ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

RECOVERY OF WATER AND CHEMICALS FROM TEXTILE WASTEWATER WITH CERAMIC MEMBRANES

Ph.D. THESIS

Meltem AĞTAŞ

Department of Environmental Engineering

Environmental Sciences Engineering and Management Programme

DECEMBER 2021

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Thesis Advisor: Prof. Dr. İsmail KOYUNCU

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

SERAMİK MEMBRANLARLA TEKSTİL ATIKSULARINDAN SU VE KİMYASAL GERİ KAZANIMI

DOKTORA TEZİ

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Meltem AĞTAŞ, a Ph.D. student of İTU Graduate School student ID 501142702 successfully defended the thesis/dissertation entitled "RECOVERY OF WATER AND CHEMICALS FROM TEXTILE WASTEWATER WITH CERAMIC MEMBRANES", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,

FOREWORD

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November 2021 | Meltem AĞTAŞ
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ABBREVIATIONS

BAT	: Best Available Techniques
BOD	: Biochemical Oxygen Demand
BREF	: Best Available Techniques Reference Documents
BSA	: Bovine Serum Albumin
CFV	: Cross-flow Velocity
CNT	: Carbon Nanotube
COD	: Chemical Oxygen Demand
ESEM	: Environmental Scanning Electron Microscope
HNT	: Halloysite Nanotube
IPPC-IED	: Integrated Pollution Prevention and Control-Industrial Emmisons Directive
kDa	: Kilo Dalton
LMH	: Litre per square meter per hour
MBR	: Membrane Bioreactor
MF	: Microfiltration
MRSL	: Manufacturing Restricted Substances List
MWCO	: Molecular Weight Cut Off
NF	: Nanofiltration
PE	: Polyethylene
PES	: Polyethersulfone
RO	: Reverse osmosis
SCADA	: Supervisory Control and Data Acquisition
SEM	: Scanning Electron Microscope
SS	: Suspended Solids
TMP	: Transmembrane Pressure
TOC	: Total Organic Carbon
TSS	: Total Suspended Solids
UV	: Ultraviolet
ZDHC	: Zero Discharge of Hazardous Chemicals

SYMBOLS

°C	: Celsius
A	: Area
c	: Spesific Heat Capacity
g	: Gram
J	: Flux
L	: Liter
m	: Mass
m^2	: Square metre
m^3	: Cubic meter
mg	: Miligrams
mm	: Milimeter
N	: Nitrogen
nm	: Nanometer
P	: Phosphorus
Q	: Required heat
wt	: Weight
Δm	: Collected amount of permeate
Δt	: Time interval
ρ	: Density

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RECOVERY OF WATER AND CHEMICALS FROM TEXTILE WASTEWATER WITH CERAMIC MEMBRANES

SUMMARY

Decreased water resources in our world necessitate the treatment and reuse of polluted water. Water recovery is of vital importance, both in terms of sustainability and economy, especially in industries that consume large amounts of water. One of the industries that consume a high amount of water is the textile industry. In the textile industry, 0.06-0.40 m^3 water/kg product is used according to literature. In parallel with the amount of water used in the processes in the textile industry, a high amount of wastewater is generated. These wastewaters are known to contain high COD, different dyes, heavy metals, etc. For this reason, it is not possible to discharge these wastewaters into the environment without proper treatment.

Many traditional methods for the treatment of textile wastewater such as coagulation-flocculation, activated carbon adsorption, ozonation and biological treatment are used. However, these methods cannot meet strict discharge limits or are not economically viable. Therefore, membrane processes come to the fore in textile wastewater treatment since they are recommended for textile wastewater treatment in the BAT (Best Available Techniques) reference document. As a result of textile wastewater treatment with membrane processes, high-efficiency treatment is provided and the treated wastewater can have the potential to be reused.

Polymeric membranes are generally preferred in treatment processes. However, since textile wastewaters have high temperatures and extreme pH values, the use of polymeric membranes is not suitable. The textile industry produces wastewater with temperatures that can go up to 90-95 °C. Generally, wastewater must be cooled down before membrane treatment. For efficient treatment, membranes have to be thermally stable; most polymeric membranes tend to degrade at high temperatures and therefore, they are not suitable for hot wastewater treatment.Therefore, the use of ceramic membranes in the treatment of textile wastewater is a viable method. Besides, when ceramic and polymeric membranes are compared, it can be said that ceramic membranes are having more advantageous in terms of high thermal, mechanical, and chemical stability, well-defined pore size distribution, and high flux.

In this thesis, a comprehensive study was carried out on the pilot-scale water and chemical recovery using ceramic membranes from real textile wastewater and the development of halloysite nanotube doped membranes for the treatment and recovery of real textile wastewater. First, a pilot-scale ceramic ultrafiltration/nanofiltration system was operated for hot water recovery by treating real textile wastewater in a selected textile factory. Later, in the same facility, real textile wastewater with caustic content was used in order to make chemical recovery. Based on the successful results of these studies, after it was proven that water and chemical recovery can be made with ceramic membranes, halloysite nanoclay added membranes were produced in order to make this process more economical, and treatment trials were carried out with real wastewater from the same facility and important results were obtained.

SERAMİK MEMBRANLARLA TEKSTİL ATIKSULARINDAN SU VE KİMYASAL GERİ KAZANIMI

ÖZET

Dünya üzerindeki su kaynakları, artan nüfus ve sanayileşmenin sonucu olarak günden güne azalmaktadır. İnsani kullanımın yanı sıra, endüstrilerin üretim ve diğer prosesleri için kullandığı su miktarı da ciddi boyutlardadır. Tekstil, kozmetik, kağıt ve benzeri endüstriler, hem yüksek miktarlarda su tüketmekte hem de bu miktara paralel olarak yüksek miktarlarda atıksu oluşumuna neden olmaktadır. Örneğin, literatüre bakıldığında tekstil endüstrisinde kg başına ürün için 0.06-0.40 m^3 su harcandığı görülebilmektedir. Miktarın yanı sıra, tekstil atıksularının toksik olduğu da bilinmektedir. Bu nedenle, tekstil atıksularının uygun bir arıtım olmadan çevreye deşarj edilmesi mümkün değildir. Bunun yanı sıra, tekstil atıksularının uygun biçimde arıtılması, geri kazanılması ve proseslerde yeniden kullanılması hem ekolojik sürdürülebilirlik hem de ekonomik açıdan büyük önem arz etmektedir.

Tekstil atıksularının arıtımı için birçok geleneksel yöntem kullanılmaktadır. Koagülasyon-flokülasyon, adsorpsiyon, ozonlama, biyolojik arıtım gibi birçok yöntem uzun yıllardır tercih edilmektedir. Fakat bu yöntemler, hem sıkı deşarj limitlerini sağlamada hem de atıksuların yeniden kullanımı için yeterli arıtımı sağlamada yetersiz kalabilmektedir. Bunların yanı sıra bu yötemlerin, hem ekonomik hem de çevresel açılardan da dezavantajları bulunmaktadır. Örneğin koagülasyon-flokülasyon prosesi sonrası fazla miktarda çamur oluşmakta, biyolojik arıtım da ise atıksu içerisindeki boyalar yeterince giderilememektedir. Bu noktada membran prosesler öne çıkmaktadır. Son yıllarda membran prosesler su ve atıksu arıtımında oldukça popüler bir yöntem haline gelmiştir. Özellikle tekstil atıksularının arıtımı için, mevcut en iyi teknikler (Best Available Techniques-BAT) referans dökümanlarında membran prosesler önerilmektedir.

