FOULING ANALYSIS FOR DIFFERENT ULTRAFILTRATION MEMBRANES IN REACTIVE DYEING WASTEWATER TREATMENT

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

RUKEN DİLARA ZAF

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
ENVIRONMENTAL ENGINEERING

SEPTEMBER 2017

Approval of the thesis:

FOULING ANALYSIS FOR DIFFERENT ULTRAFILTRATION MEMBRANES IN REACTIVE DYEING WASTEWATER TREATMENT

Submitted by **RUKEN DİLARA ZAF** in partial fulfillment of the requirements for the degree of **Master of Science in Environmental Engineering Department, Middle East Technical University** by,

Prof. Dr. Gülbin Dural Ünver
Dean, Graduate School of **Natural and Applied Sciences** _____

Prof. Dr. Kahraman Ünlü
Head of Department, **Environmental Engineering** _____

Prof. Dr. Ülkü Yetiş
Supervisor, **Environmental Engineering Dept., METU** _____

Assoc. Prof. Dr. Zeynep Çulfaz Emecen
Co-Supervisor, **Chemical Engineering Dept., METU** _____

Examining Committee Members:

Assoc. Prof. Dr. Tuba Hande Bayramoğlu
Environmental Engineering Dept., METU _____

Prof. Dr. Ülkü Yetiş
Environmental Engineering Dept., METU _____

Assoc. Prof. Dr. Zeynep Çulfaz Emecen
Chemical Engineering Dept., METU _____

Assoc. Prof. Dr. Gökşen Çapar
Water Management Institute, Ankara University _____

Asst. Prof. Dr. Derya Dursun Balcı
Environmental Engineering Dept., METU _____

Date: September 6, 2017

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: Ruken Dilara Zaf

Signature:

ABSTRACT

FOULING ANALYSIS FOR DIFFERENT ULTRAFILTRATION MEMBRANES IN REACTIVE DYEING WASTEWATER TREATMENT

Zaf, Ruken Dilara
M.S., Department of Environmental Engineering
Supervisor : Prof. Dr. Ülkü Yetiş
Co-advisor : Assoc. Prof. Dr. Zeynep Çulfaz Emecen

September 2017, 105 pages

Textile industry produces wastewater that is often very rich in salt and color, containing residues of dyes and other chemicals. Treating this wastewater to exceptionally high quality standards, typically for reuse purposes, necessitates advanced treatment methods among which membrane technology is a leading one. However, membrane fouling which can be caused by dissolved and particulate solids appears as the major limitation with the use of membranes in wastewater reclamation that leads to reduced efficiency and a shorter membrane life. In this branch of a more comprehensive project on water recovery from reactive dyeing wastewater (RDW), the relationship between membrane fouling and membrane type was investigated in ultrafiltration (UF) process. The aim of the work is pointing the most suitable membrane type for RDW treatment with regards to its fouling behavior and treatment performance. Within this context, commercial membranes such as polyether sulfone (PES), regenerated cellulose (RC), thin film composite (TFC) and poly(piperazine amide) (PPZ) were used. These membranes were compared based on their permeate flux changes, fouling tendencies/cleanabilities and color, total organic carbon (TOC), turbidity and conductivity treatment efficiencies. As a concurrent execution, in order to correlate membrane surface and fouling characteristics, the contact angles and

roughness of these different UF membranes were investigated. The overall results achieved indicated that TFC membrane showed the best performance by providing lowest fouling tendency, acceptable cleanability and good treatment performance with the highest color removal among the tested membranes. In the meanwhile, 5 kDa RC membrane was found as the weakest one because of its smallest TOC and color removal whereas the cleanabilities of PES and 1 kDa RC membranes were observed as the lowest ones among all membranes. The highest flux decline was observed during PPZ membrane filtration which also had the highest average roughness (Ra) and contact angle.

Key words: Membrane fouling, ultrafiltration, reactive dyeing wastewater, textile industry

ÖZ

REAKTİF BOYAMA ATIK SU ARITIMINDA KULLANILAN FARKLI ULTRAFİLTRASYON MEMBRANLARININ KİRLENME ANALİZİ

Zaf, Ruken Dilara
Yüksek Lisans, Çevre Mühendisliği Bölümü
Tez Danışmanı : Prof. Dr. Ülkü Yetiş
Ortak Tez Yöneticisi : Doç. Dr. Zeynep Çulfaz Emecen

Eylül 2017, 105 sayfa

Tekstil endüstrinden elde edilen atık su, genelde renk ve tuzca çok zengin olup, boya ve diğer kimyasalların kalıntılarını barındırmaktadır. Bu tip atık suların tekrar kullanılabilir hale gelecek kadar yüksek standartlarda arındırılması, gelişmiş teknikler gerektirmektedir. Membran teknolojisi bu tekniklere öncülük etmektedir. Ancak, çözünmüş ve partikül halindeki katılardan kaynaklanan membran kirlenmesi, membranların verimini ve kullanım süresini azaltması sebebiyle, bu yöntemin atık su arıtımındaki daha geniş çapta kullanımını sınırlamaktadır. Reaktif boyama atıksularından (RBA) su geri kazanımı üzerine yapılan daha kapsamlı bir çalışmanın bu tezde yer alan kısmında, membranların kirlenmesi ve membran cinsi arasındaki ilişki ultrafiltrasyon (UF) yöntemi kullanılarak araştırılmıştır. Çalışmanın amacı RBA arıtımında kullanılabilecek ve kirlenme davranışı ve arıtım performansı açısından en uygun membranı ortaya koymaktır. Bu doğrultuda, bilinen ticari mebranlardan polietersülfon (PES), rejenere selüloz (RS), ince film kompozit (TFC) and poly(piperazine amide) (PPZ) membranlar kullanılmıştır. Bu membranlar süzüntü akısı değişimleri, kirlenme yönelimleri/temizlenebilirlikleri ve renk, toplam organik karbon (TOK), bulanıklık ve iletkenlik arıtım verimlilikleri açısından karşılaştırılmıştır. Bunların yanı sıra, UF membranlarının yüzey ve kirlenme

karakteristiklerini ilişkilendirmek amacıyla, kullanılan farklı membranların temas açıları ve pürüzlülükleri ölçülmüştür. Yapılan bütün ölçüm ve çalışmalar sonucunda, TFC membranın, test edilen membranlar arasında en iyi performansı gösterdiği bulunmuştur. Sonuçlara göre, bu membran, en düşük kirlenme yönelimi, kabul edilebilir düzeyde temizlenebilirlik ve en yüksek renk giderimiyle birlikte iyi bir arıtma performansı sergilemiştir. Aynı zamanda sonuçlar, 5 kDa RS membranın TOK ve renk giderimi bakımından, PES ve 1 kDa RS membranlarının da temizlenebilirlik açısından en düşük performansa sahip olduklarını göstermiştir. PPZ membran filtrasyon sırasında en yüksek akı düşüşünü gösterirken, aynı zamanda en yüksek ortalama pürüzlülük ve temas açısı değerlerine sahip olduğu gözlenmiştir.

Anahtar kelimeler: Membran kirlenmesi, ultrafiltrasyon, reaktif boyama atıksuları, tekstil endüstrisi

ACKNOWLEDGEMENTS

Foremost, I would like to express my sincere gratitude to my advisor Prof. Dr. Ülkü Yetiş for the continuous support of my MSc study and research. Her guidance helped me in all the time of research and writing of this thesis.

Besides my advisor, I would like to thank to the professors in our project team, Prof. Dr. Levent Yılmaz and Assoc. Prof. Dr. Zeynep Çulfaz Emecen, for their encouragement and insightful comments in that three years.

I am very grateful to Gökçe Dilli Alp who helped me in critical times with some important analysis and had heartfelt sincerity during all period.

I must express my gratitude to my good friends and colleagues, Mert Erkanlı and Burcu Koçer Oruç, for being more than teammates, the encouraging discussions, and for all the fun we have had in the last three years. My sincere thanks also goes to my beautiful and hardworking officemates, Zeynep Özcan, Elif Sena Uzunpınar and Dr. Hale Demirtepe, for their patience and support during the hard times. They are always a source of happiness for me. And also, I would like to thank to Kumru Kocaman and Özge Yücel who have always been with me and spent many beautiful and difficult moments together. I also would like to thank to Alper Yavaş and Cansu Demir for their support.

I am very lucky to have such special friends, Perihan Öztürk, Özgür Balkılıç, Gamze Karaca and Ali Yücel Türegün, in my 'Canım Kitap'. They shed light on me, illuminate my life with their love and joyfulness. Not only in the thesis period, but also in every struggle I've ever met in life, they were always with me. I am sure that we are stronger and more beautiful when we are together. And also, Eren Düzenli and Emre Gökyer who give me joy and love, thank you for being a part of my life.

I also would like to express my gratefulness to my oldest and faithful friends Hülya, Seren, Caner, Doruk, Diren, Damla and Hayati. Their endless love and support is always deep in my heart.

Finally, I would like to express my deepest love and thank to my family; my father, mother and younger brother, for their always being there for me and encouraging me on the way of all my wishes.

This study was supported by The Scientific and Technological Research Council of Turkey (TUBITAK) through Project No: 114Y102.

"…

The industry is living with few problems which are self-created. The problems are repeated because people try to take the same steps which look attractive and money earning, without realizing that these are the roots of the problems. It is not that they do not know, but they try to take a chance; just like driving on the wrong side of the road to reach early.

…"

B. Purushothama,

"Solutions to Problems in Textile and Garment Industry", 2015

TABLE OF CONTENTS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

CHAPTER 1

INTRODUCTION

As world population increases, it becomes increasingly difficult to satisfy the need for water. According to the estimations, more than half of the world population could suffer from water scarcity in the year 2025. The human factor plays a critical role in worsening of this scarcity by inappropriate water management, water resources pollution and water wasting. Industry which is the second largest water consumer coming right after agricultural usage, plays a quite big role in the growth of this problem. Along with, textile industry is the leading one among all (Marrot & Roche, 2002; Ranade & Bhandari, 2014). As a consequence of the freshwater scarcity and strict regulations about effluent disposal to environment, reclamation of wastewater, especially in textile industry, has become quite significant (Chollom etal., 2015).

One of the most important environmental problems arising from textile industry is its highly toxic and colored wastewater. Among the dyes in textile wastewaters, reactive dyes are the most unfavorable type due to their low fixation degrees, and their high toxicity and persistence in the environment. However; they are the main synthetic dyes used in the coloring of cotton due to their strong technical properties. (Allegre et al., 2006; López-Grimau et al., 2015). Conventional wastewater treatment processes such as activated sludge or chemical precipitation are not usually sufficient for removal of reactive dyes. It is because important portion of dyes in the wastewater escape from these kind of treatment processes or the processes have important limitations. Several other advanced treatment techniques; such as advanced oxidation, or activated carbon adsorption can be applied for textile wastewater reclamation. However, there are some problems in implementing these techniques.

For example, although they are very effective at color removal, advanced oxidation methods are problematic for high wastewater flow rates. Because, these techniques are costly, and therefore feasible when applied for low flowrates (Holkar et al., 2016). Similarly, adsorption which can be applied as tertiary treatment is also a high-cost process for wastewaters with high flowrates.

Treating textile wastewaters to exceptionally high quality standards, typically for reuse purposes, necessitates advanced treatment methods among which membrane technology is the leading one with its high selectivity and simple operation. Many studies have been conducted on treatment of textile effluents by membrane technology. These researches are carried out either by only membrane used applications (Ciardelli et al., 2001) or combinations with other treatment methods (Radhakrishnan et al.,2015).

Generally, nanofiltration (NF) and reverse osmosis (RO) processes are preferred in direct membrane treatment applications while ultrafiltration (UF) and microfiltration (MF) are considered as pretreatment methods (Barredo-Damas et al., 2006; Cheïma Fersi & Dhahbi, 2008; Thamaraiselvan & Noel, 2015). Sójka-Ledakowicz et al. (1998) have tried NF and RO options in obtaining high quality water from cotton dyeing effluent for reuse purposes. They claimed that permeate of NF can possibly be used in rinsing process and RO can produce a permeate usage of which is possible with technological water. In 1991, Watters et al. conducted a research on treatment of textile effluent only by UF and indicated that the UF effluent was not totally purified from color. Later, Allegre et al., (2006) investigated the treatment and reuse of reactive dyeing wastewater (RDW), and showed that UF may only be used as a pretreatment for RO or in combination with biological treatment. In driving this conclusion, they considered the reclamation of textile effluent as clean water. In a recent study, Erkanlı et al. (2017) pointed out that UF treatment can effectively be used for recovery of brackish water from RDW. Lin et al. (2016) also applied UF with subsequent UF-diafiltration process. They claimed that tight UF membranes can be very effective for separation and recovery of dyes and salts in textile wastewater. But, in none of these previous studies, fouling behavior of different UF membranes was investigated.

Definitely, flux decline due to membrane fouling which can be caused by dissolved and particulate solids is one of the major bottlenecks in membrane filtration. It appears as the major limitation with the use of membranes in wastewater reclamation that leads to reduced efficiency and a shorter membrane life. Fouling happens during the filtration operation with clogging of membrane pores by several mechanisms. As a result, significant decrease of permeate flux can be observed and the effluent quality can be affected adversely (Kumbasar & Körlü, 2001).

In fact, numerous studies have been done to investigate membrane fouling or resistance development in the membrane filtration of different wastewater effluents. For example, Babu & Gaikar (2001) compared the performances of cellulose triacetate (CTA) and regenerated cellulose (RC) membranes in the means of their relative fouling during the UF of bovine serum albumin (BSA) solutions. They concluded with the result that RC is a better membrane for protein removal by its lower fouling tendency because of its higher hydrophilic nature.

In this context, enhancement of anti-fouling properties of membranes is very essential. In order to achieve this goal, one should examine firstly the fouling behaviors of membranes. Xu et al. (2016) tried several modifications on polyether sulfone (PES) membrane by natural amino acids grafting on its surface in order to enhance the anti-fouling properties of the membrane. And as a result, the PES membranes modified with charged amino acids were found as having improved antifouling characteristics against protein adsorption.

In this study, membrane fouling problem in the reclamation of RDW from textile industry is addressed. The aim of the work is pointing the most suitable UF membrane type for RDW treatment with regards to its fouling behavior and treatment performance. UF application was chosen because UF can enhance the chance of the reclamation of brackish water for reactive dyeing bath. By using a real textile effluent, effects of salinity and possible other auxiliaries used in real cases were also investigated. As the majority of the studies in literature focused on membrane based treatment of synthetic wastewaters, using real RDW as feed water made this work more challenging and innovative.

The RDW samples were taken from a textile mill where dyeing and following rinsing steps are realized. In order to observe the fouling more clearly, only dyeing bath effluent was used in the filtration tests. This wastewater was containing reactive dyes, salt, soda and caustic so that foulant concentrations in this wastewater were higher than the ones in the wastewater coming from proceeding rinsing steps. Consequently, membranes would be less prone to fouling when they are used in filtration of rinsing effluents.

Within this context, conventional commercial membranes such as polyether sulfone (PES), regenerated cellulose (RC), thin film composite (TFC) and poly(piperazine amide) (PPZ) were used. These membranes were compared based on their permeate flux changes, fouling tendencies/cleanabilities and color, total organic carbon (TOC), turbidity and conductivity treatment efficiencies. As a concurrent execution, in order to correlate membrane surface and fouling characteristics, the contact angles and roughness of these different UF membranes were investigated.

CHAPTER 2

BACKGROUND INFORMATION

2.1.Textile Industry

By 2011, the world population has passed the 7 billion mark, and today it is increased to approximately 7.5 billion. Essential requirements for all the people are food and clothing. In order to fulfill this need textile and clothing industry became an irreplaceable part of mankind. On the one hand when the size and importance are taken into consideration, textile and clothing industry can be placed in the second place (Shishoo, 2012). On the other hand when the effluent volume and content is thought, the wastewater from textile industry can be classified as the first ranked source of industrial pollution. Along the processes used in textile industry, dyeing and finishing steps are the biggest water utilizers (Sen & Demirer, 2003). According to estimations, 100,000 different commercial dyes are available in the market and over 0.7 million tons of dye-stuff are produced each year (Robinson et al., 2001). In addition, these dyes and other chemicals used in dyeing are developed as resistant to influences coming from environment (Hendrickx & Boardman, 1995). Because of that and the inefficiency in dyeing process, tons of these dyes are present in the effluents and their treatment by conventional processes is not possible most of the times (Chequer et al., 2013).

A brief information about textile manufacturing processes and the important characteristics of textile effluents will be given in the following subtitles.

2.1.1. Textile manufacturing processes

Depending on the fiber used in the mill, manufacturing processes can differ from each other. Natural and synthetic fiber types can be seen in Table 2.1. Nevertheless, production steps can be divided into two main processes as wet and dry processes in general (Verma et al., 2012).

Dry processes generally produce solid waste e.g. waste fabric from mechanical operations while wet processes (Figure 2.1) such as bleaching, dyeing, finishing etc. producing wastewater.

Table 2.1. Some fibers used in textile manufacturing (Multilateral Investment Guarantee Agency, 1996)

Natural Fibers	Synthetic Fibers
Wool	Nylon
Cotton	Acrylic
Silk	Polyester

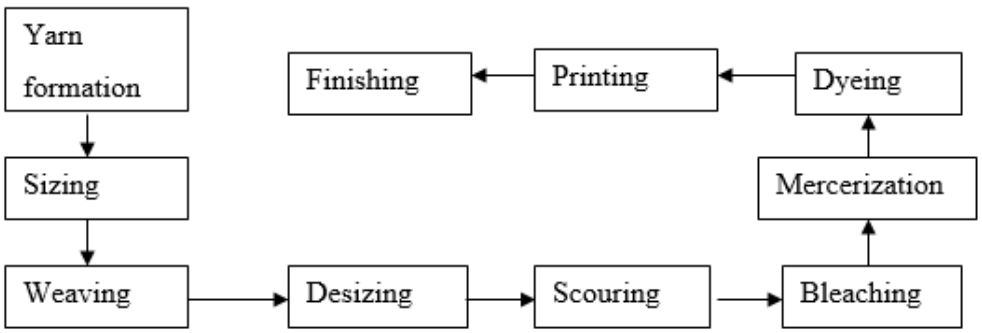

Figure 2.1. General wet processing flow diagram in a textile mill (Holkar et al., 2016)

Sizing

Aim of the process is preparing the yarn for further processes which can give damage to it. Sizing includes chemicals such as starch and acrylates increasing the yarn resistance to abrasion or tension while weaving, bleaching, mercerizing, dyeing and finishing (Petrini et al., 2015).

Desizing

After sizing, weaving step takes place. While the sizing agents are protecting the yarn during weaving, these agents should be removed for further processes. Desizing is done for removing the chemicals which can affect dyeing by reacting with dye molecules. The most general way of desizing is using enzymes to clean the yarn from starch or synthetic sizing agents. Starch can be converted into water soluble molecules after desizing (Holkar et al., 2016).

Scouring

Even after desizing, some impurities can still create problems for further processes. For natural fibers, these impurities can be grease, oils, minerals, antistatic agents etc. Scouring is applied in order to remove these pollutants using alkaline solutions (Patel, 2015).

Bleaching

Bleaching process is done for whitening the yarn (Babu et al., 2007). Hypochlorite was the most common bleaching agent earlier. Nowadays, hydrogen peroxide and peracetic acid, which are biodegradable, are used to remove the natural color of the yarn (Holkar et al., 2016).

Mercerization

Purpose of mercerization is improving the dye uptake ability, luster and stability of the cotton fabric. Sodium hydroxide (NaOH) is used for mercerization (Holkar et al., 2016). The cotton fabric swells in this alkali solution so that the luster of threads increases (Patel, 2015).

Dyeing

Dyeing process depends on the fiber to be dyed. Table 2.2 shows some fiber types and appropriate dyes for them. It must be known that there is no dye which can paint all

possible fibers and no fiber that all existing dyes can be applied on (Chequer et al., 2013).

During the process, fiber is treated with dye and auxiliary chemicals (Figure 2.2) such as surfactants, chelating agents, acids/bases etc. Depending on the end use of the fabric, different techniques can be used in order to provide appropriate fastness of color (Moore et al., 2004). Dyeing requires a large amount of water especially cotton which is the most common used fabric around the world (B. R. Babu et al., 2007).

Table 2.2. Dye distribution according the fibers (Environmental Technology Best Practice Programme, 1997; Holkar et al., 2016; Wang et al.,2011)

Fibers	Dyes
Cotton	Reactive dyes, Direct dyes, Vat dyes, Azo dyes, Pigment, Sulphur dyes
Wool	Acid dyes
Polyester	Disperse dyes, Azo dyes
Silk	Direct dyes, Acid dyes

Printing

Printing can be separated from dyeing only by the dye application practice. In this step, particular parts of the fabric is subjected to the color. In order to prevent dye spread, a thick paste of dye is applied on the fabric. The effluent characteristics are also very similar to dyeing effluent. (Bisschops & Spanjers, 2003; Holkar et al., 2016).

Finishing

The aim of the different finishing processes is to upgrade the value of the textile and make them more acceptable to the consumer. It involves various treatments techniques after preliminary treatments to remove any impurities. Some of the finishing processes are bleaching, glazing, softening etc (Abrahant et al., n.d.; Moore et al., 2004)

In literature, dyeing and finishing processes are accepted as the most water intensive steps of textile manufacturing. Kant stated that according to The World Bank data, textile dyeing and finishing are responsible from 17 to 20 percent of industrial water pollution (Kant, 2012). Especially dyeing wastewater will be discussed in detail in the following parts of the thesis.

Definition	Composition	Function
Salt	Sodium chloride Sodium sulphate	Neutralize zeta potential of the fibre; Retarder
Acid	Acetic and sulphuric acid	pH control
Base	Sodium hydroxide Sodium carbonate	pH control
Buffers	Phosphate	pH control
Oxidizing agents	Hydrogen peroxide Sodium nitrite	Insolubilize dyes
Reducing agents	Sodium Hydrosulphite Sodium sulphide	Solubilize dyes; Remove unreacted dye

Figure 2.2. Some auxiliary chemicals used in dyeing process (Correia et al., 1994)

2.1.2. Wastewater characteristics

As being one of the most water intensive industries, textile industry is also one of the most chemically intensive industries. The toxic content of its wastewater is a big threat for environment and human health (Kant, 2012).

As it can be seen from Table 2.3, wet processes of textile industry have effluents including wide range of pollutants such as pH, COD, BOD, TDS, TSS, temperature and color. By the chemicals used as auxiliary for the processes, the toxicity of

wastewater especially from dyeing, printing and finishing processes is very high (Verma et al., 2012).

Table 2.3.Effluent characteristics of textile industry wet processes

Process	**Effluent Characteristics**
Sizing	High BOD, medium COD
Desizing	BOD, high COD, temperature
Scouring	Oily fats, BOD, high pH, temperature, dark color
Bleaching	High pH, TDS
Mercerization	High BOD, high pH, suspended solids
Dyeing	High toxicity, BOD, high dissolved solids, high pH, color
Printing	High toxicity, high COD, high BOD, high dissolved solids, high pH, color
Finishing	Low alkalinity, low BOD, high toxicity

Dyeing process is responsible from a wide portion of the total wastewater coming from the industry (Verma et al., 2012). According to Kant (2012), this portion corresponds to 15-20 percent of the total effluent. Although there is such a great concern, diversity of operational modes and dyes makes the identification of dyeing wastewater very complicated (Correia et al., 1994). Operational mode can be batch or continuous according to the fabric characteristics and the required dyeing excellency (Chequer et al., 2013).

The toxic effect of dyeing wastewater arises mainly from the heavy metal content of dyestuff such as acid dyes containing chromium or direct dyes with copper etc. Some reagents used in process can also include heavy metals like mercury (Correia et al., 1994).

In the earlier times, natural dyes were used to dye the fabric. However, because of the weak fastness gained by the natural dyes, a need for some modifications had raised. Mordants such as chromium, have started to be used in order to improve the fastness and color fixation. This was the discovery of synthetic dyes (Kant, 2012).

2.2. Reactive Dyeing Wastewater (RDW)

Among all natural and synthetic fibers, cotton is the most commonly used one globally. Considering their useful technical properties, reactive dyes are used in dyeing more than half of the global cotton production. However, the nature of reactive dyes is very dangerous and they are most unfavorable type of dye for the environment (Allegre et al., 2006). Hessel (2007) claimed that in order to dye 1 kg of cotton; 40 g reactive dye, 70-150 L water and 0.6 kg NaCl usage is required. As they provide high washing fastness and intense colors for cotton, reactive dyes have a wide application in this high water demanding industry. Their low fixation degree results in existence of high amount of unfixed dye in the wastewater coming from dyeing or rinsing bath (López-Grimau et al., 2015).

Even if the exact characteristic of RDW depends on the recipe used in dyeing, some constituents are essential for every recipe. These pollutants in RDW can be listed as:

-**Dyestuff**: Unfixed hydrolyzed reactive dyes, approximately 20-30% of the applied dye. This portion is guilty for effluent coloration.

-**BOD/COD**: Coming from organic compounds or dyeing auxiliaries.

-**Salinity**: Salts used for the dye fixation.

-**Suspended solids**: Especially fiber.

-**pH** (around 10) and high **temperature** (Allegre et al., 2006; Wenzel et al., 1996)

2.3.Treatment Methods for RDW

As a result of their high pollution load, treatment of RDW is a big concern. Several studies are applied for finding the most efficient and economic techniques including biological, physical, chemical or combined treatment methods such as physicochemical methods(Z. Wang et al., 2011).

Activated sludge process which is the most traditional treatment technique is not a good alternative for RDW because of its providing poor degradation of residual dyes (López-Grimau et al., 2015). Reactive dyes have low biodegradability so that they can resist to biological treatment. According to researches; only 53% of 87 dyestuff is biodegradable (Al-Kdasi et al., 2004). The desired removal of color and other non-biodegradable constituents can be achieved by adding specific adsorbents such as activated carbon to the system (Allegre et al., 2006).

