (saf) olarak üretilmiştir.

Karakterizasyon testlerinin sonuçlarına bakıldığında, membranların olması gerektiği gibi içi boşluklu ve yuvarlak şekli sağladığı görülmüş, düzgün bir üretim gerçekleştirildiğine karar verilmiştir. Ayrıca BisBAL ilavesinin membran yapısına etkisi de açıkça görülmektedir. Saf membranlarda parmağımsı yapı görülürken, ilaveli membranların yapısının süngerimsi hale geldiği gözlemlenmiştir. Ayrıca BisBAL ilaveli membranların daha iyi geçirgenlik ve mekanik dayanıklık edinmesinin yanı sıra kirlenme özelliklerinde ve temas açılarında düşme gözlenmiş olup, daha hidrofilik ve daha az kirlenme kapasitesine sahip oldukları söylenebilmektedir.

Membranların antibakteriyel özellikleri, Mikroorganizma Kültür Koleksiyonları Enstitüsü (KÜKENS)'den alınan *E. coli* suşu ile ayrıca belirlenmiştir. Saf kültür bakterilerinin membranlar üzerinde büyümeleri 6 gün boyunca, 37 °C sıcaklık ortamında, agarlarda gözlemlenmiştir. BisBAL ilaveli membranların üzerinde, saf

membranlara nazaran daha az büyüme görülmüştür. Tüm bu sonuçlar dikkate alındığında, BisBAL ilaveli membranların antibakteriyel özellik kazandığı söylenebilir.

İnce boşluklu membran modülleri; lab ölçekli (6lt.), havalandırmalı kesikli membran biyoreaktörde 30 gün boyunca işletilmiştir. Sentetik atık su kullanılan bu sistemde, BisBAL ilaveli membranların antibiyotıkanma özellikleri araştırılmıştır.

Membran biyoreaktör işletimi boyunca, akı, kimyasal oksijen ihtiyacı ve atık suyun askıda katı madde ile askıda uçucu katı madde miktarları günlük olarak ölçülmüş ve hesaplanmıştır. Atık suyun ortalama askıda katı madde miktarı 16000 mg/l civarındadır. BisBAL ilaveli membrana ait kimyasal oksijen ihtiyacı giderim yüzdeleri ve akı miktarları, saf membrane göre daha yüksek değerlerde ölçülmüştür.

Biyokirlenme ile ortamdaki hücre dışı polimerik madde ve çözünmüş mikrobiyal ürün (EPS-SMP) miktarı arasında, literatür taraması kısmında detaylıca bahsedildiği üzere, bir paralellik söz konusudur. Bundan dolayı işletimin sonunda membranların üzerinde biriken kek tabakalarının EPS-SMP miktarları ölçülmüş ve beklenildiği üzere BisBAL ilaveli membranda daha az miktarda EPS-SMP varlığı görülmüştür.

Tüm alınan sonuçlar, BisBAL ilavesinin antibiyotıkanma özelliğini destekler nitelikte çıkmıştır. Ayrıca, konfokal lazer mikroskobu kullanılarak biyofilm tabakası kalınlığı ölçülmüştür. Membran biyoreaktör işletiminin 25., 27. ve 29. günlerinde, membranların biyofilm tabakası kalınlıkları ölçülmüş, saf membrandaki tabakanın daha fazla ve zamanla daha fazla artan miktarlarda olduğu gözlemlenmiştir. BisBAL ilaveli membranın daha ince bir tabaka biyofilmle kaplı oluşu ve evvelki sonuçlar göz önüne alındığında BisBAL ilavesinin üretilen membrana anti-biyotıkanma özelliği kazandırdığı söylenebilmektedir.

1. INTRODUCTION

1.1 Importance of The Study

Water scarcity is one of the most important problems of the world. In 21st century, demand of water is getting higher day by day because of increasing population and limited supplies. By 2025, 1.8 billion people where in countries or regions will be faced with absolute water scarcity according to United Nations Water Report (Url-1).

With this scenario, it was predicted that almost half of the world may effect from water crisis. Water scarcity is not only natural but also human-made phenomenon. Population growth, climate change, polluted resources have negative impact on water reserves and caused to 'water problem' which has to be solved urgently. So, water and wastewater management are one of the important key for the solution. Especially, water treatment and reuse are the most significant issues for preserving current sources. It can be claim that purification of water and wastewater can overcome water scarcity problem.

At the last years, membrane filtration systems have been a popular alternative as an advance treatment processes compared to conventional ones because of their advantages such as low space requirement, easily applicable, no necessity of chemical additions.With the improvements of technologies, managing and solving the world's emerging water crisis can achieved practically.

1.2 Mission and Scope of The Study

Membrane filtration technologies have various applications such as complement or replacement with conventional processes for removing of particulate and organic matter. Also, they are integrated with bioreactors which called as membrane bioreactors (MBRs) and applicated for wastewaters instead of activated sludge processes (Mansouri et. al. 2009). Membrane fouling is a major problem in membrane filtration processes in water and wastewater treatment systems. Especially, biofouling has negative impact on performance of system such as flux decreasement, filtering quality, lifetime of membranes. Growth and deposition of bacterias on the surface of

membranes are called biofilm layer and it causes biofouling. This blockage has to be prevented for operating of the system efficiently. There are some approaches for mitigation of biofouling such as coating of membrane surface and fabrication of the membranes with antibacterial materials.

In this study; fabrication and characterization of polyethersulphone (PES) ultrafiltration hollow fiber membranes with an additive (BisBAL) which has an antibacterial feature and application of membrane bioreactor for investigating its anti-biofouling effects are objected. Literature review about hollow fiber membrane, membrane bioreactor and antibacterial additive (BisBAL) were given, fabrication&characterization and application results were discussed and finally prospective ideas were presented respectively throughout the thesis.

2. LITERATURE REVIEW

2.1 Membrane Technology

Meaning of "membrane" as word is a separation barrier between two phases. In other way; it can be defined as a 'filter' which can be able to restrict the transport of various components in a selective manner (Wang et. al. 2010).

Membranes and membrane processes are not a recent invention. Membranes were firstly introduced as an analytical tools at laboratories. Than, they developed into industrial products and methods (Strathmann et. al. 2006). Industrial applications of synthetic membranes were started in the 1960s.

But, the earliest study about membrane phenomena was recorded at the middle of the eighteenth century (Strathmann et. al. 1985). Historical developments of membrane technology are listed in Table 2.1.

Table 2.1 : Historical developments of membranes (pre-1980s) (Wang et. al. 2010).

Year	Development
1784	'Osmosis', permeation of water
1833	Diffusion of gases law
1855	Phenomenological diffusion laws
1860-1880s	Osmotic pressure, semi permeable membranes
1907-1920	Microporous membranes
1920s	Reverse osmosis prototype
1930s	Electrodialysis membranes
1950s	Microfiltration, hemodialysis, ion exchange membranes
1963	Reverse osmosis membranes
1968	Spiral-wound reverse osmosis modules
1977	Thin film composite membranes
1970-1980	RO, UF, MF, electrodialysis membranes
1980s	Industrial gas separation membranes processes
1989	Submerged membrane (membrane bioreactor)

With the rapid development of membrane processes and technologies, membranes were started to use for numerous industrial applications such as purification, desalination, wastewater reclamation, gas and vapor separation, energy conversion and storage, air pollution control and hazardous industrial waste treatment, hemodialysis, proteins and microorganisms separation, etc. (Strathmann et. al. 2006). We can see that the membrane science and technology has been experienced for a long period of development in laboratory studies. Even with all of these studies and applications, membrane technology has still more space for improvement to satisfy future applications (Wang et. al. 2010).

2.1.1 Types of membrane seperation

A membrane can be defined basicly as a material which allows components to pass through in it. Some components may be more readily pass through from membrane than others because of membranes' perm-selectivity. The degree of selectivity and permeability depends on the pore characteristics (size, distribution, porosity) of the membrane. Depending on the pore structure, pressure-driven membranes can be classified by their pore sizes as four key groups which are reverse osmosis (RO), nanofiltration (NF) ultrafiltration (UF) and microfiltration (MF) membranes (Judd, 2011). Sizes and seperation targets of these membranes were given at Figure 2.1.

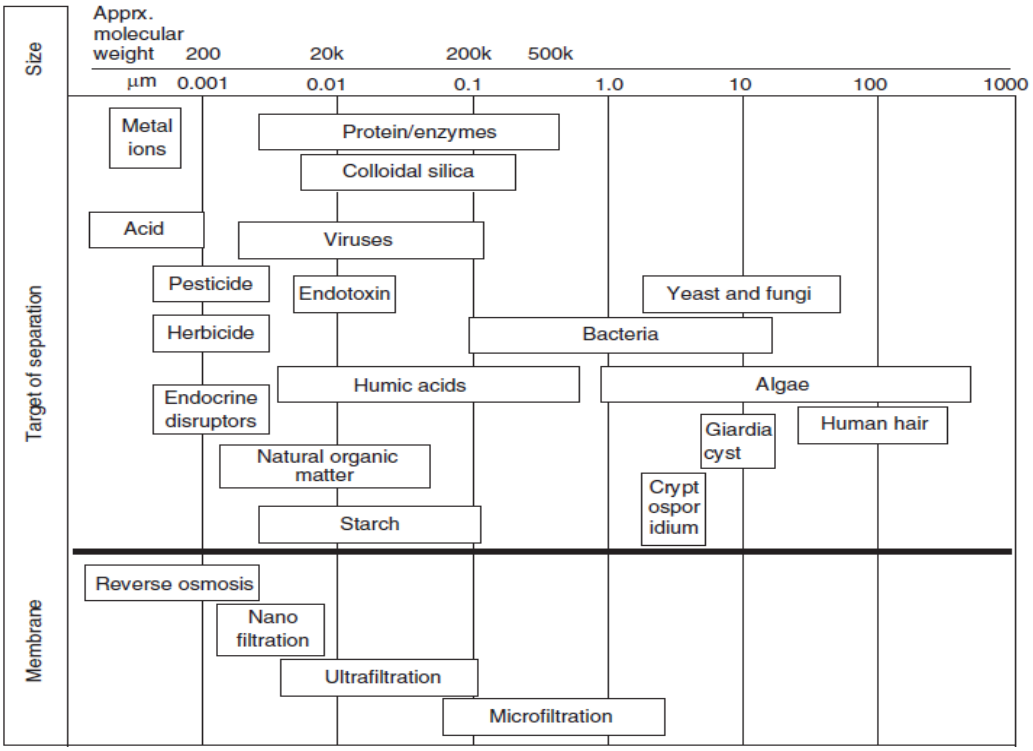


Figure 2.1 : Seperation range of membranes (Hai et. al. 2011).

Microfiltration (MF):

Typical pore size ranging of MF membranes are between 0.05 and 10 μm. Because of their pore sizes, MF membranes have high permeability and can be operated in low pressure. They can be fabricated from different materials (polymeric, inorganic) and also its structure can be symmetric or asymmetric (Fane et. al. 2011).

Ultrafiltration (UF):

Typical pore size ranging of UF membranes are from 1 to 100 nm. With these sizes, removal of bacterias, viruses, colloids, and macromolecules from water are possible.

Molecular weight cutoff (MWCO) is the molecular weight of the solute which is typically in the range of 1-300 kDa for UF membranes. If MWCO has bigger size than this range, rejection ability of membrane can be low and pore size can increase. Permeability has a range between 20 and 500 l m^{-2} h^{-1} bar^{-1} and the normal operating pressure is generally about 1-5 bar (Fane et. al. 2011).

Reverse osmosis (RO):

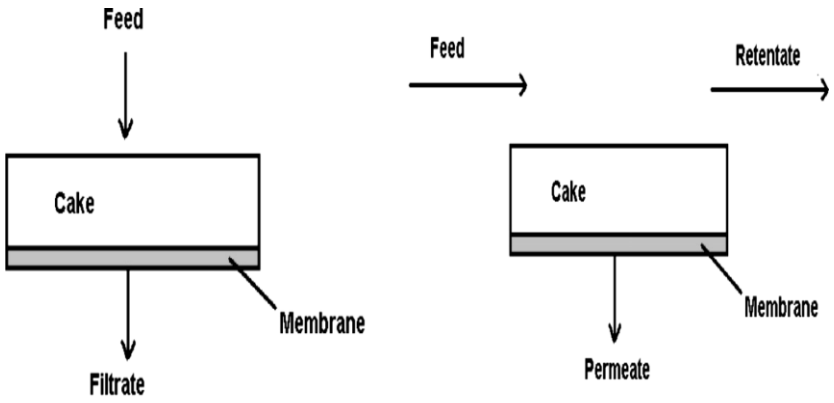
Pores of RO membranes are subnanometer and they can remove small organic molecules and also dissolved ions (including monovalent ions as Na^{+} and Cl^{-}). And, separation properties of RO membranes are specified as water permeability and sodium chloride rejection.

RO membranes are divided into two main group as sea water RO (SWRO) membranes and brackish water RO (BWRO) membranes.

SWRO membranes have high sodium chloride rejection (>99%) but, low water permeability. Also they need high pressures. BWRO membranes have low sodium chloride rejection (>95%) but higher water permeability and lower operating pressure than SWROs (Fane et. al. 2011).

Nanofiltration (NF):

NF membranes have similarities with RO membranes such as holding ability of dissolved ions as well as some small organic molecules. NFs have low rejection percentages to monovalent ions such as Na (10–90%). But, if we compared NF with RO, NFs have better water permeabilities at significant low pressures. (Fane et. al. 2011). In applications, membrane filtration operations are divided into two groups as dead-end and cross-flow which are showed schematically at Figure 2.2.



a) **b)**

Figure 2.2 : Types of membrane operations; a) Dead-end b) Cross-flow.

In dead end filtration, feed flow is forced into the membrane by driven forces for filtration seperation. If the feed solids have bigger pore size than membrane, they are easily deposit and accumulate on the surface of membrane.

In cross-flow filtration, feed flow is going paralel with the membrane surface and filtration flow is going through into membrane and permeation is occur. There is a 90 degrees angle between feed and filtration flow. So, this is called as 'cross flow'. Because the direction of filtration flow, matter accumulation on the membrane can be prevented. So, cross-flow filtration is a good choice for a high concentration of filterable matter (Mutamim et. al. 2013).

2.1.2 Membrane materials

Many different materials such as polymer, ceramic, metal, carbon, and glass can be used for fabrication of membranes. Polymeric materials are the most popular ones. These materials should have thermal and chemical stability in case of changes at temperature and pH values.

Also, mechanical strength and easy processing are important. Structure and properties of some popular membrane materials are introduced below.

Cellulose and Cellulose acetat (CA); cellulose is highly hydrophilic and generally used for dialysis membrane preparation. Generally, cellulose acetate is used for MF, UF, RO membranes as a material. They are both stable at pH: 4-6,5 and easily influenced from hydrolysis and microbial attack.

Structure of Cellulose and Cellulose Acetate (CA) are given at Figure 2.3.

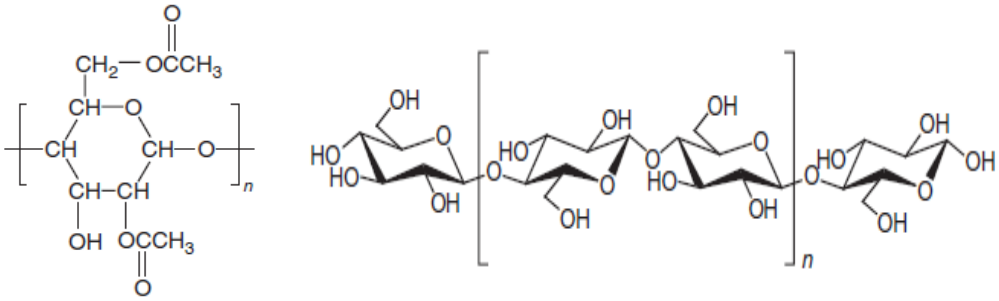


Figure 2.3 : Structure of Cellulose and Cellulose Acetate (CA).

Polysulfone (PS) is an amorphous polymer and have a great chemical and thermal stability. So, it is used for UF, MF, gas separation membranes and also the porous support layer of many RO, NF.

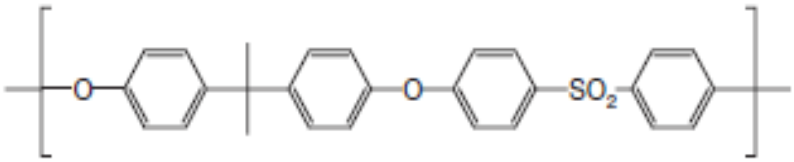


Figure 2.4 : Structure of Polysulfone (PS).

Polyethersulfone (PES) membranes are chemically and thermally stable and less hydrophobic than PS membranes. PES membranes are mainly used for UF, MF, and dialysis.

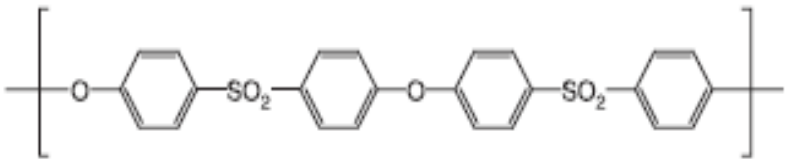


Figure 2.5 : Structure of Polyethersulfone (PES).

Polyacronitrile (PAN) has great resistance to hydrolysis and oxidation. Commonly used for UF membranes and porous supports of composite membranes.

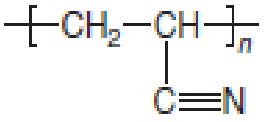


Figure 2.6 : Structure of Polyacronitrile (PAN).

Polyvinylidene fluoride (PVDF) is a popular material for MF by phase-inversion method. It is semi-crystalline, hydrophobic and it has resistance against chemicals (especially many acids at wide range of pH) and great thermal stability.

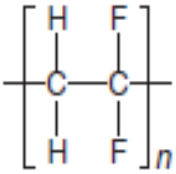


Figure 2.7 : Structure of Polyvinylidene fluoride (PVDF).

Hydrophilicity is an important feature for membrane materials. When the membrane surface has hydrophilic characteristics, it resists to organics in other words fouling tendency of membrane is decreases. But, hydrophobic membranes are more stable than hydrophilic ones. CA is naturally hydrophilic, others are naturally quite hydrophobic at different levels which are introduced at the Figure 2.8.