Membran proseslerde genel olarak polimerik membranlar tercih edilmektedir. Ancak tekstil atıksuları genellikle yüksek sıcaklıklara ve çok düşük ya da çok yüksek pH değerlerine sahip olduğundan, polimerik membranların kullanımı uygun değildir. Tekstil endüstrisi, 90-95 °C'ye kadar çıkabilen sıcaklıklarda atıksular üretmektedir. Polimerik membran kullanıldığında, atıksu membran arıtımından önce soğutulmalıdır. Etkili arıtma için membranların termal olarak dayanıklı olması gerekir; fakat polimerik membranların çoğu yüksek sıcaklıklarda bozulma eğilimindedir ve bu nedenle sıcak atıksu arıtımı için uygun değildirler. Bu nedenle tekstil atıksularının arıtılmasında seramik membranların kullanılması uygulanabilir bir yöntemdir. Ayrıca seramik ve polimerik membranlar karşılaştırıldığında, seramik membranların yüksek termal, mekanik ve kimyasal dayanıklılık, homojen gözenek boyutu dağılımı ve yüksek akı açısından daha avantajlı olduğu söylenebilir. Özellikle tekstil sektöründe sıcak atıksu arıtımında kullanıldığında, artan sıcaklık ile düşen viskoziteye bağlı olarak seramik membran akı değerleri artacaktır. Ek olarak, seramik membranların yüksek pH ve kimyasal direnci nedeniyle, membranlar daha agresif bir temizleme işlemine

dayanabileceğinden membran performansı daha verimli bir şekilde geri kazanılabilir. Tekstil atıksuyunun özellikleri ile seramik membranların özellikleri birlikte düşünüldüğünde bu membranların tekstil atıksu arıtımında kullanılması literatürde de önerilmektedir.

Seramik membranlar ile yapılan çalışmalar incelendiğinde, genel olarak labaratuvar ölçeğindeki çalışmaların yoğunlukta olduğu görülmektedir. Buna karşın pilot ve gerçek ölçekteki çalışmalar oldukça azdır. Laboratuvar ölçeğindeki çalışmalar birçok çalışmanın çıkış noktası olmasına ve çok değerli olmasına rağmen, gerçek uygulamalar için pilot çalışmaların gerekli olduğu düşünülmektedir. Pilot ve gerçek uygulamaların yaygın olmamasının en önemli sebeplerinden biri seramik membranların maliyetli olmasıdır. Bu sorunun aşılabilmesi için de düşük maliyetli seramik membranların üretilebilmesi önem taşımaktadır.

Bu tez kapsamında, gerçek tekstil atıksularının gerçek şartlar altında pilot ölçekli seramik ultrafiltrasyon/nanofiltrasyon sistemi ile arıtılarak su ve kimyasal geri kazanımının yapılması amaçlanmıştır. Buna ek olarak bu proseslerin daha ekonomik olabilmesi açısından, halloysit nanokil katkılı seramik membranların üretimi ve gerçek tekstil atıksuyu arıtım performanslarının incelenmesi de tezin ana amaçlarındandır.

Bu amaçlar doğrultusunda, ilk olarak pilot ölçekli seramik ultrafiltrasyon/nanofiltrasyon sistemi sıcak su geri kazanımı için seçilen tekstil fabrikasında işletilmiştir. Tüm denemeler, gerçek şartlar altında gerçek tekstil atıksuyu kullanılarak yapılmıştır. Elde edilen sonuçlar değerlendirildiğinde, arıtılan sıcak tekstil atıksuyunun membran çıkışında sıcaklığının yaklaşık ortalama 15 derece kadar düştüğü bu ek olarak verimli bir şekilde arıtıldığı gözlemlenmiştir. Böylece proseste kullanılacak suyun 0 °C’den 95 °C’ye ısıtılmasının yerine, elde edilen sıcak membran süzüntüsünün 95 °C’ye ısıtılması ekonomik anlamda kar sağlayacaktır. Buna ek olarak elde edilen membran çıkış suyu ile tesis içerisinde kumaş boyama denemeleri yapılmış ve yapılan üç denemeden ikisi başarılı olmuştur.

Tez kapsamında yapılan bir sonraki çalışmada ise, tekstil atıksularından kimyasal geri kazanımı hedeflenmiştir. Bu doğrultuda pilot ölçekli seramik ultrafiltrasyon/nanofiltrasyon sistemi yine aynı tekstil fabrikasında kostik içerikli atıksular ile işletilmiştir. Bu çalışmanın sonuçlar değerlendirildiğinde, yapılan tüm denemelerde en az %50 sodyumun geri kazanıldığı görülmektedir. %50 geri kazanım sağlanması, proseste kullanılan sodyum maliyetinden en azından bu oranda tasarruf edilmesi anlamına gelmektedir. Kimyasal geri kazanımın yanı sıra, bir diğer önemli nokta da aynı zamanda su geri kazanımının da gerçekleşmesidir. Membran filtrasyon sonucunda elde edilen süzüntü yeterli miktarlarda arıtıldığından ve kostik içerdiğinden tesis içerisinde uygun proseslerde tekrar kullanılabilir. Bu durum, gerçek ölçekli kullanım için oldukça umut verici bir sonuç olarak değerlendirilmektedir.

Tekstil atıksularının seramik membranlarla etkin bir şekilde arıtılıp geri kazanılabileceği tez kapsamında yapılan pilot ölçekli çalışmalar ile kanıtlandığından, tezin bundan sonraki amacına odaklanılmış ve seramik membranların yaygın olarak uygulanabilmesinin önündeki en büyük sorunlardan olan yüksek membran maliyetlerinin üstesinden gelmek için seramik membran üretimi gerçekleştirilmiştir. Bu amaçla ülkemizde de mevcut bir kil minerali olan halloysit nanokil kullanılarak nispeten düşük sıcaklıklarda ultrafiltrasyon ve sıkı ultrafiltrasyon seviyesinde membranların üretimi yapılmıştır. Üretilen membranlar karakterize edildikten sonra, ilk çalışmada kullanılan gerçek tekstil atıksuları ile arıtım ve performans testleri yapılmıştır. Elde edilen sonuçlar incelendiğinde, membranların beklenen arıtım seviyelerine ulaştıkları gözlemlenmiştir. Ayrıca, son olarak yapılan sıcak atıksu arıtım testlerinde ise membran akılarının arttığı fakat giderim verimlerinin belirgin oranda düşmediği görülmüştür.

Tezde yapılan tüm çalışmalara bütünsel olarak bakıldığında, su ve kimyasalların seramik membranlar ile geri kazanıldığı ve yeniden kullanılma potansiyelinin olduğu sonucuna varılabilmektedir. Böylece hem çevresel hem de ekonomik olarak kazanımlar elde edilebilecektir. Ayrıca son dönemlerde oldukça önem verilen tehlikeli atıkların sıfır deşarjı konseptine de katkı sağlanabileceği anlaşılabilmektedir.

1. INTRODUCTION

Usable water resources on earth are gradually decreasing with rapid population growth and industrialization. In addition to human water use, especially various industries consume large amounts of water within the scope of their own processes. It is known that the textile industry is one of the leading industries in water use in the world. As a result of the high amount of water use, a large amount of wastewater occurs. In order to protect water resources and reduce water use, the treatment, recovery and reuse of wastewater from the textile industry are important. Traditional methods used for textile wastewater treatment (coagulation-flocculation, advanced oxidation processes, adsorption, etc.) are insufficient in many respects. At this point, the use of membrane processes for textile wastewater becomes important. Since polymeric membranes, which are generally used in membrane processes, are not resistant to the high temperature and extreme pH values of textile wastewater, ceramic membranes are more suitable for this purpose.

In this thesis, a comprehensive study was carried out on the pilot-scale water and chemical recovery using ceramic membranes from real textile wastewater and the development of halloysite nanotube doped membranes for the treatment and recovery of real textile wastewater. Purpose of thesis, unique aspect and organization of the thesis are given below.

1.1 Purpose of Thesis

Within the scope of this thesis, it was aimed to carry out three main studies.