Activated carbon -more generally adsorption techniques- has a great capacity for decolorisation (Holkar et al., 2016). However direct contact with RDW creates a clogging problem because of the high suspended solid content of RDW. And also, while they can successfully adsorb water soluble dyes, such as reactive dyes, it can be inadequate for removal of insoluble dyes (Z. Wang et al., 2011). The high cost of activated carbon itself and regeneration is another limitation. As a result, pretreatment i.e. flocculation–decantation treatment is necessary for activated carbon application in order to make the adsorbent life longer and have more efficient treatment (Allegre et al., 2006).

Coagulation-flocculation processes are physicochemical processes producing large amount of sludge. The production and the treatment of that sludge are the major limitations for coagulation-flocculation process. They are more effective on removal of insoluble dyes such as disperse dyes, while the decolorisation efficiency is very low for soluble dyes i.e. reactive and vat dyes. The process generally used for organic removal (Allegre et al., 2006; Holkar et al., 2016).

Advanced oxidation processes (AOPs) are designed to destroy compounds which are very difficult to be oxidized by conventional oxidation. Dyestuff and complex organics at low concentration cannot be treated by conventional oxidation.

AOPs generate and use hydroxyl free radical ($HO\cdot$) as strong oxidant to eliminate color and organics in RDW. UV radiation, ozone, hydrogen peroxide and Fe^{2+} are some of the agents used by combinations in AOP (Al-Kdasi et al., 2004).

The techniques mentioned above have several advantages and limitations with different real RDW applications. For example, in the case of oxidation and physical treatment methods, while they are very effective on color removal, the wastewater volume is a problem. That means they can only be applied on small volumes. On the other hand, membrane filtration does not have a volume limitation while the cost is its major disadvantage (Holkar et al., 2016).

Membrane process is mainly used for recovery and reuse of water for the production processes (Holkar et al., 2016). One should consider the desired permeate quality while choosing the particular membrane process (MF,UF,NF or RO). For RDW treatment, they provide high separation of hydrolyzed dyes thus color, organics and dyeing auxiliaries (Allegre et al., 2006).

2.4. Membrane Technology

When it is looked for the history of membranes, at the end of World War II, membrane technology was started to be used for drinking water treatment. This was the first significant application of membrane. The critical step for transformation of membrane from being a laboratory mechanism to being a tool for industrial application was taken in the early 1960's (Baker, 2012).

At the beginning of 1960's, Loeb and Sourirajan had discovered the first asymmetric polymer membrane and the industrial applications of membranes started to be feasible (Noble & Stern, 1996). The reason of this discovery being very seminal was the membrane having high flux and mechanical support (Baker, 2012).

Between 1960 and 1980, the position of membrane process had changed significantly. High performance membranes were built by including interfacial polymerization and multilayer composite casting and coating. Nowadays, membranes having 0.1 μm or less thin selective layers are designed by several companies (Baker, 2012).

Today, membrane processes have a large application area such as sea water desalination, separation of vapors or gases, treatment of industrial wastewater and important constituents' recovery, concentration or purification of macromolecular mixtures for certain industries (Strathmann et al., 2006).

2.4.1. Principles of Membrane Filtration

Membrane is a selective barrier which can use the permeation rate of different components or their size difference for separation. There are two basic models to characterize the permeation mechanism: solution-diffusion and pore-flow model (Figure 2.3).

Nonporous membranes such as RO membranes work with solution-diffusion mechanism. This means that dissolution and following diffusion of permeants occurs through the membrane by a concentration gradient. So that, separation takes place with the difference on the dissolution and diffusion rates of different permeants (Baker, 2012).

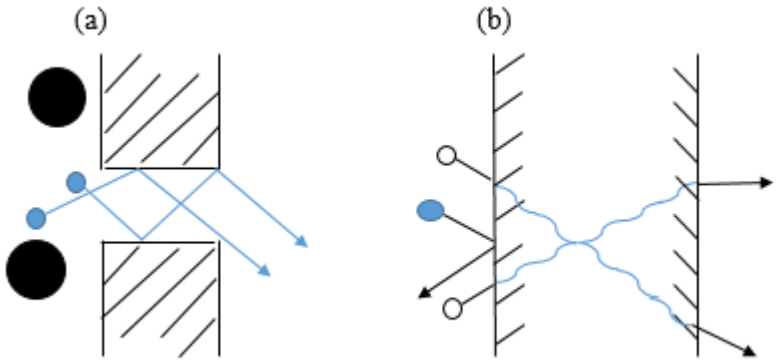

Figure 2.3. Illustrations of transport mechanisms (a) size exclusion and (b) solution-diffusion models

In order to obtain practical fluxes in solution-diffusion controlled processes, membranes should be very thin and also large concentration gradients should be achieved. Otherwise, the flux will be very low because of the slow nature of diffusion (Baker, 2012).

Table 2.4. Transport mechanisms used in some type of membrane processes (Drioli, 2016)

Process	Transport mode	Driving force
Microfiltration	Size exclusion	Pressure difference
Ultrafiltration	Size exclusion	Pressure difference
Nanofiltration	Size exclusion, solution diffusion, charge exclusion	Pressure difference
Reverse Osmosis	Solution diffusion	Pressure difference
Pervaporation	Solution diffusion	Chemical potential or concentration difference
Electrodialysis	Charge exclusion	Electrical potential difference

In the pore-flow model, the separation mechanism is size exclusion. Mainly microfiltration and ultrafiltration processes are working with this mechanism. This type of permeant transport is described by the Darcy's law. Briefly, it is a pressure-driven process in which permeants are transported through the membrane by convective flow (Drioli, 2016). While some of the constituents can permeate, some are rejected from membrane pores because of their size. Generally pore-flow mechanism provides higher fluxes than solution-diffusion can afford. (Baker, 2012). Transport mechanisms used in some of the membrane operations can be seen in Table 2.4.

Membranes can be placed in either dead-end or cross-flow modules. These operations differ from each other by the direction of feed flow according to membrane position and pressure gradient. A schematic diagram of operations is shown in Figure 2.4.

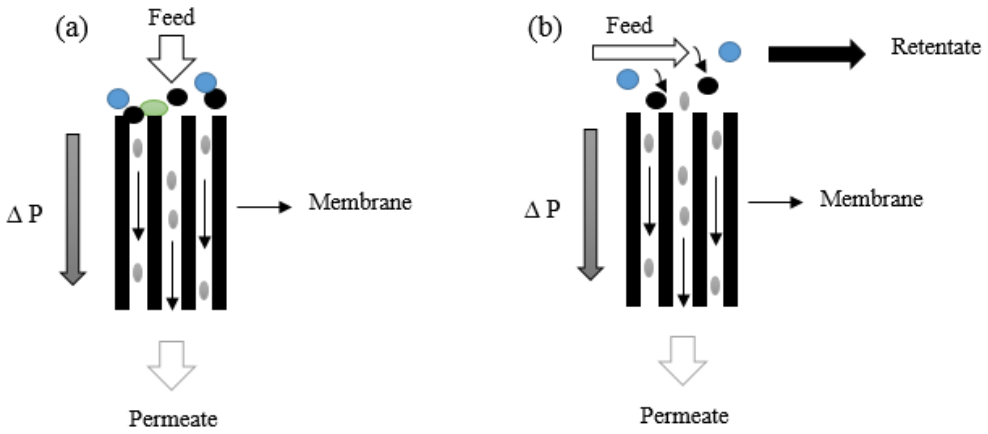

Figure 2.4. Illustration of (a) dead-end and (b) cross-flow operations

The retentate solution is not seen in Figure 2.4a. At the time=0, the feed is introduced to membrane however; after the filtration starts, the name of 'feed' stream turns into 'retentate'.

The valuable stream of the process depends on the aim of operation. That means if the purpose is concentrating a solution, then the retentate can be the product stream. While in purification case, both the permeate and retentate streams can generate the preferred product depending on the constituents wanted to be removed (Mulder, 1996).

Apart from transport mechanisms and operational modes, morphological differences of different membranes are also important to classify the membranes. All commercial membranes can be classified as one of the two main types according to their morphology: Symmetric and asymmetric membranes (Figure 2.5).

Symmetric membranes have homogenous structures. The total thickness of membrane determines the extent of resistance and by reducing membranes' thickness, the flux obtained can be increased. In the case of asymmetric morphology, the composition of membrane is either physically or chemically heterogeneous (Baker, 2012; Mulder, 1996).

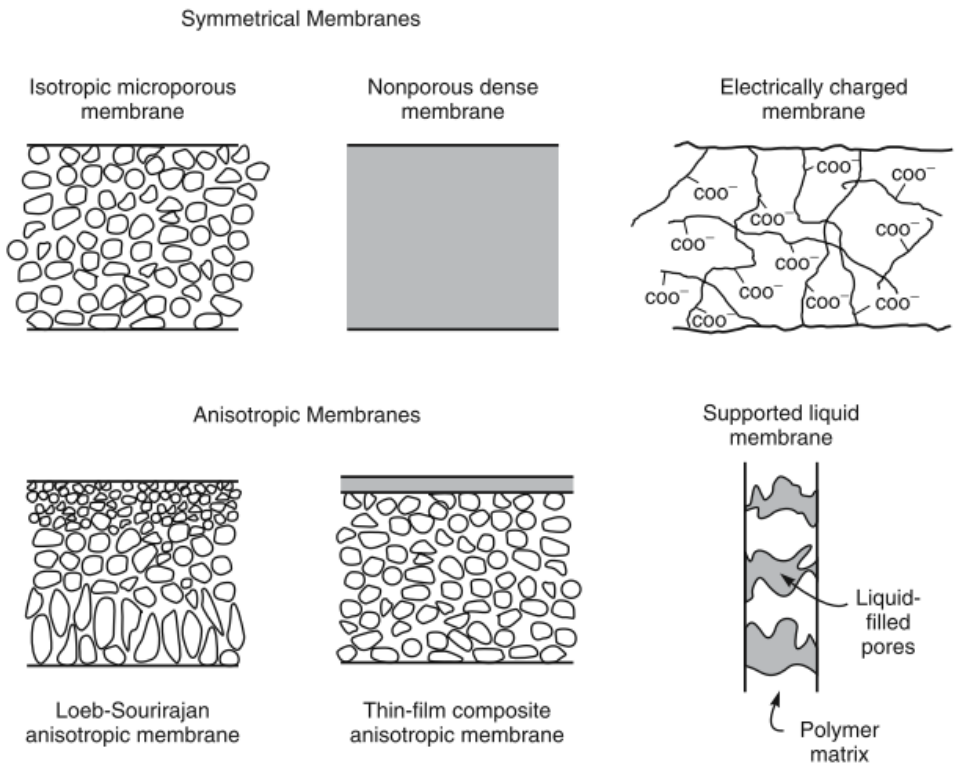

Figure 2.5. Symmetric and asymmetric membrane types (Baker, 2012)

Nearly all membranes which are available commercially have asymmetric structures because of that they can provide higher fluxes than symmetric ones (Baker, 2012).

As mentioned earlier, Darcy's Law represents the transport mechanism in pore-flow model. It covers the relation between the pressure gradient and the volume flux over the membrane (Drioli, 2016). The flux equation derived from Darcy' Law is given as

$$\mathbf{J}=\frac{\Delta \mathbf{P}}{\boldsymbol{\mu}*\mathbf{R}} \qquad \text{(Eqn. 1)}$$

where J is the permeate flux, ΔP is pressure gradient, μ is the viscosity of permeate and R is resistance of a medium to flow. Volume flux is calculated as permeate volume per time and per area by the definition and the common unit is L/m^2*h (LMH).

During filtration, total resistance (R_{total}) to flow increases by the addition of the resistance by concentration polarization (R_{cp}) and fouling ($R_{fouling}$) to the intrinsic

membrane resistance (R_{mem}). Fouling phenomena will be discussed more in detail in Section 2.4.2.

Another important term used for analyzing membrane characteristic is permeance which is the penetration and permeation ability of components through a membrane (Drioli, 2016). While flux is a measure of filtration rate depending on driving force applied, permeance is a property independent from extent of driving force. In the case of pressure driven operations, permeance is calculated with the equation below:

Permeance (LMH/bar) = Flux(LMH)/Pressure Difference(bar) (Eqn. 2)

From the definition of membrane, selectivity is the underlying parameter for a successful filtration (Mulder, 1996). Separation takes place by the help of the permeance or permeability (permeance times membrane thickness) difference of the species. The selectivity (α) for a binary mixture with the components a and b can be determined as below (Drioli, 2016):

$\alpha_{a,b} = P_a/P_b$ where P_a and P_b are the permeances of the components a and b.

Selectivity can also be expressed by retention of components. While the solvent of mixture can pass through the membrane, solutes can be partially or fully retained in the retentate stream. It is shown via percentages and calculated as:

$R(\%) = 1 - (C_{perm}/C_{feed})$ (Eqn. 3)

where C_{perm} is the concentration of the solute in permeate and C_{feed} is the concentration of solute in feed at t=0 (Mulder, 1996).

Pressure driven membrane processes namely microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), are distinguished by the retained particle size (Porter, 1989). Figure 2.6 explains the scale of the pore sizes and the compounds that they can remove.

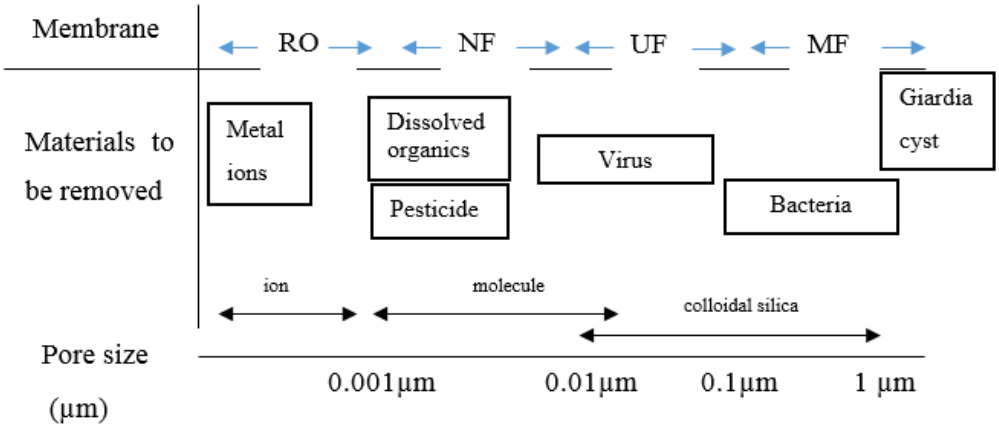

Figure 2.6. Pore size distribution of different membrane processes ("3R Technology," n.d.)

RO is one of the first applications of membrane technology which was used to convert seawater to drinking water. Earlier, cellulose acetate (CA) was used in RO membrane manufacturing, and now in addition to CA, thin film composite using different polyamides is one of the primary materials used in both RO and NF applications (AWWA, 2007).

While MF and UF processes can be classified as low pressure required membrane applications; RO and NF need higher pressure gradients. RO membranes are generally characterized according to their NaCl retention (Munir, 2006). So that the required pressure for RO is dependent on the total dissolved solid concentration because of the osmotic pressure created by them (AWWA, 2007). The application areas for RO technology can be listed as seawater desalination, brackish water treatment, drinking water production and wastewater treatment (Jiang et al., 2017).

NF has a wide range of application possibilities. Even if NF can be an alternative for RO membranes in removing inorganic salts and small organics, they differ from each other in many details. For example, NF results in lower rejection of monovalent ions however it provides higher flux and less energy requirements (Muntha et al., 2017) . As well as water softening and desalination processes, pulp and paper, food, chemical and pharmaceutical industries are also common industries in which NF can find a place for itself (Nunes & Peinemann, 2006).

As it is mentioned before, MF and UF membranes work with size exclusion so that removal of ions is not possible with their large pores. They are mainly used for removing particulate matter. Materials used in their manufacturing are polymers such as polypropylene, polysulfone, polyether sulfone, cellulose acetate, polyvinylidine fluoride etc. (AWWA, 2007).

UF membranes are commonly used to remove macromolecular particles for example proteins. Because of that, the characterization of UF membranes can be made by its protein rejection ability. The molecular weight cut off is a specification used for defining the size (molecular weight) of the particles which are 90% rejected by the membrane (Cheryan, 1998; Drioli, 2016). And instead of pore size, MWCO is used for characterization for UF membranes (and also for NF membranes). Dalton (Da) is the unit for MWCO.

Lastly, there are several advantages and disadvantages of membrane process. The energy saving gained by applying membrane technology instead of other separation processes is one of the most important advantages of membranes. Further advantages can be listed as easy operation and high separation efficiency and so on (Ranganathan et al., 2007). However, the limitations are also critical for membrane users and environment. For example process can require special equipment or cleaning and concentrated waste can be real problems (Cheryan, 1998). Most importantly, membrane fouling which makes the membrane life shorter is an obstacle for guaranteeing the economic viability of membranes (Thamaraiselvan & Noel, 2015).

2.4.2. Membrane Fouling

Membrane fouling is the most important limitation which slows the growth of membrane application. Basically, it represents the flux decline which can be seen during and also after filtration process. The reason for flux decline is an increase on resistances coming from different origins. The possible reasons for resistance building are shown in Figure 2.7. Fouling can also cause selectivity loss or further unwanted selectivity (Smolders, 1990).

The tendency for fouling differs for each membrane. As well as the nature of solutes to be fouled, the surface morphology and physicochemical properties of membrane affect the membrane performance and the extent of fouling. (Cheryan, 1998; Muntha et al., 2017).

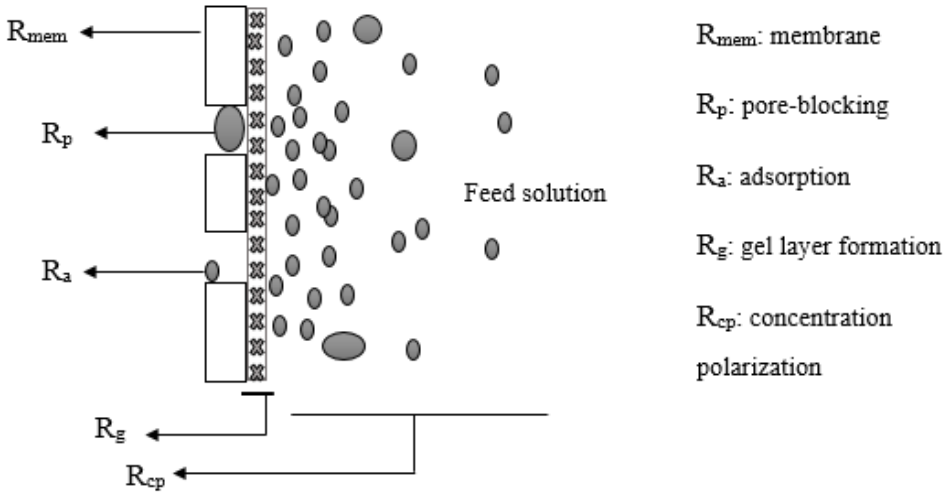

Figure 2.7. Possible reasons for flux decline

In Figure 2.7, components of total resistance affecting the permeate flux are visually summarized. The reasons for flux decline can be divided as CP (which is reversible and inherent) and fouling (partially or fully irreversible), separately.

That means total resistance can be subdivided in three: 1) intrinsic membrane resistance, 2) resistance from CP and 3) fouling resistance (including adsorption, gel layer and pore blocking resistances).

$$R_{total} = R_{mem} + R_{cp} + R_{fouling} \quad \text{(Eqn. 4)}$$

where R_{total} refers to total resistance, R_{mem} to intrinsic membrane resistance, R_{cp} to CP resistance and $R_{fouling}$ to fouling resistance. So that; the flux equation can be written as:

$$\boldsymbol{Flux} = \frac{\text{driving force}}{\text{viscosity} * \text{Rtotal}} \quad \text{Eqn. (5)}$$

Components of feed mixture have different permeation rates so that one can permeate more easily than other components. In some cases, some solutes totally retain in the feed side. Either partially or fully retained, they accumulate near to surface of membrane. As a result, the concentrations at the membrane surface and in the bulk solution are different from each other. This difference results with a resistance to flow. Finally, the permeation changes through the membrane. This resistance is called as the CP resistance (R_{cp}) and it is an inherent result of membrane separation (Baker, 2012; Mulder, 1996).

CP occurs only during filtration; that means after filtration, by the elimination of permeation, the effect of CP will also be removed. Cheryan (1998) claimed that if it is only a polarization it can be reversed and is not a true fouling. This reversible resistance is still a serious problem because of the flux decline that it caused during the operation.

There are some precautions to minimize the effect of CP. Increasing the turbulence or cross flow velocity in the feed stream can be a hydrodynamic improvement, for example. Alternatively, decreasing the pressure gradient (transmembrane pressure) can result in a decrease on CP (Cheryan, 1998; Drioli, 2016).

As being an important part of total resistance, fouling can create resistance by occurring in different forms. The dominating form of fouling can change by several parameters, such as:

-Type of membrane (i.e. RO or UF can have different fouling mechanisms)

-Physicochemical characteristics of membrane (depending on materials)

-Concentration and nature of components (solutes and solvents)

-Interactions between membrane surface and solute or solute and solute

-Hydrodynamics of process (Cheryan, 1998; Field, 2010)

By the effect of above parameters, the buildup of material can be as adsorption, pore-blocking or gel (cake) layer formation. Adsorption occurs by the existence of specific interactions between solutes and membrane (Field, 2010). Amount of adsorbed materials can differ by the type of solute, membrane material etc. For example, in the separation of proteins, hydrophilic membranes would be a better choice because of the higher adsorption tendency of hydrophobic membranes with proteins (Smolders, 1990). Pore blocking is simply the closure (total or partial) of membrane pores. So that dense membranes using processes such as RO are not suitable for pore-blocking (Franken, 2009).

$$R_{fouling} = R_a + R_p + R_g \quad \text{(Eqn. 6)}$$

where R_a stands for adsorption resistance, R_p for pore blocking resistance and R_g for gel layer resistance.

In an ideal filtration theory, flux would increase as long as transmembrane pressure (TMP) increases. However, in real case, there is a limiting flux at critical TMP. That means after a certain TMP value, there is no further flux increase (Karode, 2001). Polarization resistance occurs by the concentration difference between bulk solution and boundary layer as long as the solutes remain in solution (Franken, 2009). When the rejected particles start to deposit on the membrane surface, this resistance is no longer caused by CP but by gel layer that formed on the surface. The limiting flux is observed at a certain gel concentration (Karode, 2001). When there is gel layer formation, generally it is the predominant form of fouling in the process. Sometimes this layer can behave as a second membrane and cause a better quality effluent by reducing the flux / increasing the selectivity (X.-M. Wang & Waite, 2008).The decrease in average flux causes a high capital expense which is the most undeniable result of fouling. Additionally, the cleaning agents used for restoring the flux can shorten the membrane life. Materials having low tolerance for different pH values can be affected by powerful cleaning agents very easily. CA is one of these sensitive materials while other polymeric membranes such as polysulfone (PS) and PES are more durable under the same cleaning procedures (Cheryan, 1998).

2.4.3. Membrane Materials

Membrane materials can be classified firstly as synthetic and natural membranes. Most of the materials used for industrial and municipal applications are synthetic and they can be subdivided into inorganic and organic (polymer) membranes.

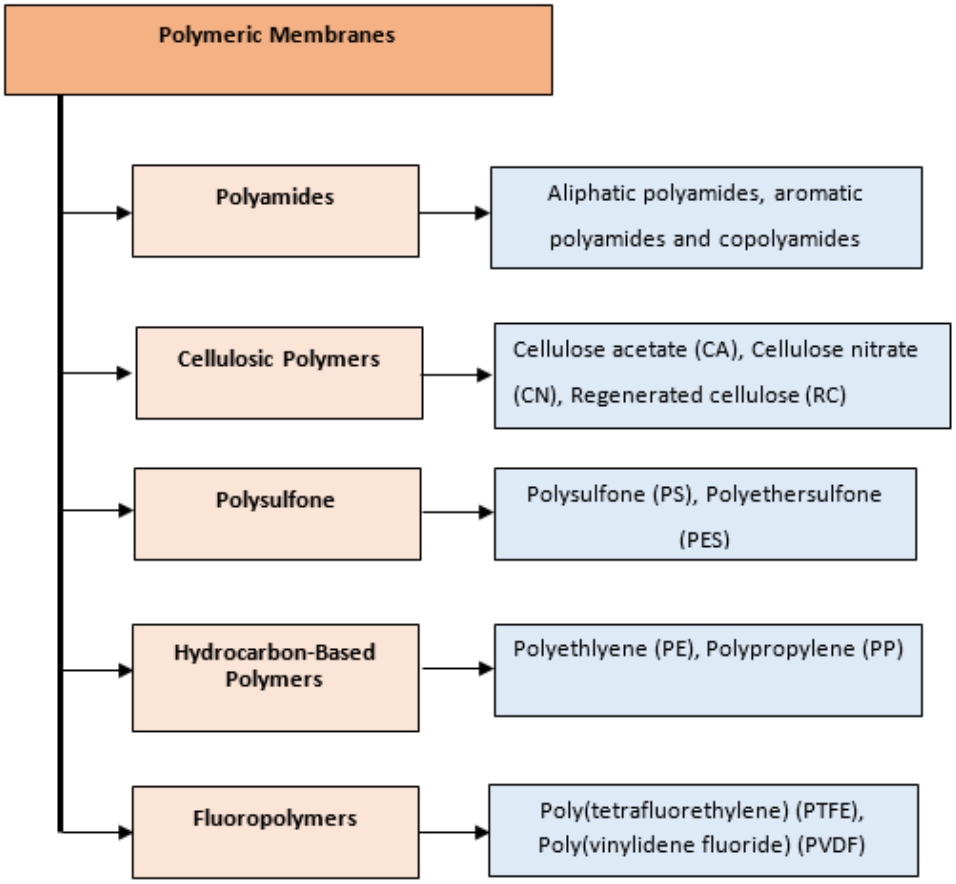

Figure 2.8. Polymer types used in membrane manufacturing (Saleh & Gupta, 2016)

Inorganic membranes are made of ceramics, glass, zeolite or metals. Although they have high thermal stability and chemical and pH resistance, they are typically brittle and have larger footprints than organic membranes. Polymeric materials are the most common ones used in membrane manufacturing. As there are large number of different polymers, the most suitable one for the specific operation should be selected and used for higher efficiency (Saleh & Gupta, 2016). Ciardelli (2001) claimed that polymeric membranes are very promising for the textile industry effluents. Some of the possible

polymers used for membranes are listed in Figure 2.8. In addition, composite membranes where an ultrathin layer is placed on a polymeric asymmetric membrane are very common for wastewater treatment by ultrafiltration (Ciardelli et al., 2001).