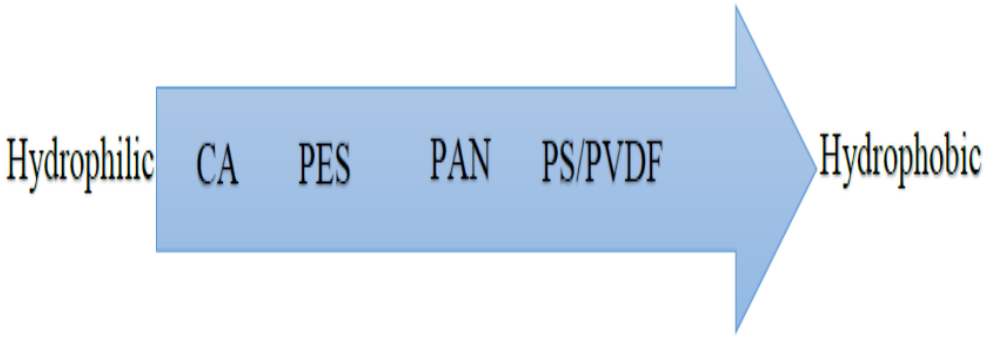


Figure 2.8 : Hydrophilicity levels of common membrane materials.

We can modified the hydrophobic polymers such as blending with a hydrophilic ones or adding some pore formers for being more stable and also having less fouling features (Pearce, 2007).

2.1.3 Configuration of membranes

The configuration of the membranes is important for membrane processes. An ideal membrane configuration should have some conditions such as high membrane area, high degree of mass transfer ability, energy efficent, economic and cleanable. And it can be applicable as a module. (Judd, 2011). Selection of module type is an important parameter on application of membrane systems.

A membrane module has to be supporting the membrane layer and providing fluid management efficiently. There are four major modules which are flat sheets, spiral wound, tubular and hollow fibers. Tubular and flat sheets needs a supportance layer which has to be porous, resistant to pressure and cooperative with removal. Hollow fibers are self-supported and they can be able to operate both outside-to-in or inside-to-out. Comparative features of these modules are given below at Table 2.2 (Cardew et. al. 1988).

Table 2.2 : Advantages and disadvantages of membrane modules.

	Advantages	**Disadvantages**
Flat sheet	*Low energy requirements *Cleanable by dissassembling *Various range of product available	*High cost *Not reusable *Seal problems
Hollow Fiber	*Compact system *Low liquid hold up *Low cost *Backflushable	*Not suitable for viscous systems *Limited range of product available *Easily fouled with particulates
Spiral wound	*Compact system *Low hold up *Low cost	*Have dead spots *Not backflushable
Tubular	*Tolerable with high suspended solids *Viscous fluids can use *Cleanable (mechanically)	*High energy requirement *High cost *High hold up *Large space demand

2.1.4 Fabrication of membranes

There are a various polymer membrane fabrication techniques which are depends on choice of polymer and desired structure of the membrane. The most common

techniques for preparation of polymeric membranes are interfacial polymerization, stretching, track-etching, electrospinning and phase inversion. These methods are described below.

Interfacial polymerization (IP) is the most important method for fabrication of RO and NF membranes with thin-film composite (TFC). At this method; thin polymer film is created by reaction of two different monomers. These membranes have good salt rejection and high water flux. The various factors such as concentrations of monomers, solvent types, reaction time and post-treatment conditions affect the features of membranes.

Streching is a solvent free technique which was developed in 1970s. The polymer is heated to the melting point and extruded into thin sheet forms followed by stretching for making it porous. Stretching has two steps which are cold stretching followed by hot stretching.

Cold stretching is used for making micropores. Hot stretching is for controlling the final pore structures of membranes. Microporous membranes are commonly used for MF and UF. These are fabricated by extrusion followed by stretching technique.

Track-etching is famous for controllable pore size distribution of the membrane. Pore size and pore density are independent parameters and can be controlled in a wide range from a few nanometers to tens of micrometers. Basicly, a nonporous polymeric film is irradiated with energetic heavy ions leading to the formation of linear damaged tracks across the irradiated polymeric film. Porosity of membrane depends on the duration of irradiation and size of pores which are controlled by the etching time and temperature.

Electrospinning is a new technique to fabrication of porous membranes for various applications such as filtration and desalination. When the electrostatic potential is enough between the polymer solution droplet and the grounded collector, liquid jet gets charged and shaped as electrofiber formation. The unique features of these fibrous membranes are the controllable aspect ratios (length-diameter ratio) and morphologies.

Phase inversion method is a process that the polymer solution is transformed to solid state from liquid phase under control. This transformation can be completed by several methods such as immersion precipitation, thermally induced phase separation, evaporation-induced phase separation and vapor-induced phase separation.

- Immersion precipitation: Polymer solution is immersed in a coagulation bath (water). There is an exchange of solvent from polymer solution and water in coagulation bath.
- Thermally induced phase separation: Quality of solvent is negatively changes with temperature decrease. So, solvent is removed by extraction, evaporation or freeze drying after demixing.
- Evaporation-induced phase separation (solution casting method): after making polymer solution in solvent or mixture of a volatile non-solvent, the solvent is vaporized and leading to precipitation.
- Vapor-induced phase separation: The polymer solution is exposed to water and its absorption makes demixing and also precipitation.

Summary of common fabrication techniques of polymeric membranes for water treatment processes are introduced at Table 2.3.

Table 2.3 : Common fabrication techniques of polymeric membranes.

Water treatment process	Fabrication techniques
MF	Phase inversion Stretching Track-etching
UF	Phase inversion Solution wet-spinning
NF	Phase inversion Interfacial polymerization Layer-by-layer deposition
RO	Phase inversion Solution casting

However, among these techniques, immersion precipitation is the most common method for the fabrication of polymeric membranes (Laila et. al. 2013).

2.1.4.1 Fabrication of hollow fiber membranes by phase inversion

The membrane preparation techniques of flat-sheet membranes were adapted for producing new kind of membranes which are formed as thin tubes or fibers.

The first development of hollow fiber membranes, which was one of the major events in membrane technology, was presented by Dow Chemical in 1966.

A significant advantage of hollow fiber membranes is their high surface areas. The diameter range of hollow fibers are varied from 50 to 3000 μm. The structure of fibers can be uniformly dense, but microporous structure which have a dense selective layer on the outside or the inside surface is preferred.

Application of hollow fiber membrane is realized with modules which are include bunch of fibers. These fibers packed into bundle and potted into tubes to formed as a module. With these modules, surface area is dramatically increased. Also, a module has contain no broken or defective fibers. So, production of hollow fiber requires high reproducibility and strict quality control.

The types of hollow fiber membranes are illustrated in terms of diameter in Figure 2.9.

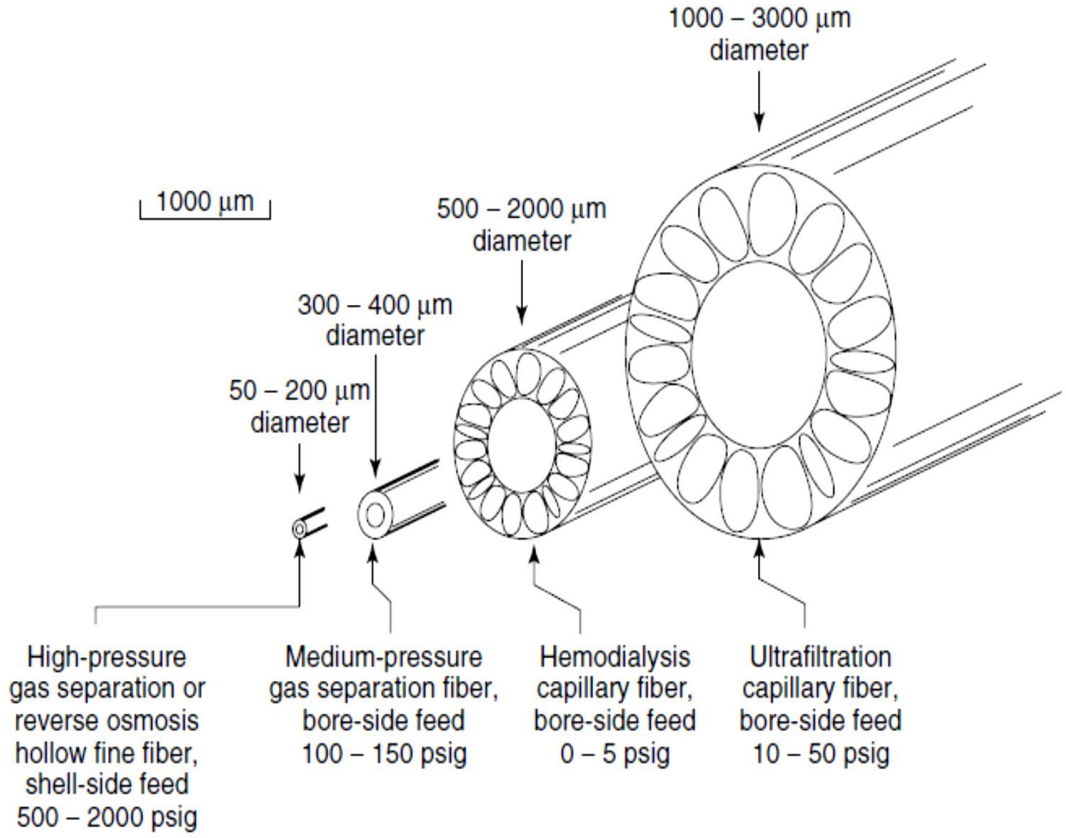


Figure 2.9 : Schematic view of the principal hollow fiber membrane types.

Fibers of 50- to 200-μm diameter are called as hollow fine fibers. These fibers can be stand on high (1000 psig or more) hydrostatic pressures from the outside, so they are generally used for reverse osmosis and high-pressure gas separation applications.

If the diameter of fiber is bigger than 200–500 μm, the feed fluid is applied to inside bore of the fiber and permeate is removed from the outer shell. These are used for low-pressure gas separations and hemodialysis or ultrafiltration applications. If the diameters of fibers are high (bigger than 500 μm), they are called as capillary fibers.

There are two common methods for production of hollow fibers:

- Solution spinning
- Melt spinning

Solution spinning (includes wet, dry and dry-wet spinning) is the most common technique which is generally used for fabrication of large, porous hemodialysis and ultrafiltration fibers. 20–30 wt % polymer solution is extruded and precipitated into water in coagulation bath. If it enters into bath directly, this is called as wet spinning. If solidification occurs by air instead of coagulation bath, this is called as dry spinning. And, if polymer solution is firstly introduced by air then goes into water, it is called as dry-wet spinning. Air gap is so important factor for membrane formation.

In melt spinning, melted polymer is extruded and precipitated into air, then it is solidified by cooling down (Laila et. al. 2013; Baker, 2004).

Quality of membrane is strongly influenced by production conditions. Especially, spinning parameters, which are type of polymer and solvent, additives, air gap length, viscosity, dope extrusion rate, coagulation bath temperature and composition, take-up speed, bore and outer fluid type, are important for the performance of hollow fiber membranes (Şengür, 2013).

2.2 Membrane Bioreactor (MBR) Technology

Membrane bioreactor (MBR) is a hybrid technology of biological treatment processes and membrane seperation. MBR systems can provide the treatment of wastewaters with high removal efficiency of biological oxygen demand (BOD) and chemical oxygen demand (COD) also water reclamation with low production of excess sludge (Menga et. al. 2009; Le-Clech et. al. 2006).

The MBR process was found at 1960s with the commercialization of ultrafiltration (UF) and microfiltration (MF) membranes. The original process that is an activated sludge bioreactor with flat sheet membrane was introduced by Dorr-Olivier Inc.

At 1989, submerged membrane bioreactors were applied. Until then, MBRs were designed as the membranes where outside of the reactor (Le-Clech et. al. 2006).

Basic schematic view of MBR configurations are given at Figure 2.10.

Side stream MBRs, which the membrane and bioreactor are located seperately, are easily maintained systems, but the operational cost is higher because of the recirculation loop installation.

In submerged MBR systems, the feed wastewater interacts with biomass directly. There is no need for a recirculation loop, because biological process occurs around the membrane and it has less operational than external MBR systems (Mutamim et. al. 2013).

Nowadays, there are wide range of MBR systems commercially, most of them are submerged membranes but also external modules are exist (Le-Clech et. al. 2006).

The MBR systems have many advantages over conventional wastewater treatment processes such as smaller footprint and reactor requirements, higher volumetric loading and effluent quality, better disinfection capacity and less sludge production (Judd, 2011).

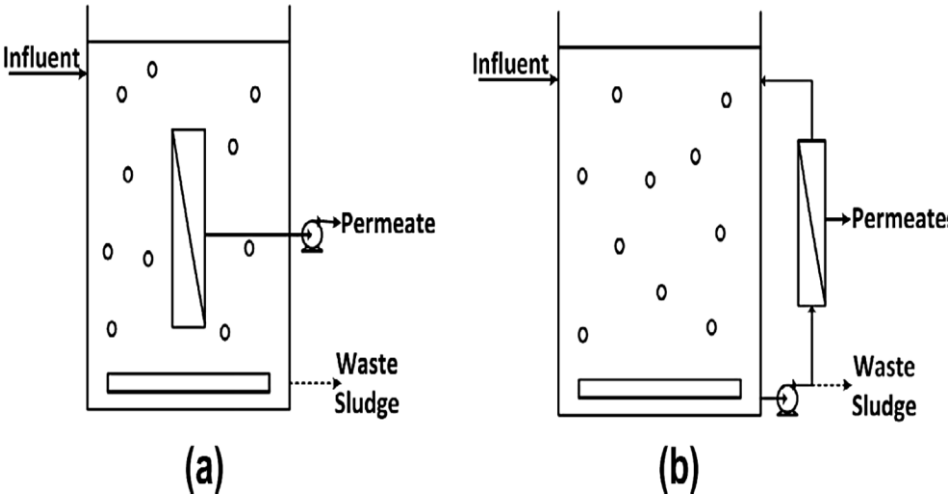


Figure 2.10 : MBR configurations; a) submerged MBR B) side-stream MBR.

But also there are some challenges in MBR systems such as high cost of membranes and low performance of system due to membrane fouling. So; fouling is the biggest problem of membrane separation processes.

Many researchers have been studied to understand MBR fouling and development of high-flux and low-cost membranes.

2.2.1 Fouling in Membrane Bioreactors

The major problem of membrane processes is the flux and yield decrease with time because of fouling. Membrane fouling is an acummulation of matters on the membrane surface or internal membrane structure.

There are various accumulation types on membranes such as adsorption, pore blockage, gel/cake layer formation that are cause to fouling. Schematic view of major fouling mechanisms are given at Figure 2.11.

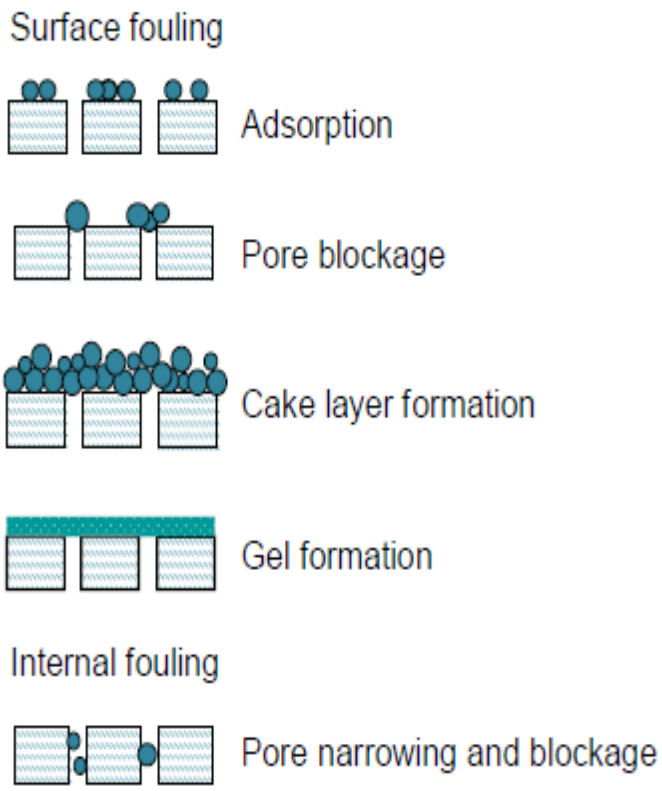


Figure 2.11 : Major fouling types.

If particules are smaller than the pores, they can enter into the pores. If particle size is about same or bigger than pores, they can be adsorbed to the membrane surface and may accumulate onto it. So, pores are blocked and obviously it affects the membrane seperation negatively. If these particals are cleanable by physical means, it is classified as reversible fouling. If it is not because of the adsorption, it is called as irreversible fouling (Mutamim et. al. 2013).

Fouling is a complex mechanism and not entirely understood. All operations and environment conditions are related to each other and these parameters can change the fouling in many ways. Basicly; it depends on the features of feed solution (nature,

concentration, pH ect.), properties of membrane (hydrophobicity, charge, roughness, pore size, porosity) and operating conditions (temperature, pressure, cross-flow velocity). General topics which effects to fouling of submerged membranes are given at Figure 2.12 (Le-Clech et. al. 2006).

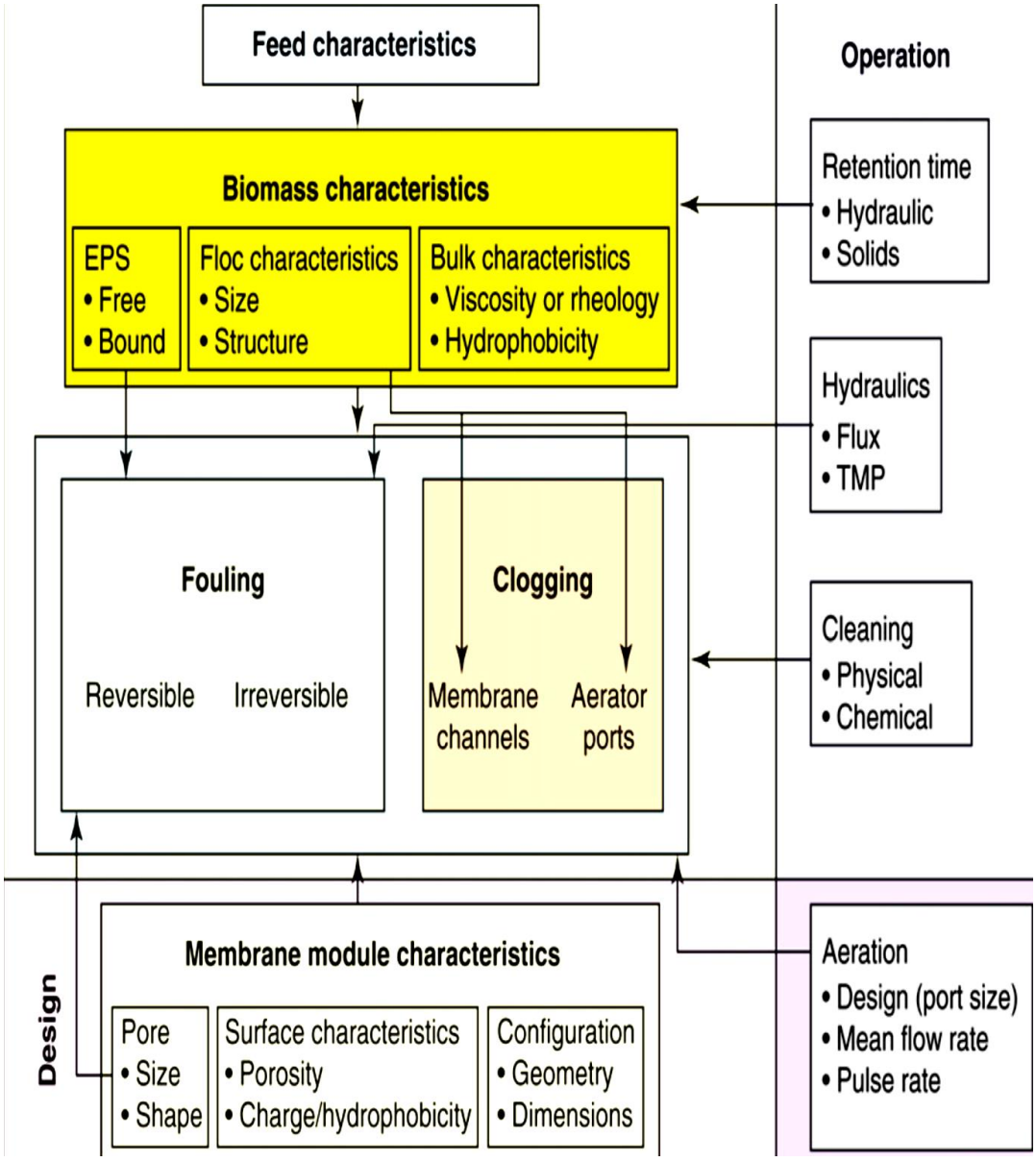


Figure 2.12 : Factors effecting fouling for submerged MBRs (Le-Clech et. al. 2006).