- Treating real hot textile wastewater with a pilot ultrafiltration/nanofiltration ceramic membrane technology and recover hot water to reuse in the plant again. In addition to this, making an economic analysis of the study.
- Treating the real caustic bath wastewater (pH>13) with a pilot ultrafiltration/nanofiltration ceramic membrane technology and recover water

and caustic solution. In addition to this, making an economic analysis of the study.

- Fabrication of halloysite nanotube (HNT) -doped ultrafiltration (UF) and tight-ultrafiltration ceramic membranes with the layer deposition method using relatively low temperatures, and the treatment of textile wastewaters with the produced membranes.

1.2 Unique Aspect

The originality of this thesis is the in-situ treatment of real textile wastewater, the recovery of chemical and hot water, and the acquisition of real field data with the pilot ceramic membrane system, which does not have many applications in the literature. In addition, the usability of the recovered water in the processes has been examined and proven. Another uniqueness is the production of ceramic ultrafiltration and tight ultrafiltration membranes more economically at relatively low temperatures by using halloysite nanotube, which is a type of clay that is widely found in our country, and its use in the treatment of real textile wastewater and successful results are obtained.

1.3 Organization of the Thesis

The thesis contains an introduction followed by a review article (Chapter 2) and three data chapters (Chapters 3-5). Afterward, the comprehensive conclusion of the thesis and recommendations for future studies are presented in the sixth chapter (Chapter 6). In Chapter 2, the properties of ceramic membranes and the use, advantages, and disadvantages of ceramic membranes in textile wastewater treatment and recovery processes are represented and explained in detail. In Chapter 3, the pilot ceramic ultrafiltration/nanofiltration system for hot water recovery from real textile wastewater, which is one of the main objectives of the thesis, was operated in the selected textile factory and the results were collected. Therefore, cross flow ceramic membrane filtration experiments were performed and flux and removal efficiencies were calculated. Temperature changes between feed and permeate streams were monitored. In addition to this, dyeing experiments were carried out with treated water obtained from the ultrafiltration+nanofiltration operation mode which were made with hot mixing wastewater. Also, an economic evaluation was implemented. In Chapter 4, as a continuation of the work done in Chapter 3, the wastewater from processes containing caustic in the same factory was treated with a pilot ceramic ultrafiltration/nanofiltration system, and chemical and water recovery was aimed. In addition, a determination of how the obtained permeate will be used in the facility and whether the whole process is economically viable was carried out. Since it has been proven in Chapters 3 and 4 that textile wastewater can be effectively treated and recovered with ceramic membranes, the next aim of the thesis has been focused and ceramic membrane production has been carried out in order to overcome the high membrane costs, which is one of the most important obstacles in the use of ceramic membranes. Hence, in the 5th chapter, fabrication of HNT-doped ultrafiltration (UF) and tight-ultrafiltration ceramic membranes with the layer deposition method using relatively low temperatures, and the treatment of textile wastewaters with the produced membranes were examined. Treatability studies were carried out using 3 different real textile wastewater taken from the same factory which wastewater was used in the studies in Chapters 3 and 4, with the tight UF membrane obtained and also hot wastewater treatment tests were performed. In the last chapter, Chapter 6, the general results of the whole thesis are explained and recommendations for future studies are presented.

2. CERAMIC MEMBRANE OVERVIEW AND APPLICATIONS IN TEXTILE INDUSTRY: A REVIEW[1]

2.1 Introduction

Increasing population, impetuous urbanization, improper use of water resources and climate change are increasing the need for safe water. It is very difficult for them to lead a healthy life as approximately 15 percent of 7 billion people in the world do not have access to clean water (Sheikh et al., 2019).

The world has a lot of critical environmental problems and industrial wastewaters which has dangerous and detrimental contaminants in it is one and an important part of these problems. The main ones from these industries are the textile, mining, pharmaceutical, pulp and paper and petrochemical industries. All of these industries have detrimental effects on soil, air and water ecosystems because of their wastewaters (Samaei et al., 2018). When the textile industry is evaluated with a global approach, the demand for textile products is increasing with a constant rate and it is expected that it will continue to increase given the economic developments and population growth (Sandin and Peters, 2018).

In the textile sector, China is a leader country in fabrication and export. In the global textile exporter list regarding 2016, China was in the first place with nearly 106 billion US dollars export and Turkey was in fifth place after European Union, India and the USA (Rovira and Domingo, 2019). In the Turkish manufacturing sector, the textile industry employs 27% of all workers. The textile industry in Turkey consists of small and large scale establishments and a lot of complicated processes. Because of the regulations and strict discharge standards, efficient water and chemical usage became more important in the Turkish textile sector and cleaner production procedures are started to implement based on Turkish BREF and IPPC-IED directive. Most of action carried out to modify processes and equipment to decrease water and chemical usage

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[1] This chapter is based on the paper "Meltem Ağtaş, Mehmet Dilaver and İsmail Koyuncu. Ceramic membrane overview and applications in textile industry: a review. Water Science & Technology, 2021.DOI: 10.2166/wst.2021.290. "

(Ozturk et al., 2016). Within this context, using water recovery and reuse applications in the food, textile, metal, paper and chemical industries where water consumption is intense; it will contribute significantly to the reduction of raw water consumption, wastewater discharged to the receiving water bodies and the amount of pollutants contained in the wastewater (Dilaver et al., 2018).

In finishing and dyeing processes in a conventional textile factory, an averagely 150 m^3 of water has to be used for manufacturing every tone of the fabric product. Besides the use of water, in different textile mill processes such as bleaching, finishing, dyeing and printing, 3600 different types of dyes and 8000 types of various chemicals are put to use and therewith human health and aquatic ecosystem can be affected by these compounds because of the pollution of soil and water (Hussain and Wahab, 2018). US Environmental Protection Agency made a classification for wastes from textile and divided into groups. These groups were named as hard to treat, hazardous and toxic, high volume and dispersible. Textile industry wastewater generally contains high amounts of colour, salt, turbidity, chemical oxygen demand, total dissolved solids and complex chemicals. In addition, the temperature and pH of these wastewaters can be in extreme conditions (Dasgupta et al., 2015). For the treatment of textile industry effluent, generally physicochemical and biological treatment methods were applied. Nevertheless, these methods aren't sufficient enough to remove surfactants, salts, some kind of dyes and so on. To obtain high quality water after treatment, advanced technologies are required to be used (Cinperi et al., 2019). Membrane technology can be identified as a suitable choice for the textile wastewater treatment since most of textile effluents have high temperature and high basic nature. For commercial applications, polymeric membranes are quite popular but ceramic membranes are more resistant to temperature and have high mechanical and chemical stability compared to polymeric membranes (Zebić Avdičević et al., 2019). For instance, more effective chemicals can be used for the membrane cleaning procedure without the risk of damaging the membrane (Lee et al., 2013). Another advantage of ceramic membranes is having longer service life than polymeric membranes. But the cost of ceramic membranes can be shown as a drawback although in recent years the cost of ceramic membranes has been decreasing (Zebić Avdičević et al., 2017).

The data obtained in the search made in the literature using the keywords 'ceramic membrane' (demonstrates the results of 'Scopus' search) are given in Figure 2.2,

Figure 2.3 and Figure 2.4, between 1966-2020. When the graph is analysed, it is seen that there has been a rapid increase in studies involving ceramic membranes since 1990. When we look at the countries where the studies are carried out, it is seen that China is in the first place and USA comes after. When we look at the kind of studies, it is seen that the publication is the most widely published as article and then the conference paper and reviews come (data obtained from Scopus, 7th June 2020).

In this review, studies on characterization and treatment of textile industry wastewater have been studied and the properties and applications of ceramic membranes have been emphasized. In addition, it was aimed to highlight the importance of ceramic membranes in the treatment and recovery of textile wastewater. For this reason, important studies in recent years have been gathered together to the best of our knowledge.