TFC membranes consist of a mechanical porous support and a thin membrane layer formed by interfacial polymerization (Noble & Stern, 1996). As the thin layer is the selective part of the membrane, the flux obtained by these kind of membranes is relatively higher (Nunes & Peinemann, 2006) However the characteristics of TFC membranes change according to the specific thin layer polymer such as polyamide or polyethylene.

Cellulose based UF membranes are known by their low fouling tendency. Because of their hydrophilic nature, even only a clean water rinsing can be enough for regenerated cellulose (RC) membranes to return the flux to its initial value (Søtoft et al., 2015). On the other hand, their performance is not stable under high temperatures (Drioli, 2016).

PS and PES membranes have high pH and temperature stability. They can be used in MF, UF or NF applications and also they can provide the mechanical support for composite membranes (Saleh & Gupta, 2016). However; the main limitation for PS and PES membranes is their hydrophobic nature which can lead to a tendency for fouling (Cheryan, 1998) .

Polyamide (PA) based membranes are known by their high resistance to extreme pH and temperature (Bailey, 1981). They are usually used in RO and NF applications. The major problem faced with PA membranes is their low chlorine resistance. They can be easily attacked by chlorine due to their electrophilic nature created by carbonyl groups. This change in the physical and chemical nature of PA layer causes a decrease on the membrane performance and shortening of membrane life (Drioli, 2016).

2.4.4. Membrane Surface Characteristics

In the determination of the fouling behaviors of membranes during the filtration process, understanding of their nature is very essential. Surface characteristics, namely, roughness, charge, pore distribution and wettability (degree of hydrophilicity) can give an idea about their fouling tendency at the contact moment. It is because of that the solute adsorption on the surface depends on solute-membrane interactions, attraction or repulsion between surface and particle etc. (Drioli, 2016). For example, by the deviations on the surface topography, permeance quality and flux can be affected. These deviations are represented as roughness. Or else, because of the interactions between water molecules and OH^- groups in membrane structure, there is an acceptation as hydrophilic membranes being less prone to fouling than hydrophobic ones (Yu et al., 2008).

In order to investigate the physical and chemical characteristics of membrane surfaces, several analytical techniques have been used. Some of these are NMR spectroscopy (for determination of permeability), streaming potential (for membrane surface zeta potential), atomic force microscopy (AFM) (for membrane structure, morphology, roughness), contact angle (for the degree of hydrophilicity) and X-ray photoelectron spectroscopy (XPS) (for surface chemical functional groups) etc. Correlation of membrane fouling by permeate flux decline percent with that measured membrane surface characteristics is a possible strategy for understanding the reasons for fouling (Vrijenhoek et al., 2001) .

CHAPTER 3

LITERATURE REVIEW

In the aim of better use of freshwater resources, reuse of wastewater is currently a strategic approach. This practice also important for preventing the aquatic environment from deterioration which is caused by wastewater disposal. Membrane processes are now used to achieve the recyclable quality of water. RO and NF can successfully remove most of the contaminants, including dissolved organic materials. On the other hand, RO and NF need quite high energy resulting high operational costs. Comparatively, UF processes are more cost-effective by their high permeate flux (Shon etal., 2006).

In order to obtain high quality effluent for reuse, UF is generally used as a pretreatment method for NF or RO applications. More specifically, in the textile wastewater treatment, UF application is mostly accepted as a pretreatment with MF (Barredo-Damas et al., 2006; Cheïma Fersi & Dhahbi, 2008; Thamaraiselvan & Noel, 2015). In 1991, Watters et al. conducted a research on treatment of textile effluent only by UF. After various runs with a PS UF membrane, dye removal was obtained in the range of 30-90%. When Allegre et al., (2006) was studying on treatment and reuse of reactive dyeing wastewater, they claimed that by the help of the information gained by the Watters' study, UF may only be used as a pretreatment for RO or in combination with biological treatment. By contrast with this discourse, Simonič (2009) had found that some UF membranes can reach approximately 98% color and 61% COD removal for treatment of dyeing bath wastewater.

For a study conducted with real textile effluent in order to investigate the color and COD removal by hybrid biosorption and UF (Radhakrishnan et al., 2015), a PES based UF membrane (with MWCO of 50 kDa) was used. The best combination was determined as biosorption followed by UF with quite high color (99%) and COD (90-93%) removal. However, the application of direct UF resulted with a lower efficiency by 70% color and 65% COD retention. Also, when they measured the initial clean water and permeate fluxes, it was seen that there was 32.5% decline between these two fluxes. They claimed that it was due to cake layer formation on the PES membrane surface.

In another study, the fouling mechanisms were investigated for MF, UF and NF membranes used in textile wastewater treatment (Fersi et al., 2009). It was observed that the main reason of flux decline for UF membrane was CP (with 97% contribution to R_{total}). And also, they observed a sharp flux decrease at the beginning of filtration. According to the investigations on cake formation constants, a rapid cake layer formation was responsible for this sudden flux decline.

Apart from being an advantageous option with their permeate flux, UF membranes suffer from fouling phenomena which can cause a serious flux decline as mentioned in the study of Radhakrishnan et al. (2015). Irreversible portion of fouling is mostly caused by adsorption when protein solutions are filtrated. Besides, the removal of proteins from membrane is not easy even by washing with buffer solutions. The characteristics of membrane material play an important role to choose the suitable membrane for a specific process. For example, Babu & Gaikar (2001) compared the performances of cellulose triacetate (CTA) and RC membranes in the means of their relative fouling during the UF of bovine serum albumin (BSA) solutions. They concluded with the result that RC is a better membrane for protein removal by its lower fouling tendency because of its higher hydrophilic nature. CTA membranes showed higher resistance (caused by adsorbed proteins) than RC membranes. Additionally, they found out that with presence of salt in the feed solution, resistance caused by protein deposits increased.

As Reddy et al. (2005) said that application of selective modifications on membrane surfaces is a common interest to convert hydrophobic membranes' surfaces into more hydrophilic. This approach is widely accepted due to the improved antifouling properties gained by these modifications. As an example, Xu et al. (2016) tried several modifications on PES membrane by natural amino acids grafting on its surface. In the research, BSA and lysozyme including solutions were used as feed water. The results showed that for both of the feed solutions, grafted PES membranes with neutral amino acids performed much higher $R_{fouling}$ than the non-grafted PES membrane. However, the PES membranes modified with charged amino acids showed improved antifouling characteristics against protein adsorption. Additionally, they showed higher clean water fluxes and enhanced flux recovery.

Investigation of membrane material properties is very essential to understand the behavior of selected membrane for any kind of use. For example, CA and polyamide TFC membranes are the two leading types of membranes used in NF and RO applications. When a comparison is carried out between these two types of membranes, it can be said that while TFC has higher salt rejection, organic removal and pH tolerance, CA can be more advantageous in the means of being less susceptible to biofouling or having higher chlorine resistance (AWWA, 2007). So that, one should consider both the feed water characteristics and membrane material's nature in order to create optimal conditions for treatment. For instance; one of the main pollutants in RDW is its high salt content used for dye fixation. In order that, salt effect should be considered while choosing the membrane used in RDW treatment.

Luo & Wan (2011) investigated thoroughly the salt effect on four conventional commercial polymeric NF membranes which have PA and PPZ as surface materials. By using a solute transport model, they found out that the increase in salt concentration resulted with a decrease in solute-to-pore size ratio and increase on effective thickness of the membrane. Their explanation for these changes was increment of pore size by the effect of salt. The background of this idea was the knowledge of that some water molecules adsorbed on membrane pore walls (Dias & de Pinho, 1999). By the interactions between water and salt ions, the adsorbed water layer on the pore walls could have been thinner and as a result of this physical thinning, the effective pore size

and membrane thickness became wider. This effect was observed both for PA and PPZ membranes. Tsuru et al. (2000) was observed the same effect on adsorbed water layer when temperature is high but the research was carried on inorganic membranes.

As salt content of RDW can affect the performances of polyamide based membranes as mentioned, also the dyes in this wastewater can react with the polyamide surfaces. J. Babu & Murthy (2017) claimed that most of the dyes used in textile industry react with and resultantly dye polyamide surfaces. Consequently, an undesirable heavy fouling can be observed during filtration of RDW with polyamide membranes.

Another important parameter used for the fouling investigation is membrane roughness (Bes-Piá etal., 2010; Luján-Facundo et al., 2015; Zamiah et al., 2012). Fouling and roughness are interactive concepts as change on one of them can affect the other one. For example, Xiao et al. (2012) conducted a research on a UF membrane used in a full-scaled drinking water treatment plant. They used scanning electron microscopy (SEM) and atomic force microscopy (AFM) for investigation of organic fouling and accumulation behavior of foulants. The AFM results of virgin and fouled membranes showed that the accumulation of foulants caused an increase in surface roughness. Besides, several researches made on different membranes and wastewaters displayed the result that when roughness of a virgin membrane is higher than another one, it has also higher fouling tendency (Elimelech et al., 1997; Schäfer et al., 1998).

Apart from surface enhancements applied for improvement of anti-fouling properties of membranes, cleaning of membranes can also reversed the fouling effect. However, traditional cleaning methods can be still insufficient to remove all effects of fouling. One should understand the interactions between the membrane used and the foulants to apply the optimum procedure (Shi et al., 2014). For instance; in order to dissolve the accumulated inorganic salts and metal oxides, acid cleaning is preferred (Trägårdh, 1989). As being a strong oxidizing agent, nitric acid can be used also for organic fouling removal. On the other hand, this kind of strong acids may cause deterioration on membrane structure. So that, weak acids are more preferable in chemical cleaning (Shi et al., 2014). Cheryan (1998) gave some industry specific examples in his handbook. He claimed that when the main reason for fouling is salt deposition as in cheese whey treatment, the best cleaning efficiency can be reached by acid cleaning

followed by alkali cleaning. For milk processing effluent, while alkali followed acid cleaning is giving the best results, alkali cleaning is insufficient when it is applied alone. Frequent membrane cleaning is a part of membrane filtration processes for most of the users; however this could affect membrane lifespan adversely (Jiang et al., 2017).

As summarized here, membrane fouling phenomena is widely investigated by different aspects. As mentioned in Chapter 1, application of real textile effluent is rarely encountered in the literature. Additionally, application of UF is not preferred as a singular process for a saline feed water. Because the goal is generally reclamation of clean water in these kind of researches, NF or RO are the first methods coming to the minds. However in this study, real RDW containing remarkable salinity was used as feed water for UF by the goal of brackish water reclamation. And also, as a novel approach, the salinity effect on UF membranes was investigated while the essential aim was investigation of fouling behaviors of different UF membranes.

While choosing a proper membrane for a specific process, treatment efficiencies of certain pollutants are considered more than the membrane fouling. This leads a more limited life for membrane and decreases the economic feasibility of membrane process. To sum up, fouling behaviors should be considered as much as removal efficiencies of different membranes to obtain the optimum set-up for a particular application.

CHAPTER 4

MATERIALS AND METHODS

4.1. Membranes

In this study, five different (difference in material or MWCO) UF membranes were used. Properties of used membranes can be seen in Table 4.1.

Table 4.1. Properties of UF membranes used in the study

Manufacturer	Membrane	Material	MWCO ($gmol^{-1}$)	pH range
GE Osmonics	UF-GH	TFC	2000	1-11
GE Osmonics	UF-PT	PES	5000	1-11
Millipore	PLAC	RC	1000	-
Millipore	PLCC	RC	5000	-
Trisep	UF-UA60	PPZ	3500	2-11

4.2. Wastewater

RDW taken from a cotton textile mill located in Denizli was used in the filtration experiments. The wastewater samples were collected separately from four different step as it can be seen in Figure 4.1 , and wastewater #1 (dyeing bath effluent) was used in all filtration tests conducted in this study. The characteristics of wastewater #1 is shown in Table 4.2.

Table 4.2. The average characteristics of wastewater #1

Wastewater #1	TOC	SAC (m^{-1})			Turbidity	Conductivity
	mg/L	436nm	525nm	620nm	NTU	mS/cm
Dyeing Bath	500	381	326	42	277	83

This wastewater coming from the dyeing bath contains reactive dyes, salt, soda and caustic. Soda and caustic are used because dye fixation can be done successfully only in alkaline environments. The recipe of dyeing bath solution can be found in Appendix A. After this first step, neutralization step which can also be called as hot rinsing takes place. This bath is followed by soap washing bath then lastly by warm rinsing bath. Rinsing and soap washing steps are very important in order to remove the unfixed portion of reactive dyes (American Association of Textile Chemists and Colorists, 1981).

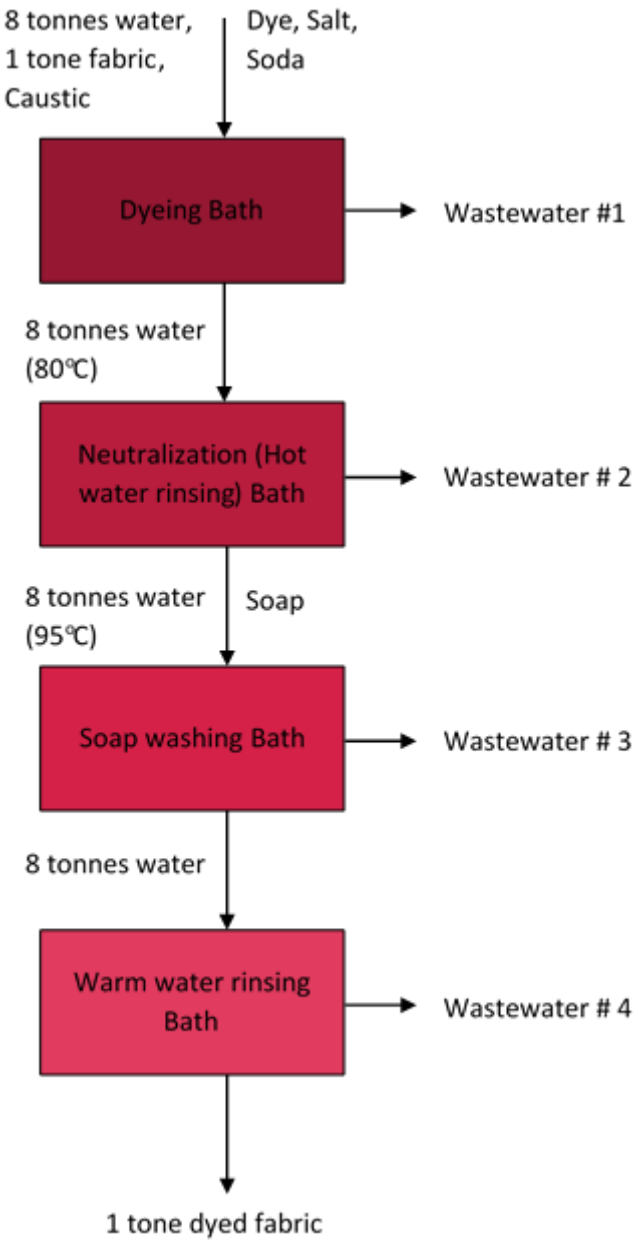

Figure 4.1. Simple flow chart of dyeing process in the mill

4.3. Methodology of Filtration Tests

In filtration experiments, 200 mL Amicon stirred cell was used as dead-end filtration unit. A simple figure which shows feed and permeate flow can be seen in Figure 4.2.

First step of filtration tests was compaction which was conducted under higher pressure (3 bar) than filtration pressure (2 bar). During compaction, ultra-pure water (UPW) was used as feed water. Compaction continued until a steady-state flux was reached. After compaction, chemical cleaning was applied to each membrane. This step was added to methodology in order to prevent unexpected effects of any coating which commercial membranes could have. Chemical cleaning procedure was including four steps. First one was putting the membrane in an acid solution (prepared with 65% HNO_3) having a pH of 3.0±0.1. Membrane had retained in that solution during 15 minutes. The second step was replacing the membrane into UPW for another 15 minutes. In the meantime, UPW was changed three times. After removing excess acid completely by UPW cleaning, membrane was removed in a base solution (prepared with NaOH) having a pH of 10.0±0.1. This step also took 15 minutes. As the final step, UPW cleaning was applied one more time in order to make excess base disappear from the membrane surface.

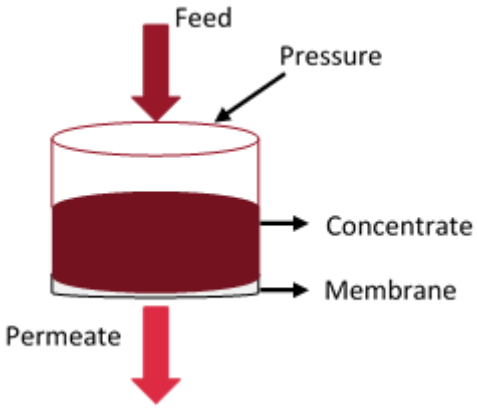

Figure 4.2. Illustration of dead-end filtration unit and flow directions of feed and permeate

The last step before filtration was permeance determination. Under different pressures (1 and 2 bar), UPW fluxes were measured. After that, by the addition of compaction flux (at 3 bar), a flux versus pressure graph was prepared. The membrane permeance (L/m^2hbar) was the slope of that graph.

After membrane clean water permeance was detected, wastewater filtration was carried out. Wastewater coming from dyeing bath was used as feed water and stirred at 150 rpm. TMP in every filtration step was 2 bar.

Filtration operation continued until volume reduction factor (VRF) reaches 2.5. While keeping the VRF constant; feed volume was not the same in every experiment. Besides the permeance of each membrane was different. Therefore; filtration by each membrane completed in different time periods.

Filtration step was followed by UPW flux measurements under 2 bar. The sequence of these measurements was as follows: UPW flux right after filtration (without cleaning), UPW flux after physical cleaning and lastly UPW flux after chemical cleaning. Physical cleaning was done by stirring the UPW at 250 rpm during 15 minutes. There was no pressure applied during this procedure.

The flux calculations of each step were done using the following equation

$J= V/(S*t)$

where J ($L\ h^{-1}\ m^{-2}$) is the permeate flux, V (L) is the permeated volume of UPW or wastewater for a given time, S (m^{-2}) is the effective surface area of the membrane, t (h) is the time.

4.4. Methods of Treatment Analysis

In order to determine the TOC content of the samples, a Shimadzu 5000A model TOC analyzer that employed "the 680°C combustion catalytic oxidation method" was used. The 680°C combustion catalytic oxidation method heats the samples to 680°C in an oxygen-rich environment inside TC combustion tubes that are filled with a platinum catalyst and achieves their total combustion in this way. An infrared gas analyzer detects the formed CO_2. The oxidized sample was then subjected to the acid spreading process and converted in carbon dioxide, in order to measure the IC (inorganic carbon) in the sample. As was mentioned, the infrared gas analyzer was used to detect CO_2, and IC concentration was obtained. The difference between TC and IC was then calculated by the instrument according to Standard Method No 5310 B (APHA, AWWA, & WEF, 1999) so as to obtain the TOC value. The standards for 0-200 mg/L range were used for the generation of TC and IC calibration curves.

By using HACH model 2100 turbidimeter and following the Standard Method No. 2130B, the turbidity of samples was measured. In order to measure conductivity and pH, a HACH Sension 378 pH/Conductivity/DO meter was used; and during the analyses of conductivity and pH, Standard Method No 2510B and 4500-H^+ were respectively followed (APHA, AWWA, & WEF, 1999).

The color of wastewater samples was measured by using a Varian Cary 100 model spectrophotometer and following the method of EN ISO 7887. Since the wavelengths between 400-500 nm, 500-600 nm and 600-700 nm respectively give absorbance for yellow and its shades, red and its shades and blue and its shades; measurements were made at three different wavelengths (436 nm, 525 nm and 620 nm.). To read the absorbance of samples, absorption cuvettes of 10 mm spectral band were used. Before the readings, feed samples were passed through 0.45 Whatman Glass Fiber filter so as to remove the suspended material that would interfere with and disturb the readings. For permeate samples, this procedure was not followed. By means of the formula provided below and by using absorbance values, spectral absorption coefficient (SAC) was obtained:

$$SAC(\lambda) = \frac{A}{d} x\ f$$

Where; A: Absorbance of the sample (cm^{-1})

d : Spectral band (mm)

f: Constant to obtain spectral absorption coefficient in m^{-1} unit

SAC : Spectral Absorption Coefficient (m^{-1})

4.5. Surface Characteristics Analysis

Atomic force microscopy (AFM), scanning electron microscopy (SEM), contact angle and Fourier-transform infrared spectroscopy (FTIR) analysis were performed to correlate the filtration results of the membranes with the surface properties. In AFM analysis, measurements were carried out by PSIA Corporation, XE-100E device (in non-contact mode) using ACTA 10M type Cr-Au cantilevers and at a scan rate of 0.37 Hz. By using this device, the surface roughness of each membrane was determined. The analysis was carried out at the laboratory of Hacettepe University, Chemical Engineering Department. The contact angle measurements were also done at the same laboratory by using Krüss DSA 10 Mk2 drop shape analyzer.

SEM imaging was made for examination of membrane surface topography. The microscope used in the analysis was FEI Nova NanoSEM 430. Membranes were coated by 10nm gold. This analysis was conducted at METU, Metallurgical and Materials Engineering Department.

For FTIR analysis, Perkin Elmer Spectrum UAT Two was used at METU, Chemical Engineering Department.

CHAPTER 5

RESULTS AND DISCUSSION

In order to analyze fouling behaviors of different types of membranes and investigate their performances; firstly, a series of filtration tests were carried out and evaluations were made based on clean water and wastewater flux changes, resistances and rejections (TOC, color, conductivity and turbidity). Afterwards, the membranes characterized in terms of flux, resistance and treatment performances were correlated with their contact angles, AFM and SEM images.

5.1. Filtration Tests and Treatment Analysis

By the aim of examination of membranes' fouling tendency, each type of membrane has been used for filtration of wastewater #1 under the same operational conditions. In order to show the reproducibility, two different pieces of each membrane have been tested. Their results were shown as Test-1 and Test-2 in flux and resistance analysis.

5.1.1. Fouling Analysis (Flux and Resistance Analysis)

RC Membranes

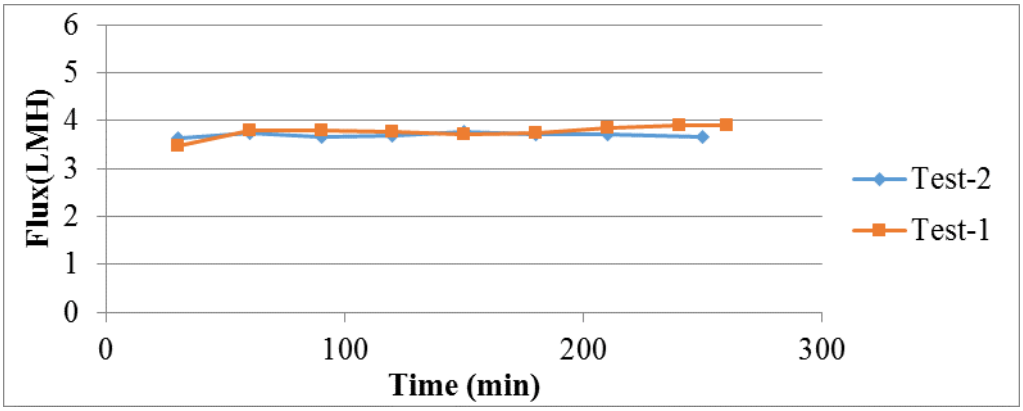

Figure 5.1. Filtration flux for 1 kDa RC membrane

Two regenerated cellulose (RC) membranes (1 kDa and 5 kDa) were tested to investigate the fouling behavior of cellulose membranes in dyeing wastewater filtration. In Figure 5.1, filtration fluxes of two different 1 kDa RC membranes are shown. As it can be seen from the figure, wastewater fluxes (Jrw) were quite stable during filtration for both of the membrane pieces tested at around 3.8 LMH. So that; there was no increased (progressive) fouling with no serious flux decline during approximately 270 min filtration. In literature, RC membranes are known by their hydrophilic nature caused by hydrogen bonding between water and hydroxyl groups in their structure. However they are not water-soluble because of the intermolecular hydrogen bonding between the hydroxyl groups (Vázquez et al., 2009). This physicochemical property makes them less prone to fouling than hydrophobic ones.

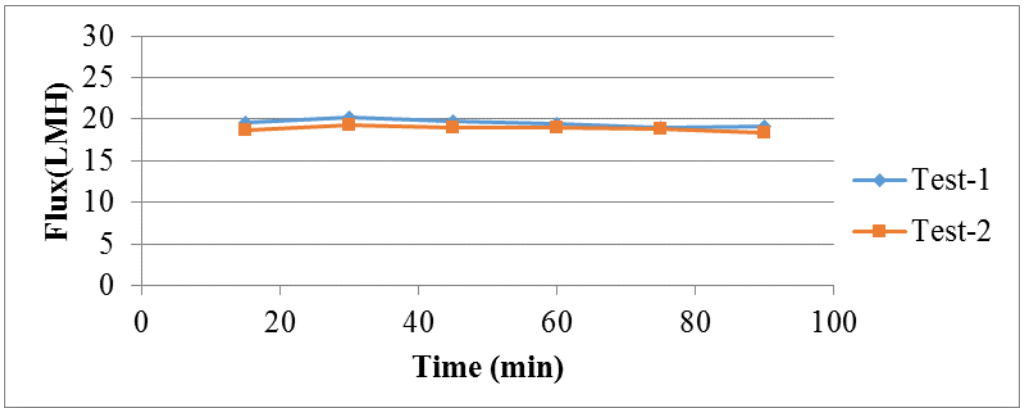

Figure 5.2. Filtration flux for 5 kDa RC membrane

When the tests were carried out with 5 kDa membrane, the same flux stability was observed (Figure 5.2) and there was no increased fouling during filtration with both pieces of membranes tested. As expected, wastewater filtration flux with 5 kDa membrane was higher than with 1 kDa and stable at around 18-20 LMH level. In parallel, average initial clean water fluxes (Jcwi) of 1 kDa and 5 kDa membranes were different; 6.5±0.5 LMH and 26.25±0.25 LMH, respectively; which were quite higher than the wastewater fluxes (Jrw) of the membranes (Table 5.1). It is clear that this difference was caused by CP and/or adsorptive fouling mechanisms.