If mixed liquor suspended solids (MLSS) are high, fouling potential increases. High viscosity decreases membrane permeability. Operating under critical flux can prevent the fouling. And, when hydraulic retention time decreases, membrane fouling increases. Also SMP and EPS are important parameters of fouling mechanism. For example; bound EPS influences on specific cake resistance. Especially, SMP is correlated with fouling rate (Menga et. al. 2009; Sillanpää, 2014).

Also, fouling is classified into two main groups according to fouling material types as scaling (colloidal, organic, inorganic) and biofouling (microbial/biological) (Sillanpää, 2014).

2.2.1.1 Biofouling

Biofouling can be defined as an undesired accumulation of microorganisms at membrane that may happened by deposition, growth of microorganisms or flocculation. Generally, bacterias are accumulated by attachment (bioadhesion, bioadsorption) or growth. These accumulation on membranes can be defined as biofilm layer. So, biofilms are usually composed from layers of alive and dead microorganisms and their associated extracellular products (Guo et. al. 2012).

It can be said that the cell biomass and the extracellular polymeric substances (EPS) cause to biofouling. The extracellular polymeric substances (EPS) in microbial composition include charged groups (carboxyl, phosphoric, sulfhydryl, phenolic and hydroxyl) and polar groups (aromatics, aliphatics in proteins and hydrophobic regions in carbohydrates). Because of the availibility of hydrophilic and hydrophobic groups, EPS can be defined as amphoteric. And this feature is very important for microbial aggregates and their formation in membrane bioreactors. The hydrophobic areas in EPS may provide the adsorption of organic pollutants (Guo et. al. 2012).

EPS are divided into two groups:

- Bound EPS
- Soluble EPS (SMP)

Bound EPS are eliminated by bacterial hydrolysis. Dissolved products of bound EPS are called as soluble EPS in other name soluble microbial products (SMP) that are biodegradable. Each has various organic macromolecules such as polysaccharides, proteins, humic substances, nucleic acids, (phospho)lipids and other polymeric compounds (Guo et. al. 2012). EPS are directly related with specific cake resistance. If EPS is high, cake resistance will be high, too (Mutamim et. al. 2013). So, it is clear that some bacterias in the sludge play a significant role in membrane biofouling. Understanding of bioflocculation behaviour and mechanisms of cell attachment in MBRs will be the key component for the biofouling control (Menga et. al. 2009). There are various factors that related to biofouling of MBRs. Table 2.4 describe some important factors and their relationships with biofouling on MBRs.

Table 2.4 : Biofouling effects of some parameters (Guo et. al. 2012).

Fouling Factors	Effects on biofouling
MLSS	When MLSS concentration increases, protein and carbohydrate fractions of EPS and SMP gets higher.
F/M	High F/M ratios causes generation of SMP and bound EPS, filtration decreases.
HRT	At low HRT, EPS are released from the bacterial cells, SMP rises. Decreasement of HRT causes growth of filamentous bacterias and the large, irregular flocs. High HRT leads to foulant accumulation.
SRT	At shorter SRT, the concentrations of EPS and SMP deposit on membrane at higher amounts.
Nutrients	Lack of nitrogen increases the protein rate in the EPS. Lack of phosphorous increases SVI values and decreases the protein level of EPS. Insufficiency of nutrients may caused to flocculation.
Temperature	Biomass is decomposed by increasement of temperature. Also, SMP and turbidity are increased and proteins in EPS are decreased. But, low temperature raises the filamentous bacteria that are produced more SMP.

2.2.2 Fouling Mitigation

After the occurance of fouling, physical or chemical cleaning can be applied for the removal. If fouling is reversible, backwashing (physical cleaning) is enough. If fouling is irreversible, chemical cleaning is necessary although operation cost is higher. Also, the membrane surface may be damaged (Le-Clech et. al. 2006).

Because of these reasons, fouling should be prevented which can be provided by some limitations. For example, some operation conditions or feed characteristics are directly effected on fouling as mentioned before. So, applying the optimum conditions on MBRs may prevent fouling on membranes. Another way is to prevent fouling before its occurrence by improving the anti-fouling properties of the membrane with some special additives such as BisBAL which has anti biofouling characteristics.

2.3 BisBAL

Bismuth is the 83rd element of the periodic table. As a word, it is derived from the German word 'wismuth' (white mass) (Brock, 1993). It is the heaviest member of the Pnictogen group and called as ‘‘green’’ element. Because, elemental bismuth and its compounds are more non-carcinogenic and non-toxic than other heavy metals. Also, they have less bioaccumulative features (Badireddy et. al. 2014). When bismuth is combined with thiols, it is named as Bismuth-thiols which have better antibacterial properties than bismuth (Domenico et. al. 1997). Bismuth-thiols (BTs) are a group of antibacterial agents that have anti-biofilm characteristics against gram-positive and gram-negative bacteria.

Bismuth acts as a metabolic poison inside the cell and inhibits growth and causes to cell death. Also, BTs interfere with the bacterial adherence and colonization (Varposhti et. al. 2014). Bismuth thiols are available as seven different types which are 1,3-propanedithiol, dimercaprol (BAL), dithiothreitol, 3-mercapto-2-butanol, b-mercaptoethanol, 1-monothioglycerol, and mercaptoethylamine in order of decreasing synergy (Domenico et. al. 1997). Among these bismuth-thiol compounds, bismuth dimercaptopropanol (BisBAL) is very effective as an antimicrobial agent. It can prevent biofilm formation in medical devices and microfiltration membranes even at sub-minimum inhibitory concentrations (Badireddy et. al. 2013). The bismuth-BAL compound (BisBAL) is very active against most bacteria according to the studies by broth dilution, agar diffusion and dilution analyses (Domenico et. al. 1997).

BAL and BisBAL structures are given below at Figure 2.13.

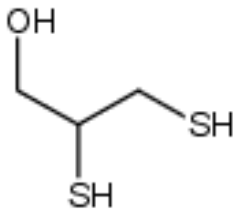
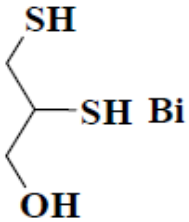
BAL ($C_3H_8OS_2$)	**BİSBAL**
	

Figure 2.13 : Chemical structures of BAL and BisBAL.

2.3.1 Anti-biofouling effects of BisBAL

Biofilms (suspended or surface adherent) are composed from microorganisms and adhesive matrix of extracellular polymeric substances (EPS) which happens on many places at right conditions (presence of water and nutrients). They causes biofouling that makes the decreasement of flux and yield. So, they have to be prevented. Inhibiting accumulation of biofilm-forming bacteria and cleaning the existing biofilms are serious operational problems in many technological systems (Badireddy et. al. 2014). An alternative approach for controlling this biofilm formation is inhibition of the biofilm matrix material by agents. An excellent agent for inhibition of EPS production (as blocking of extracellular polysaccharide (EPS) synthesis and consequently reduce to biofilm accumulation) are bismuth compounds. (Badireddy et. al. 2014; Hai et. al. 2011). Inhibition of biofilm formation mechanism is defined basicly as the bacterial respiratory enzymes which are inactivated by BTs. The exopolysaccharide expression is suppressed and inhibit biofilm formation of Gram-positive and -negative bacteria. Also, bacterial adherence and colonization is prevented (Chellam, 2014).

Especially BisBAL is a very powerful antimicrobial agent within bismuth thiols in comparison to either Bi^{3+} or BAL alone (Domenico, 2002).

The datas where from patent are showed us that there was a 10-20% decreasement in BisBAL activity under anaerobic conditions. So, aerobic applications of BisBAL should be better (Domenico, 2002).

Although the step by step mechanisms of action of BisBAL are not fully understood, we can observed its effectivity according to the results of the related studies about BisBAL that are briefly explained as:

Domenico et al. 1999 showed that bismuth dimercaprol (BisBAL) inhibits capsule expression with phagocytosis and the reactivity of certain antibodies increases against core epitopes of lipopolysaccharides (LPS)s or outer membrane proteins.

Badireddy, 2008 demonstrated the decreasement of total polysaccharides and proteins in free and bound EPS that are produced by *Escherichia coli* and *Serratia marcescens.*

Codony et al. 2003 compared BisBAL efficiency with other disinfected ways such as chlorination, using of copper (Cu) and silver (Ag) ions, high temperature for multi-species biofilms grown from municipal water. BisBAL action was relatively slow, but

it had a significantly-increased effectiveness, producing a 100-fold reduction in viable bacteria at 24 hours. This study indicates that BisBAL is a potential disinfection alternative to chlorine.

BTs have an antimicrobial activity against a very broad spectrum of Gram-positive and Gram-negative bacteria such as *Pseudomonas, Bacillus, Mycobacteria* that are mostly caused to biofouling in water systems (Domenico, 2003).

2.4 Industrial Applications of Bismuth-Thiols

Bismuth-thiol technology has significant potential for diverse industrial applications.

In Agriculture industry; BTs are used for preventing of crop losses. Due to resistant microbes and their biofilms on crops, BT compounds are capable of preserving plant health and crop productivity.

In Oil&Gas sectores; Biocorrosion on the pipelines is a major problem for oil and gas industry. The current solutions contains highly toxic chemicals which are dangerous for human health. These chemicals releases deadly hydrogen sulfide (H_2S) gas which causes to deaths. Instead of these unwanted chemicals, BTs are the best solutions.

In Pulp&Paper Industry; Undesired microbial growth is a big problem in the pulp and paper industry. Paper manifacturing processes are the favourable places where the microorganisms can live easily because of all the nutrients (starches ect.) and process temperature (typically 30-50 ^{o}C). Current technology which used for preventing of microbial resistance has a danger for environment and human health. So, application of BTs are safer and environmentally-friendly solution.

In Ship paints Industry; BTs have been demonstrated to be effective both against marine bacteria. Instead of toxic chemicals, BTs are more useful and safer.

In Water Technology; BTs will be capable of reducing maintenance costs for membrane microfiltration applications. Backflushing necessity is decreased and filter life is increased by the applications of bismuth-thiols. Also, BTs used for industrial cooling water systems for reducing associated biocorrosion (Url-2).

3. MATERIALS & METHODS

3.1 Fabrication and Characterization of Hollow Fiber Membranes

3.1.1 Membrane materials

Polyethersulfone (PES) was taken from BASF The Chemical Company as a mebrane polymers. PVP-K90 (Mw=1,500,000) which was taken from ISP (US) as a pore former. *N*-methyl-2-pyrrolidone (NMP) was used as solvent. BisBAL was available in MEMTEK (National Research Center on Membrane Technologies) from previous researches.

3.1.2 Preparation of spinning solutions

For choosing the ultimate spinning parameters and solution composition, many experiments were done in previous researches. The pristine membranes were prepared: PES was dried at 100 ^{o}C for 2 hours and after it dissolved in NMP at 90 ^{o}C. Then, PVP K90 were added in solution. The enhanced membranes with Bismuth-BAL chelate (BisBAL) were prepared: PES was dried at 100 ^{o}C for 2 hours. 30 μm BisBAL solution was mixed with solvent (NMP). Dried PES was dissolved into NMP-BisBAL mixed solvent. Then, PVP K90 were added in solution.

3.1.3 Spinning of hollow fiber membranes

Hollow fiber fabrication was done by phase inversion method (immersion precipitation). Hollow fiber membrane fabrication system (PHILOS, South Korea) is given at Figure 3.1. Spinning line of this system consists of driving roll in coagulation bath, godet roll in rinsing bath and and take-up roll in storage bath. Polymer (dope) solution and bore liquid was pumped into spinneret by gas (nitrogen) pressure. Rates of liquids and extruded fibers were adjusted according to the desired properties. Polymer solution and bore liquid goes through into the spinneret where hollow structure occurs. Nascent fibers goes to firstly driving roll in coagulation bath and secondly godet roll in rinsing bath, then lastly take up roll, respectively.

Also, schematic view of spinning line is given in Figure 3.2

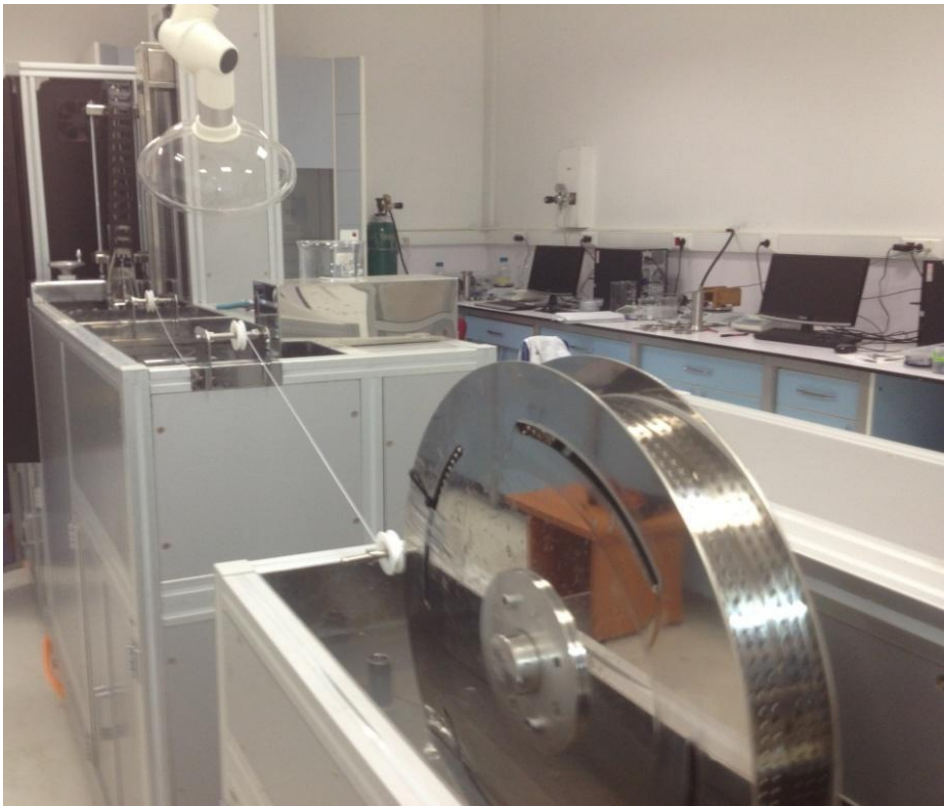


Figure 3.1 : Hollow Fiber Membrane System.

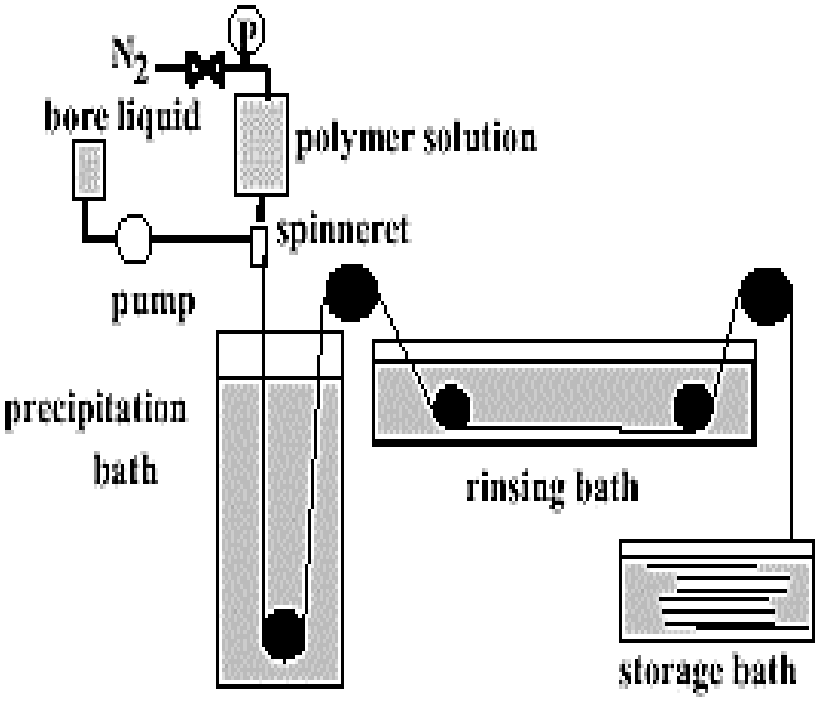


Figure 3.2 : Schematic view of spinning line.

3.1.4 Treatment & Post-treatment of Hollow Fiber Membranes

Hollow fibers were taken from take up roll and flushed for solvent removal from membranes (12 hours). After that the fabricated membranes were put into 4000 ppm sodium hypochloride (NaOCl) solution for post treatment (during 2 days). Then, membranes were waited in distilled water till the experimental uses.

3.1.5 Preparation of Hollow Fiber Test Modules

After the treatment, dead end HF modules were prepared. HF membranes were cut and put into plastic tubes (diameter: 8 inches). Then, silicon was injected into the tubes for sealing them. These prepared modules (active membrane areas: 20 cm^2) are shown at Figure 3.3. Finally all modules were put into distilled water for both preservation and testing.

Figure 3.3 : Hollow Fiber Test Modules.

3.1.6 Viscosity

Viscosity of dope solution was measured by AND vibro viscosimeter SV-10 (UK) (Figure 3.4). After the calibration with distilled water at 25ºC, viscosity value of dope solution (30 ml.) was used to determine at room temperature.