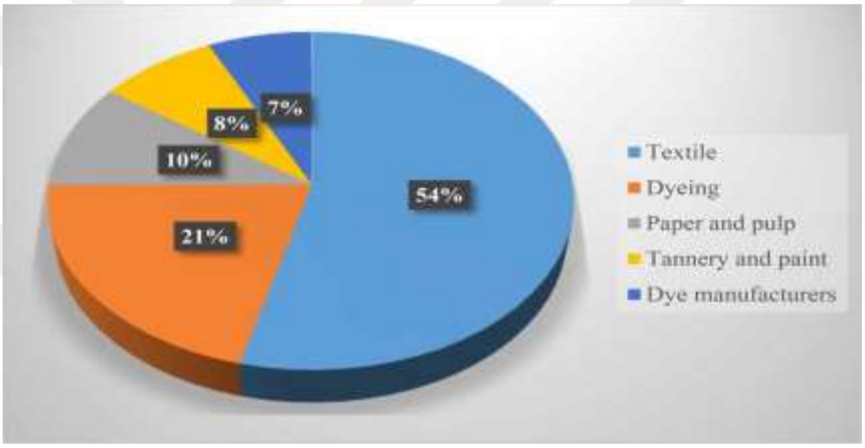

Figure 2.1 : Industries responsible for the presence of dye effluent in the environment (Katheresan et al., 2018).

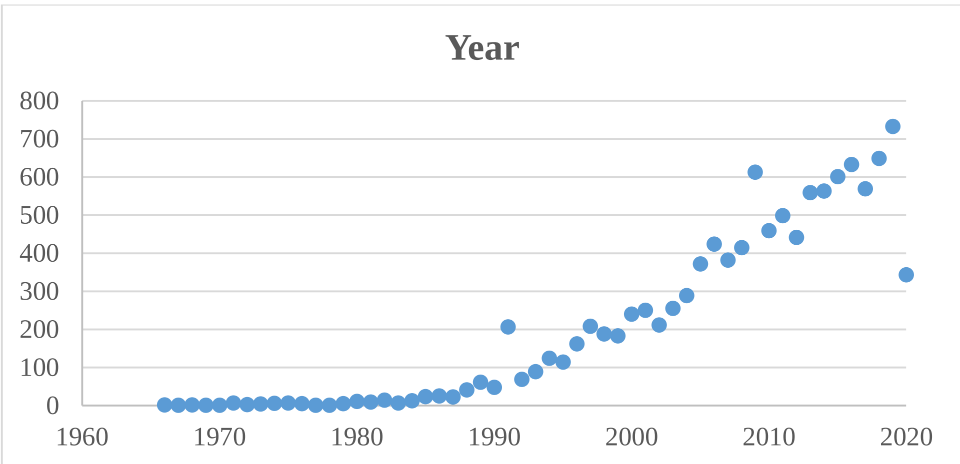

Figure 2.2 : The number of publication on ceramic membrane based on year. The data is based on the citation database Scopus in June 2020.

2.2 General Information About Textile Processes

Textile industry is an industry that consumes large amounts of water and therefore limits global water resources. Especially in wet processes, due to high water usage, the textile industry produces high amount of wastewater with high pollution (Hussain and Wahab, 2018). For instance, in dyeing process, approximately 100-150 L of water per 1 kg fiber can be used. Not only water but also different type of dyes and chemicals are required for this process and consequently process wastewater contains of unused dyes, salts and surfactants (Zheng et al., 2016). The processes in textile industry start with treatment of raw materials. For fabrication of woven and knitted products, to give products aesthetic and physical properties; printing, dyeing, bleaching, coating, impregnating and similar processes can be applied (Bullon et al., 2017).

In Figure 2.5, flow chart of an exemplary factory is given. Alkaya and Demirer included this factory in their work. This company is located in Bursa with 10.000 m^2 factory area and produces woven products. They use cotton, polyester and lycra based materials for fabrication. The average fabric production of 2009, 2010 and 2011 is approximately 2226 tons/year (Alkaya and Demirer, 2014).

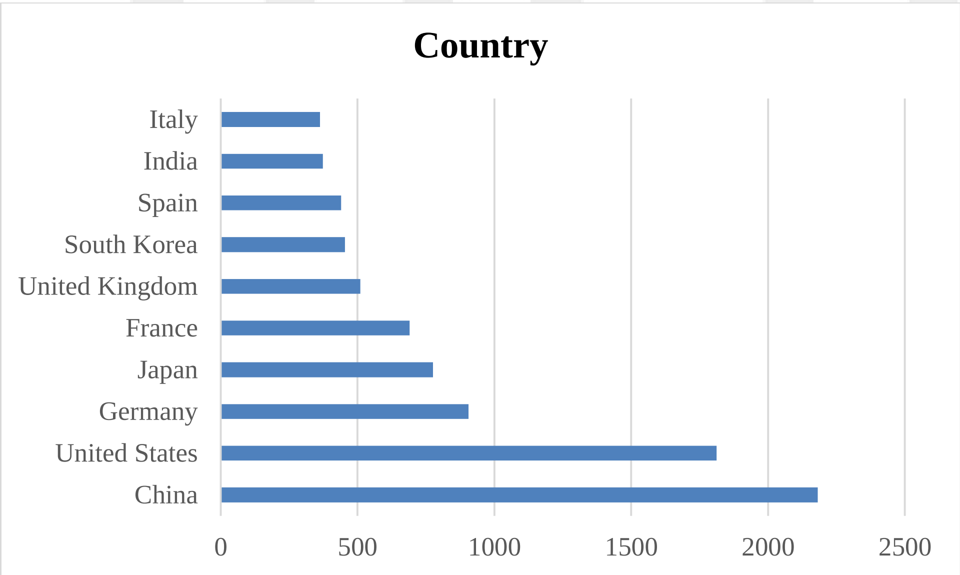

Figure 2.3 : The number of publication on ceramic membrane based on country. The data is based on the citation database Scopus in June 2020.

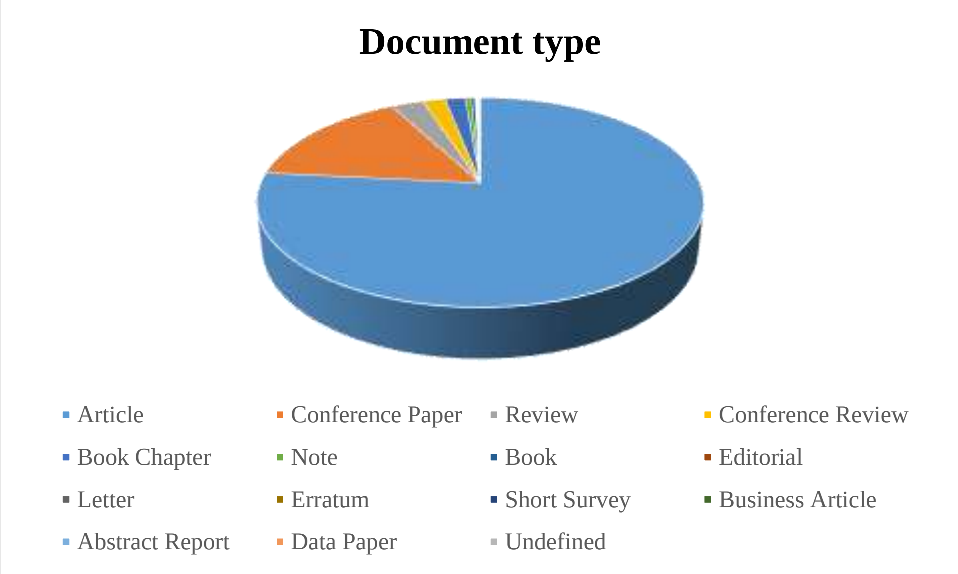

Figure 2.4 : The number of publication on ceramic membrane based on document type. The data is based on the citation database Scopus in June 2020.

The processes that are considered important in the flow chart of the textile industry are mentioned below.