When resistance results were evaluated for both 1 kDa and 5 kDa membranes, it was seen that, for 1 kDa RC membrane, CP and fouling resistances were very close to each other and they were remarkably higher than the resistances observed in 5 kDa membrane (Figure 5.3). For 5 kDa RC membrane, the main reason for flux decline was CP. The flux decline seen at the beginning of filtration was 94% reversed only by replacing the feed with UPW without any cleaning, implying that the decline was due to CP. Afterwards, the fouling effect on flux was completely removed by chemical cleaning as can be seen in Table 5.1. Thus; it is seen that 5 kDa RC membrane was not fouled while 1 kDa RC membrane could show higher fouling tendency. As it can be seen from Figure 5.3, each test conducted with 1 kDa membrane resulted with an irreversible portion of fouling even after the chemical cleaning.

This unexpected fouling of RC membrane could be the result of 1 kDa membrane being very tight for an UF membrane. The reason for higher fouling tendency of 1 kDa membrane can be seen more clearly when the treatment performances of these two membranes are investigated. In Section 5.1.2, it will be mentioned that 1 kDa RC membrane had much higher TOC and color removal capacities than 5 kDa RC membrane. So that; the lower MWCO of 1 kDa membrane resulted in both better treatment efficiency and more concentrated retentate region resulting the possibility of higher fouling tendency. And also, it can be said that the dominating fouling mechanisms were different for 1 kDa and 5 kDa RC membranes when the feed water is RDW.

Table 5.1. All flux changes by 1 and 5 kDa RC membranes

Flux (LMH)	1 kDa RC		5 kDa RC	
	Test-1	Test-2	Test-1	Test-2
Initial clean water flux (Jcwi)	7.02	6.00	26.03	26.50
Final wastewater flux (Jrw)	3.90	3.70	19.10	18.40
Clean water flux after filtration (Jcwf)	5.04	4.40	24.46	24.80
Clean water flux after physical cleaning (Jcwp)	6.30	4.90	25.09	25.50
Clean water flux after chemical cleaning (Jcwc)	6.40	4.90	27.10	30.20

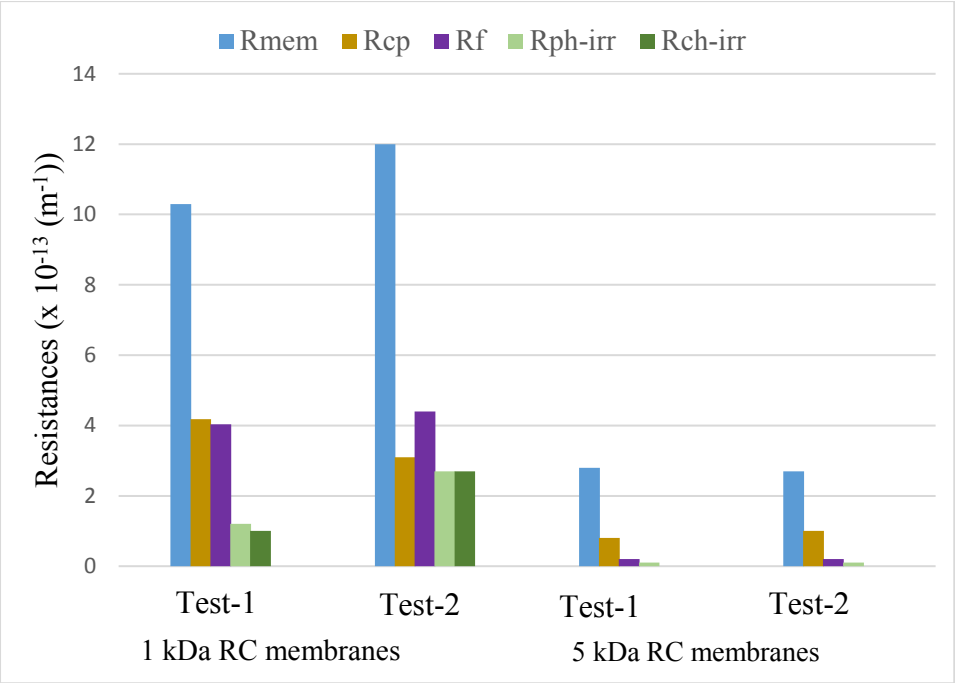

Figure 5.3. Resistance analysis of 1 and 5 kDa RC membranes

PES Membrane

As it is mentioned in Section 2.4.3, PS and PES materials are relatively hydrophobic in nature. PES membranes are more popular in treatment processes because of having better thermal and mechanical stability and higher chemical resistance than PS membranes (Idris et al., 2007). The fact remains that membrane wettability is very important to have an idea about its fouling and PES membrane is expected as to be prone to fouling.

Figure 5.4 shows the changes in 5 kDa PES membrane flux during filtration. During the first test run with the first piece of membrane, wastewater flux decreased from 19.5 LMH to 14.2 LMH, and during the second test, the change started at 20.6 LMH and stopped at 15.3 LMH when VRF was 2.5. So, there was about 26 % decrease in wastewater flux at the end of filtration test. Unlike RC membranes, the decreasing flux during filtration may indicate that the membrane was subjected to an increased fouling during filtration period.

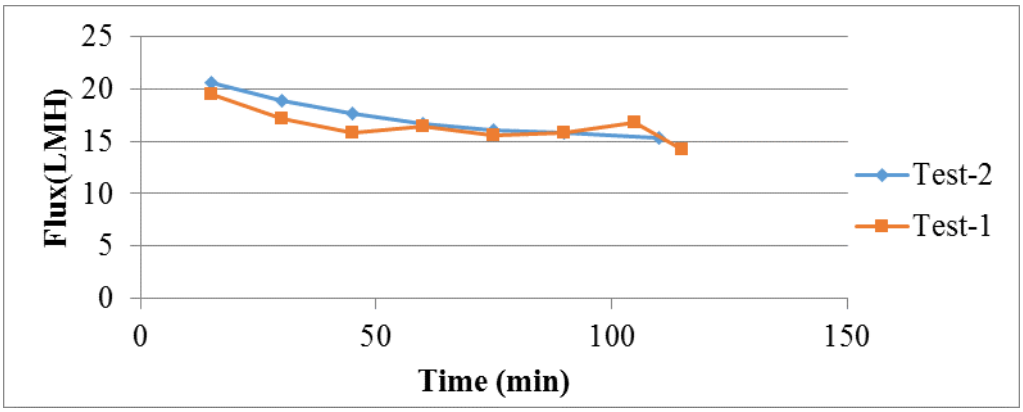

Figure 5.4. Filtration flux for 5 kDa PES membrane

Table 5.2. All flux changes by 5 kDa PES membrane

Flux (LMH)	5 kDa PES	
	Test-1	Test-2
Initial clean water flux (Jcwi)	39.90	39.90
Final wastewater flux (Jrw)	14.20	15.30
Clean water flux after filtration (Jcwf)	29.80	25.80
Clean water flux after physical cleaning (Jcwp)	36.60	32.80
Clean water flux after chemical cleaning (Jcwc)	35.70	33.60

The high initial flux (Jcwi) could take PES membrane a step forward from RC membranes. As it can be seen from Figure 5.5, resistances stemming from fouling were not high as much as 1 kDa RC membrane (Figure 5.3). And especially, 1 kDa RC membrane had quite disadvantageous initial flux when it is compared to 5 kDa RC and PES membranes. However; when it is looked more carefully, even if PES membrane

had 35% higher Jcwi than 5 kDa RC membrane, PES was also subjected to higher flux decline. Besides, the fouling was not completely reversible in the case of PES membrane. According to Table 5.2 , after physical cleaning, flux recovery was 87% and even after chemical cleaning, it was around 87%. This irreversible portion of fouling makes PES material concluded as more prone to fouling than RC.

Chemical cleaning which was the last step of filtration tests, showed some different effects on different membranes. For example, 5 kDa RC membrane had higher Jcwc (flux after chemical cleaning) than its Jcwi. The difference was not dramatic for the first test however; second test showed 14% increase between the Jcwi and Jcwc. Some portion of flux increase is not improbable after chemical cleaning. Actually, this kind of enlargements are reported in literature. For example, Meng (2017) claimed that pore size and surface porosity of PES/PVP membranes are enlarged when they are in contact with NaOH. On the other hand, in some of the experiments conducted for this research, PES membrane showed flux decline after chemical cleaning. Effects of chemical cleaning on membranes will be discussed in more detail in Section 5.5.

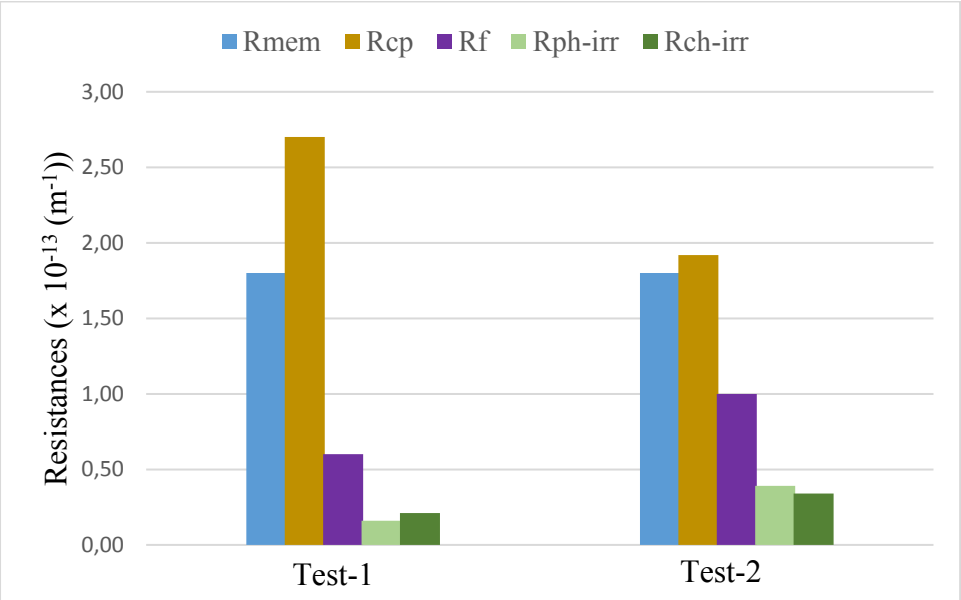

Figure 5.5. Resistance analysis of 5 kDa PES membrane

PPZ Membrane

Filtration flux observed with PPZ membrane is presented in Figure 5.6. As seen, two tests were performed with this membrane using two different pieces and a very similar, serious flux decline was observed. In the first test; flux decreased from 35.5 to 27.2 LMH, and in the second test; the decline was from 39.6 to 23.9 LMH. On the average there was 32% reduction in filtration flux with this membrane. This result indicates that fouling was a part of these experiments.

When clean water flux with these fouled membranes were measured, it was seen that there was a surprising serious increase in clean water flux as compared to the initial clean water flux (Table 5.3). Even more surprisingly, there was reduction in flux after both physical and chemical cleaning.

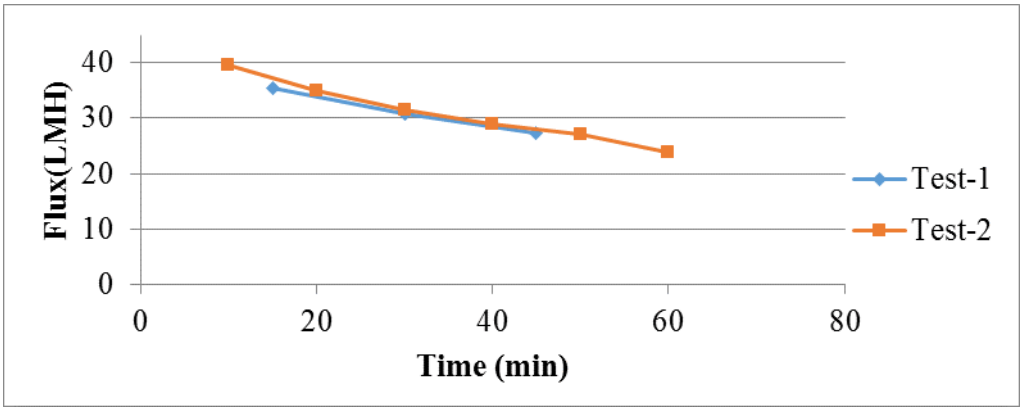

Figure 5.6. Filtration flux for 3.5 kDa PPZ membrane

Table 5.3. All flux changes by 3.5 kDa PPZ membrane

Flux (LMH)	3.5 kDa PPZ	
	Test-1	Test-2
Initial clean water flux (Jcwi)	34.50	32.70
Final wastewater flux (Jrw)	27.20	23.90
Clean water flux after filtration (Jcwf)	48.20	60.50
Clean water flux after physical cleaning (Jcwp)	37.10	45.00
Clean water flux after chemical cleaning (Jcwc)	38.40	44.20

Table 5.3 shows that all fluxes after filtration (Jcwf, Jcwp and Jcwc) were greater than Jcwi. After an evaluation carried out on these two filtration results, clean water fluxes after filtration (Jcwf) values were found as exceptionally high. Thus; as it can be seen from Figure 5.7, PPZ membranes did not show any portion of fouling resistance. According to mathematical analysis, total resistance coming from CP and fouling (Rcp+Rf) revealed as lower than resistance coming from only CP (Rcp). Also, the summation of intrinsic membrane resistance (Rmem) and fouling resistance (Rf) was calculated as smaller than the resistance from only the membrane (Rmem) which was tested at the beginning of tests. That means the negative value of fouling calculated from the difference between Jcwf and Jcwi was misleading. To be clearer, the Rcp values seen in Figure 5.7 do not show the real effect of CP because they were calculated by deduction of Rf from the summation of Rcp and Rf. Thus; the Rcp values look like higher than they really should be. Besides there was neither physically nor chemically irreversible flux decline observed as a result of unexpected flux increase after filtration. However, the effect of filtration on clean water flux was decreased when cleaning was applied (Table 5.3).

By all these information, it can be said that, filtration of RDW can be changing some physicochemical properties of PPZ membrane by the pollutants in the wastewater. It was determined that high salt content of RDW affected the flux of PPZ and all membranes were tested to understand the salinity effect on them (see Section 5.4).

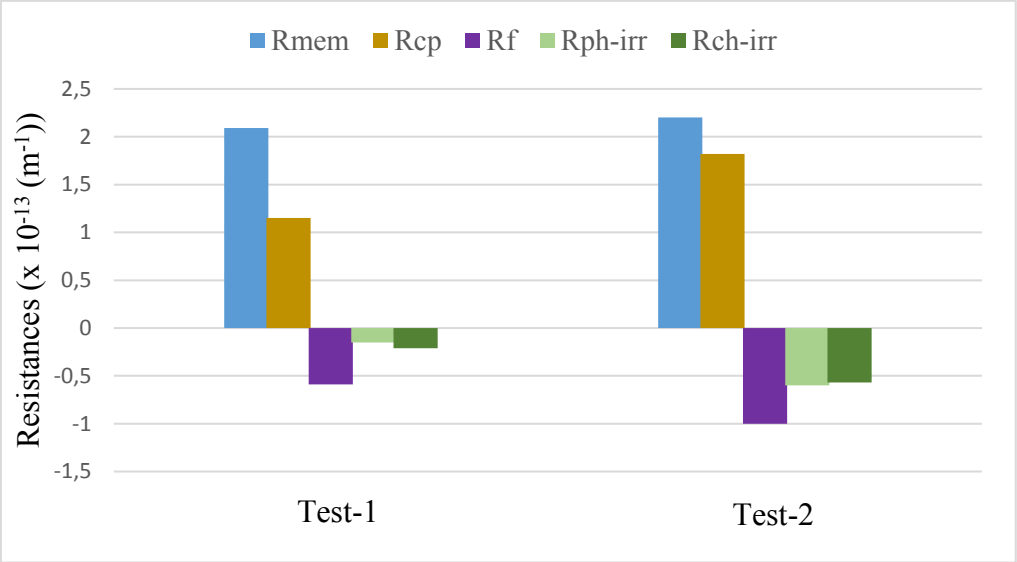

Figure 5.7. Resistance analysis of 3.5 kDa PPZ membrane

TFC Membrane

As in RC membranes cases, there was no flux decline observed during filtration of RDW by TFC membrane (Figure 5.8). As shown, the wastewater fluxes observed with different TFC membrane pieces were slightly different. But, in both cases, there was no increased fouling during filtration period. On the other hand, Figure 5.9 shows that there was active resistance caused by fouling for each tests. Significant portion (around 87%) of this resistance was chemically reversible. Additionally, the observed flux decline was 86% reversed after physical cleaning and 96.3% reversed after chemical cleaning (Table 5.4).

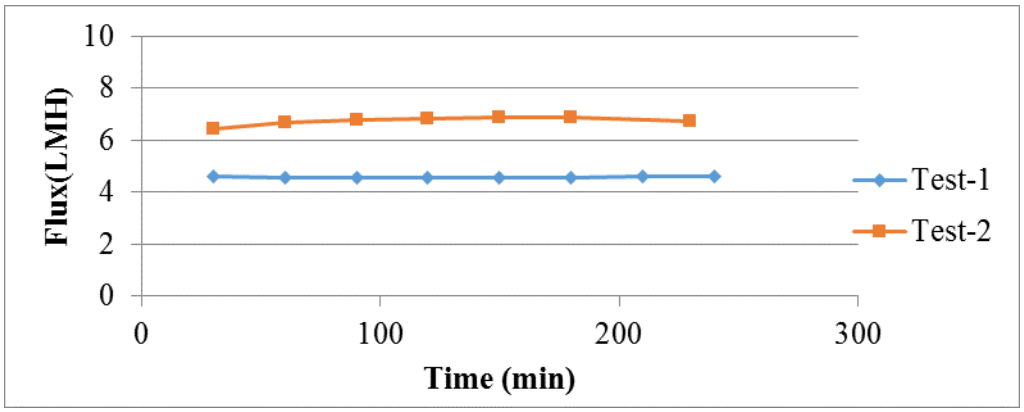

Figure 5.8. Filtration flux for 2 kDa TFC membrane

Table 5.4. All flux changes by 2 kDa TFC membrane

Flux (LMH)	2 kDa TFC	
	Test-1	Test-2
Initial clean water flux (Jcwi)	8.60	10.80
Final wastewater flux (Jrw)	4.60	6.70
Clean water flux after filtration (Jcwf)	6.60	8.50
Clean water flux after physical cleaning (Jcwp)	7.20	9.50
Clean water flux after chemical cleaning (Jcwc)	8.20	10.50

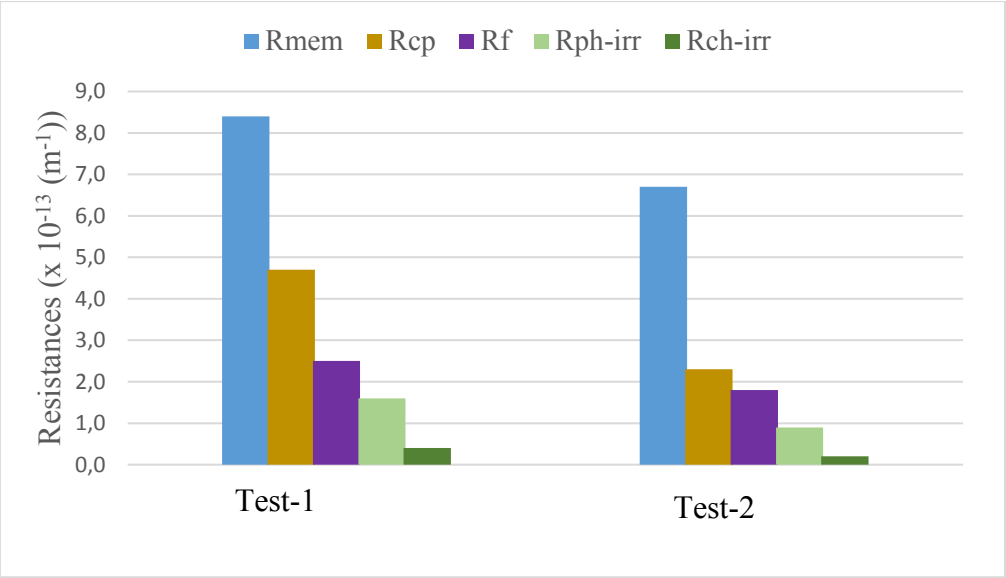

Figure 5.9. Resistance analysis of 2 kDa TFC membrane

Comparison of Different Membranes Tested

In Table 5.5, a comparative analysis of fouling behavior of the different membranes tested is given. As can be seen from this table, 1 kDa RC and 5 kDa PES membranes had been seem to be affected from fouling in a similar way. Their flux decline percentages and resistances remained after cleaning procedures were quite close to each other. On the other hand, their behavior were different during filtration period. While 1 kDa RC was preserving its flux during filtration period, PES membrane showed 26.4±0.7% flux decline. It can be a result of their being affected by different fouling mechanisms. For example, 1 kDa RC membrane could be fouled by pore blocking at the first moment of filtration. For PES membrane, the reason for flux decline could be gel layer formation and by the increased concentration near the membrane surface, the flux was decreasing during filtration. As a result, their fouling and cleanability behaviors were similar even if their filtration behaviors were different.

Table 5.5. Comparative fouling analysis of different membranes

MEMBRANES	Did increased fouling exist during filtration?	Flux change (%) (Between Jcwi and Jcwc)	Physically irreversible resistance (%)	Chemically irreversible resistance (%)
1 kDa RC	NO	13.5±4.5% decline	45.5±16.5%	43.5±18.5%
5 kDa RC	NO	9.0±5.0% increase	57.5±0.5%	-
2 kDa TFC	NO	3.7±1.3% decline	57.0±7.0%	13.2±2.7%
3.5 kDa PPZ	YES	23.0±12.0% increase	-	-
5 kDa PES	YES	13.2±2.7% decline	33.1±6.5%	34.5±0.5%

In 5 kDa RC and PPZ cases, there was unexpected flux increase between their Jcwi and Jcwc. After filtration, normally it is assumed that the flux is recovered step by step while the effects of fouling are eliminated by cleaning. However, the recovery would be expected to stop when flux is recovered 100%. This is the maximum percentage expected. There can be different reasons for these kind of enlargements. For 5 kDa RC, it is obvious that chemical cleaning had affected the performance of the membrane because the increase was seen after chemical cleaning. In PPZ case, starting from the filtration flux (at t=0), all measured fluxes were higher than Jcwi. So that, for PPZ membrane it can be said that feed water changed some properties and as a result, the performance of membrane.

Besides, the results gained by all membranes (except from PPZ membrane) showed that there was a rapid flux decrease between their clean water fluxes and the initial fluxes of filtration. This result is supporting the finding by Fersi et al. (2009) mentioned in Chapter 3. They observed that there was a sharp decline at the beginning of filtration by UF membrane because of rapid cake formation on membrane surface.

The performance results presented in Table 5.5 indicated that TFC membrane is the membrane having the best performance. This induction was made by its not having flux decrease during filtration, lower flux decline observed between Jcwi and Jcwc and high resistance elimination after chemical cleaning. Apart from the membranes showing unexpected and dubious flux increases, TFC membrane had the highest cleanability among them. In the next section, RDW treatment performances of all membranes will be examined.

5.1.2. Treatment Performances of the Membranes

In order to investigate the treatment performances of membranes; TOC, color, turbidity and conductivity removal efficiencies were measured after each filtration test. The results are shown in Figure 5.10, Figure 5.11, Figure 5.12, Figure 5.13.

In Figure 5.10, TOC retention percentages of different membranes are shown. As it can be seen from the figure, 1 kDa RC membrane had the highest TOC removal efficiency while 5 kDa RC membrane had the lowest. This could be the reason for 1 kDa RC membrane to have lower cleanability than 5 kDa RC one. Besides, 1 kDa RC membrane showed the highest TOC removal and the lowest cleanability among all membranes. It might be because of the highly removed organics retained in the membrane pores, so that cleaning was inefficient. The difference between TOC retentions of the two RC membranes were quite high (around 22%). On the other hand; PES, TFC and PPZ membranes had similar retentions to each other as having 62-73% TOC removal. When color removal performances were compared, TFC and PPZ were the most efficient ones among all membranes (Figure 5.11). Especially, considering the removals at 525 nm would be more accurate because the color of RDW samples was dark red. As it is for TOC removal, 5 kDa RC membrane showed also the lowest color removal.