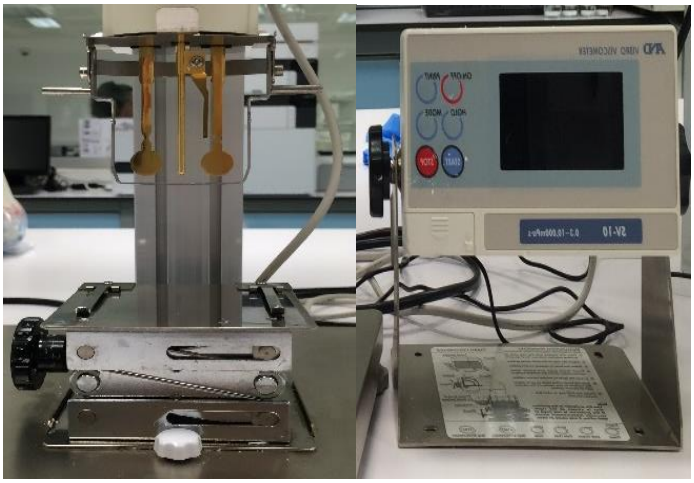


Figure 3.4 : Viscosimeter (AND vibro SV-10).

3.1.7 Permeability

Pressure drived filtration cell taken from Sterlitech Corporation (USA) was used after modified for hollow fiber application. (Figure 3.5). Volume of cell is 300 ml. Maximum pressure and temperature of cell is 69 bar and 121^{o}C.

Before permeability tests, compaction test were done during 30 min with distilled water for removal of solvent or unreacted polymer remainings. After the compaction test for 3 different pressures, filtration flux were measured again with distilled water and results were transferred to an excel file.

Flux was calculated according to the equation below. Flux graphs was drawn by excel. Slope of the graphs gives permeability of HF membranes. Flux values were calculated according to equation **(3.1)**

$$J=\frac{V}{At} \qquad \textbf{(3.1)}$$

where;

J: Flux (L/m2.hr),

V: Volume of permeation (liter),

A: Area (m2),

t: time (hour).

Figure 3.5 : Modified Sterlitech for HF membranes.

3.1.8 Fouling experiments

Rejection performances of the HF membranes were done by using (BSA) bovine serum albumin aqueous solution (100ppm) at room temperature.

The data of BSA rejection were taken from the permeation and feed solutions. Concentrations of BSA solutions were measured by UV Spectrophotometer (Hach Lange DR500) (Figure 3.6). BSA rejection was calculated from the equation **(3.2)** which was given below.

$$R = 1 - \frac{Cp}{Cf} x\ 100 \qquad \textbf{(3.2)}$$

where;

R: Rejection (%),

Cp : Permeate concentration (wt%);

Cf: Feed concentration (wt%).

Figure 3.6 : UV Spectrophotometer (Hach Lange DR500).

Also; Flux recovery ratio (FFR%), total fouling ratio (Rt), reversible fouling ratio (Rr), irreversible fouling ratio (Rir) was calculated according to the equation **(3.3), (3.4), (3.5), (3.6), (3.7)** which were given below (Vatanpour et al., 2011).

$$\text{FRR (\%)} = \frac{Jw,2}{Jw,1} \text{ x } 100 \qquad \textbf{(3.3)}$$

$$\text{Rt} = \left(1 - \frac{Jp}{Jw,1}\right) \text{ x } 100 \qquad \textbf{(3.4)}$$

$$Rr=\left(\frac{Jw,2-Jp}{Jw,1}\right) x\ 100 \quad \textbf{(3.5)}$$

$$Rir=\left(\frac{Jw,1-Jw,2}{Jw,1}\right) x\ 100 \quad \textbf{(3.6)}$$

$$Rt=Rr+Rir \quad \textbf{(3.7)}$$

where;

Rt: Total fouling ratio (%),

Rr: Reversible fouling ratio (%),

Rir: Irreversible fouling ratio (%),

Jw,1: Water flux,

Jw,2: Water flux of cleaned membranes,

Jp: Flux for protein solution.

3.1.9 Stereo microscopy

After preperation of the samples (cutting and inserting into the metal plate), images were taken by stereo microscope for the observation of HF membranes' structures (Figure 3.8).

Figure 3.7 : Stereo microscopy.

3.1.10 Optical profilometer

The samples were placed into the optical profilometer (Zygo New View 7100) and imaged by the device for the observation of surface roughness (Figure 3.9). Light transmitted through or reflected from sample and formed an image of surface macrostructure with a 50x lens system.

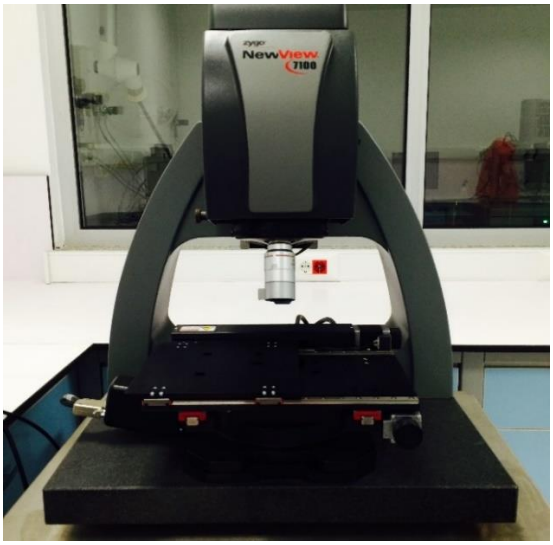


Figure 3.8 : Optical profilometer.

3.1.11 Scanning Electron Microscopy (SEM)

SEM (FEI Quanta FEG 200) (Figure 3.11) was used to examine the surface morphology of hollow fiber 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.

SEM device where in MEM-TEK is showed at Figure 3.11.

Figure 3.9 : SEM (FEI Quanta FEG 200).

3.1.12 Contact angle

Hyrophobicity of membranes were determined by contact agles and these were measured by Attension T200 Theta (Figure 3.7). After dropped to distilled water on the surfaces of dry membranes, datas were collected (from 3 different points).

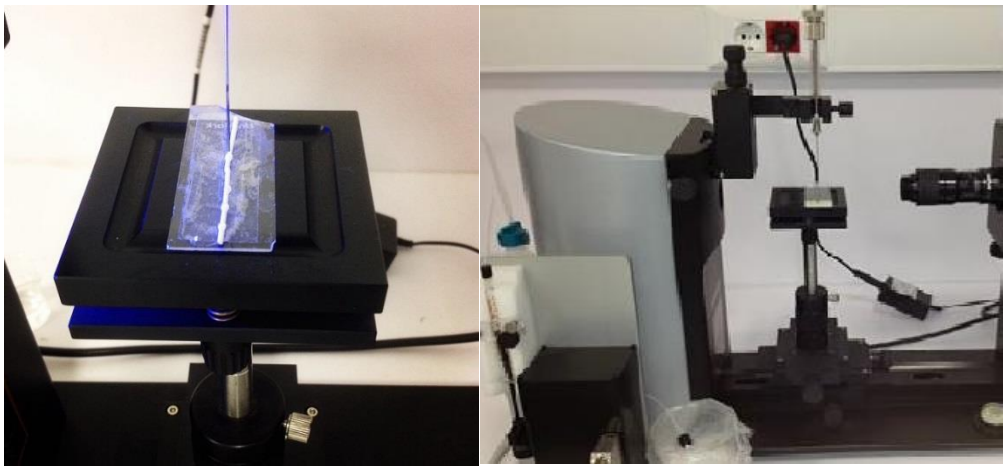


Figure 3.10 : Contact Angle (Attension T200 Theta).

3.1.13 Mechanical stability

Mechanical stabilities of hollow fibers were measured by the device (SII DMS 6100 Exstar) which is showed at Figure 3.10.

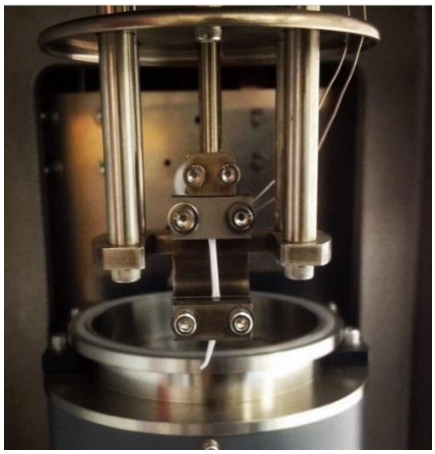


Figure 3.11 : Mechanical stability test equipment.

Membranes were placed into device and the measurements were done. Datas were taken in every 3 seconds and loaded till 5000N by steps as 150Ns.

The software of the device was calculated the tensile strength, percentage elongation at break and Young's modulus according to equations **(3.8), (3.9), (3.10)** that were given below (Rugbani, 2009).

$$\text{Tensile Strength} = \frac{F}{A0} \quad \textbf{(3.8)}$$

$$\text{Elongation} = \frac{\Delta L}{L0} \quad \textbf{(3.9)}$$

$$\text{Young's Modulus(E)} = \frac{\text{Tensile strength}}{\text{Tensile strain}} \quad \textbf{(3.10)}$$

where;

F: Force applied to the sample (N),

A0: Cross sectional area of sample before elongation,

ΔL: The displacement at maximum load (mm),

L0: Length of sample at starting point.

3.1.14 Porosity

Porosity (Ɛ %) of the membranes was measure by the equations (Vatanpour et al., 2012) which were given below:

$$\varepsilon = \frac{(w1-w2)}{\rho x A x L} \quad \textbf{(3.11)}$$

where;

w1: Weight of the wet membrane (g),

w2: weight of the dry membrane (g),

ρ: Water density (0.998g/cm3),

A: membrane effective area (m^2),

L: membrane thickness (m).

3.2 MBR Application of Hollow Fiber Membrane with BisBAL additive

3.2.1 Flux

Aerated batch reactor was applied for the HF membrane modules during a month. Dead end filtration modules (Figure 3.13) were immersed into the batch reactor (6lt).

Filtration was done by vacuum driven (0.7-0.8 bar). In same reactor, pristine and enhanced membranes were applicated. Water, that is treated from active sludge by membranes, was collected on daily basis. Fluxes were calculated according to equation **(3.1)** with using the weight of the cumulative water in boxes.

Schematic representative of batch submerged membrane bioreactor was given at Figure 3.12.

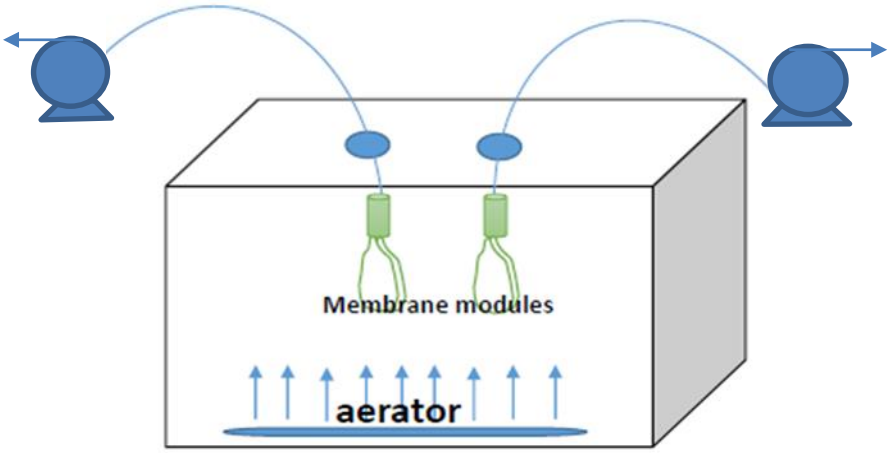


Figure 3.12 : Schematic representative of batch submerged membrane bioreactor.

3.2.2 COD

Water, which was treated by membranes (enhanced with BisBAL and pristine), was collected and measured on daily basis. COD analyses was done with closed-reflux method as defined in Standard Methods. Samples were filtered by microfilters (0.45 μm) and pour into the COD digestion tubes. Treated sample diluted with distilled water (1:5) as 2.5 ml. 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 150 ^{o}C 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. added 1-2 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 (3.13).

$$COD = \frac{((A-B)Nx8x1000)}{Vsample} \qquad \textbf{(3.13)}$$

where;

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

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

N: Normality of FAS solution.

3.2.3 SS-VSS

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. Dried sample ignited at 550 °C for 30 minutes in oven. The weighted lost on ignition of the solids represents the volatile solids in the sample.

$$\text{SS}\ \left(\frac{\text{mg}}{\text{l}}\right) = \left(\frac{(\text{A-B})}{\text{V}}\right) \text{x}1000 \qquad \textbf{(3.14)}$$

$$\text{VSS}\ \left(\frac{\text{mg}}{\text{l}}\right) = \left(\frac{(\text{C-A})}{\text{V}}\right) \text{x}1000 \qquad \textbf{(3.15)}$$

SS and VSS were calculated by the equations (3.14) and (3.15).

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 EPS-SMP

Extracellular polymeric substance (EPS) and soluble microbial product (SMP) analysis were done with the physical-chemical (sodium hydroxide -formaldehide) extraction method at the end of operation.

Activated sludge sample (5 mL) was taken from the batch reactor and the suspension was centrifuged (4000×g, 10min, 40C). The supernatant was decanted into a sterile tube and recentrifuged (13.200×g, 20min, 40C) for removal of the suspended solids completely with this physical extracting. The supernatant has soluble microbial

products (SMP). 6 µL formaldehyde (37%) was added into the precipitant for 1 h at 4 ◦C. Then, added 0.5 mL NaOH (1N) for 3 h at 4 ◦C. And it was centrifuged (13.200×g, 20min, 4 ◦C). The supernatant from this chemical extracting method, has extracellular polymeric substance (EPS).

Carbohydrate concentrations and protein concentrations of SMP and EPS were analyzed by the phenol–sulfuric acid and Lowry methods.

Protein analysis method: Lowry solution which was prepared with mixing of A,B and C solutions with the rate of 100:1:1 (A:B:C). [(A): NaOH (2.86 g) and Na_2CO_3 (14.31 g) dissolved in distilled water and diluted to 500 ml., (B): $CuSO_4.5H_2O$ (1.42 g) dissolved in distilled water (100 ml), (C): 2.85g Na_2tartarate.$2H_2O$ was dissolved in distilled water (100 ml)]. Lowry solution (0.7 ml) and the sample (0.5 ml) were mixed and waited for 20 min at room temperature in a dark place. 5 ml of Folin solution (2N) was mixed with 6 ml of distilled water. 0.1 ml of folin solution was mixed with 0.5 ml of the sample and waited in a dark place for 30 min. Then, samples were colored from light to dark blue according to their protein concentrations. Measurements were done by using a UV spectrophotometer at 660 nm. Samples and the referance solution were done with paired for providing of measurement repeatability.

Bovin Serum Albumin (BSA) was used as the standard protein solution for the calibration. The absorption-concentration graph is given at Figure 3.14.

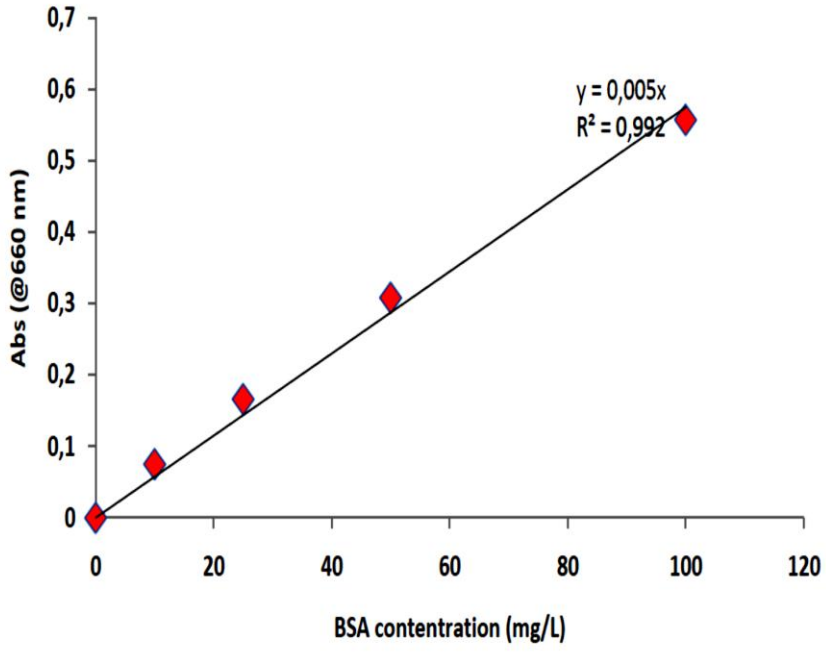


Figure 3.13 : Calibration graphic of protein.

Carbohydrate analysis method: 25 µl. of Phenol solution (80%) and 2.5 ml. Of H_2SO_4 (95-97%) were added to 1 ml of sample and waited in a water bath for 15 min. Colors of the samples were varied from light yellow to dark yellow according to their carbohydrate concentrations. Measurements were done at 490 nm wave length by UV spectrophotometer.

Glucose was used as the standard carbohydrate solution for the calibration The absorption-concentration graph was drawn with the obtained values. Calibration graph is given at Figure 3.14.

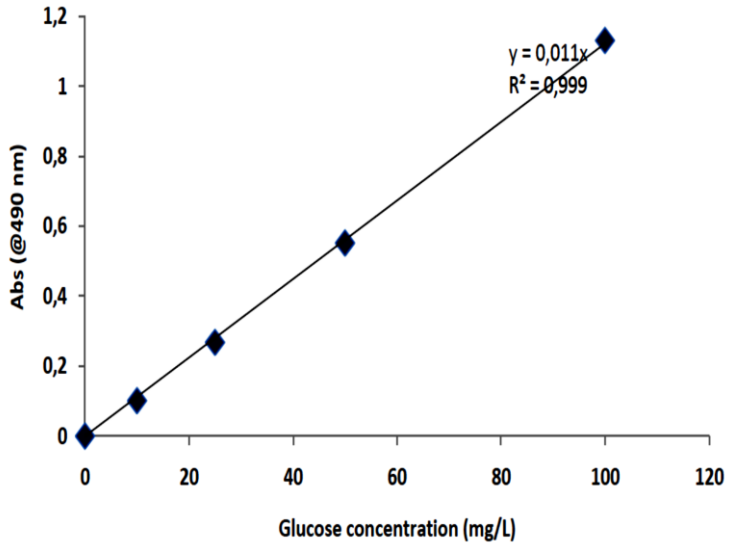


Figure 3.14 : Calibration graph of carbohydrate.

3.2.5 Confocal scanning laser microscopy

In confocal scanning laser microscopy, high-resolution optical images can obtain with depth selectivity. Confocal microscopy was imaged with point-by-point and reconstructed with a computer, allowing three-dimensional reconstructions of objects topologically. After the detection of fluorescently labeled foulants on the membrane surface, images are taken by confocal microscopy (Figure 3.15) to evaluate the efficiency of cleaning measures for deposit removal.