Before weaving or spinning process, the sizing process is applied to yarns to make yarns more durable and prevent fiber break down. Wastewater generated from sizing process has a high level of pollution parameters such as Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and suspended solids (SS) even a low amount of wastewater is generated. (Bisschops and Spanjers, 2003).

Scouring and bleaching processes are generally applied consecutively. The purpose of the scouring process is to remove substances such as oil, wax and fat from the product to increase the absorbency level using an alkaline chemical (Harane and Adivarekar, 2017).

In the mercerization process, alkali solutions are used for enhancing the tension of fiber, improving fiber's surface gleam and ameliorate the affinity of dye. Accordingly, the wastewater generated as a result of the mercerization process has a high base content and is mixed with wastewater from other processes to be treated (Zhang et al., 2014).

Dyeing operation is a process that is used to colour the product, using many types of dyes, different equipment and methods and can be done at different points of production. (Varol, 2008).

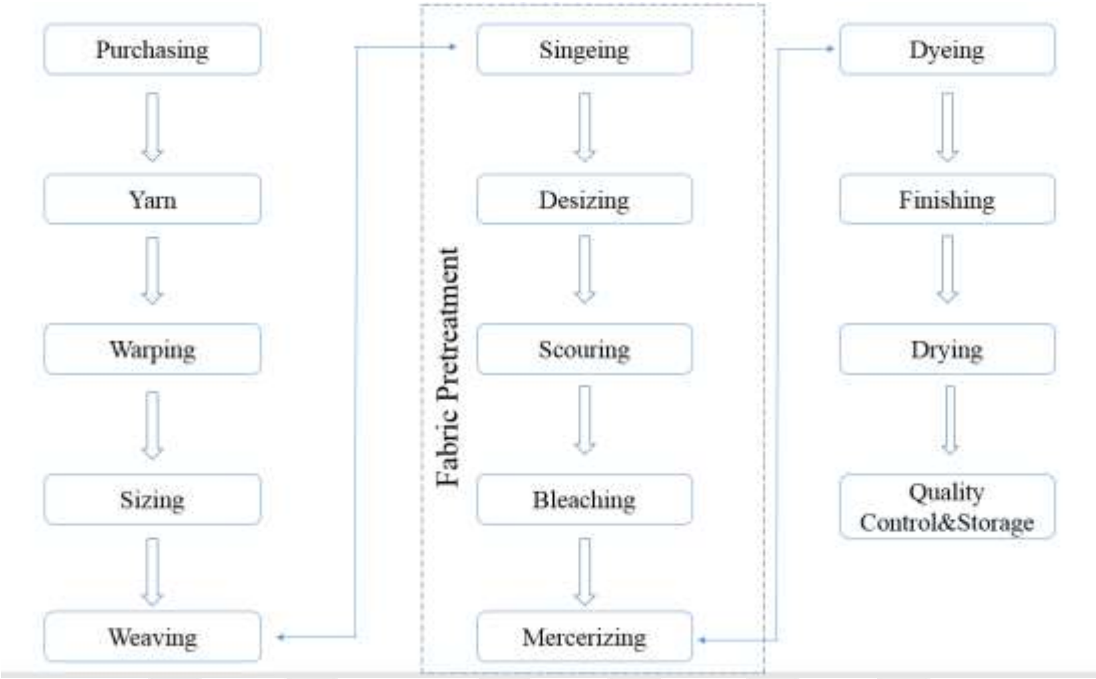

Figure 2.5 : Example of a textile mill flow diagram (Bursa, Turkey)(adapted from Alkaya and Demirer, 2014).

For making the fabric more favourable for final use, the fabric goes through some processes to alter its outlook or performance. Finishing operations are important in many aspects. For instance, it is able to change the texture of the product, make products appropriate for a specific use, and advance the appearance of the product (Bullon et al., 2017).

2.2.1 Textile wastewater characterization

Textile industry wastewaters contain different biological and physicochemical parameters such as salinity, pH, temperature, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total nitrogen (TN), total dissolved solids (TSS), total phosphorus (TP), non-biodegradable organic compounds, heavy metals (Cr, Cu, Zn, Ar, etc.) and wide range of type of dyes (Berradi et al., 2019). The dyes used in the textile industry are based on various chemical structures, for instance sulphur, azoics, triphenyl methane and others. Depending on the technological developments, chemicals used in colouring processes have also developed. In particular, different chemicals are used to provide properties such as softness, flame retardant and wrinkle-free effect to the end product. Approximately 90% of the chemicals used in this last stage remain on the fabric and the rest passes into the wastewater through washing processes (Nimkar, 2018).

There are a lot of studies including textile effluent characterization in literature. In this study, the most general and current ones are tried to be mentioned. In a recent study is being conducted by real wastewater from disperse printing and reactive printing washing baths hot discharges mixing point, average values for COD, total hardness, TOC were 580 mg/L, 49 mg $CaCO_3$/L and 161 mg/L respectively (Ağtaş et al., 2020). Tomei and friends (2016) studied analysing performance of real textile wastewater (dyeing bath of a textile factory) bio-decolourization. According to experiments they have performed, COD, BOD_5, TSS and TOC values were 1017 mg/L, 9.8 mg/L, 535 mg/L and 158 mg/L respectively. pH was reported as approximately 9 (Tomei et al., 2016). Bilinska (2019) investigated treatment of textile wastewater with electrocoagulation and ozone processes. Studied wastewater's pH was 11.82 and conductivity was 57.56 mS/cm. They also measured NaCl as 53.66 g/L, COD as 1315±5 and as TOC 264±20 mg O_2/L. Since high pH and high salinity values are common properties for textile wastewater, their results are expectable (Bilińska et al., 2019). When these results are examined, it can be said that even for similar processes, wastewater characterization can be varied in a wide range. In Yaseen's (2019) paper, this variety attributed to textile wastewater consisting of different effluents which are outlet streams of particular processes or passed through specific stages. For instance, in textile manufacturing steps, different dyes and additives are used and these are the reason of metal presence in this process' wastewater (Yaseen and Scholz, 2019). Wastewater characterization (average values) in literature is given in Table 2.1.

Table 2.1 : Wastewater characterization (average values) in literature.

Parameter	Literature values
COD (mg/L)	580[a],1017[b],1315[c],281[d],1581[d],1560[e], 185.6[f],329.4[g]
Hardness (mg $CaCO_3$/L)	49[a],500[e]
Colour	0.33[a*],137[d**],713[d**],2.98[f*]
Conductivity (µs/cm)	57.56[c],27700[d],92200[d],568[f],8620[g]
TOC (mg/L)	161[a],158[b],264[c],390[e],49.05[f]
BOD_5 (mg/L)	9.8[b]
TSS (mg/L)	535[b],34[d],196[d]
pH	9[b],11.82[c],10.5[d],10.7[d]
NaCl (g/L)	53.66[c]

(*value for 525 nm, ** unit as Pt-Co.)

[a] (Ağtaş et al., 2020), [b] (Tomei et al., 2016), [c] (Bilińska et al., 2019), [d] (Ozturk et al., 2016b), [e] (Blanco, Torrades, et al., 2014), [f] (Güyer, Nadeem, et al., 2016), [g] (Fersi and Dhahbi, 2008).

2.2.2 Textile wastewater treatment methods

As mentioned in the previous section, textile wastewater has a characteristic that includes a wide variety of parameters such as COD, colour, hardness, conductivity, TSS, BOD and so on.

For treatment of this kind of wastewater, various treatment technologies have been studied and applied up until now. To select a proper method for treatment, there are several factors which have to be considered. Textile factory's process chart, type of chemicals and dyes which are used in these process', local standards of discharge and cost of treatment options are important. If wastewater is aimed to be recovered or reused, it may be necessary to change the perspective for treatment options and in this case wastewater streams may need to be separated and managed separately (Jegatheesan et al., 2016).