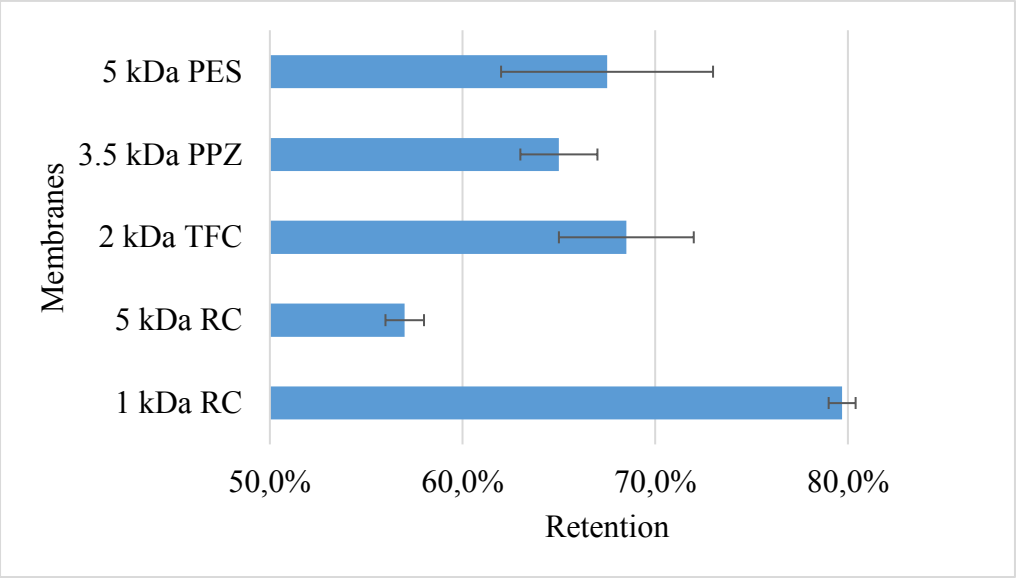

Figure 5.10. TOC retention by different membranes

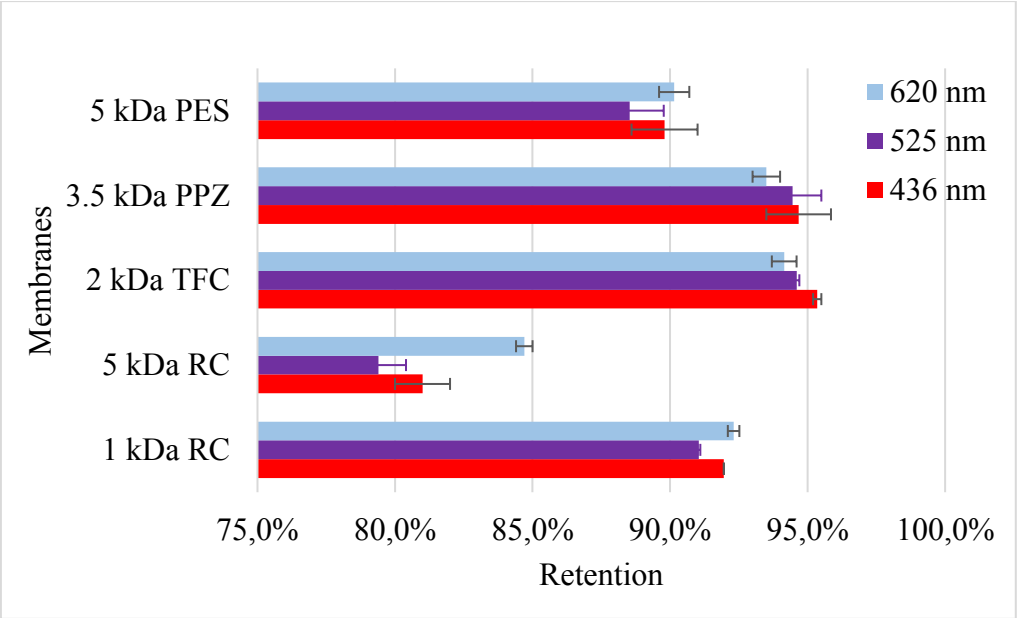

Figure 5.11. Color retention by different membranes

Turbidity was the parameter for which there is no significant difference between membrane removals. When their standard deviation values were taken into consideration, all membranes were seen as having around 99% turbidity removal (Figure 5.12). However; the permeate turbidity is an important criteria for making a better investigation. In some filtration tests, permeate turbidity values were observed as above 10 NTU. This is quite higher than expected values from an UF permeate. Another unexpected finding was that membranes with lower MWCO showed higher turbidity left in permeate region than larger MWCO having membranes. Normally, 1 kDa membrane should not pass more solids than 5 kDa membrane. As non-dissolved components cause turbidity in wastewater, their size and distribution in the used feed water could be different for each filtration process. Additionally, their interactions can cause a misleading analysis. For example, if the feed water used in one filtration has turbidity causing materials tending to agglomerate by the effect of surfactants, the turbidity of permeate could be read higher than it normally should be. It looks like non-homogenous turbidity or various interactions affected the final turbidity of permeate.

In Figure 5.13, conductivity removals by the membranes tested are compared. Very low retentions were observed for all the membranes as UF membranes can remove quite a low amount of dissolved solids. Observed conductivity retention was attributed to the rejection of ionic species by size exclusion, charge and electrostatic interactions of ions with the membrane surface (Sert et al., 2017). Indeed, these low retentions can be an advantage for the purpose of brackish water reuse in dyeing process by minimizing the spending salt amount (Erkanlı et al., 2017).

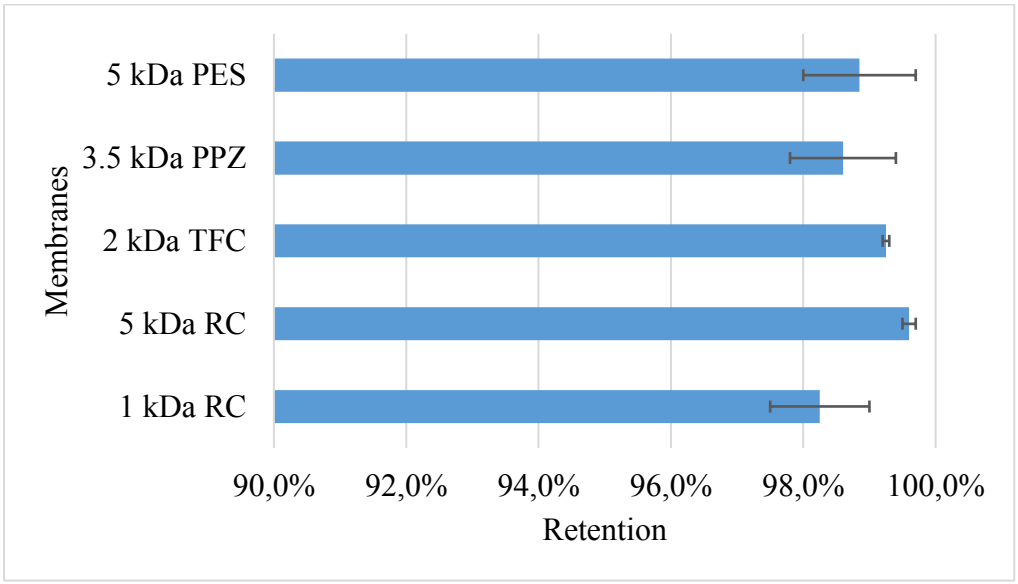

Figure 5.12. Turbidity retention by different membranes

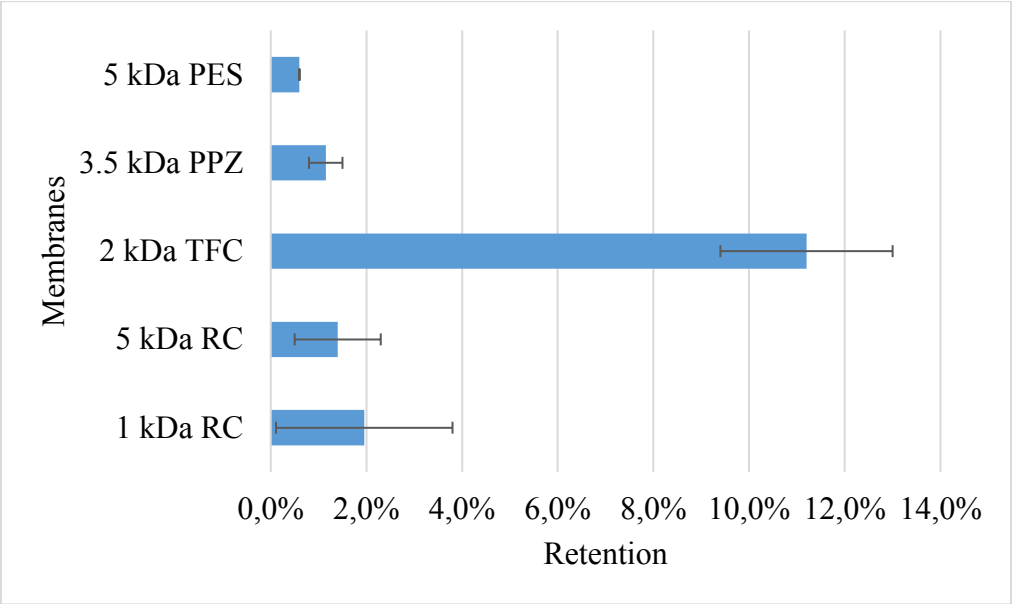

Figure 5.13. Conductivity retention by different membranes

5.2.Surface Characteristics

5.2.1. AFM and SEM analysis

In this study, surface roughness of the membranes were measured by non-contact mode AFM. The average values of roughness are represented in Table 5.6 and the topography images obtained are given in Figure 5.15. As explained earlier, roughness defines the surface morphology and it is widely used to interpret the relative fouling tendency of different membranes (Bes-Piá et al., 2010).

Table 5.6. Average roughness (Ra) values of membranes

Membrane	1 kDa RC	5 kDa RC	5 kDa PES	2 kDa TFC	3.5 kDa PPZ
Ra (nm)	4.2±0.8	3.0±0.7	4.3±1.2	5.8±0.3	8.0±0.3

Among different roughness values, average roughness (Ra) was chosen as the decisive roughness to be discussed as it is mostly in literature. According to their Ra values, PPZ membrane was the roughest one while the others have similar roughness. The 3-D topography image (Figure 5.15d) and the surface line profile (Figure 5.14d) confirmed that PPZ membrane has a lot of peaks and valleys on its surface. The color transitions seen on the 3-D images show the difference in height between these peaks and valleys. Surface line profiles (Figure 5.14) were obtained by AFM cantilever scanning along a 5 μm line on the membrane surface. The height differences between peaks and valleys can also give an idea about the roughness profile. As it is seen in the line profile of PPZ, the peak points were around 20 nm while the bottom of the valleys were around -20 nm. Therefore, PPZ was seen as having the highest difference (in nm) on its surface morphology.

3-D images of 1 kDa and 5 kDa RC membranes were found similar. They had extremely identical peak line on their surface (Figure 5.15a and Figure 5.15b). This can be structural caused by the casting of RC coating on nonwoven (See SEM images, Figure 5.16 and Figure 5.17). However, apart from this line, their surface were very smooth by no obvious color transition seen on the images.

The line profiles of these two RC membranes also showed that they are relatively smoother than other membranes. The smallest height differences were detected on the surface of 5 kDa RC membrane by the exception of the peak seen between 3rd and 4th μm of the line. The similar peak was observed for 1 kDa RC membrane at the end point of the line. These peaks were the representation of the peaks seen in their 3-D topography images.

The Ra value of PES membrane was quite close to 1 kDa RC membrane. However; when their 3-D topography images were compared, PES was seen rougher than 1 kDa RC membrane. On the other hand, Ra values were calculated by using the average roughness of 3 different line profiles. Thus; they are more reliable than the 3-D images. And also, their Ra standard deviation values are not remarkably different than each other. As a result, it can be said that they are moderately rough among all membranes. As Al-Jeshi & Neville (2006) mentioned about, even though the Ra value, topography image and surface line profile were supporting each other for PPZ membrane, this correlation could fail in some cases as a result of non-uniform structure of membranes as it happened in this case.

Lastly, TFC membrane was the second roughest membrane after PPZ according to Ra comparison. The line profile of this membrane (Figure 5.14c) showed that it had denser peaks and valleys than PPZ surface (Figure 5.14d). 3-D image of TFC membrane also showed that it had very compact surface by deviations. While these high deviations made TFC membrane look like as rough as PPZ, the sizes of the peaks and valleys of PPZ were higher than in the line profile. So that; Ra of PPZ was higher than TFC and highest one among all membranes.

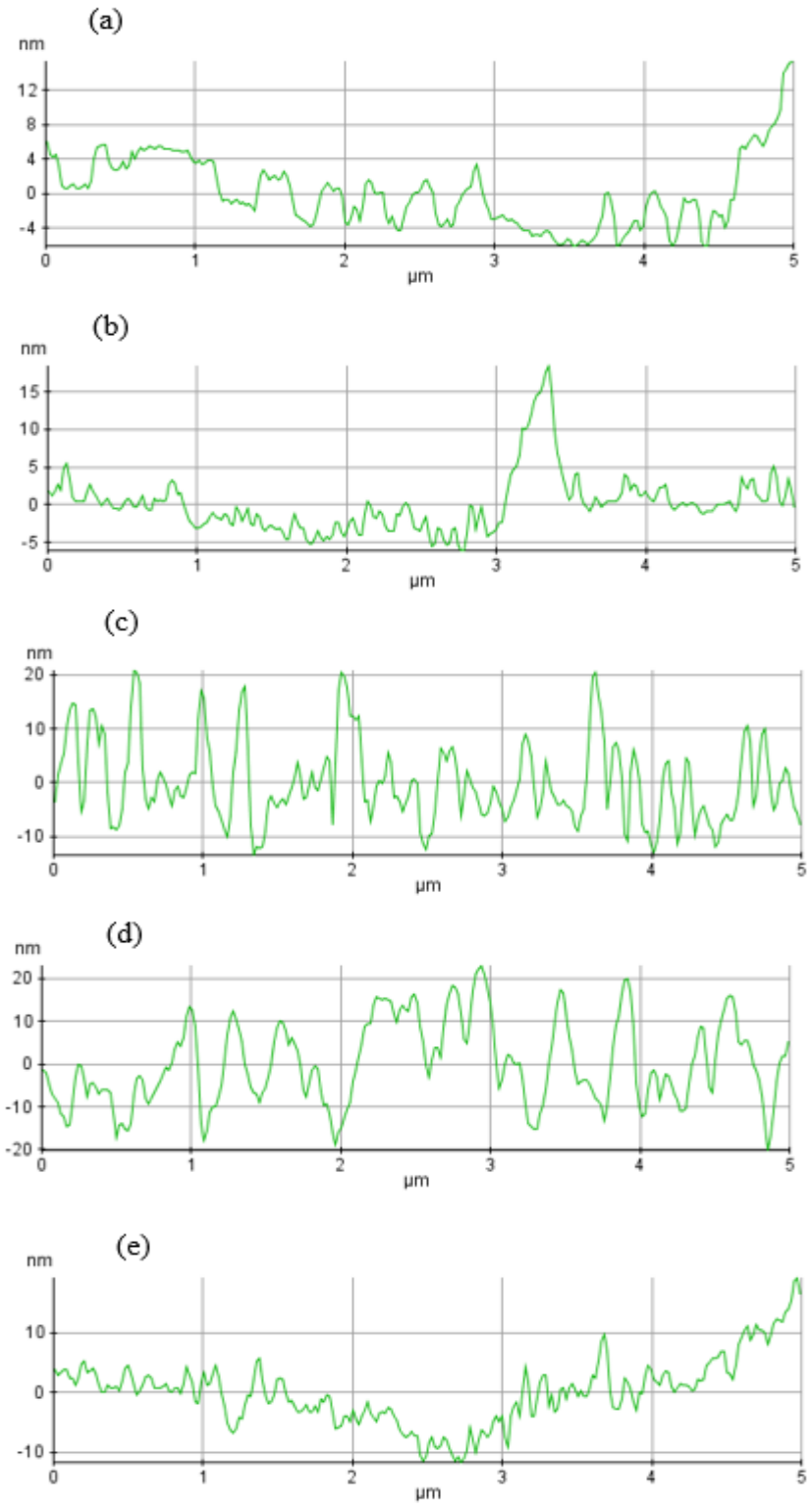

Figure 5.14. Line profiles of membrane surfaces (a) 1 kDa RC (b) 5 kDa RC (c) 2 kDa TFC (d) 3.5 kDa PPZ and (e) 5 kDa PES

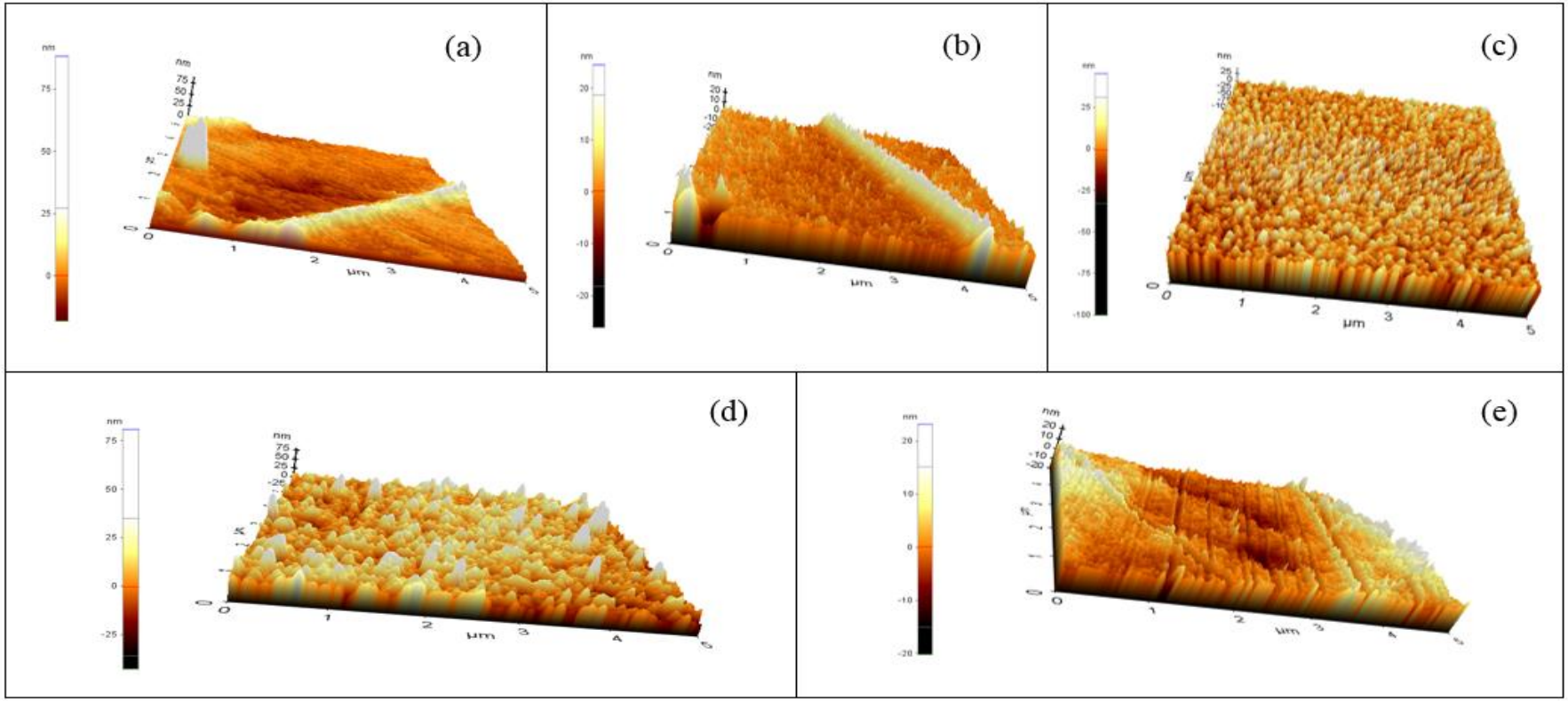

Figure 5.15. 3-D topography images of membranes (a) 1 kDa RC (b) 5 kDa RC (c) 2 kDa TFC (d) 3.5 kDa PPZ and (e) 5 kDa PES

The SEM images taken for this study did not reveal a distinctive characteristic difference between membranes' topography. Figure 5.16 and Figure 5.17 show SEM images of RC membranes. Surface images (Figure 5.16a and Figure 5.17a) verified that there were structural peak lines on both of the RC membranes' surfaces as observed in 3-D AFM images and line profiles. Besides, as seen in AFM images, the surfaces of RC membranes were not seen rough neither in SEM images. The cross-section images of RC membranes showed that these membranes are supported by nanofiber nonwovens.

The roughness density difference observed in 3-D images of TFC and PPZ membranes was also seen at their top surface images (Figure 5.18a and Figure 5.19a). Additionally, when the surface images of all membranes are compared, their being rougher membranes became visible also in SEM images.

It can be seen from Figure 5.20b that PES membrane has large macrovoids which results from finger-like structure. This structure may be the reason for high flux obtained with PES membrane. Other membranes did not display these kind of macrovoids. Especially, RC membranes have very dense structure (Figure 5.16b and Figure 5.17b). It is quite hard to observe that however; PPZ and TFC membranes have a thin top layer above their sponge-like supports (Figure 5.18b and Figure 5.19b).

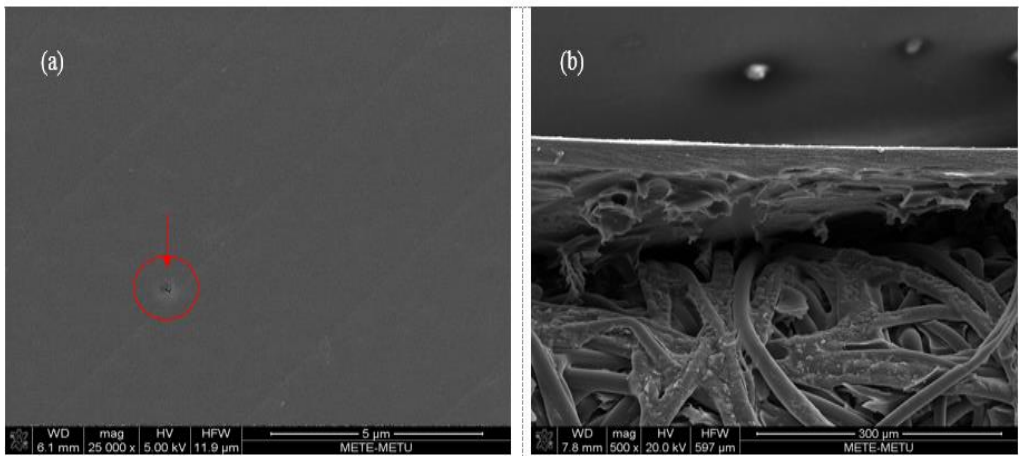

Figure 5.16. 1 kDa RC SEM images (a) top surface* (b) cross-section

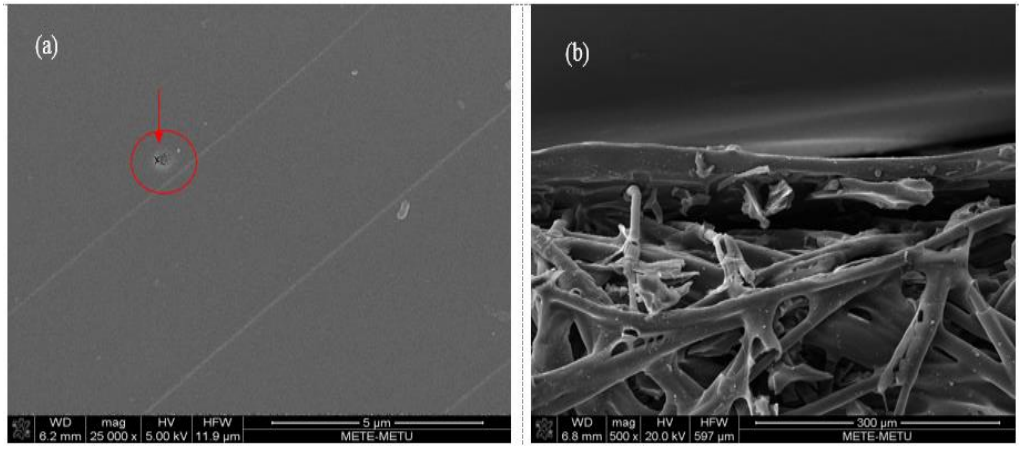

Figure 5.17. 5 kDa RC SEM images (a) top surface* (b) cross-section

* The red arrows seen on the top surface images showed the burning part of RC membranes because of the high energy electron beam.

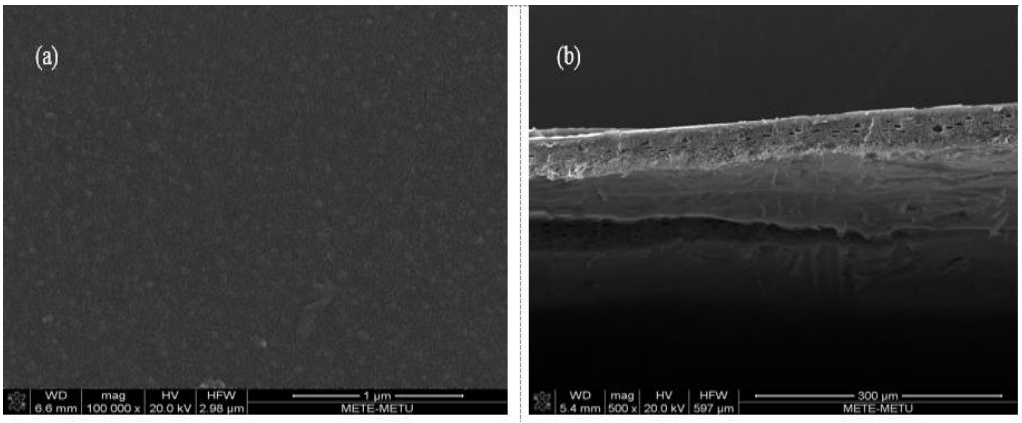

Figure 5.18. 2 kDa TFC SEM images (a) top surface (b) cross-section

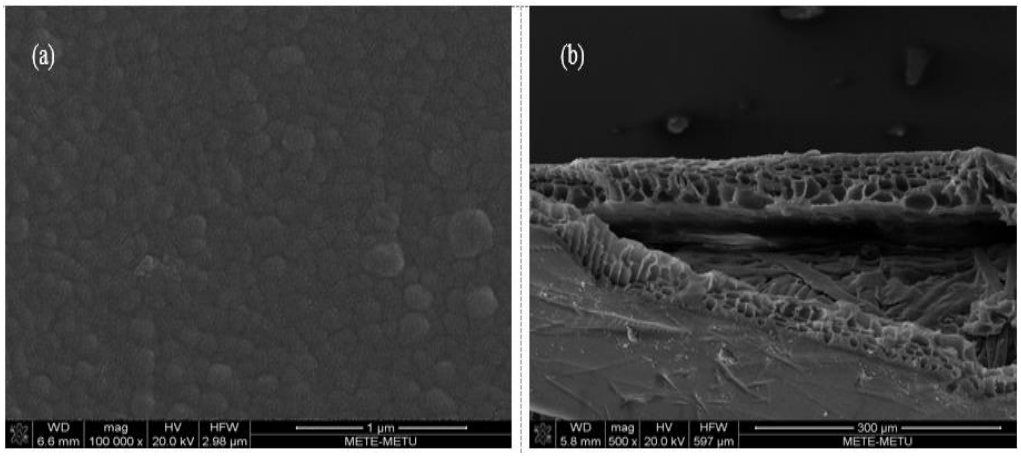

Figure 5.19. 3.5 kDa PPZ SEM images (a) top surface (b) cross-section

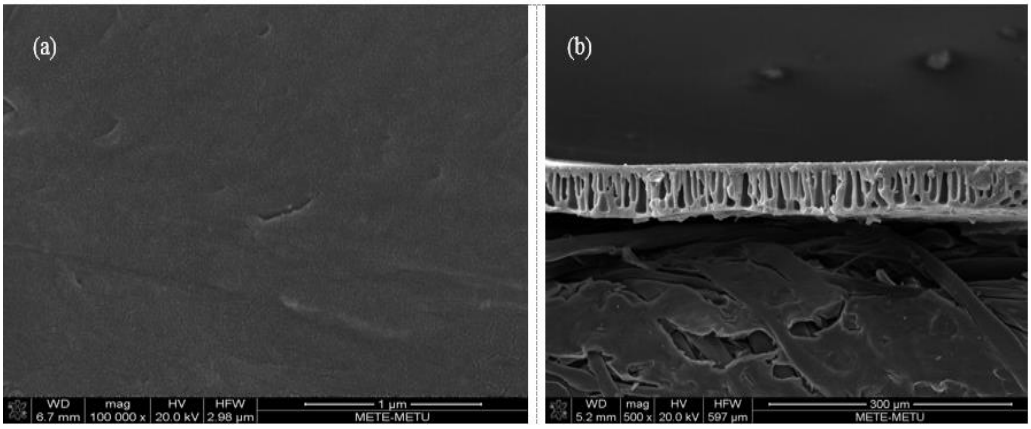

Figure 5.20. 5 kDa PES SEM images (a) top surface (b) cross-section

5.2.2. Contact Angle Measurements

The reported average contact angles were analyzed by the measurements from three or four different places (with tens of measurement on one point) of the same membrane piece. As it can be recognized from Figure 5.21, it was not possible to measure contact angles for RC membranes (1 and 5 kDa) because of their high hydrophilic surface absorbing the water droplets. Thus, RC membranes had smallest contact angles (nearly zero) among the studied membranes.