3.2.6 Growth of *Escherichia coli* (*E. coli)* on hollow fiber membranes

Antibacterial activity of BisBAL were assessed by using Gram negative bacteria *E. coli* culture which (0.1ml) is diluted in water (1 liter). Dead End filtration membrane modules were used to vacuum *E. coli* solution for 10 min.

Then, modules were cut and inserted on agar medium and incubated at 37 ºC for 6 days. Growth of bacteria was observed visually.

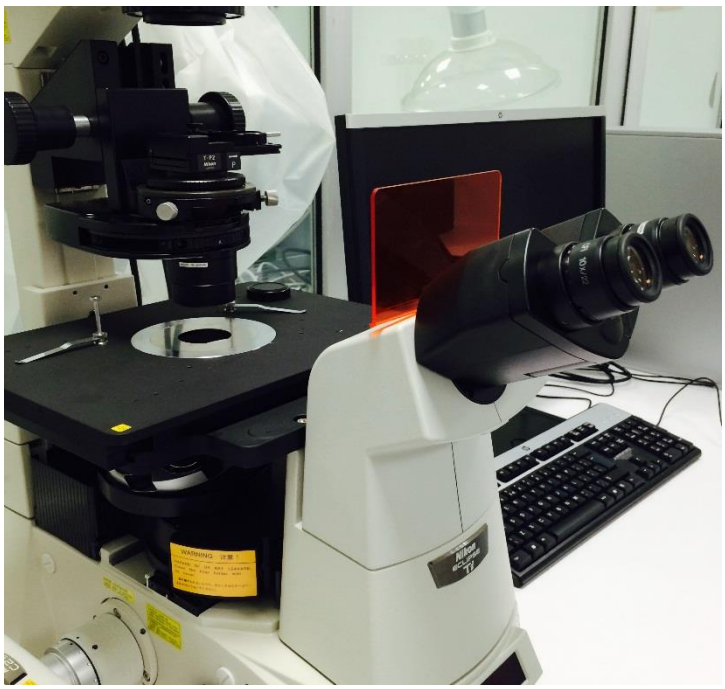


Figure 3.15 : Confocal scanning laser microscopy.

4. RESULTS & DISCUSSIONS

4.1 Fabrication and Characterization of Produced Membranes

4.1.1 Deciding the solution composition

Many previous trials had been done for finding the most appropriate recipe for fabrication of hollow fiber membranes. (Durmaz, 2014) demonstrated that %16 PES and %20 PES flat sheet membranes with 30 μm BisBAL had the best results.

So, polymer type was selected as PES and optimum BisBAL rate was selected as 30 μm. based on the results of this previous study. Our purpose was fabrication of hollow fiber ultrafiltration (HF-UF) membranes with high flux values as well as high selectivity. For obtaining the required membrane property, trials have been conducted and their dope solution compositions were given in Table 4.1.

Table 4.1 : Results and compositions of previous trials.

Trial No.	Dope solution composition	Result
1	%20PES, %7PVP K30, %73NMP, 25°C	Good mechanical stability but it has no flux.
2	%20PES, %7PVP K90, %73NMP, 25°C	It has a flux but a little.
3	%20PES, %7PVP K90, %73NMP, 35°C	It has better flux than trial no. 2.

According to the results, temperature, PVP molecular weight and polymer concentration are important parameters for obtaining high flux values with high selectivity. These parameters had impact on the viscosity of the dope solution. It is known that higher fluxes are possible at low viscosity values. Because of that, polymer concentration was decreased. Also, in the previous studies, when the amount of polymer concentration was decreased, the permeability of PES membranes were increased (Durmaz, 2014).

After the optimization of the dope solution, solution (contaning 18%PES, 7%PVP K90, 75%NMP) was selected and spinned at 35°C for the fabrication of hollow fiber membranes in context of this study.

4.1.2 Optimization of the spinning parameters

Hollow fiber membranes were fabricated by phase inversion method. Phase inversion process depends on spinning parameters such as take-up speed, air gap, viscosity of the dope solution, coagluation bath temperature, coagulation bath composition, bore liquid and outer liquid composition. Pristine and enhanced membranes (with 30μm BisBAL) were produced considering only take-up speed and air-gap parameters.

After fabrication of membranes with different take-up speed and air gap, membranes were characterized with permeability, porosity, mechanical stability, contact angle and morphology assessment with optical profilometer, stereo microscopy, scanning electron microscopy, also fouling tests were performed. Permeability, anti fouling capacities and morphologies of the membranes were considered for the selection (Table 4.2).

Table 4.2 : Selected spinning conditions.

Parameters	Selected Spinning Conditions
Dope solution velocity (ml/min)	36
Bore liquid velocity (ml/min)	18
Outer liquid velocity (ml/min)	0
Take- up speed (m/s)	7,1
Air gap (cm)	0
Coagulation bath temperature (°C)	35

4.1.3 Viscosity

Phase inversion process is affected by viscosity changes because exchangement rate of solvent and non-solvent can be changed by viscosity. Low viscosity degree of dope solution caused to early coagulation which makes flux rate to decrease. Viscosity values of dope solutions are 9.3 Pa.s and 7.5 Pa.s for pristine and enhanced membranes

in order of term. According to the results, which were given at the following sections, enhanced (with BisBAL additive) membrane had better flux results than pristine even its high viscosity value. It can be said that BisBAL addition into the PES delays coagulation time and provides better flux results.

4.1.4 Characterization tests

Fabricated membranes with the selected spinning condition were tested for assessing the characterization of their structures and anti biofouling features. Results were given at the following sections.

4.1.4.1 Morphologies of fabricated membranes

Fabricated hollow fiber membranes were imaged by stereo microscopy, scanning electron microscopy (SEM) and optical profilometer, that results were given at Figure 4.1-4 in order of term, for understanding their morphologies. .

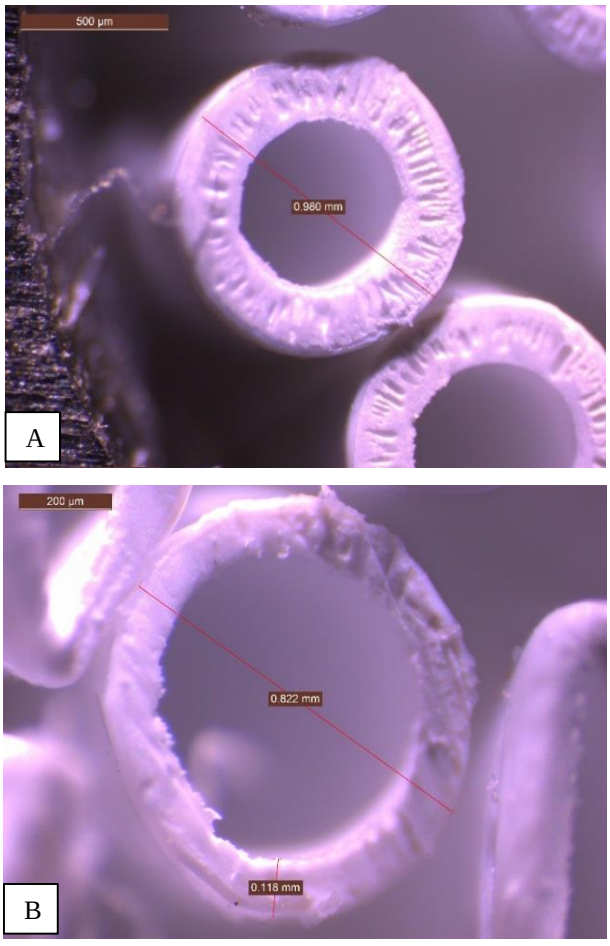


Figure 4.1 : Stereo microscopy images of fabricated hollow fiber membranes: (A) pristine, (B) enhanced with BisBAL additive.

In Figure 4.1, cross section views of membranes were taken by stereo microscopy. It can be seen that fabricated membranes had circular shapes as desired. It was observed that enhanced hollow fiber membrane was thinner than pristine. Inner and outer diameters of membranes were 0,514 and 0,98 for pristine, 0,597 and 0,822 for enhanced membrane in order of term. The additive of BisBAL into PES matrix changed the structure of membranes. Pristine membrane had finger-like structure. Structure of enhanced membrane seemed as sponge-like. However details can not be observed through stereo microscope images, just a general idea can be obtained by using stereo microscopy, more detailed view of the membranes can be seen through their SEM images which were given at Figure 4.2 and 4.3.

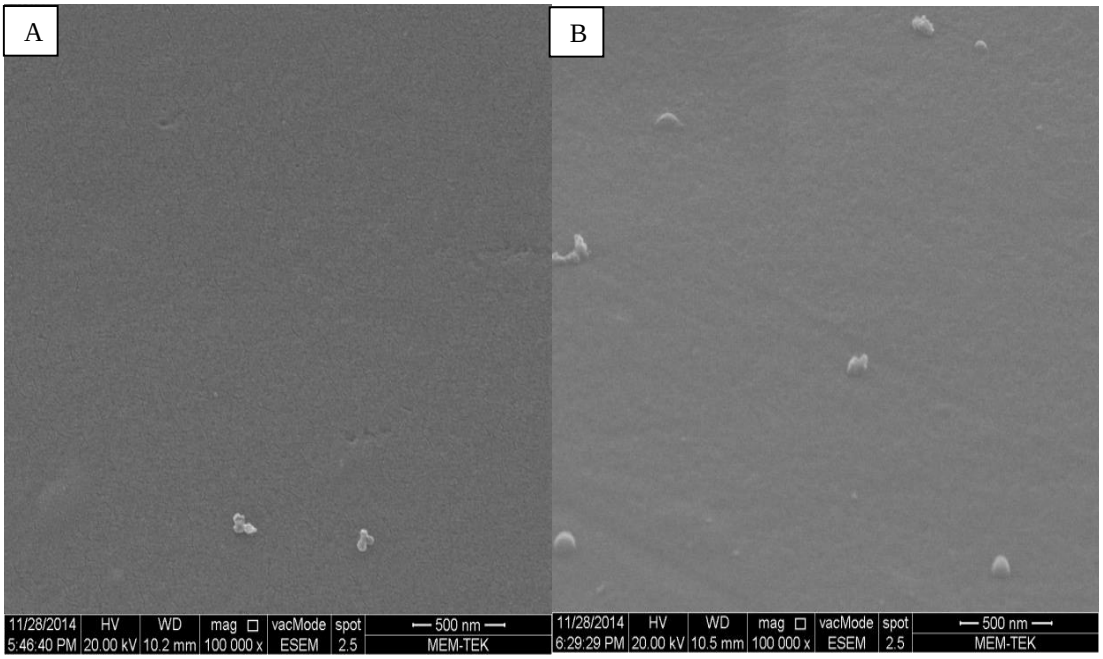


Figure 4.2 : Outer surface SEM images of membranes: pristine (A), enhanced (B) with BisBAL additive.

Images of outer surface (Figure 4.2) were taken by 100000X magnification to obtain general morphology of the membranes whether they had defects on them or not. There were no defects on the surfaces caused by fabrication.

It can be seen the surfaces of both membranes were formed as uniform and proper. Pores were not visible because of spinning conditions such as air gap (0 cm).

Images of cross section views (Figure 4.3) of membranes were taken by 150X and 300X magnification to find out structures of the membranes. Sponge-like structure of enhanced membrane can be observed clearly in Figure 4.2 (B).

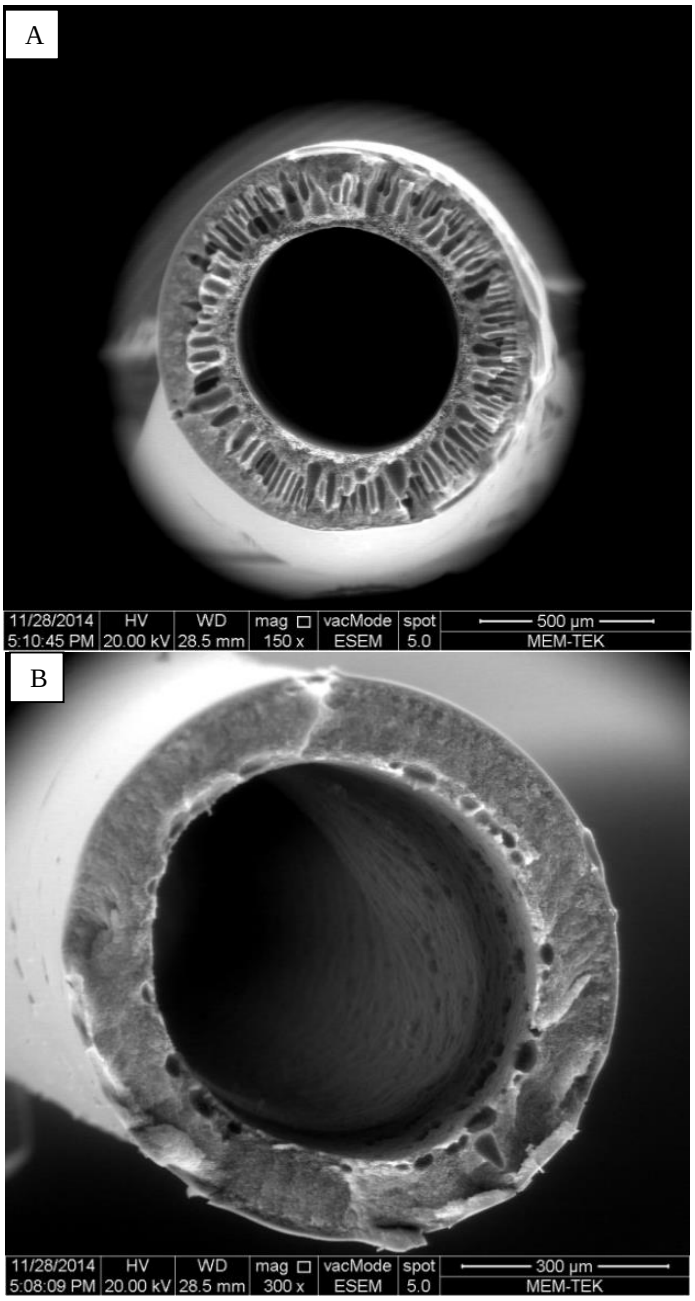


Figure 4.3 : Cross section SEM images of fabricated hollow fiber membranes: (A) pristine, (B) enhanced with BisBAL additive.

Surface roughness was very important to understand the fouling properties of the manufactured membranes. Fouling is more expected at high roughness degrees. Surface roughnesses were imaged by optical profilometer for each membrane and average surface roughness of fabricated hollow fiber membranes calculated which were 0,19 and 0,35 nm for pristine and enhanced membranes (Figure 4.4). Roughness of membrane was increased with additive. Images provided from optic profilometer which were given in Figure 4.5.

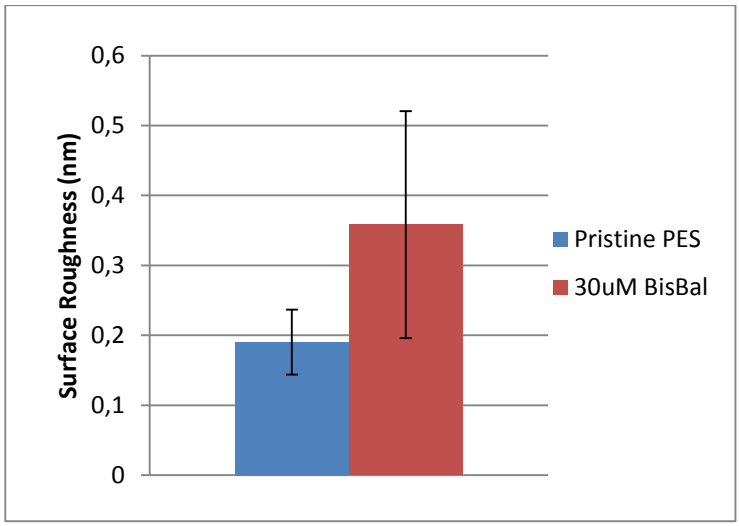


Figure 4.4 : Average surface roughness values of hollow fiber membranes.

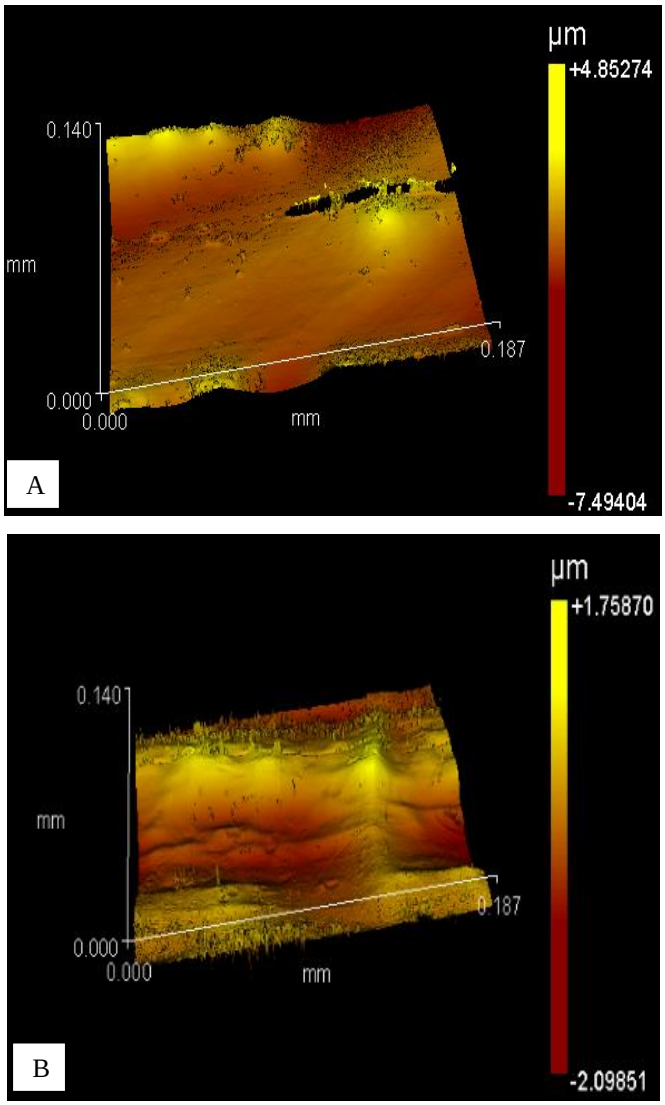


Figure 4.5 : Optical profilometre images of fabricated hollow fiber membranes: (A) pristine, (B) enhanced with BisBAL additive.

Normally, high fouling rates are expected at high roughness values because foulants can hold on surface easily. But, fouling degree was decreased by BisBAL additive even its higher surface roughness.

4.1.4.2 Contact Angle

Contact angles of membranes were measured for investigating their hydrophobicity characteristics. Contact angle value of enhanced hollow fiber membrane with BisBAL additive was lower than pristine. Values were 67,3° and 71,3° for enhanced and pristine membranes as given at Figure 4.6.