Many treatment techniques have been applied for textile wastewater treatment. Physical methods such as coagulation-flocculation, adsorption, advanced and chemical oxidation, biological methods and membrane processes are available in the literature (Holkar et al., 2016; Yukseler et al., 2017). Considering all the various pollutants which are found in textile wastewater, dyes are thought to be as the most persistent source of pollution (Lafi et al., 2018). Also, the types of dyes vary depending on the material. Different dyes used for different materials are given in Figure 2.6 (Holkar et al., 2016).

For dye-containing wastewater, the coagulation process has been used as a pre-treatment or main treatment option for many years. Its low investment cost also allowed it to be used frequently. But there is a major drawback for this process which is sludge generation. Besides, the coagulation process can't be effective for removal of some kind of soluble dyes (Verma et al., 2012).

Adsorption, which is another method frequently used in dye removal, is preferred due to its ease of use and high removal efficiency. Carbon nano tubes, zeolite, graphene, activated carbon obtained from some different materials are commonly used for adsorption process (Abd-Elhamid et al., 2019). Activated carbon is an efficient, common adsorbent but there are some limitations because of the cost of providing and regeneration of adsorbent (Streit et al., 2019). Since the regeneration of the adsorbent is expensive and there is a loss of material while regenerating, there are restrictions in the application of the process (Khandegar and Saroha, 2013).

In the past years, advanced oxidation techniques have also been an extensively studied method for dye removal. These techniques are mainly based on the degradation of impurities by chemical methods and oxidation of pollutants until they are mineralized by using reactive oxidants e.g. hydroxyl radical. Radicals for oxidation are produced in situ and they degrade the organic matters with fast chemical reaction rates (Nidheesh et al., 2018). Ozone has advantages such as not forming sludge and eliminating colour and organic matter in one step. In a study using the oxidation process with ozone, the degradation of three types of azo dyes was modelled and the results were supported by experiments.

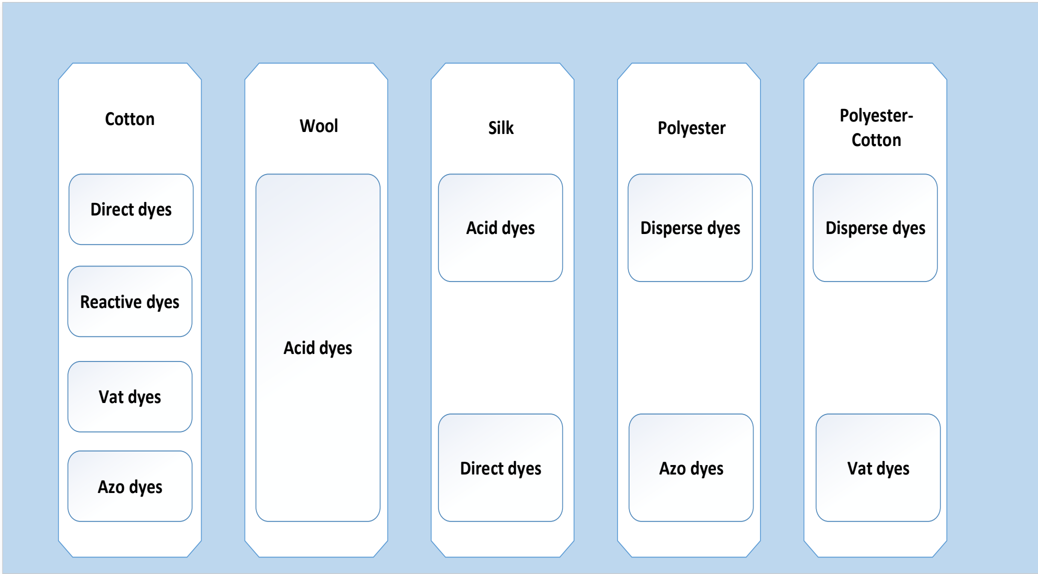

Figure 2.6 : Type of dyes for different materials (adapted from Holkar et al., 2016).

Correlation coefficients which indicated compatibility between model and the experiments were found approximately as 0.97. High degradation rates were also obtained (Muniyasamy et al., 2020). Although the ozone process has its advantages, high costs, as well as the formation of by-products that may be toxic or carcinogenic as a result of the process are the main disadvantages (de Souza et al., 2010).

Biological treatment methods have been categorized as an effective and environmentally-conscious process for treating textile wastewater when compared to other methods since they are more expensive and may have by-products after treatment. In literature there are lots of studies about biological methods for textile industry effluents because of the biological degradation of dyes under aerobic/anaerobic circumstances. For further and more efficient treatment of these effluents, membranes and biological activated sludge can be used together which is called membrane bioreactors (MBRs). Besides MBR technology has lots of advantages which are high water quality, lower sludge requirement and lower maintenance need (Khouni et al., 2020).

Although all the processes mentioned above have obvious advantages and disadvantages, in most processes, dyes and salt, which are valuable chemicals, cannot be recovered or reused. When approached from a holistic point of view, water resources will be protected by both the process being sustainable and the efficient treatment of textile wastewater and its recovery, and the amount of water used by the industry will decrease. In this context, the use of membrane technologies instead of traditional methods is more suitable in terms of having high treatment efficiency of membranes and being more environmentally friendly (Yang et al., 2020; Yang et al, 2020; Lu et al., 2020). There are many studies in the literature using membrane processes. In a very recent study, ultrafiltration membranes were fabricated by using polyimide (PI) polymer and according to filtration results, approximately 98% of dye retained on the membrane while monovalent and divalent salts have passed into the permeate stream. It was stated that the fabricated membrane can be used for separating dye-salt mixtures (Yang et al., 2020).

As it is known, textile wastewater can contain high salt and acidic compounds. Production of membranes resistant to these conditions is also studied in the literature. For example, with a doped polymeric NF membrane produced for this purpose, high dye removal was achieved in saline and acidic dye solution (Lu et al., 2020).

In Table 2.2 discharge limits for the textile industry in different countries is given. As it can be seen from the table, although some values are the same or similar for all countries in the table, some values are quite different. It can be seen that the same parameters are not evaluated especially in each country.

In addition to legal discharge limits, there is an approach regarding hazardous chemicals that companies should not use while manufacturing. This approach was named Zero Discharge Hazardous Chemical (ZDHC) and designated the Manufacturing Restricted Substance List (MRSL). Companies that adopt this concept by not using these dangerous and prohibited chemicals manage to produce cleaner (URL-1). Since the same organization will adopt the zero discharge concept after 2020, it is thought by the authors of this article that the use of membranes will be very useful in this regard.

Table 2.2 : Discharge limits for the textile industry in different countries (Senthil Kumar and Saravanan, 2017; Resmi Gazete, 2004).

	China*		**Germany***	**USA***	**India***	**Turkey****		
Parameter	**Direct discharge**	**Indirect discharge**	**Point of discharge**			**Open Fiber, Yarn Production and Finishing**	**Woven Fabric Finishing and Similar Processes**	**Cotton Textiles and Similar Processes**
pH	6-9	6-9	-	6-9	6-8.5	6-9	6-9	6-9

Table 2.2 (continued) : Discharge limits for the textile industry in different countries (Senthil Kumar and Saravanan, 2017; Resmi Gazete, 2004).

	China*		Germany*	USA*	India*	Turkey**		
Parameter	**Direct discharge**	**Indirect discharge**	**Point of discharge**			**Open Fiber, Yarn Production and Finishing**	**Woven Fabric Finishing and Similar Processes**	**Cotton Textiles and Similar Processes**
Chemical oxygen demand (mg/L)	80	200	200	80	250	350	400	250
Biochemical oxygen demand (mg/L)	20	50	20	50	30	-	-	-
Total suspended solids (mg/L)	50	100	-	30	100	-	140	160
Total dissolved solids (mg/L)	-	-	-	2000	5034	-	-	-
Colour	50	80	-	-	20	280 (Pt-Co)	280 (Pt-Co)	280 (Pt-Co)
Ammonia nitrogen (mg/L)	10	20	10	0.0002	-	5	5	5

Table 2.2 (continued) : Discharge limits for the textile industry in different countries (Senthil Kumar and Saravanan, 2017; Resmi Gazete, 2004).