TFC membrane had most hydrophilic active layer after RC membranes. It had lower contact angle as 40.7°±3.0°, than PES and PPZ membranes. Contact angle of PES and PPZ membranes were 48.3°±0.7° and 60.0°±0.7°, respectively. PES can be called as the second most hydrophobic membrane in the study. In the literature, there are several studies confirming the results found in this study. For example, Bes-Piá et al. (2010) summarized some membrane materials and their contact angles according to their manufacturers and literature. In this summary, one of the PPZ membranes had contact angle as 51.4° and another one had as 60.0°. While Xu et al. (2016) was reporting the contact angle of a PES membrane as 54.5°, Fan et al. (2016) reported as 44°.

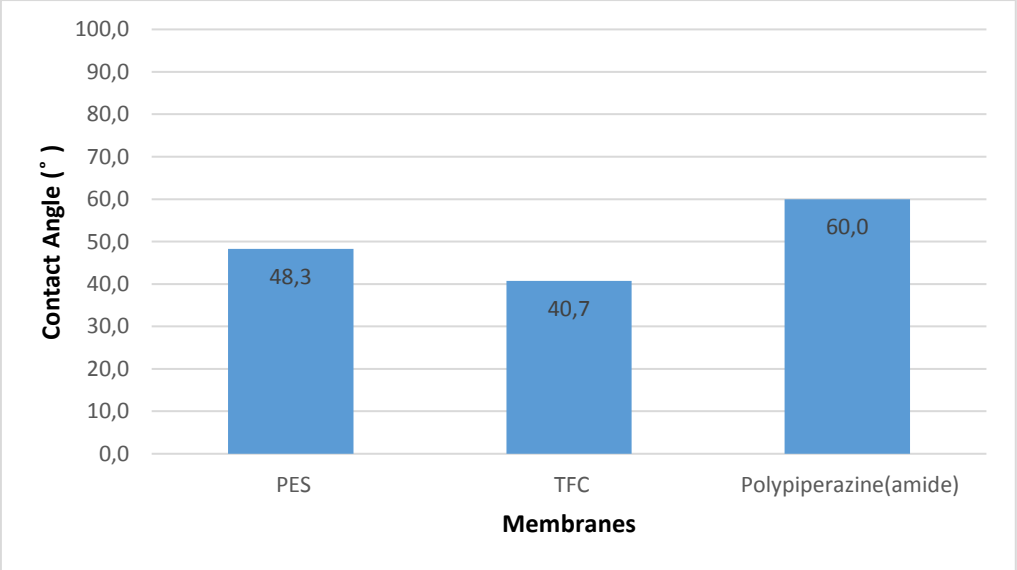

Figure 5.21. Contact angle results of PES, TFC and PPZ membranes

5.3. Interpretation of Membrane Behaviors with Surface Characteristics

Up to now, along with the membrane behaviors during and after filtration, membranes' topography, roughness and contact angle results are discussed separately. Establishing a correlation between the filtration behaviors and surface characteristics can reveal some important relationship between them.

In literature, roughness and hydrophilicity are generally associated with fouling phenomenon. Several modifications were made on membrane surfaces to decrease the roughness and/or increase the hydrophilicity of membrane; so that membranes would be less vulnerable for fouling (Al-Amoudi & Lovitt, 2007). For example; acrylate (Reddy et al., 2005) and poly(ethylene oxide) (PEO) (Asatekin et al., 2009) were used to modify the surfaces of some hydrophobic UF membranes in order to enhance the anti-fouling properties of membrane and use them during dyeing wastewater filtration (Thamaraiselvan & Noel, 2015).

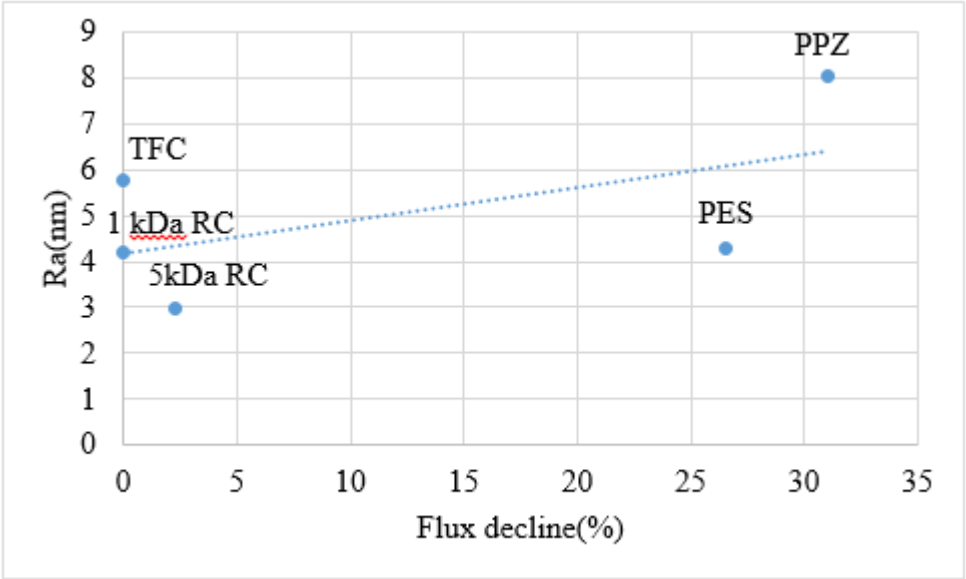

Figure 5.22. Relationship between flux decline and membrane surface average roughness

First of all, the relationships between Ra and flux decline (during filtration) of membranes are represented in Figure 5.22. There was not a linear relationship found between roughness and flux decline. However; PPZ membrane which showed the highest Ra had also highest flux decline. Furthermore; due to its relatively hydrophobic nature observed in Section 5.2.2, it was expected that fouling tendency of PPZ would be higher.

In order to search for a possible correlation between contact angle and flux decline, Figure 5.23 was drawn. As it can be observed from this figure that the two most hydrophobic membranes which are PPZ and PES had the highest flux decline percentages. Consequently, it can be said that; while roughness and flux decline did not show a direct correlation, the relationship between contact angle and fouling seems to be more reliable.

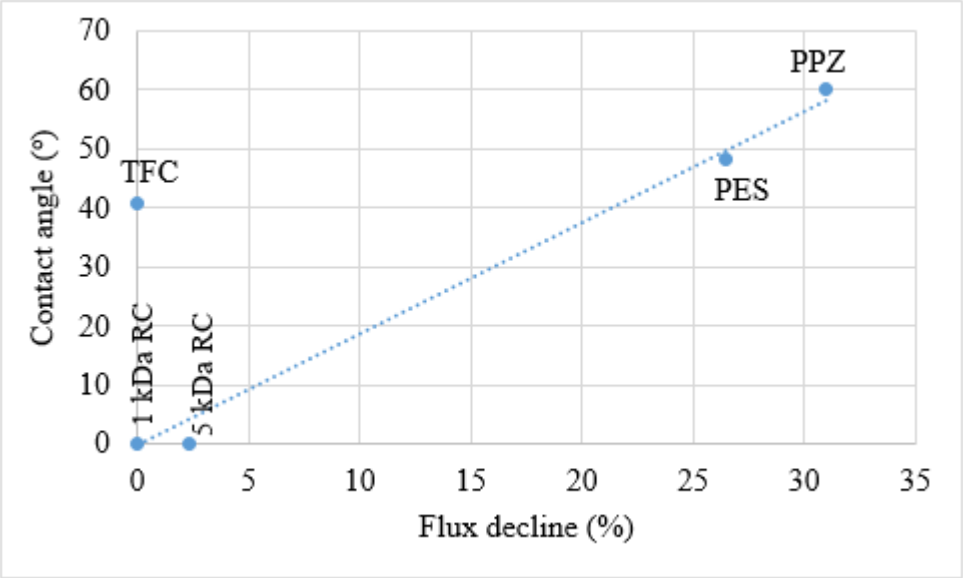

Figure 5.23. Relationship between flux decline and membrane surface contact angle

TFC membrane which was the second roughest membrane, did not have any portion of flux decline during RDW filtration. From the knowledge gained from literature, the increase in surface roughness is expected to make the membrane more prone to fouling (Hobbs et al.,2006.; Zamiah et al. , 2012; Zhao et al., 2015). On the other hand; some different cases are also reported in literature. For instance; Zamiah et al. (2012) claimed that despite high roughness; increased hydrophilicity of membrane surface and pore walls can lower the fouling by the help of shear force removing the adsorbed particles from membrane surface. Such results imply that even if TFC membrane had closest Ra to PPZ membrane (Figure 5.22), its higher hydrophilicity (lower contact angle; Figure 5.23) might have prevented the flux decline due to fouling.

Filtration behavior and surface characteristics of 5 kDa RC membrane were supporting each other as in the PPZ membrane case. With this membrane, there was no observed flux decline during filtration and also the fouling resistance was completely removed after chemical cleaning. These outcomes can be thought as results of 5 kDa RC membrane's having extreme hydrophilic nature and lowest roughness.

When 1 kDa RC and PES membranes' behaviors were examined all at once, the roughness and hydrophilicity effects on membrane fouling could be seen more clearly. As mentioned in Section 5.1.1, their overall flux decline between Jcwi and Jcwc was observed as quite similar even if their filtration behaviors were different. In Section 5.2.1, it was seen that also their Ra values were nearly same. The only significant difference was seen on their contact angle results. So that; the increased fouling during filtration by PES membrane can be the result of its hydrophobicity. Because when the membrane had a hydrophilic nature as 1 kDa RC, increased fouling was not observed during filtration. Additionally, all the membranes which had no increased fouling during filtration (RC and TFC membranes) were found as more hydrophilic than the ones had increased fouling (PES and PPZ).

To sum up, by comparing their irreversible fouling resistances after chemical cleaning, the cleanabilities of PES and 1 kDa RC membranes were observed as the lowest ones among all membranes. Also, they had the highest flux decline between their Jcwi and Jcwc. By all of the other membranes (5 kDa RC, TFC and PPZ), 5 kDa RC membrane showed the weakest performance for RDW treatment with the lowest color and TOC removal. Although 2 kDa TFC membrane did not have the most hydrophilic and smoothest surface, its low fouling tendency, good treatment performance with the highest color removal make it the most suitable membrane for RDW treatment among the tested ones.

5.4. Salinity Effect on Different Membranes

During PPZ membrane filtration tests, it was observed that there was an unexpected increase in clean water flux after wastewater filtration. This increase was attributed to possible effect of wastewater salinity on the membrane. In order to understand this behavior or to search for possible reasons, some additional experiments were conducted with this membrane using new membrane pieces to determine if they behave in a similar way. Besides, the other membranes were also tested.

Before the tests with the new pieces of PPZ membrane, a detailed flux analysis was performed and Figure 5.24 showing the flux changes of Test-1 and Test-2, respectively, were drawn. As seen in the figures, Jcwf of the PPZ membrane was exceptionally high (about 40 % and 85% higher than Jcwi, for the Test-1 and Test-2, respectively) during the whole clean water filtration period. In order to understand the reason for this tremendous increase in clean water flux, a series of salt solution filtration tests were carried out varying salt content of the clean feed water. These tests were run with clean water in order to eliminate possible effects of other wastewater constituents. Firstly, a salt solution, which had a conductivity close to real wastewater (~70 mS/cm), was prepared and filtrated through PPZ membrane (Figure 5.25). Then, two different membrane pieces were used to filter salt solutions with different conductivities around 20 and 200 mS/cm. The flux behaviors of these experiments can be found in Figure 5.26 and Figure 5.27, respectively.

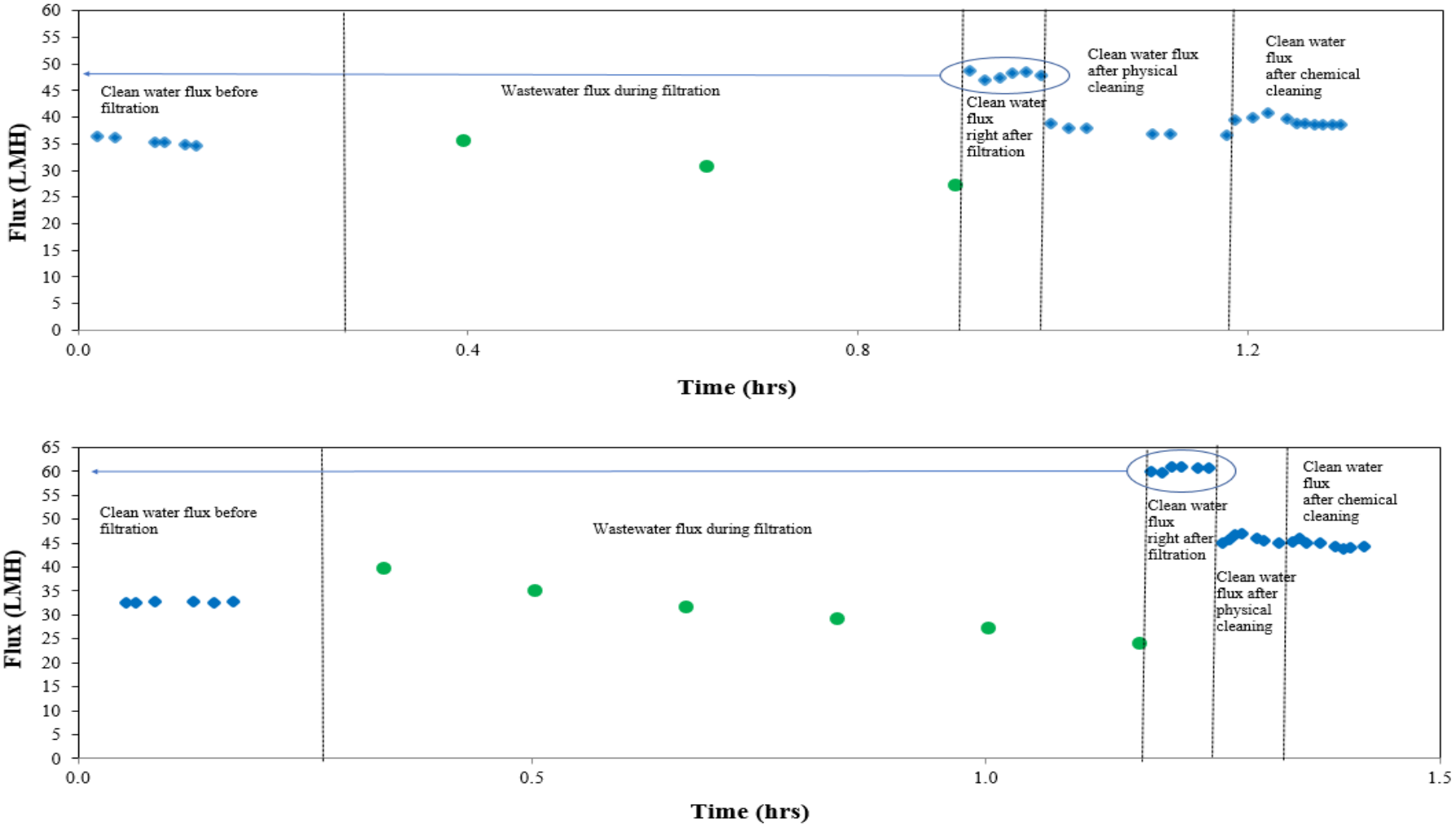

Figure 5.24. PPZ membrane flux changes during RDW filtration (Test-1 andTest-2)

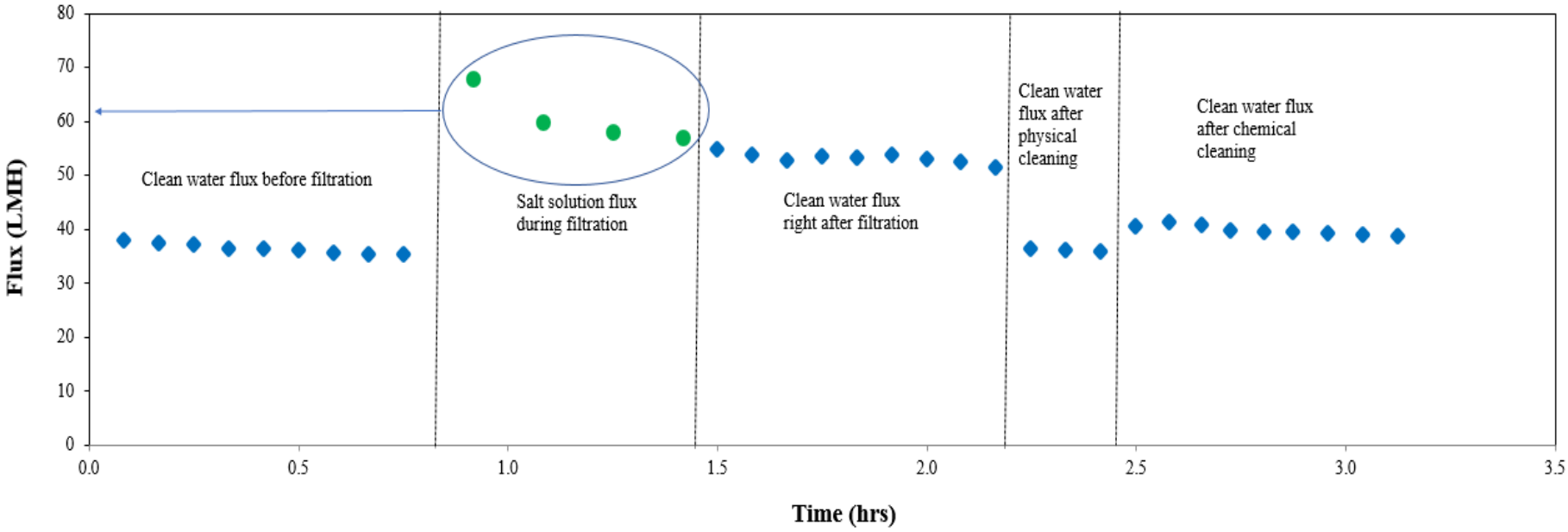

Figure 5.25. PPZ membrane flux changes during salt solution filtration (conductivity~70 mS/cm)

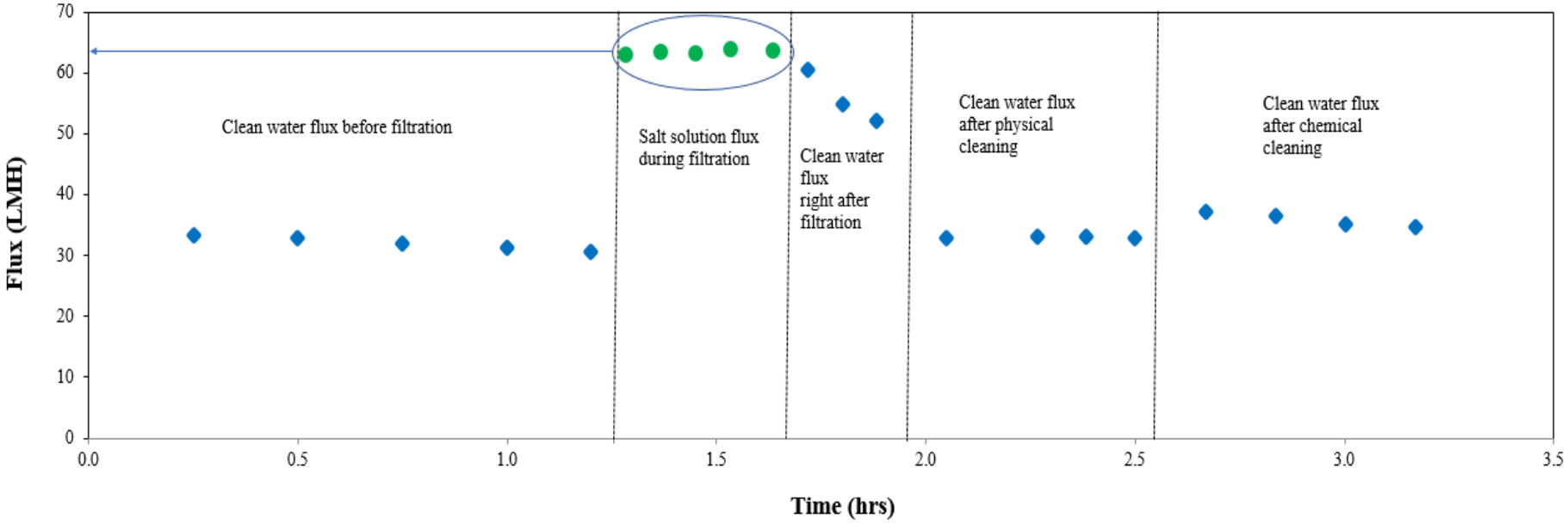

Figure 5.26. PPZ membrane flux changes during salt solution filtration (conductivity~20 mS/cm)

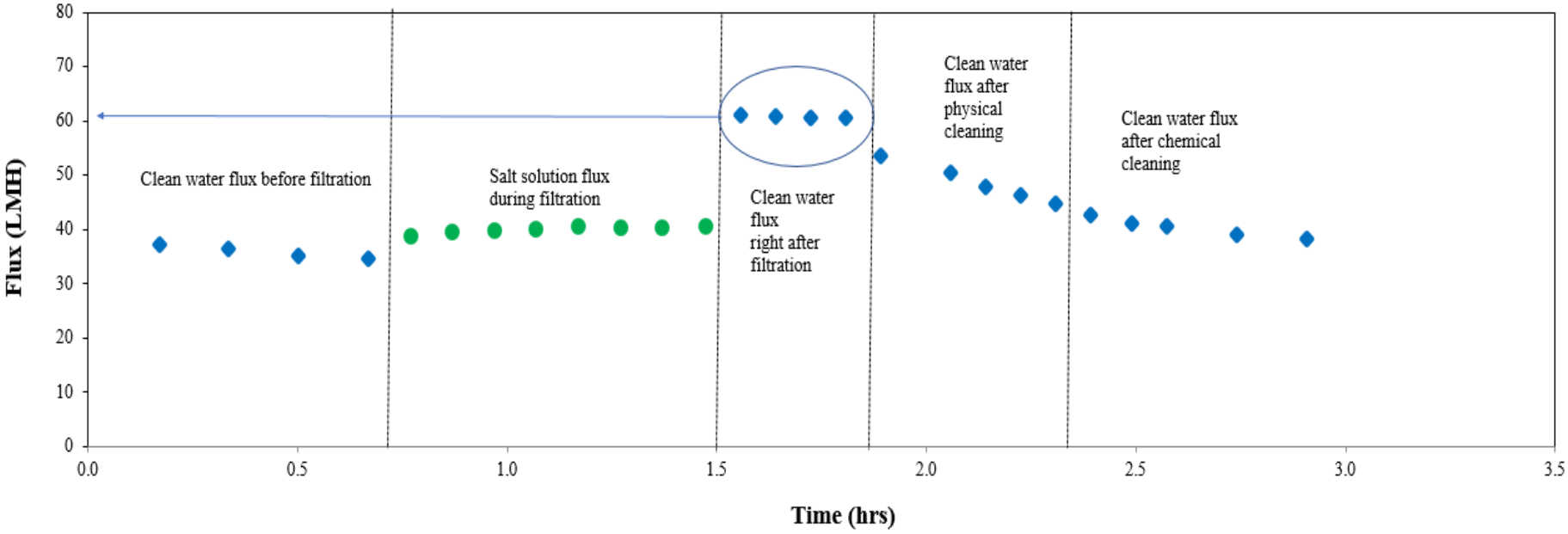

Figure 5.27. PPZ membrane flux changes during salt solution filtration (conductivity~200 mS/cm)

In case of clean water filtration (i.e. when there is no TOC, color or turbidity causing particles in the feed water), salt content affects the clean flux in such a different manner. That is to say, with the impact of other pollutants in RDW, it was observed that the major increase took place not *during* but *after* filtration. In the experiments conducted with salt solutions, even though it had the same level of conductivity with RDW, since there was no other pollutant (no material that can foul the membrane), we observed the flux increase *during* filtration (Figure 5.25). In line with the expectations, it was observed the same result for lower conductivity (~ 20 mS/cm) as well (Figure 5.26). However, as the salt concentration increased (~ 200 mS/cm), the flux increase was observed *after* filtration again (Figure 5.27), just like it was in RDW filtration experiments. Thus, it can be said that the increase of salt concentration after some level might have created a blocking affect for the flux increase *during* filtration. And by UPW permeation after filtration, when this concentrated salt was removed, the flux increase started to be observed right *after* filtration.