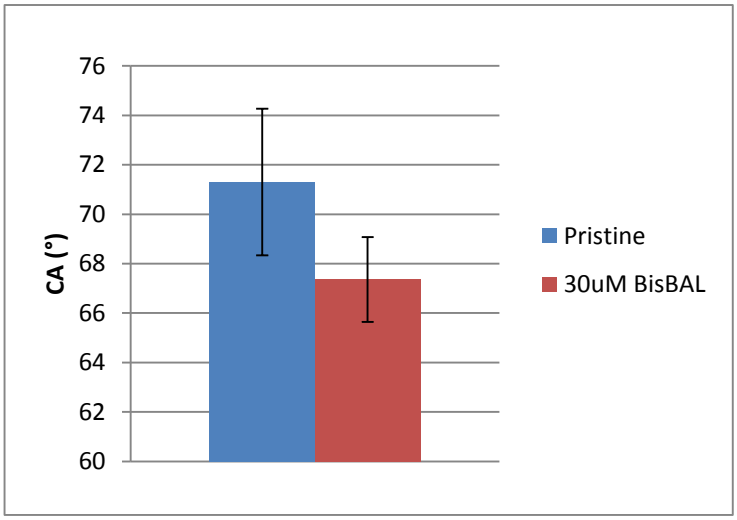


Figure 4.6 : Contact angles of hollow fiber membranes.

It was related to hydrophilic properties of Bismuth Thiols. Decreasement of contact angle value with BisBAL additive showed that the enhanced membrane was more hydrophilic than pristine. Also, higher surface roughness may provide the lower contact angle degree**.**

4.1.4.3 Permeability

Production of membranes were done by phase inversion. Phase inversion can change with thermodinamic and kinetic conditions. When the exchange rate between solvent to non-solvent (in this case, it was water) is slow, coagulation is delayed. Therefore, more sponge-like morphology is expected. If the exchange rate is fast, dope solution is coagulated in a higher rate, so that membrane morphology has more finger-like structures.

Conductivity of metallic bismuth is better at liquid phase than solid (Url-2). So, increasement of polymer solutions' conductivity can effect its exchange rate which can change the structure. Besides low viscosity degree of dope solution causes to early coagulation which makes permeability to decrease.

Additive of BisBAL could set up this negative effect of low viscosity on membrane permeability. All af these conditions had synergistic effect on permeability degree of membrane. It was observed that BisBAL have positive effects on permeability of membrane even its lower viscosiy value than pristine.

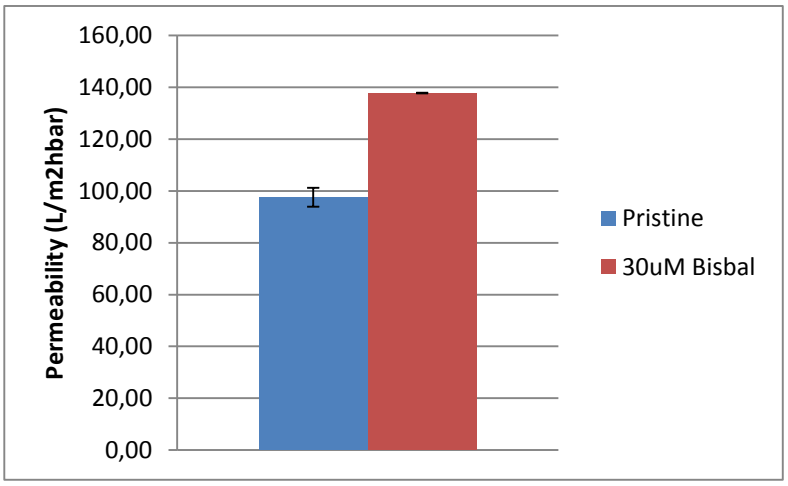


Figure 4.7 : Permeabilities of hollow fiber membranes.

Addition of BisBAL increased permeability of hollow fiber membrane. Permeability degrees were 97,6 and 137,81 l/m^{2}hbar for pristine and enhanced membranes through selected spinning conditions (Figure 4.7).

4.1.4.4 Porosity

Porosity of membranes are depends on many parameters such as polymer type and fabrication conditions. Membrane morphology and pore distribution are changed with these parameters which affects porosity of membranes (Şengür, 2013).

Membrane porosities were presented in Figure 4.8. Percentage of enhanced membrane porosity was little bit more than pristine membrane. But, there was no significant difference between hollow fiber membranes. It was expected result because the both hollow fiber membranes had the same spinning conditions and polymer type. Difference on permeability may caused from thickness and density of semipermeable layer.

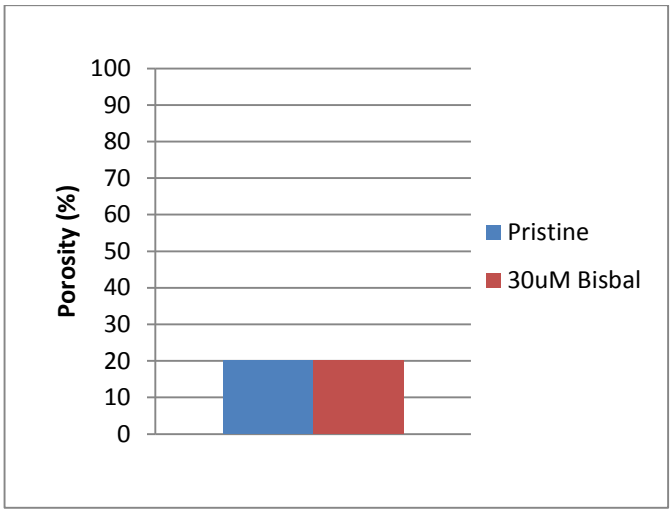


Figure 4.8 : Porosities (%) of hollow fiber membranes

Porosity of membranes were % 20,12 and %20,18 for pristine and enhanced in order of term.

4.1.4.5 Mechanical stability

Young's modulus degrees were 149 and 217 MPa which was presented in Figure 4.9. The addition of BisBAL into the polymer matrix suggested an increasement on mechanical stability. BisBAL additive into PES membrane provided an increasement on its structural morphology according to results of Young's Modulus test. In SEM images, it was seen that enhanced membrane had sponge-like structure which increased mechanical stability.

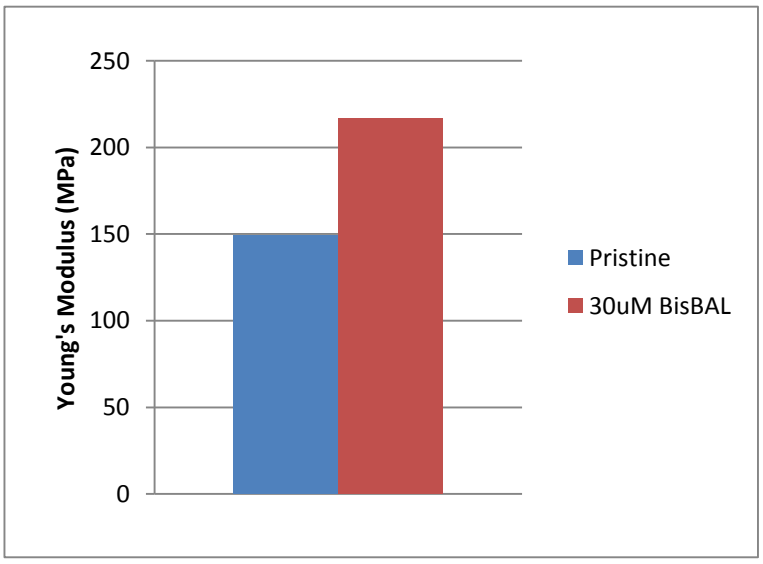


Figure 4.9 : Mechanical stabilities of hollow fiber membranes.

4.1.4.6 Fouling experiments

Flux recovery (FRR%), Total fouling (%) that include Reversible (Rr) and irreversible fouling (Rir) ratios and BSA rejection rates of pristine and enhanced with BisBAL additive hollow fiber membranes are given at Figures 4.10-12.

Water flux recovery rate means that the recycling water flux after fouling with BSA. It is an important parameter for understanding of anti-fouling properties. In Figure 4.10, flux recovery ratios of hollow fiber membranes were presented as % 30,7 and % 83,9 for pristine and enhanced membranes in order of term. Higher value of FRR means that having better antifouling capacity. BisBAL additive were caused to increasement on flux recovery percentage of membrane.

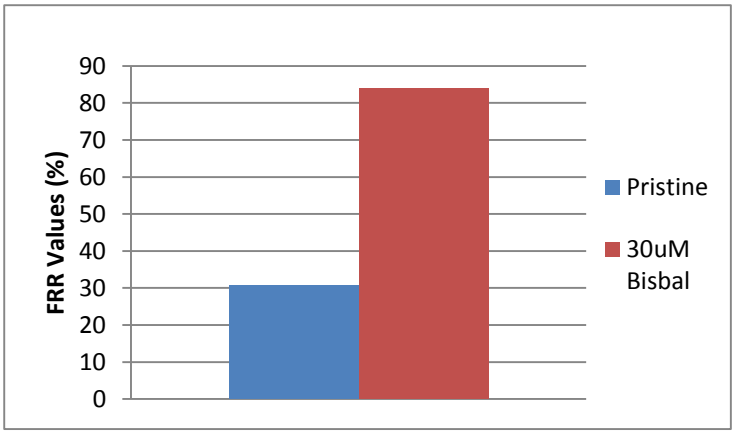


Figure 4.10 : Flux recovery ratios of hollow fiber membranes.

There are two types of fouling as reversible and irreversible. Reversible fouling is caused by weak protein adsorption and can remove by hydraulic cleaning. But irreversible fouling that is caused by strong adsorption of protein molecules can not removed easily. In Figure 4.11, percentages of total fouling and its fractions (reversible and irreversible) were given. Results of pristine and enhanced membranes which were represented by number 1 and 2 at graphic in terms of order. According to Figure 4.11, total fouling value of enhanced membrane was lower than pristine but there was no significant difference between membranes. Anyway, reversible fouling rate was increased dramatically on enhanced hollow fiber membrane. BisBAL additive was changed the behaviours of adsorption and not allowed to strong bound with organic matters. So, membrane can be able to clean easily which means the lower operation cost.

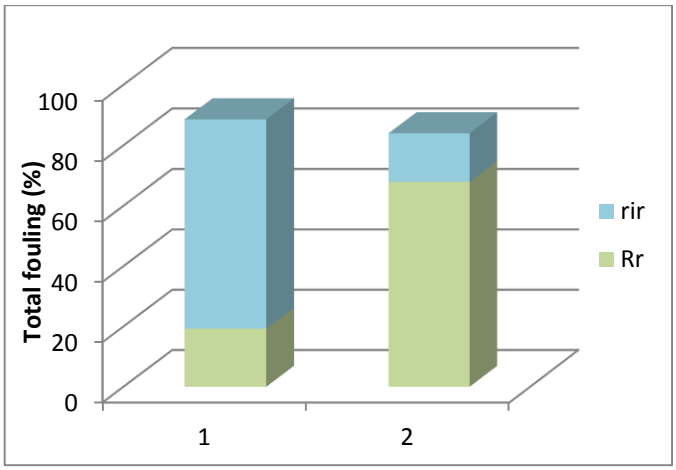


Figure 4.11 : Total fouling (reversible and irreversible) percentages of membranes.

BSA rejection percentages of hollow fiber membranes were given at Figure 4.12. There was an increasement (from 12,7 to 63,2) with BisBAL additive. Normally, lower rejection is expected if flux is higher. According to permeability results, enhanced membrane had bigger flux value than pristine. So, it can be said that the additive of BisBAL increased the rejection rate even flux was high.

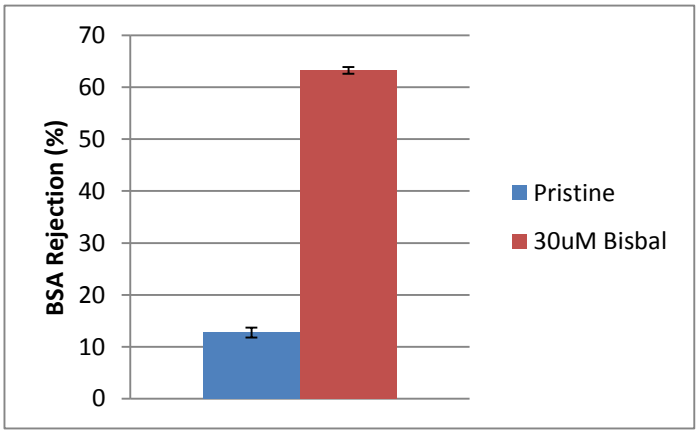


Figure 4.12 : BSA rejections of hollow fiber membranes.

Fouling mechanisms of membranes can effected by some parameters such as hydrophobicity, surface roughness, porosity and structure. Higher fouling capacity of fabricated pristine membrane can be explained due to its low contact angle degrees which shows high hydrophobicity. BisBAL additive changed the properties of membrane as explained at previous sections and increased its antifouling characteristics. To investigate the fouling capacity, fabricated hollow fiber membranes were applied with membrane bioreactor during 30 days and the results were explained at the following sections.

4.1.4.7 Growth of Escherichia Coli (*E.Coli*) on hollow fiber membranes

Escherichia coli (*E.Coli*) is a gram-negative, facultatively anaerobic and rod-shaped bacteria and one of the species in wastewaters which cause fouling on membrane systems. Antibacterial activity of BisBAL were obversed visually on membranes by using *E.Coli* for 6 days. Results of experiments were given at Figure 4.13. Less growth rate of bacteria on enhanced membrane was observed than pristine which proved the antibacterial property of BisBAL .

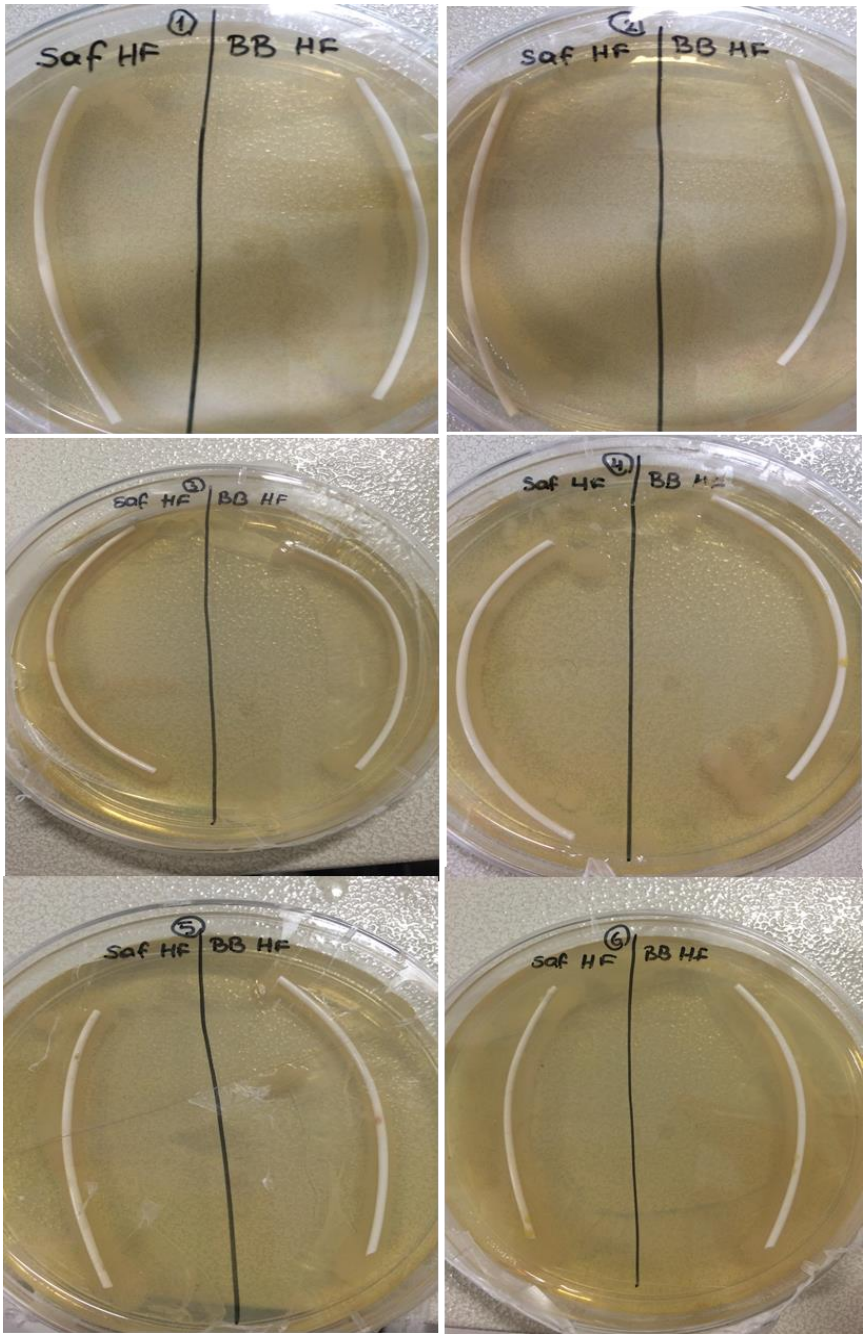


Figure 4.13 : Growth of *E.Coli* on membranes for 6 days.

4.2 MBR Application Results

Submerged membrane bioreactor (with synthetic wastewater) were operated during 30 days. Fabricated HF UF membranes as pristine and enhanced with BisBAL were used in batch sMBR. Fluxes, COD removals, suspended solids and volatile suspended solids of mixed liquor were measured on daily basis. To investigate the antifouling properties of BisBAL additive, EPS-SMP amounts of membranes were measured at the end of operation. And, aggregation on surface was imaged by confocal microcopy. Also, *E. coli* growth on membranes were observed visually.

4.2.1 SS-VSS

Average amount of suspended solids and volatile suspended solids of mixed liquor were 16205 and 13338 mg/l in order of term. VSS values were lower than SS values as expected. Daily amounts of SS and VSS were presented at Figure 4.14.