	China*		Germany*	USA*	India*	Turkey**		
Parameter	**Direct discharge**	**Indirect discharge**	**Point of discharge**			**Open Fiber, Yarn Production and Finishing**	**Woven Fabric Finishing and Similar Processes**	**Cotton Textiles and Similar Processes**
Chlorine dioxide (mg/L)	0.5	0.5	-	-	-	-	-	-
Free chlorine (mg/L)	-	-	-	1	1 (residual)	0.3	0.3	0.3
Sulphide (mg/L)	0.5	0.5	-	0.2	100	1	1	1
N total (mg/L)	15	30	20	-	-	-	-	-
P total (mg/L)	0.5	1.5	3	0.005	-	-	-	-
Nitrite (mg/L)	-	-	1	-	-	-	-	-
Nitrate (mg/L)	-	-		20	-	-	-	-
Iron/manganese (mg/L)	-	-	-	-	0.25	-	-	-
Total chromium(mg/L)	-	-	-	-	-	2	2	2

Table 2.2 (continued) : Discharge limits for the textile industry in different countries (Senthil Kumar and Saravanan, 2017; Resmi Gazete, 2004).

	China*		Germany*	USA*	India*	Turkey**		
Parameter	**Direct discharge**	**Indirect discharge**	**Point of discharge**			**Open Fiber, Yarn Production and Finishing**	**Woven Fabric Finishing and Similar Processes**	**Cotton Textiles and Similar Processes**
Fish bioassay (ZSF)	-	-	-	-	-	4	4	4
Oil and grease (mg/L)	-	-	-	-	-	10	-	10
Phenol (mg/L)	-	-	-	-	-	-	1	-

2.2.3 Textile wastewater recovery and reuse approaches

The textile industry has a lot of different production processes that consume energy, water and raw materials and as a result of these processes, a high amount of wastewater is formed containing many different chemicals. To disposal of these effluents into the environment poses a risk for both human health and the ecosystem. Also, considering the amount and characteristic of textile wastewater, it is considered to be a more polluting industry than other industries (Alkaya and Demirer, 2014). Recycling and reuse of wastewater are getting more important because of decreasing water supplies, discharge regulations and treatment and supply costs (Güyer et al., 2016). There are some studies in the literature for water and chemical recovery from textile industry wastewater.

The data obtained in the search made in the literature using the keywords textile wastewater recovery' (demonstrates the results of 'Scopus' search) are given in Figure 2.7, Figure 2.8 and Figure 2.9 between 1971-2020. When the graph is analysed, it is seen that there has been a rapid increase in studies involving ceramic membranes since

2010. When we look at the countries where the studies are carried out, it is seen that India is in the first place, China comes after and Turkey is in the third place since these three countries have a large market in the textile industry, these figures are expected. When we look at the kind of studies, it is seen that the publication is the most widely published as article and then the conference paper and reviews come (data obtained from Scopus, 19th July 2020).

Table 2.3 : Water reuse reference values for textile industry (adapted from Lafi et al., 2018).

Parameter	Criteria
COD (mg/L)	60-80
Conductivity (µS/cm)	1000
pH	6-8
Turbidity (NTU)	1
Color	None
Suspended Solids (mg/L)	5
Dissolved Solids (mg/L)	500
Total Hardness (mg $CaCO_3$/L)	25-50

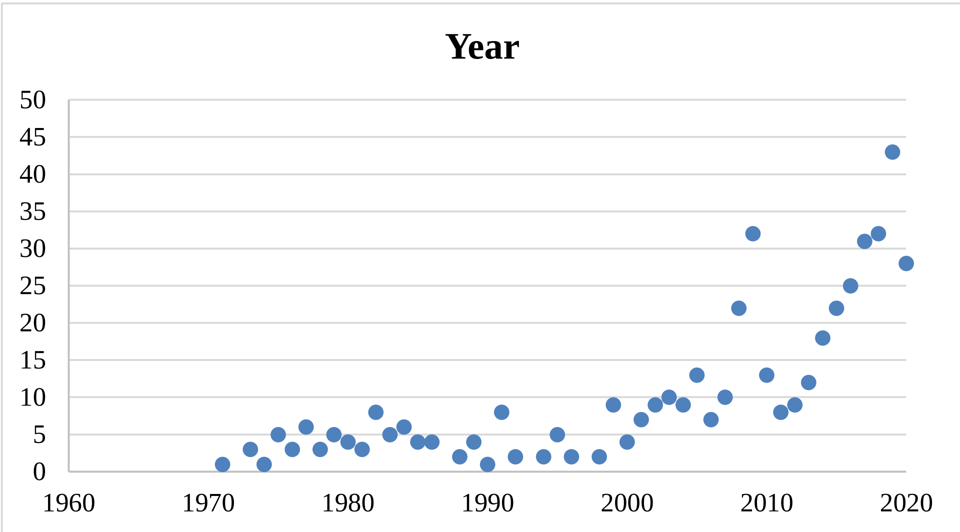

Figure 2.7 : The number of publication on ceramic membrane based on year. The data is based on the citation database Scopus in July 2020.

For recycling or reusing wastewater of cotton fabric processes, advanced oxidation technology was used. Ozone oxidation, Ultraviolet (UV) and H_2O_2 oxidation were applied to wastewater in different combinations. Resulting effluent was tested in dyeing experiments to investigate if it is reusable or not in the fabrication processes again. It was found out that no adverse effects have been observed on product quality (Güyer et al., 2016). In the study conducted in a textile factory to recycle wastewater and reuse it in various processes at the facility, studies were carried out with composite wastewater and separate wastewater streams from 3 different processes. For this purpose, membrane bioreactor, reverse osmosis and nanofiltration processes which were all pilot-scale were used in different combinations. Disinfection with ultraviolet light was also applied to the treated water. After dyeing experiments with treated water, it was reported that MBR-RO-UV and MBR-NF-UV combinations didn't have a negative effect on the quality of the product (Cinperi et al., 2019). In another study where pilot-scale MBR+NF processes were used together, the studies were carried out on-site and the concentrate of the NF process was recirculated back to MBR to gain a large amount of water recovery. It was indicated that NF concentrate has a noteworthy effect on the removal of pollutants in the MBR. Besides, the payback period was calculated for this process and found to be 3.11 years (Li et al., 2020). In Balcık-Canbolat's (2017) study, the RO process was evaluated for the recovery of water by using real dye effluent which was treated biologically before RO process. They also investigated the effect of the nanofiltration process as a pre-treatment before RO. According to results, it can be said that RO was very effective to obtain an adequate level of treated water quality (Balcik-Canbolat et al., 2017).

Since zero liquid discharge or near zero liquid discharge concept has been drawing more attention in the industrial sector because of the maintain water conservation to prevent high water consumption and meet discharge regulations, different processes are being used together for water recovery. To remove ions which cause scaling from textile wastewater concentrate of RO process, pellet reactor and UF process were used. The filtrate from these processes was reintroduced to the RO membrane to increase water recovery. It was also reported that near zero liquid discharge was achieved (Sahinkaya et al., 2018).