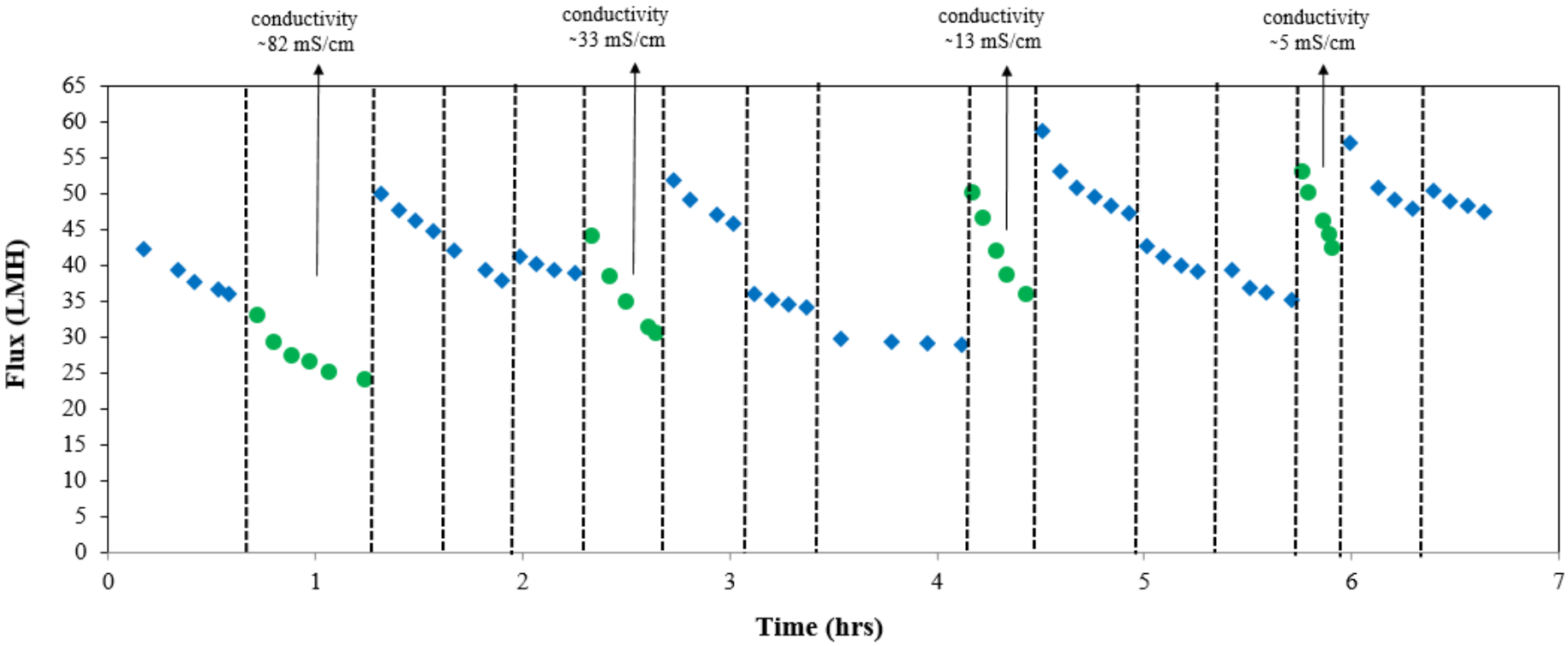

Figure 5.28. Flux results of four serial filtration carried by PPZ membrane by changing the conductivity of RDW in each filtration

In order to investigate the relation between foulants, conductivity and flux change, four filtration tests with RDW (by reducing conductivity but also keeping the concentrations of other variables nearly same) were conducted. Conductivity change was obtained by diluting the retentate solution from previous experiment. By diluting the retentate obtained after each filtration, the conductivity was decreased with respect to the dilution rate. The assumptions here were as follows: while other pollutants were 100% removed in each filtration, conductivity removal was 0%. Among the results (Figure 5.28) of these experiments, a striking one was the following: when conductivity was above a certain value, with the impact of pollutants, the flux increase was observed *after* filtration. However, as conductivity decreased in each experiment, so did the difference between Jrw and Jcwf. In other words, when conductivity decreased, filtration flux increased and there remained no significant difference between Jrw and Jcwf. In the meanwhile, in each filtration, pollution load decreased because unlike the preliminary assumptions, especially TOC removal was not close to 100%. As a result of the decrease in both conductivity and concentrations of other constituents, it was started to be seen the major increase *during* filtration, like it did in salt water filtrations (20 and 70 mS/cm).

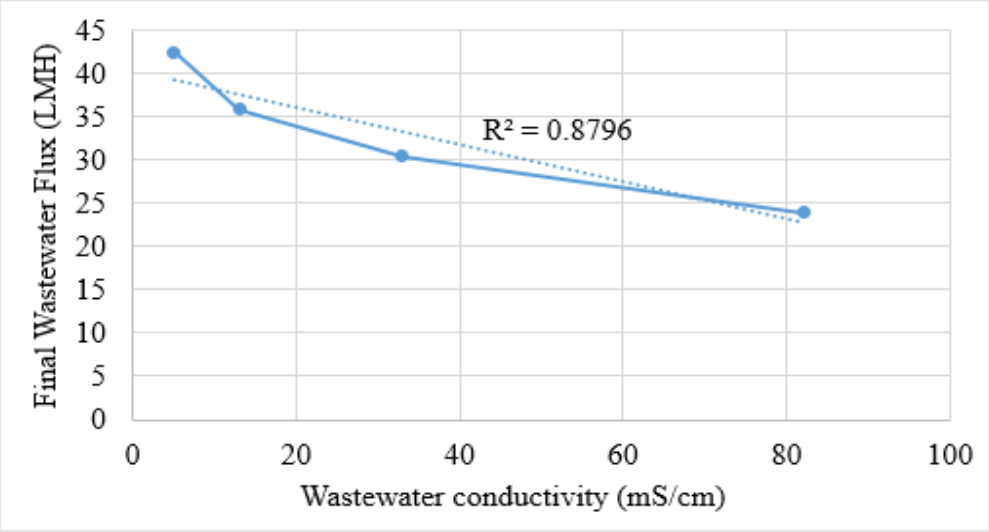

Figure 5.29. Relationship between conductivity and final flux of wastewater

To sum up, it is obvious that there was a change in PPZ membrane when it was faced with salty water/wastewater. Permeate flux was always affected by salt however; the effects were different according to the salt concentration of feed. Figure 5.29 shows that there is an adverse relationship between the conductivity and wastewater flux for PPZ membrane. Even if the final wastewater flux decreased with increase in conductivity (obviously also by the additional effect of other foulants), there was a significant flux increase between Jcwi and Jcwf in all cases. One of the studies investigated in Chapter 3 have been concluded with a similar result. According to that study, due to an interaction between salt ions and water molecules, there happened a thinning effect on adsorbed water layer on polyamide membrane pores. As a result, effective pore size and membrane thickness were observed as increased. The same interaction could have been affected the PPZ membranes used in this study.

The observed flux increase arising from salt content of feed could be thought as the result of physical and/or chemical interactions between the membrane material and salt ions. For a better investigation, FTIR analysis were carried out. This analysis would be expected to show different bond formations or breakings by the effect of salt ions, if existed. For this purpose, three PPZ membrane pieces were analyzed; first one was only cleaned by UPW, second one was used in RDW filtration and lastly the third one was used in RDW filtration and then cleaned by UPW. Figure 5.30 shows the results of FTIR analysis. It is clearly seen that, there was neither created nor broken bonds by the salt effect. So that, it can be said that the change observed on PPZ membrane was not originated from chemical interactions. The flux increase was the result of physical enlargements caused by ionic strength of salt. If this change is permanent after several filtrations, it may cause a decrease in retentions and can shorten the life of PPZ membrane.

PES, RC and TFC membranes were also examined to see if conductivity affected them in such a similar way. At the end of salt solution filtration testes carried out with these membranes, no significant effect of salt was observed on their permeate fluxes neither *during* nor *after* filtration. The salt solution filtration results for these membranes can be found in Appendix B.

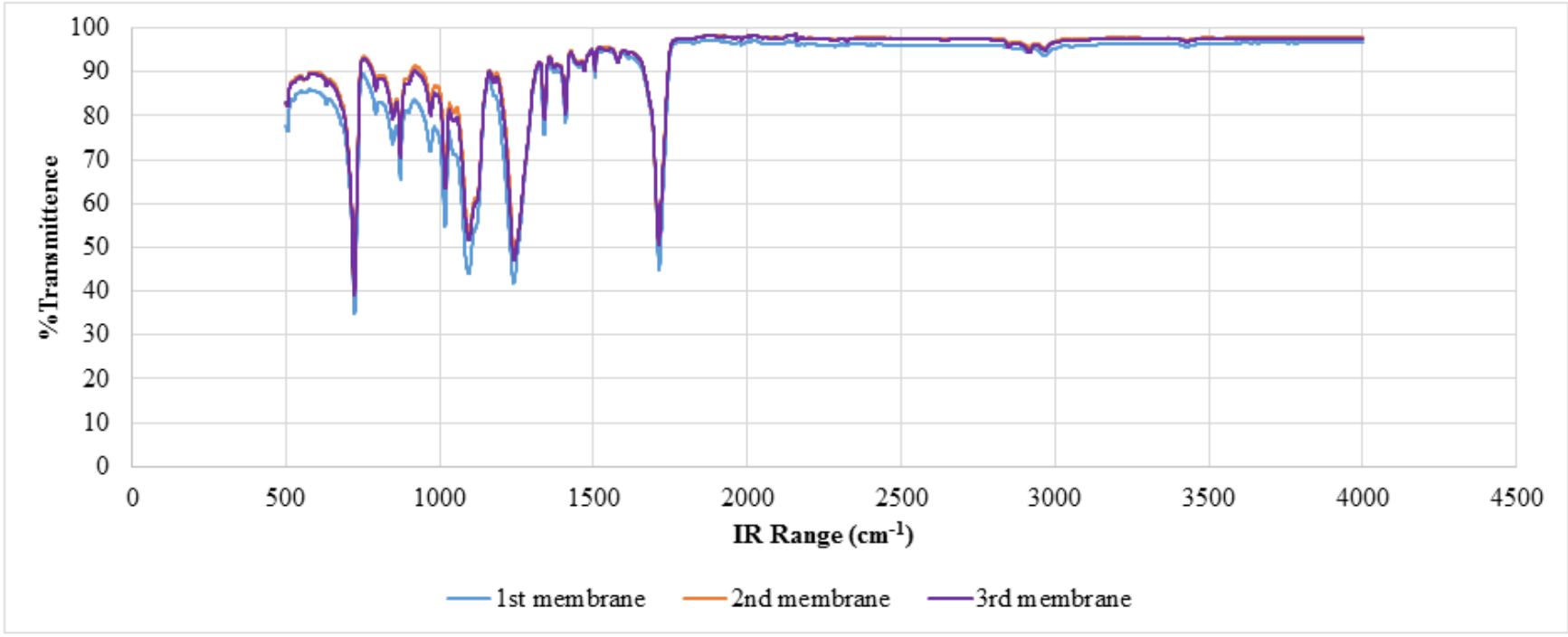

Figure 5.30. FTIR results of three PPZ membranes (1st membrane: only cleaned by UPW, 2nd membrane: used only in RDW filtration, 3rd membrane: used in RDW filtration then cleaned by UPW)

5.5. Chemical Cleaning Effect on Different Membranes

As it is mentioned in Section 5.1.1, flux of PES membrane frequently showed different trends after chemical cleaning. At the beginning of the research, filtration experiments had been carried out without chemical cleaning after compaction. In these initial studies, exceptional flux declines after both physical and chemical cleaning were observed for PES membrane. The flux results of these experiments can be found in Appendix C.

It was obvious that cleaning chemicals affected PES material different than the other membranes. By the addition of one more chemical cleaning step to ahead of filtration, the extreme effects of the chemicals on PES membrane was removed. This means that the flux decline either disappeared or was much lowered. However; the chemical cleaning effect was still investigated with all membranes, especially with PES.

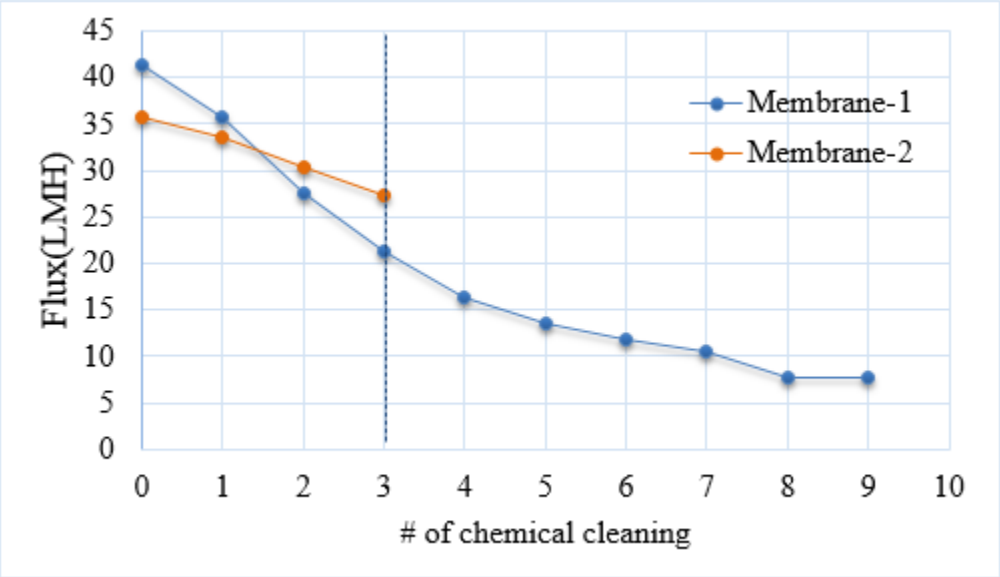

Figure 5.31. Flux changes on PES membrane after serial chemical cleanings (acid followed base cleaning)

First of all, sequential chemical cleanings were conducted on PES membrane and the UPW flux was measured after each of the cleanings. Two pieces of PES membranes were tested as parallel studies. As it can be seen in Figure 5.31, at the end of third cleaning, Membrane-1 showed a higher decline than Membrane-2. So that, it was decided to continue the tests with Membrane-1. Nine serial cleanings were applied to Membrane-1 in total. While the fluxes after eighth and ninth cleanings were same, the flux was decreased around 80% between first and last cleaning. Apart from the enormous size of flux decline, its being very consistent during nine tests proved that the permeate pathways on PES membrane became smaller by the effect of chemicals. After this result has been reached, tests were conducted to determine whether the acid or base caused this effect.

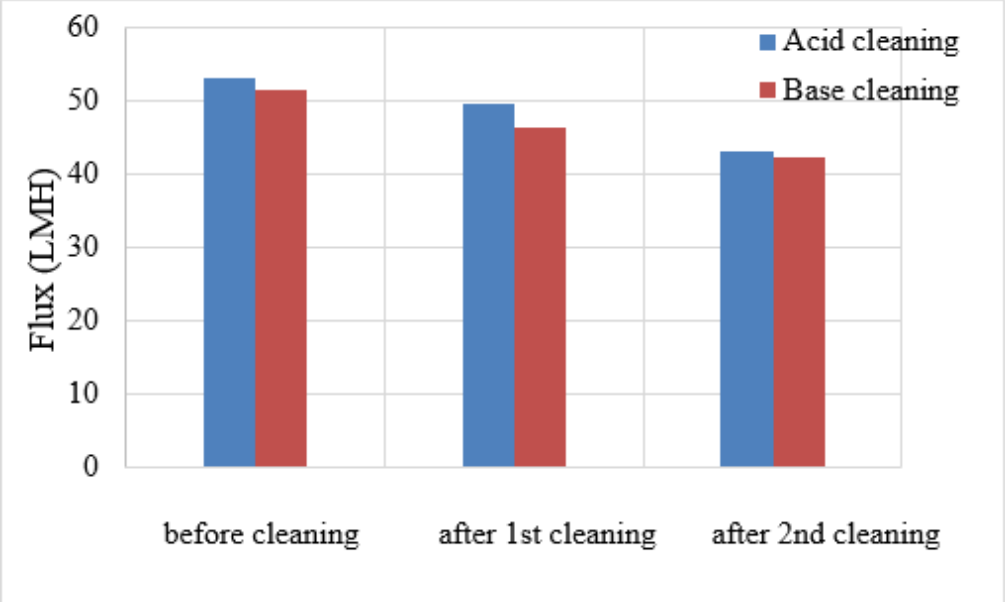

Figure 5.32. PES membrane flux changes due to acid and base cleaning

Figure 5.32 shows the flux changes on PES membrane due to acid and base cleanings. Applied acid solution (HNO_3) resulted with nearly 6%, 13% and 19% flux decline after first cleaning, second cleaning and in total, respectively. The decline observed after base solution (NaOH) application was nearly 10% after first cleaning, 8% after second cleaning and 17.5% in total. In the tests conducted with Membrane-1 with both acid and base cleanings, the total flux decline was around 33% at the end of two serial cleanings. In the light of these information, it can be said that when the acid-base cleaning procedure was followed, both of the chemicals affected the flux of PES membrane. Thus, the total decline was higher than the decline observed when acid or base cleaning was applied separately.

After seeing the effect of chemical cleaning on membrane structure, experiments were carried out to see the effect of this change on treatment performance of PES membrane. Figure 5.33 shows the comparative fluxes of the membranes. The difference between the two filtration was five chemical cleaning applied before one of them. As it can be observed, all fluxes of the test after chemical cleanings were much lower than the fluxes of direct filtration test. The influence of the resulted lower flux on treatment performance can be seen in Figure 5.34. It is clearly shown that, whatever caused the flux to be reduced, led to increased performance. This conclusion supported the theory that pores became smaller by the effect of chemical cleanings applied before filtration.

PPZ, RC and TFC membranes were investigated by the application of serial chemical cleanings. They all showed some portion of flux increase after each cleaning. The results can be found in Appendix D.

To conclude, among all membranes tested, PES membrane showed a different trend with chemical cleaning. Effects of both acid and base solutions used in cleaning procedure resulted with pore shrinking. This influence can be thought as a possible disadvantage for PES membrane filtration based treatments. This is because the chemical cleaning to be performed after each filtration is likely to shorten the life of PES membrane easier than the other membranes.

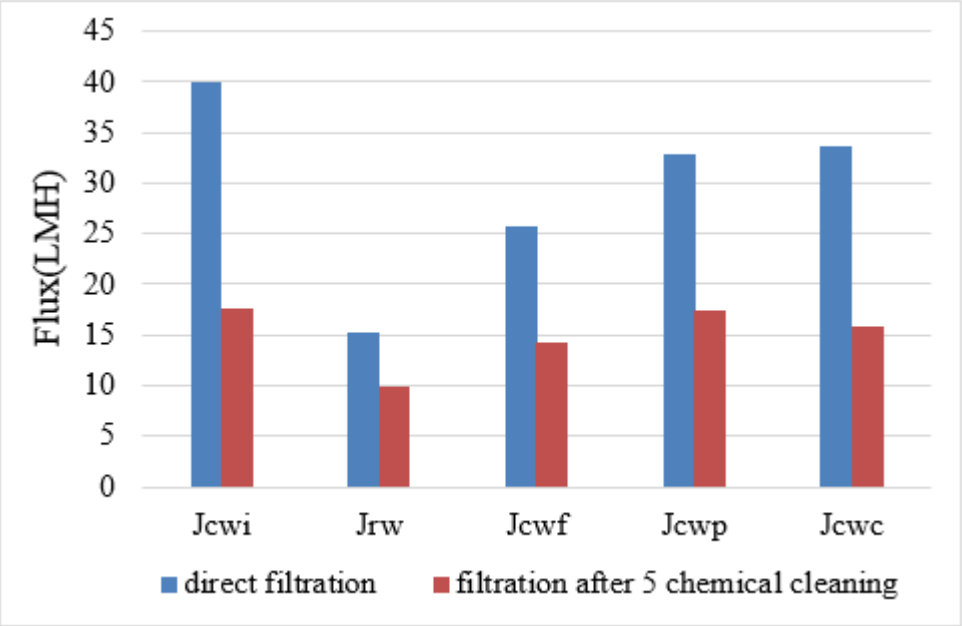

Figure 5.33. PES membrane flux results (direct filtration and filtration after 5 chemical cleaning)

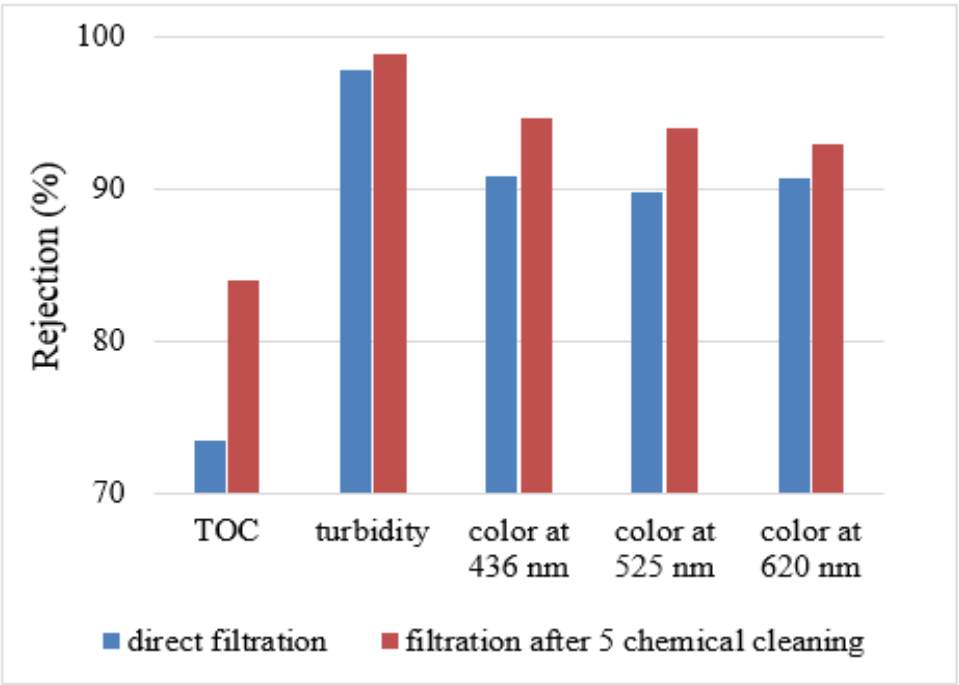

Figure 5.34. PES membrane removal efficiencies (direct filtration and filtration after 5 chemical cleaning)

CHAPTER 6

CONCLUSION

In this study, the encouraging idea was pointing the most suitable membrane for RDW (dyeing bath effluent) treatment by comparing different membranes on their fouling behaviors and treatment efficiencies. For this purpose, five different UF membranes (1 kDa RC, 5 kDa RC, 5 kDa PES, 3.5 kDa PPZ and 2 kDa TFC) were investigated based on their permeate flux changes, fouling tendencies/cleanabilities and color, TOC, turbidity and conductivity treatment efficiencies. As a concurrent execution, in order to correlate membrane surface and fouling characteristics, the contact angles and roughness of these different UF membranes were investigated. The results of the study conducted using a real effluent from a cotton textile mill can be summarized as follows:

- By comparing their irreversible fouling resistances after chemical cleaning, the cleanabilities of PES and 1 kDa RC membranes were observed as the lowest ones among all membranes. Also, they had the highest decline between their initial and after chemical cleaning UPW fluxes. By all of the other membranes (5 kDa RC, TFC and PPZ), 5 kDa RC membrane showed the weakest performance for RDW treatment with the lowest color and TOC removal.

- Contact angle results showed a better correlation with fouling tendency than average roughness values of the membranes. According to the results, the two most hydrophobic membranes (PPZ and PES) also had the highest flux decline

percentages while the two most hydrophilic membranes (1 and 5 kDa RC) did not show any significant decline on their flux during filtration process.

- The highest flux decline was observed during the filtration by PPZ membrane which also had the highest average roughness (Ra) and contact angle. This indicated that PPZ membrane is the most hydrophobic membrane among all. And also, PPZ membrane showed a different flux trend during the study. The unexpected flux increase observed with PPZ membrane was the result of physical enlargements caused by ionic strength of salt. So that, the existence of salt in the feed water affects PPZ material in such a different and complicated manner. If this change is permanent after several filtrations, it may cause a decrease in retentions and can shorten the life of membrane.

- Chemical cleaning is a necessary part of filtration process even if it can have some adverse effects on membrane structure. In the study, only PES membrane was observed as significantly affected by chemical cleaning. Effects of both acid and base solutions used in cleaning procedure resulted with PES membrane pore shrinking. This influence can be thought as a possible disadvantage for PES membrane filtration based treatments. This is because the chemical cleaning to be performed after each filtration is likely to shorten the life of PES membrane easier than the other membranes.

- According to the overall results achieved, TFC membrane is proposed as the most proper membrane for RDW treatment by providing lowest fouling tendency (lowest flux decline), acceptable cleanability and quite good treatment performance with the highest color removal (nearly 95%) among the tested membranes. However; as a distinctive treatment criteria, TOC removal capacity of 1 kDa RC is quite higher than the other membranes. This membrane can be recommended as the second best performing membrane also with its highest hydrophilicity among all.