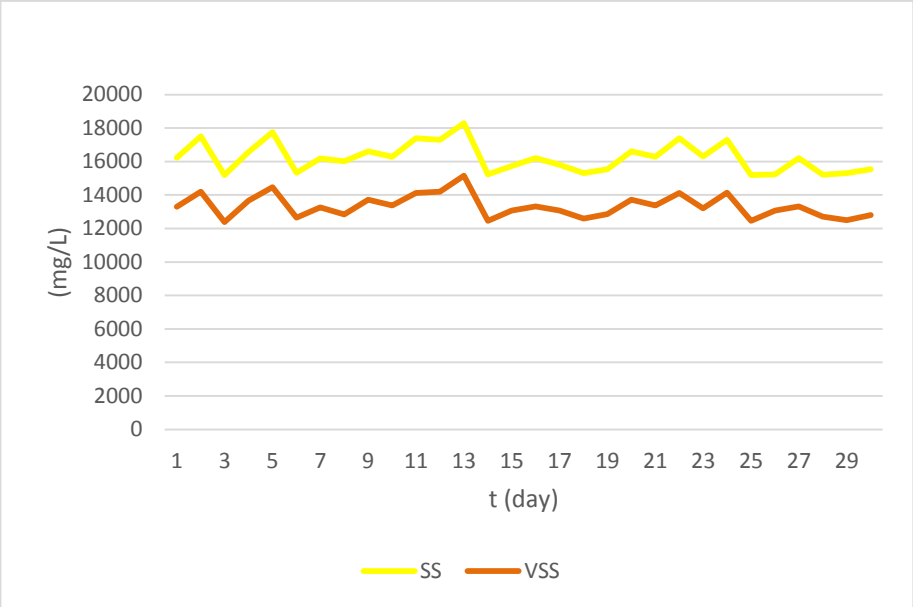


Figure 4.14 : SS and VSS values of mixed liquor.

4.2.2 Flux

Before the operation, membranes were filtered with distilled water. Fluxes were 68,9 and 141,2 l/m^{2}h for pristine and enhanced membranes in order of term. Synthetic wastewater were filtered daily with vacuume driven system by using with fabricated UF HFs which have surface areas as 20 cm^2 averagely. During the system (30 days), fluxes were measured that were presented by Figure 4.15.

Fluxes of enhanced membrane had better results than pristine. Permeability degree of fabricated HF membrane with BisBAL additive was bigger than pristine. There was a parallel correlation between permeability capacitiy and flux rates.

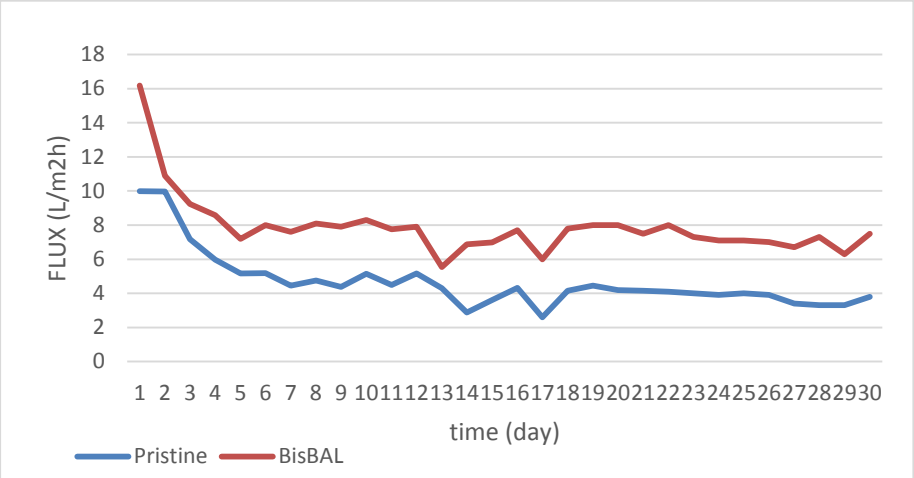


Figure 4.15 : Flux rates of hollow fiber membranes during operation.

Flux of enhanced membrane had better than pristine during 30 days as expected. Average flux rates of HF membranes are 7,9 (enhanced) and 4,6 (pristine) l/m^{2}h. Generally, HF membrane with BisBAL additive had flux rate as two times more than pristine. Because high concentration of wastewater and small surface areas of membranes, fluxes were decreased dramatically at the first day of operation. At the following operation days, results were not so unsteady. Daily flux changes by amount of suspended solids in wastewater were given at Figure 4.16. According to the graphic, fluxes had a decreasement tendency when amount of suspended solids were increased.

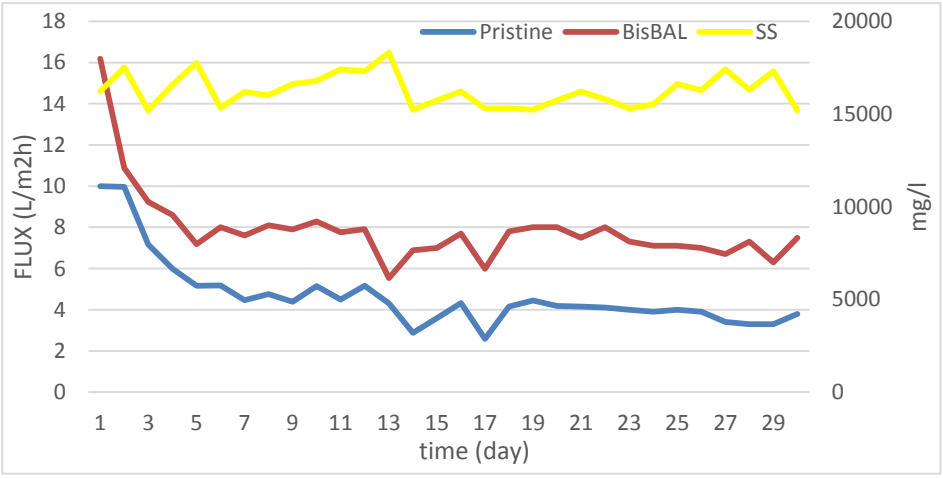


Figure 4.16 : Daily flux changes by amount of suspended solids.

4.2.3 COD

Daily measurements of COD removal percentages were given at Figure 4.17.

Average removal values were %60 for pristine and %80 for enhanced membrane with BisBAL additive. Difference between membranes may caused from their structures which was changed by additive of BisBAL.

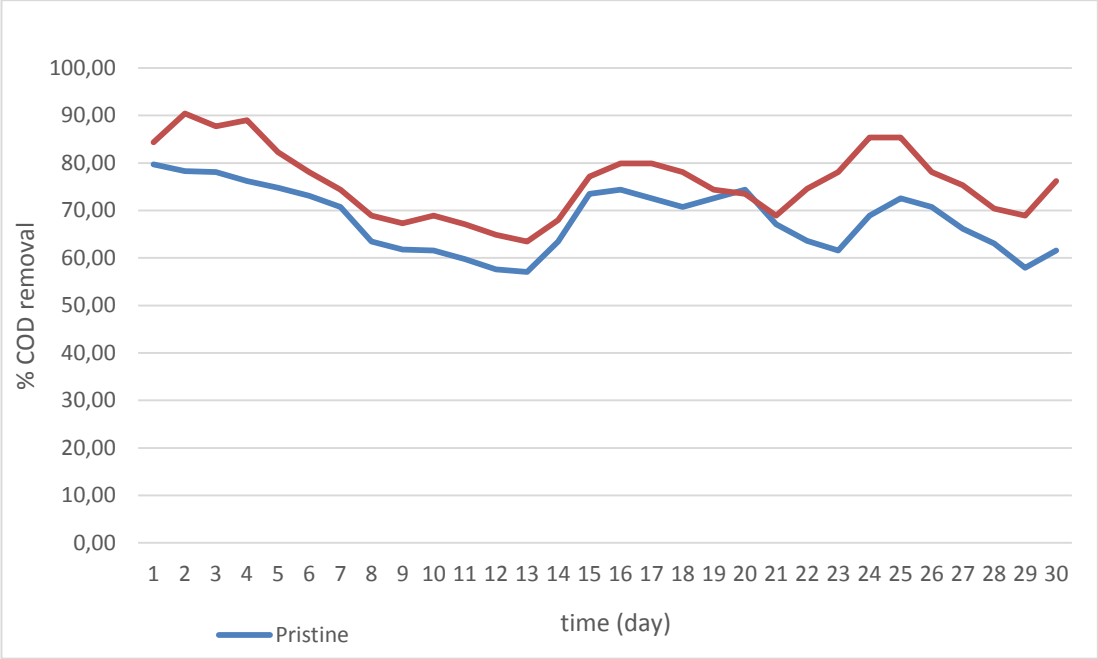


Figure 4.17 : COD removal percentages on daily basis.

4.2.4 EPS-SMP

SMP and EPS are one of the most important causes of affecting membrane biofouling which was explained in literature review section. Additive of BisBAL can decrease the amount of EPS and inhibited to biofilm formation (Badireddy et al. 2008).

At the end of operation, aggregated cake layer were collected from pristine and enhanced HF membranes. Amount of SMP-EPS were measured and calculated which was given at Figure 4.18. (Carbohydrate fractions were showed as SMPc and EPSc, also protein fractions were showed as SMPp and EPSp).

EPS-SMP values of enhanced membrane were bigger than prisitine membrane that showed the BisBAL had an antibiofouling feature. Previous researches were supported that extra polymeric substances and soluble microbial products could prevented by BisBAL.

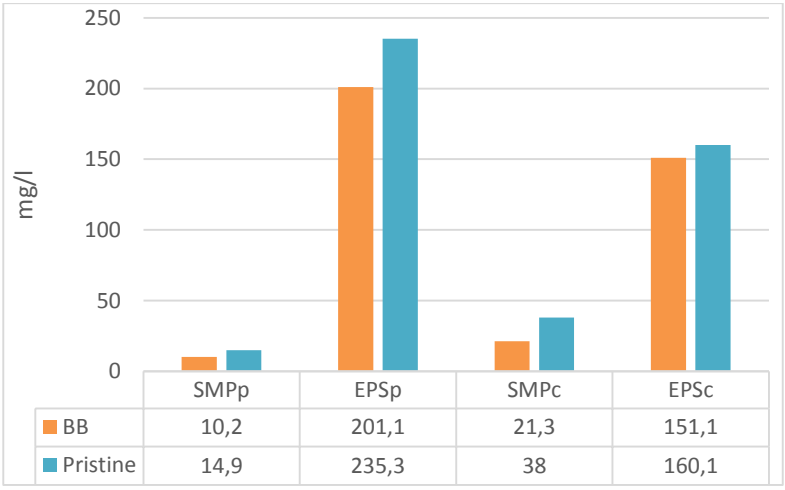


Figure 4.18 : SMP-EPS measurements of applicated HF membranes.

Bismuth chelates are excellent agents for inhibition of EPS production (as blocking of extracellular polysaccharide (EPS) synthesis and consequently reduce to biofilm accumulation) (Badireddy et. al. 2014; Hai et. al. 2011). The exopolysaccharide expression is suppressed and biofilm formation of Gram-positive and -negative bacteria are inhibited by BisBAL which is a very powerful antimicrobial agent within bismuth thiols. Also, bacterial adherence and colonization is prevented (Chellam and Romero, 2014; Domenico, 2002).

4.2.5 Confocal microscopy

According to confocal microscopy images, difference of biofilm layer thicknesses were observed clearly. Images were taken at 25th, 27th and 29th days of operation. In Figure 18-25, foulings on membranes were given.

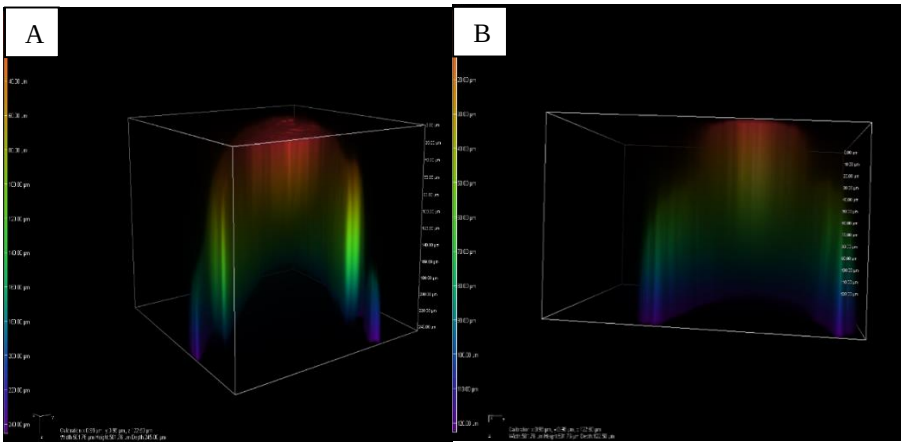


Figure 4.19 : Cross view images of applicated HF membranes (25th day): pristine (A) and enhanced with BisBAL additive (B).

According to cross view images, thickness of biofilm layers were presented by confocal microscopy (Figure 4.18).

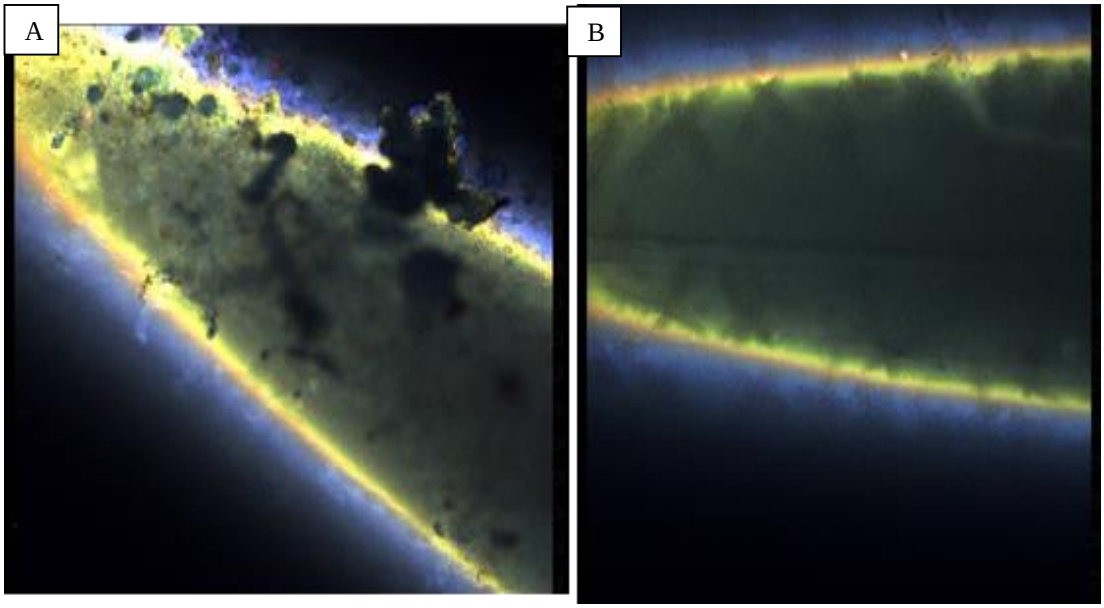


Figure 4.20 : Surface view images of applicated HF membranes (25th day): pristine (A) and enhanced with BisBAL additive (B).

Also fouling, which was higher at pristine membrane, could be observed in surface images of membranes (Figure 4.19-20).

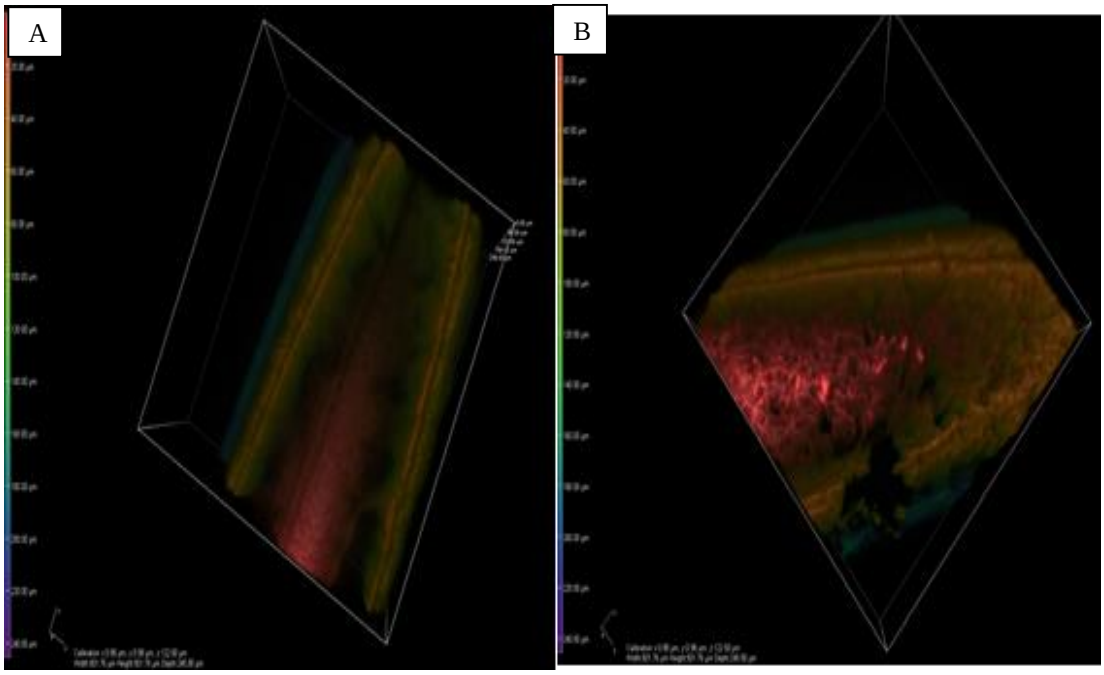


Figure 4.21 : Surface view images of applicated HF membranes (25th day): pristine (B) and enhanced with BisBAL additive (A).

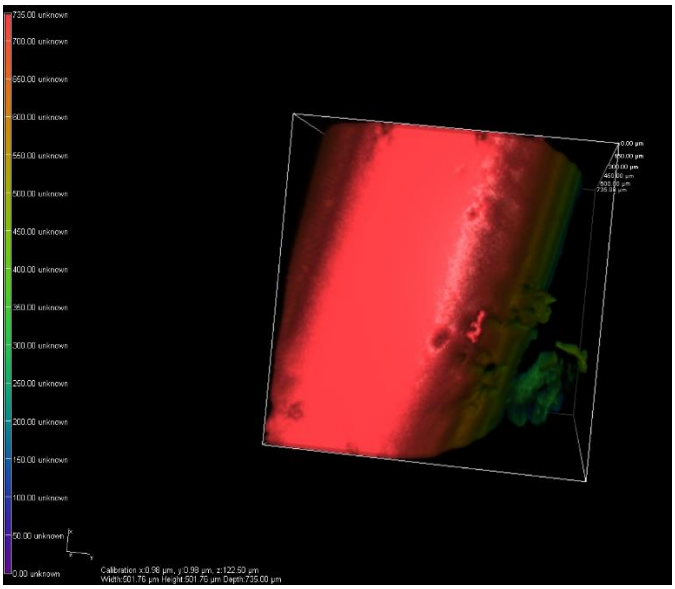


Figure 4.22 : Side view images of applicated pristine HF membrane (25th day).

Foulants where on pristine membrane could be noticed at side view images (Figure 4.21).

Antifouling properties of BisBAL were prevented from the foulants that were caused from soluble microbial products and extracellular polysaccharides.

It was known that Bismuth chelates were excellent agents for inhibition of EPS-SMP production as blocking of extracellular polysaccharide (EPS) synthesis and consequently reduce to biofilm accumulation.