CHAPTER 7

RECOMMENDATIONS

In this study, fouling characteristics of different UF membranes with the wastewater from the first stage of dyeing process was investigated. The wastewater was containing dyes, salt and some auxiliary chemicals in certain concentrations. However; according to the targeted qualities of colorization, recipe of dyeing bath is changed by employees. As only wastewater from one recipe was used during this study, the effect of different recipes was not investigated. Further studies are recommended by TFC membrane in treating different recipes. And also, even if TFC membrane was chosen as the most proper one for RDW treatment among tested membranes, some modifications can be tried on the membrane surface in order to minimize the fouling effect and having higher organic removal.

REFERENCES

3R Technology. (n.d.). Retrieved June 29, 2017, from http://www.3rtechnology.in/membrane.php

Abrahant, E. N., & Whewell, C. S. (n.d.). Textile. In *Encyclopædia Britannica, inc.*

Al-Amoudi, A., & Lovitt, R. W. (2007). Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency. *Journal of Membrane Science*, *303*(1–2), 4–28. http://doi.org/10.1016/j.memsci.2007.06.002

Al-Jeshi, S., & Neville, A. (2006). An investigation into the relationship between flux and roughness on RO membranes using scanning probe microscopy. *Desalination*, *189*(189), 221–228. http://doi.org/10.1016/j.desal.2005.08.001

Al-Kdasi, A., Idris, A., Saed, K., & Guan, C. T. (2004). TREATMENT OF TEXTILE WASTEWATER BY ADVANCED OXIDATION PROCESSES – A REVIEW. *Global Nest: The Int. J*, *6*(3), 222–230. Retrieved from https://journal.gnest.org/sites/default/files/Journal Papers/Al-kdasi-222-230.pdf

Allegre, C., Moulin, P., Maisseu, M., & Charbit, F. (2006). Treatment and reuse of reactive dyeing effluents. *Journal of Membrane Science*, *269*, 15–34. http://doi.org/10.1016/j.memsci.2005.06.014

American Association of Textile Chemists and Colorists. (1981). Dyeing Primer - Google Kitaplar. Retrieved June 9, 2017, from https://books.google.com.tr/books?id=FPz0QRwKHsMC&printsec=frontcover&dq=dyeing+primer&hl=tr&sa=X&ved=0ahUKEwjozpiw27DUAhWkAMAKHRACAboQ6AEIJjAA#v=onepage&q=dyeing primer&f=false

APHA, AWWA, & WEF. (1999). *Standard Methods for the Examination of Water and Wastewater*. Retrieved from https://www.mwa.co.th/download/file_upload/SMWW_1000-3000.pdf

Asatekin, A., Olivetti, E. A., & Mayes, A. M. (2009). Fouling resistant, high flux nanofiltration membranes from polyacrylonitrile-graft-poly(ethylene oxide). *Journal of Membrane Science*, *332*, 6–12. http://doi.org/10.1016/j.memsci.2009.01.029

AWWA. (2007). *Reverse Osmosis and Nanofiltration: Manual of Water Supply Practices M46*.

Babu, B. R., Parande, a K., Raghu, S., & Kumar, T. P. (2007). Cotton Textile Processing : Waste Generation and Effluent Treatment. *The Journal of Cotton Science*, *153*(11:141), 141–153.

Babu, J., & Murthy, Z. V. P. (2017). Treatment of textile dyes containing wastewaters with PES/PVA thin film composite nanofiltration membranes. *Separation and Purification Technology*, *183*, 66–72. http://doi.org/10.1016/j.seppur.2017.04.002

Bailey, W. J. (1981). *Ultrafiltration Membranes and Applications* (Vol. 13). http://doi.org/10.1007/978-1-4613-3162-9

Baker, R. W. (2012). *Membrane Technology and Applications*. *Membrane Technology*. http://doi.org/10.1016/S0958-2118(96)90133-0

Barredo-Damas, S., Alcaina-Miranda, M. I., Iborra-Clar, M. I., Bes-Piá, A., Mendoza-Roca, J. A., & Iborra-Clar, A. (2006). Study of the UF process as pretreatment of NF membranes for textile wastewater reuse. *Desalination*, *200*(1–3), 745–747. http://doi.org/10.1016/j.desal.2006.03.497

Bes-Piá, A., Cuartas-Uribe, B., Mendoza-Roca, J. A., & Alcaina-Miranda, M. I. (2010). Study of the behaviour of different NF membranes for the reclamation of a secondary textile effluent in rinsing processes. *Journal of Hazardous Materials*, *178*(1–3), 341–348. http://doi.org/10.1016/j.jhazmat.2010.01.085

Bisschops, I., & Spanjers, H. (2003). Literature review on textile wastewater characterisation. *Environmental Technology*, *24*(11), 1399–1411. http://doi.org/10.1080/09593330309385684

Chequer, F. M. D., Oliveira, G. A. R. De, Ferraz, E. R. A., Cardoso, J. C., Zanoni, M.

V. B., & Oliveira, D. P. De. (2013). Textile Dyes: Dyeing Process and Environmental Impact. *Eco-Friendly Textile Dyeing and Finishing*, 151–176. http://doi.org/10.5772/53659

Cheryan, M. (1998). *Ultrafiltration and Microfiltration Handbook*. *Taylor&Francis Routledge*. http://doi.org/97-62251

Chollom, M. N., Rathilal, S., Pillay, V. L., & Alfa, D. (2015). The applicability of nanofiltration for the treatment and reuse of textile reactive dye effluent. *Water SA*, *41*(3), 398–405. http://doi.org/10.4314/wsa.v41i3.12

Ciardelli, G., Corsi, L., & Marcucci, M. (2001). Membrane separation for wastewater reuse in the textile industry. *Resources, Conservation and Recycling*, *31*(2), 189–197. http://doi.org/10.1016/S0921-3449(00)00079-3

Correia, V. M., Stephenson, T., & Judd, S. J. (1994). Characterisation of textile wastewaters - a review. *Environmental Technology*, *15*(10), 917–929. http://doi.org/10.1080/09593339409385500

Dias, C. R., & de Pinho, M. N. (1999). Water structure and selective permeation of cellulose-based membranes. *Journal of Molecular Liquids*, *80*(2–3), 117–132. http://doi.org/10.1016/S0167-7322(99)80003-8

Drioli, E. (2016). *Encyclopedia of Membranes*. http://doi.org/10.1007/978-3-662-44324-8

Elimelech, M., Zhu, X., Childress, A. E., & Hong, S. (1997). Role of membrane surface morphology in colloidal fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes. *Journal of Membrane Science*, *127*, 101–109.

Environmental Technology Best Practice Programme. (1997). Water and chemical use in the textile dyeing and finishing industry. *Guide Was Produced by the Environmental Technology Best Practice Programme*, 1–28.

Erkanlı, M., Yilmaz, L., Zeynep Çulfaz-Emecen, P., & Yetis, U. (2017). Brackish water recovery from reactive dyeing wastewater via ultrafiltration. http://doi.org/10.1016/j.jclepro.2017.07.195

Fan, G., Su, Z., Lin, R., Lin, X., Xu, R., & Chen, W. (2016). Influence of Membrane Materials and Operational Modes on the Performance of Ultrafiltration Modules for Drinking Water Treatment, *2016*.

Fersi, C., & Dhahbi, M. (2008). Treatment of textile plant effluent by ultrafiltration and/or nanofiltration for water reuse. *Desalination*, *222*(1–3), 263–271. http://doi.org/10.1016/j.desal.2007.01.171

Fersi, C., Gzara, L., & Dhahbi, M. (2009). Flux decline study for textile wastewater treatment by membrane processes. *DES*, *244*, 321–332. http://doi.org/10.1016/j.desal.200

Field, R. (2010). Fundamental Of Fouling. *Membrane For Water Treatment*, *4*, 22. Retrieved from http://www.wiley-vch.de/books/sample/3527314830_c01.pdf

Franken, A. C. . (2009). *Prevention and control of membrane fouling: practical implications and examining recent innovations*. Retrieved from http://www.ispt.eu/media/CS-01-02-Final-report-Prevention-and-reduction-of-membrane-fouling.pdf

Hendrickx, I., & Boardman, G. D. (1995). Pollution Prevention Studies in the Textile Wet Processing Industry.

Hessel, C., Allegre, C., Maisseu, M., Charbit, F., & Moulin, P. (2007). Guidelines and legislation for dye house effluents. *Journal of Environmental Management*, *83*, 171–180. http://doi.org/10.1016/j.jenvman.2006.02.012

Hobbs, C., Hong, S., & Taylor, J. (2006). Effect of surface roughness on fouling of RO and NF membranes during filtration of a high organic surficial groundwater. *Journal of Water Supply: Research and Technology—AQUA*. http://doi.org/10.2166/aqua.2006.038

Holkar, C. R., Jadhav, A. J., Pinjari, D. V, Mahamuni, N. M., & Pandit, A. B. (2016). A critical review on textile wastewater treatments: Possible approaches. http://doi.org/10.1016/j.jenvman.2016.07.090

Idris, A., Zain, N. M., & Noordin, M. Y. (2007). Synthesis, characterization and performance of asymmetric polyethersulfone (PES) ultrafiltration membranes

with polyethylene glycol of different molecular weights as additives. *Desalination*, *207*(207), 324–339. http://doi.org/10.1016/j.desal.2006.08.008

Jiang, S., Li, Y., & Ladewig, B. P. (2017). A review of reverse osmosis membrane fouling and control strategies. *Science of the Total Environment*, *595*, 567–583. http://doi.org/10.1016/j.scitotenv.2017.03.235

Kant, R. (2012). Textile dyeing industry an environmental hazard. *Natural Science*, *4*(1), 22–26. http://doi.org/10.4236/ns.2012.41004

Karode, S. K. (2001). Unsteady state flux response: a method to determine the nature of the solute and gel layer in membrane filtration. *Journal of Membrane Science*, *188*, 9–20.

Kumbasar, E. P. A., & Körlü, A. E. (2001). *Textile wastewater treatment*. *Sixth International Water Technology Conference*.

Lin, J., Ye, W., Baltaru, M. C., Tang, Y. P., Bernstein, N. J., Gao, P., … Van der Bruggen, B. (2016). Tight ultrafiltration membranes for enhanced separation of dyes and Na2SO4 during textile wastewater treatment. *Journal of Membrane Science*, *514*, 217–228. http://doi.org/10.1016/j.memsci.2016.04.057

López-Grimau, V., Vilaseca, M., & Gutiérrez-Bouzán, C. (2015). Comparison of different wastewater treatments for colour removal of reactive dye baths. *Desalination and Water Treatment*, *3994*(June 2015), 1–8. http://doi.org/10.1080/19443994.2015.1031185

Luján-Facundo, M. J., Mendoza-Roca, J. A., Cuartas-Uribe, B., & Álvarez-Blanco, S. (2015). Evaluation of cleaning efficiency of ultrafiltration membranes fouled by BSA using FTIR-ATR as a tool. *Journal of Food Engineering*, *163*, 1–8. http://doi.org/10.1016/j.jfoodeng.2015.04.015

Luo, J., & Wan, Y. (2011). Effect of highly concentrated salt on retention of organic solutes by nanofiltration polymeric membranes. *Journal of Membrane Science*, *372*(1–2), 145–153. http://doi.org/10.1016/j.memsci.2011.01.066

Marrot, B., & Roche, N. (2002). Wastewater treatment and reuse in textile industries, a review. *Res. Adv. Water. Res*, *3*(January 2002), 41–53.

Meng, F., Zhang, S., Oh, Y., Zhou, Z., Shin, H. S., & Chae, S. R. (2017). Fouling in membrane bioreactors: An updated review. *Water Research*. http://doi.org/10.1016/j.watres.2017.02.006

Moore, S. B., & Ausley, L. W. (2004). Systems thinking and green chemistry in the textile industry: Concepts, technologies and benefits. *Journal of Cleaner Production*, *12*(6), 585–601. http://doi.org/10.1016/S0959-6526(03)00058-1

Mulder, M. (1996). Basic Principles of Membrane Technology. *Zeitschrift Für Physikalische Chemie*. http://doi.org/10.1524/zpch.1998.203.Part_1_2.263

Multilateral Investment Guarantee Agency. (1996). Environmental Guidelines for Textiles Industry. In *Pollution Prevention and Abatement Fruit and Vegetable Processing*. Retrieved from https://www.miga.org/documents/Textiles.pdf

Munir, A. (2006). Dead End Membrane Filtration. Retrieved from http://www.egr.msu.edu/~hashsham/courses/ene806/docs/Membrane Filtration.pdf

Muntha, S. T., Kausar, A., & Siddiq, M. (2017). Polymer-Plastics Technology and Engineering Advances in Polymeric Nanofiltration Membrane: A Review Advances in Polymeric Nanofiltration Membrane: A Review. *Polymer-Plastics Technology and Engineering*, *568*(8), 841–856. http://doi.org/10.1080/03602559.2016.1233562

Noble, R. D., & Stern, S. A. (Eds.). (1996). *Membrane separations technology: Principles and applications*. *Chemical Engineering Science* (Vol. 51). http://doi.org/10.1016/S0009-2509(96)90039-1

Nunes, S. P., & Peinemann, K. V. (2006). *Membrane Technology: in the Chemical Industry*. *Wiley-VCH-Verlag GmbH & Co. KGaA*. http://doi.org/10.1002/3527600388

Patel, H. (2015). Characterization and Treatment of Textile Wastewater Chapter 1 - Introduction. http://doi.org/10.1016/B978-0-12-802326-6.00001-0

Petrini C, I., Bajraktari, N., & Hélix-Nielsen, C. (2015). 17 - Membrane technologies for water treatment and reuse in the textile industry. *Advances in Membrane*

Technologies for Water Treatment, 537–550. http://doi.org/10.1016/B978-1-78242-121-4.00017-4

Porter, M. (1989). Handbook of industrial membrane technology. *Chemie Ingenieur Technik*, *62*(9), 619. Retrieved from http://www.osti.gov/energycitations/product.biblio.jsp?osti_id=6379997

Radhakrishnan, K., Sivaraman, P., & Thilagaraj, R. (2015). Removal of color and COD from actual textile ef fl uent by hybrid biosorption and ultra fi ltration processes. *Journal of Water Reuse and Desalination*, 505–515. http://doi.org/10.2166/wrd.2015.021

Ramesh Babu, P., & Gaikar, V. G. (2001). Membrane characteristics as determinant in fouling of UF membranes. *Separation and Purification Technology*, *24*(1–2), 23–34. http://doi.org/10.1016/S1383-5866(00)00207-0

Ranade, V. V, & Bhandari, V. M. (2014). Chapter 1 - Industrial Wastewater Treatment, Recycling, and Reuse: An Overview. http://doi.org/10.1016/B978-0-08-099968-5.00001-5

Ranganathan, K., Karunagaran, K., & Sharma, D. C. (2007). Recycling of wastewaters of textile dyeing industries using advanced treatment technology and cost analysis—Case studies. *Resources, Conservation and Recycling*, *50*, 306–318. http://doi.org/10.1016/j.resconrec.2006.06.004

Reddy, A. V. R., Trivedi, J. J., Devmurari, C. V, Mohan, D. J., Singh, P., Rao, A. P., … Ghosh, P. K. (2005). Fouling resistant membranes in desalination and water recovery. *Desalination*, *183*, 301–306. http://doi.org/10.1016/j.desal.2005.04.027

Robinson, T., McMullan, G., Marchant, R., & Nigam, P. (2001). Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*, *77*(3), 247–255. http://doi.org/10.1016/S0960-8524(00)00080-8

Saleh, & Gupta. (2016). Chapter 3 - Membrane Classification and Membrane Operations. *Nanomaterial and Polymer Membranes*, 55–82.

http://doi.org/10.1016/B978-0-12-804703-3.00003-6

Schäfer, A. I., Fane, A. G., & Waite, T. D. (1998). Nanofiltration of natural organic matter: removal, fouling and the influence of multivalent ions. *Desalination*, *118*(1–3), 109–122. http://doi.org/10.1016/S0011-9164(98)00104-0

Sen, S., & Demirer, G. N. (2003). Anaerobic treatment of real textile wastewater with a fluidized bed reactor. *Water Research*, *37*, 1868–1878. http://doi.org/10.1016/S0043-1354(02)00577-8

Sert, G., Bunani, S., Yörükoğlu, E., Kabay, N., Egemen, Ö., Arda, M., & Yüksel, M. (2017). Performances of some NF and RO membranes for desalination of MBR treated wastewater. *Journal of Water Process Engineering*, *16*, 193–198.

Shi, X., Tal, G., Hankins, N. P., & Gitis, V. (2014). Fouling and cleaning of ultrafiltration membranes: A review. http://doi.org/10.1016/j.jwpe.2014.04.003

Shishoo, R. (2012). *The Global Textile and Clothing Industry*. *The Global Textile and Clothing Industry*. http://doi.org/10.1533/9780857095626.8

Shon, H. K., Vigneswaran, S., Kim, I. S., Cho, J., & Ngo, H. H. (2006). Fouling of ultrafiltration membrane by effluent organic matter: A detailed characterization using different organic fractions in wastewater. *Journal of Membrane Science*, *278*(1–2), 232–238. http://doi.org/10.1016/j.memsci.2005.11.006

Simonič, M. (2009). Efficiency of ultrafiltration for the pre-treatment of dye-bath effluents. *Desalination*, *245*(1–3), 701–707. http://doi.org/10.1016/j.desal.2009.02.040

Smolders, C. A. (1990). Flux Decline in Ultrafiltration Processes, *77*, 101–133. Retrieved from https://core.ac.uk/download/pdf/11470922.pdf

Sójka-Ledakowicz, J., Koprowski, T., Machnowski, W., & Knudsen, H. H. (1998). Membrane filtration of textile dyehouse wastewater for technological water reuse. *Desalination*, *119*(1–3), 1–10. http://doi.org/10.1016/S0011-9164(98)00078-2

Søtoft, L. F., Lizarazu, J. M., Parjikolaei, B. R., Karring, H., & Christensen, K. V.

(2015). Membrane fractionation of herring marinade for separation and recovery of fats, proteins, amino acids, salt, acetic acid and water. *Journal of Food Engineering*, *158*, 39–47. http://doi.org/10.1016/j.jfoodeng.2015.02.020

Strathmann, H., Giorno, L., & Drioli, E. (2006). An introduction to membrane science and technology. *Journal of Proteome Research*, *10*(January 2011). http://doi.org/10.1021/pr200145a

Thamaraiselvan, C., & Noel, M. (2015). Membrane Processes for Dye Wastewater Treatment: Recent Progress in Fouling Control. *Critical Reviews in Environmental Science and Technology*, *45*(10), 1007–1040. http://doi.org/10.1080/10643389.2014.900242

Trägårdh, G. (1989). Membrane cleaning methods, *71*, 325–335. Retrieved from http://www.lenntech.com/membrane-cleaning.htm#ixzz3Q1xSxpgP

Tsuru, T., Izumi, S., Yoshioka, T., & Asaeda, M. (2000). Temperature effect on transport performance by inorganic nanofiltration membranes. *AIChE Journal*, *46*(3), 565–574. http://doi.org/10.1002/aic.690460315

Vázquez, M. I., De Lara, R., & Benavente, J. (2009). Transport and elastic parameters for dense regenerated cellulose membranes. *Desalination*, *245*, 579–586. http://doi.org/10.1016/j.desal.2009.02.023

Verma, A. K., Dash, R. R., & Bhunia, P. (2012). A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. *Journal of Environmental Management*, *93*(1), 154–168. http://doi.org/10.1016/j.jenvman.2011.09.012

Vrijenhoek, E. M., Hong, S., & Elimelech, M. (2001). Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes. *Journal of Membrane Science*, *188*(1), 115–128. http://doi.org/10.1016/S0376-7388(01)00376-3

Wang, X.-M., & Waite, T. D. (2008). Impact of gel layer formation on colloid retention in membrane filtration processes. *Journal of Membrane Science*, *325*, 486–494. http://doi.org/10.1016/j.memsci.2008.08.016

Wang, Z., Xue, M., Huang, K., & Liu, Z. (2011). Textile dyeing wastewater treatment. *Advances in Treating Textile Effluent*, 91–116. http://doi.org/10.5772/22670

Watters, J. C., Biagtan, E., & Senler, O. (1991). Ultrafiltration of a Textile Plant Effluent. *Separation Science and Technology*, *26*(10–11), 1295–1313. http://doi.org/10.1080/01496399108050533

Wenzel, H., Knudsen, H. H., Kristensen, G. H., & Hansen, J. (1996). Reclamation and reuse of process water from reactive dyeing of cotton. *Desalination*, *106*(1–3), 195–203. http://doi.org/10.1016/0011-9164(96)00109-9

Xiao, P., Xiao, F., Wang, D. S., Qin, T., & He, S. P. (2012). Investigation of organic foulants behavior on hollow-fiber UF membranes in a drinking water treatment plant. *Separation and Purification Technology*, *95*, 109–117. http://doi.org/10.1016/j.seppur.2012.04.028

Xu, C., Liu, X., Xie, B., Yao, C., Hu, W., Li, Y., & Li, X. (2016). Preparation of PES ultrafiltration membranes with natural amino acids based zwitterionic antifouling surfaces. *Applied Surface Science*, *385*, 130–138. http://doi.org/10.1016/j.apsusc.2016.05.084

Yu, H. Y., Tang, Z. Q., Huang, L., Cheng, G., Li, W., Zhou, J., … Wei, X. W. (2008). Surface modification of polypropylene macroporous membrane to improve its antifouling characteristics in a submerged membrane-bioreactor: H2O plasma treatment. *Water Research*, *42*(16), 4341–4347. http://doi.org/10.1016/j.watres.2008.05.028

Zamiah, N., Shaari, K., Rahman, N. A., & Mara, U. T. (2012). Thin film composite membrane with hybrid membrane as the barrier layer : Preparation and characterization. *IEEE Colloquium on Humanities, Science & Engineering Research (CHUSER 2012)*, (Chuser), 615–620. http://doi.org/10.1109/CHUSER.2012.6504386

Zhao, D., Yu, S., Liu, G., Yuan, Q., & Guo, H. (2015). Polypiperazine-amide nanofiltration membrane incorporated with poly (ethylene glycol) derivative for electrodialysis concentrate treatment. http://doi.org/10.1016/j.seppur.2015.08.013

APPENDICES

Appendix A

Table A.1. Recipe of dyeing bath solution

Dyestuff Used	Amount
Reactive Orange S3R	0.56%
Reactive Deep Red SB6	2%
Remazol Ultra Navy Blue RGB	0.26%
Auxiliary Chemicals	
Salt (NaCl)	60g/l
Soda	5g/l
Caustic	1.2g/l

Appendix B

Table B.1. Salt solution filtration effect on fluxes of TFC membrane

2 kDa TFC	Conductivity
	~70 mS/cm
Initial clean water flux (Jcwi)	9.40
Final salt solution flux (Jss)	8.10
Clean water flux after filtration (Jcwf)	9.00
Clean water flux after physical cleaning (Jcwp)	9.40
Clean water flux after chemical cleaning (Jcwc)	8.70

Table B.2. Salt solution filtration effect on fluxes of PES membrane

5 kDa PES	Conductivity
	~70 mS/cm
Initial clean water flux (Jcwi)	53.80
Final salt solution flux (Jss)	47.60
Clean water flux after filtration (Jcwf)	48.50
Clean water flux after physical cleaning (Jcwp)	48.20
Clean water flux after chemical cleaning (Jcwc)	41.60

Table B.3. Salt solution filtration effect on fluxes of RC membrane

5 kDa RC	Conductivity
	~70 mS/cm
Initial clean water flux (Jcwi)	26.50
Final salt solution flux (Jss)	24.60
Clean water flux after filtration (Jcwf)	26.50
Clean water flux after physical cleaning (Jcwp)	26.00
Clean water flux after chemical cleaning (Jcwc)	26.40

Appendix C

Table C.1. PES membrane filtration results (without chemical cleaning after compaction)

5 kDa PES	Filtration #1*	Filtration #2*
Initial clean water flux (Jcwi)	50.5	43.0
Final salt solution flux (Jss)	25.6	26.2
Clean water flux after filtration (Jcwf)	34.5	34.0
Clean water flux after physical cleaning (Jcwp)	31.2	30.5
Clean water flux after chemical cleaning (Jcwc)	11.8	21.2

*In these tests, the recipes of wastewater were different from each other and also from the wastewater #1 used in this research.

Appendix D

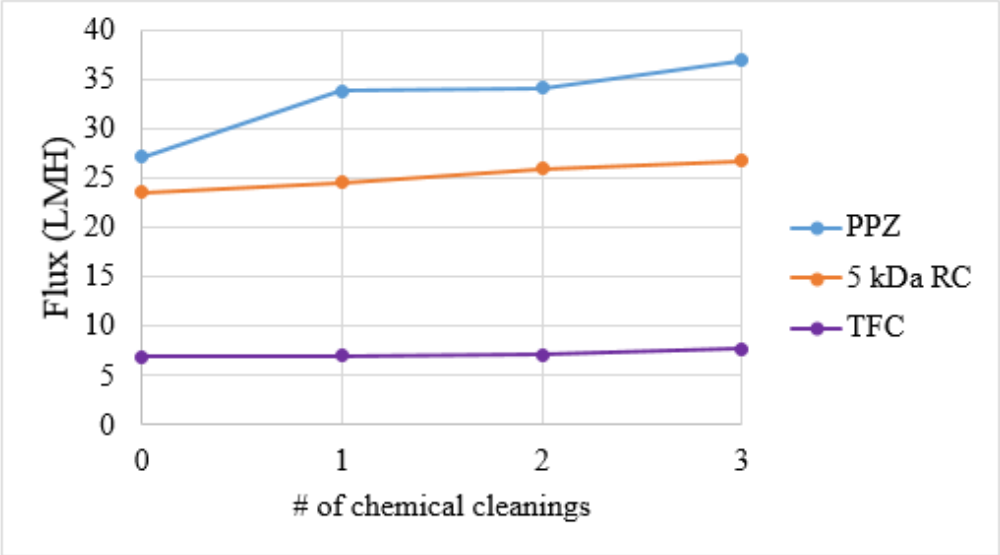

Figure D.1. PPZ, RC and TFC membranes' flux changes after serial chemical cleanings