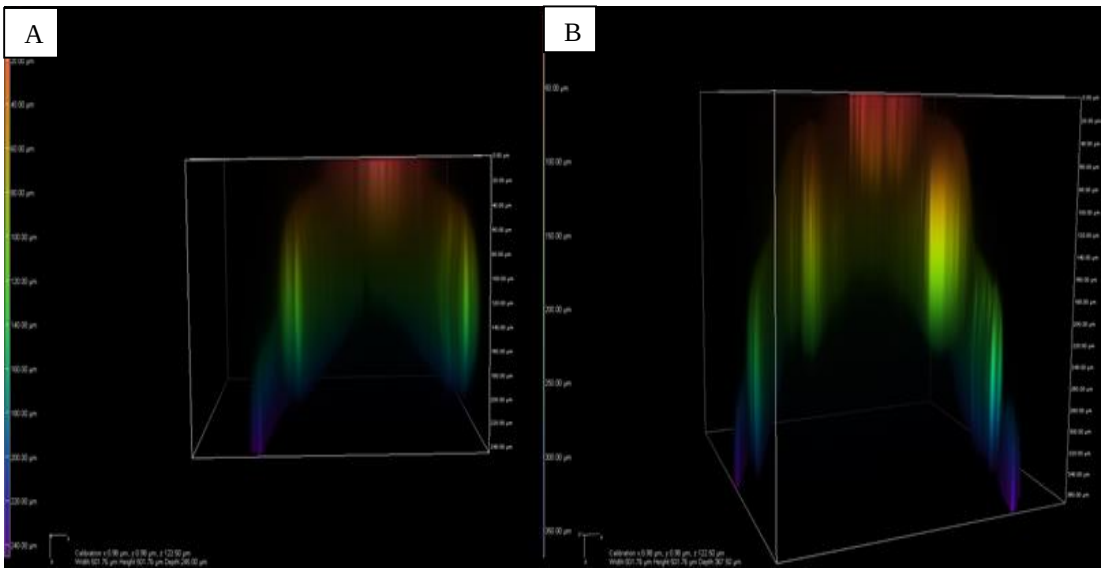


Figure 4.23 : Cross view images of applicated HF membranes (27th day): pristine (B) and enhanced with BisBAL additive (A).

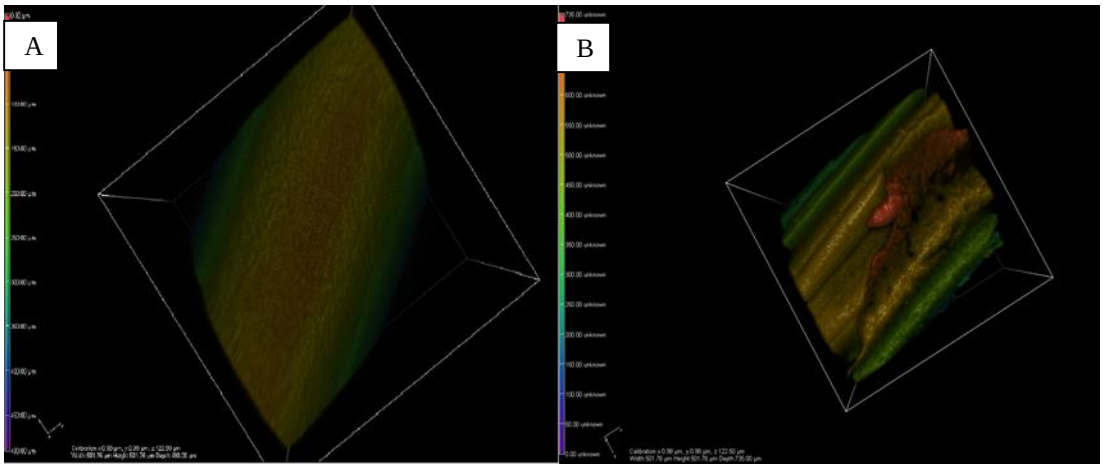


Figure 4.24 : Surface images of applicated HF membranes (29th day): pristine (B) and enhanced with BisBAL additive (A).

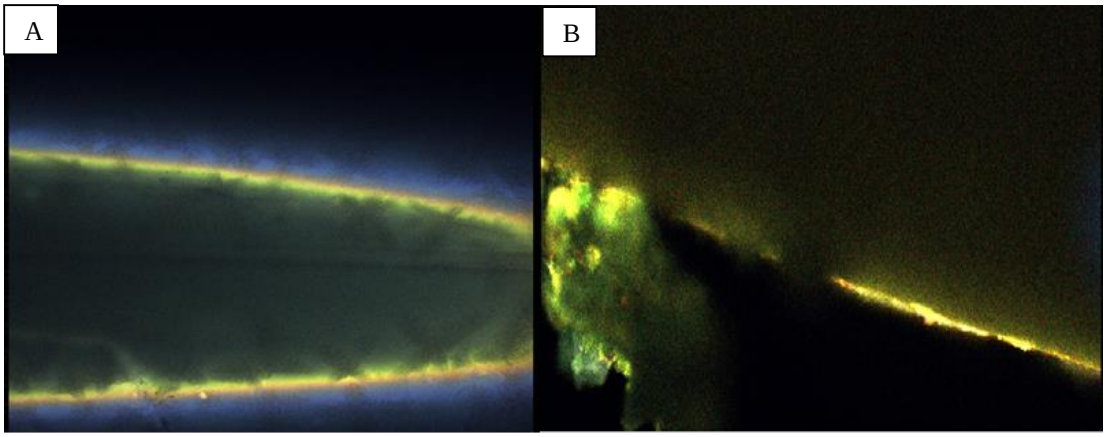


Figure 4.25 : Surface images of applicated HF membranes (29th day): pristine (B) and enhanced with BisBAL additive (A).

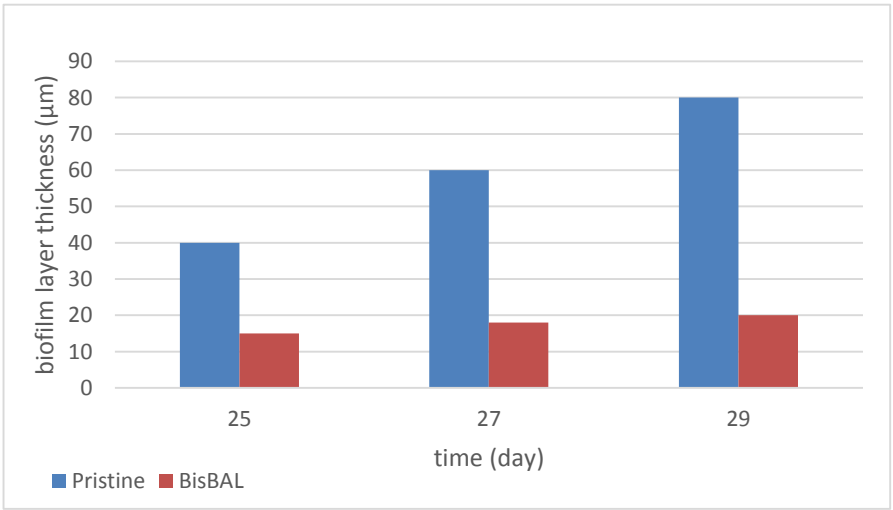


Figure 4.26 : Biofilm layer thicknesses of applicated HF membranes at different operation days (25th, 27th and 29th).

The combination of bismuth nitrate with a lipophilic thiol containing compound describes as Bismuth thiols. The antimicrobial properties of bismuth increase with thioles. They can inhibit exopolysaccharide production and decrease biofilm formations (Badireddy et. al. 2014; Hai et. al. 2011).

Biofilm layers on membrane were increased because the foulants were accumulated onto surfaces of the membranes. This undesired accumulations were caused to fouling which decreased filtering capacities of membranes. It was clearly visible that the enhanced membranes with BisBAL additive had lower degree of accumulation than pristine membrane.

It can be said that the less biofilm formation was occured by BisBAL additive. Blocking of biofilm layer formation on enhanced membrane with bismuth thiole (BisBAL) addition was observed at confocal microccopy images.

5. CONCLUSIONS AND RECOMMENDATIONS

Hollow fiber membranes were fabricated with BisBAL additive by phase inversion method and applicated in lab scaled submerged membrane bioreactor for obtaining its antibiofouling features. To reach the aim, pristine membrane recipe and spinning conditions were optimized and effects of BisBAL additive were investigated with different characterization methods. Then membranes were operated in membrane bioreactor for 30 days.

Pristine recipe of membranes was 18 % PES, 7 % PVP K90, 75 % NMP. This dope solution were spun with 30 μm BisBAL additive for enhanced hollow fiber membrane. Features of fabricated hollow fiber membranes were changed by spinning parameters and temperature. Also optimum spinning parameters were investigated. Spinning parameters and temperature of coagulation bath were decided as 0 cm (air gap), 7,1 m/s (take-up speed) and 35 ^{o}C.

Morphologies of pristine and enhanced membranes were investigated by SEM, stereo microscopy and optical profilometer images. It was seen that fabricated membranes had proper circular structures as expected. According to cross section images, it was seen that pristine membrane had finger-like structure which was changed with BisBAL additive as sponge-like. Effects of BisBAL were clearly seen in cross sections, outer layers and also diameters of membranes at all images.

Also permeability, porosity, mechanical stability, contact angles and fouling experiments were done for investigating the effects of BisBAL additive into the PES membrane matrix. Permeability and mechanical stability values increased which means membrane had higher flux and more stability with BisBAL addition. Fouling ratios (water flux recovery, total fouling which was composed of irreversible and reversible fouling, and BSA rejection rates) and contact angle degrees were decreased that means membrane had antifouling feature and more hydophilic characteristic by

BisBAL additive. Antibacterial activity were also investigated by E.coli growth on membranes which was supported the antibiofouling feature of BisBAL additive.

Fabricated membranes immersed into an aerated batch reactor and operated for 30 days. Synthetic wastewater was used for the system. Amount of suspended solids and volatile suspended solids were measured daily. Also fluxes and COD removals of pristine and enhanced (with BisBAL) membranes were measured on daily basis. Enhanced membrane had higher flux and COD removal than pristine as expected. Previous researchers claimed that EPS-SMP rates were directly related with formation of biofilm layer (biofouling). So EPS-SMP rates of pristine and enhanced membranes were analyzed at the end of operation. It was seen that enhanced membrane had less amount of EPS-SMP. According to the confocal images, formation of biofilm layer was thinner than pristine.

It was expected that the addition of BisBAL into membrane matrix will enhance antifouling properties of membranes. With respect to the results, addition of BisBAL improved the antibiofouling properties of fabricated membranes.

Biofouling is very challenging problem in membrane operation systems. It has to be controlled for an efficient process. Material developments and modifications with an additives are one of the most promising approaches for preventing the biofouling because it is easier and economical than conventional methods. Biocidal components such as BisBAL or other bismuth thiols can use for blocking of biofouling by membrane enhancements. Besides BTs can use as nanoparticles or apply with thin film coating methods on membranes. Extensive studies have focussed on generating hydrophilic structures on membrane surfaces which has lower initial fouling or microbial attachment.

According to results of this study, PES hollow fiber ultrafiltration membranes, which were modified with BisBAL additive, gained an antibiofouling feature as expected.

REFERENCES

Badireddy, A. (2008). Spectroscopic characterization of extracellular polymeric substances from *Escherichia coli* and *Serratia marcescens*: suppression using sub-inhibitory concentrations of bismuth thiols**.** *Biomacromolecules,* Vol. 9 (11). pp. 3079-3089**.**

Badireddy, A., Hernandez-Delgadillo, R., Sa´nchez-Na´jera, R., Chellam, S., Cabral-Romero, C. (2014). Synthesis and characterization of lipophilic bismuth dimercaptopropanol nanoparticles and their effects on oral microorganisms growth and biofilm formation. *J Nanopart Res.* Vol. 16. pp. 2456.

Badireddy, A., Marinakos, S., Chellam, S., Wiesner, M. (2013). Lipophilic nano-bismuth inhibits bacterial growth, attachment, and biofilm formation. *Surface Innovations*. Vol. 1.

Baker, R. (2004). Membrane technology and applications, 2nd Edition.

Brock, W. H. (1993). The norton history of chemistry, *W. W. Norton & Company.*

Cardew, P. T., Le, M. S. (1988). Membrane processes: a technology guide. *Royal Society of Chemistry.*

Chellam, S., Romero, C. (2014). Bismuth nanoparticles: antimicrobials of broad-spectrum, low cost and safety. *Nanomedicine*. pp. 429.

Codony, F., Domenico, P., Mas, J. (2003). Assessment of bismuth thiols and conventional disinfectants on drinking water biofilms**.** *J Appl Microbiol***,** pp. 288-93.

Domenico, P. (2002). Mixture of bismuth compound and dimercaprol, US Patent, No: RE37793 E1 dated 16.7.2002.

Domenico, P. (2003). Combating antibiotic resistance with bismuth-thiols. *Res. Adv. in Antimicrob. Agents & Chemother*. pp. 79-85.

Domenico, P., Salo, R., Novick, S., Schoch, P., Van Horn, K., Cunha, B. (1997). Enhancement of bismuth antibacterial activity with lipophilic thiol chelators. *Antimicrobial Agents And Chemotherapy.* pp. 1697-1703.

Domenico, P., Tomas, J., Merino, S., Rubires, X., Cunha, B. (1999). Surface antigen exposure by bismuth dimercaprol suppression of Klebsiella pneumoniae capsular polysaccharide. *Infect Immun.* Vol. 67, pp. 664.

Durmaz, G. (2014). Inhibition effect on *Streptococcus pyogenes* bacteria of Bisbal and activated sludge filtration with membranes containing BisBAL. *MSc. Thesis,* Istanbul Technical University.

Fane, A.G., Tang, C.Y., Wang, R. (2011). Membrane technology for water: microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. *Wilderer P (ed.) Elsevier*. pp. 301-335

Guo, W., Ngo, H., Li, J. (2012). A mini-review on membrane fouling. *Bioresource Technology*. Vol. 122, pp. 27-34.

Hai, F. I., Yamamoto, K. *(2011).* Membrane biological reactors. *Wilderer (Eds.), Treatise on Water Science.* pp. 571-613.

Judd, S. (2011). The MBR Book: Principles and applications of membrane bioreactors for water and wastewater treatment. *Elsevier.*

Laila, B. S., Kochkodan, V., Hashaikeh, R., Hilal, N. (2013). A review on membrane fabrication: structure, properties and performance relationship. *Desalination.* Vol. 326, pp. 77-95

Le-Clech, P., Chen, V., Fane, T. (2006). Fouling in membrane bioreactors used in wastewater treatment. *Journal of Membrane Science.* Vol. 284, pp. 17-53.

Mansouri, J., Harrisson, S., Chen V., (2009). Strategies for controlling biofouling in membrane filtration systems: challenges and opportunities. *Journal of Materials Chemistry*, 20, pp. 4567-4586

Menga, F., Chaeb, S., Drewsc, A., Kraumec, M., Shind, H., Yanga, F. (2009). Recent advances in membrane bioreactors (MBRs): Membrane fouling and membrane material. *Water Research.* Vol. 43, pp. 1489-1512.

Mutamim, N., Noor, Z., Hassan, M., Yuniarto, A., Olsson, G. (2013). Membrane bioreactor: Applications and limitations in treating high strength industrial wastewater. *Chemical Engineering Journal*. Vol. 225, pp. 109-119.

Patterson, J. (1985). Industrial wastewater treatment technology. *Butterworth Publishers.*

Pearce, G. (2007). Introduction to membranes: Membrane selection. *Filtration and Separation*. Vol. 44, pp. 35-37.

Rugbani, A. (2009). Investigating the influence of fabrication parameters on the diameter and mechanical properties of polysulfone ultrafiltration hollow-fiber membranes, MSc. Thesis, *University of Stellenbosch.*

Sillanpää, M. (2014). Natural Organic Matter in Water: Characterization and treatment methods: membranes. *IWA Publishing.* pp. 113-150.

Strathmann, H., Giorno, L., Drioli, E. (2006). An Introduction to membrane science and technology. *Consiglio Nazionale Delle Ricerche.*

Şengür, R. (2013). Fabrication and characterizatıon of polyethersulfone (Pes)/multiwalled carbon nanotube hollow fiber ultrafiltration membranes**.** *MSc. Thesis*, Istanbul Technical University.

Thomas, F., Bialek, B., Hensel, R. (2011). Medical use of bismuth: the two sides of the coin. *Clinical Toxicology.*

Varposhti, M., ; Ali, A., Mohammadi, P. (2014). Synergistic effects of bismuth thiols and various antibiotics against *Pseudomonas aeruginosa* biofilm. *Jundishapur J Microbiol*, (7). pp. 3.

Vatanpour, V., Madaeni, S.S., Moradian, R., Zinadini, S., Astinchap, B. (2011). Fabrication and characterization of novel antifouling nanofiltration from oxidized multiwalled carbon nanotube/polyether sulfone nanocomposite. *Journal of Membrane Science*, 375, pp.284-294.

Wang, L., Chen, K., Jiaping, P., Nazih K. (2010). Membrane and desalination technologies. *Handbook of Environmental Engineering.* Vol. 13, no 2.

Url-1 < *http://www.un.org.com* >, date retrieved 14.09.2014

Url-2 <*http://www.microbioncorp.com* >, date retrieved 15.10.2014

CURRICULUM VITAE

Name Surname: Fatma Nur Şeyma Yavuz

Place and Date of Birth: Sandıklı – Afyon, 17/05/1988

Address: Acıbadem/Kadıköy - İstanbul

E-Mail: seym_a@hotmail.com

B.Sc.: Chemical Engineering, Ankara University

M.Sc.: Environmental Biotechnology, Istanbul Technical University

Professional Experience and Rewards:

(June, 2014 – cont.) TUBITAK 1003 - Primary Subjects R&D Funding Program Scholarship (Production of nanocomposite hollow fiber membranes and their applications on drinking water treatment).

UNIDO, CleanTechOpen, TUBITAK: GCIP (Global CleanTech Innovation Programme) 2014. National 1st prize. (Waste to Energy)

(January, 2014 – May, 2014) TUBITAK 1001 - COST Action Project (European Cooperation in Science and Tech.) Scholarship (Determination of Impacts of Wastewaters including Antibacterials and Antibiotics on Anaerobic Metabolic Pathways and Investigation of Relationship between These Pharmaceuticals and Antibiotic Resistance Genes).

PUBLICATIONS/PRESENTATIONS ON THE THESIS

- **Şengür R**., Yavuz F.N.Ş., Ürper M., Türken T., and Koyuncu İ., 2014: Fabrication and Characterization of Polymeric Hollow Fiber Membranes with Bismuth-BAL Chelate. *International Congress - 4th IWA Regional Conference on Membrane Technologies*, November 12, 2014, Vietnam.