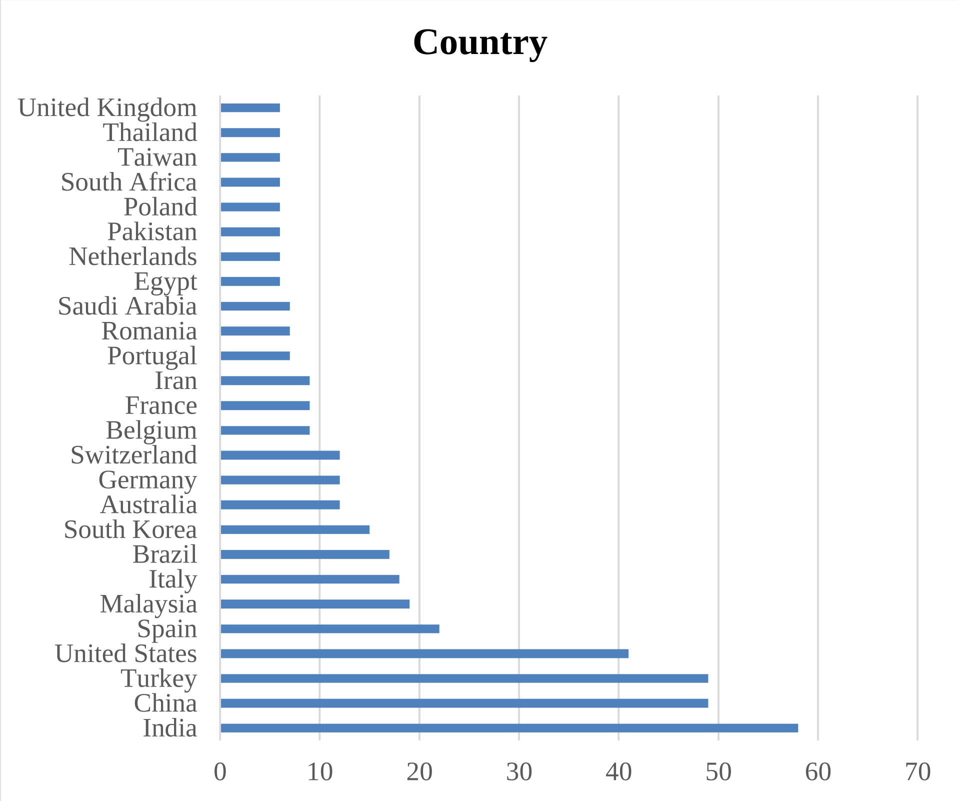

Figure 2.8 : Number of publication on ceramic membrane based on country. The data is based on the citation database Scopus in July 2020.

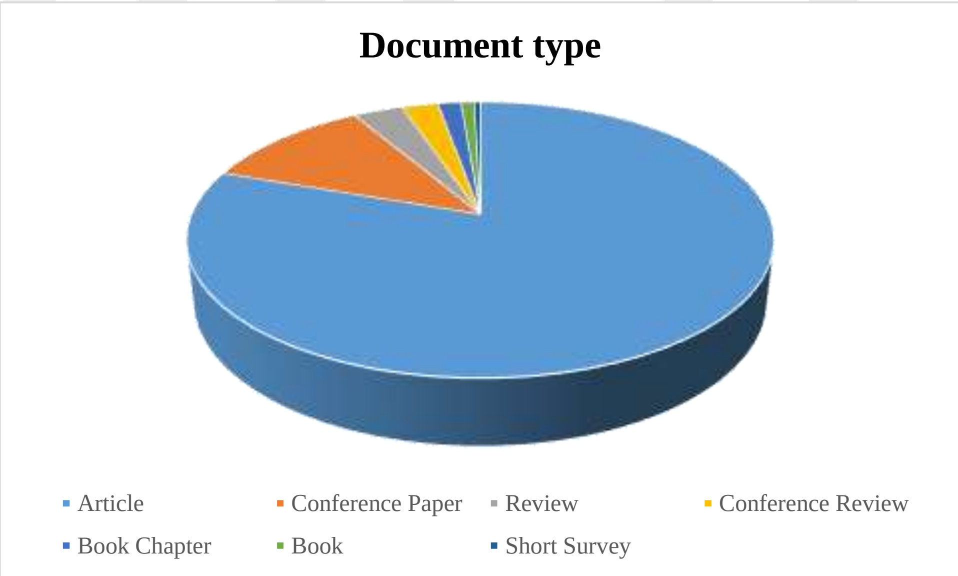

Figure 2.9 : Number of publication on ceramic membrane based on document type. The data is based on the citation database Scopus in July 2020.

Sierra-Solache and friends (2020) used the UF membrane process and biologic method which includes encapsulated fungal cells in an aerobic bioreactor to recover two kinds of dye contained wastewater. As a result of this study, they stated that the quality of treated water has the potential to use in the textile industry (Sierra-Solache et al., 2020).

Textile wastewaters can also show high alkaline properties and recovering caustic by membrane processes have been applied in a wide variety of industries. In a study conducted for caustic recovery from mercerizing process wastewater, polymeric microfiltration, ultrafiltration and nanofiltration membranes were used and the resulting caustic filtrate was intended to be used again. It was underlined that obtained permeate can be reuse in mercerization process after concentration step (Varol et al., 2015).

2.3 Ceramic Membrane Processes

In the past twenty years, it has become a remarkable option for industrial wastewater treatment. Ceramic membranes have many advantages over polymeric membranes/counterparts. Some of these are being easy to clean, high chemical, thermal and physical resistance and ease of backwash (Samaei et al., 2018). Because of the resistance of ceramic membranes to high temperatures and highly acidic and basic solutions, it has been successfully used in applications involving difficult conditions. Ceramic membranes commonly are fabricated by using alumina, titania, zirconia and silica materials (Lee et al., 2015). According to chemical stability, ceramic membrane materials are listed from the highest strength to the lowest as follows; titania >zirconia > alumina >silica (Hofs et al., 2011). It should also be noted that commercial nanofiltration or tight UF production is very limited. The reasons for this situation can be listed as follows. Since the membrane thickness does not exceed 50 nm, in addition, high quality support layer and intermediate layers are required for the nanofiltration membrane, making it difficult to manufacture defect free membranes. The need for the use of organic solvents and the need for special technical measures for this can be counted as one of these reasons (Voigt et al., 2019).

2.3.1 Ceramic membrane fabrication

As mentioned above, the main materials of ceramic membranes are usually silica, alumina, zirconia and other oxide mixtures (Li et al., 2020). The pore size of the ceramic membranes is divided into 3 groups. 1) lower than 2 nm- microporous, 2) between 2-50 nm-mesoporous and 3) gerater than 50 nm-macroporous (Nishihora et al., 2018). In general, every ceramic membrane production procedure involves sintering these materials at high temperatures and obtain a nonsymmetric membrane (Li et al., 2020). First of all, ceramic membrane production starts with the preparation of adequate powder. By using wet or dry forming methods and with the help of organic additives, the membrane begins to take its final shape. Subsequently, the heat treatment step is applied. If the main purpose is to detract organic additives from membrane texture, low temperatures would be enough and this process is called calcination. To obtain membranes with a dense or porous structure, multilayer conformation which includes a support layer for physical strength and active layer for separation is required (Buekenhoudt et al., 2010). By multi-layered fabrication, pore size and thickness of layers changes gradually (Das and Maiti, 2009). There are different techniques for ceramic membrane fabrication. The most used methods are as follows; tape casting, extrusion, slip casting, pressing and sol-gel (Issaoui and Limousy, 2019; Nishihora et al., 2018).

Tape Casting

Tape casting method is used for the fabrication of flat type ceramic membranes and the thickness of the membrane can be adjusted between 1mm to 10μm. After preparation a powder-liquid suspension which is called slip or slurry, the tape is casted as a wet-shaping process (Nishihora et al., 2018). Permanentness and rheological structure of the slurry can be controlled by dispersant and to alter durableness and flexibility of produced tapes, plasticizers and binders are important. Subsequently, produced tapes are dried to remove the solvent by evaporation. As a final step, the desired shape is given by cutting the tapes, pressed for lamination and sintering process is applied. Tape casting method is also generally preferred for large scale fabrications (Bernardo et al., 2020). In Figure 2.10, a typical ceramic membrane type-casting manufacturing device is given.

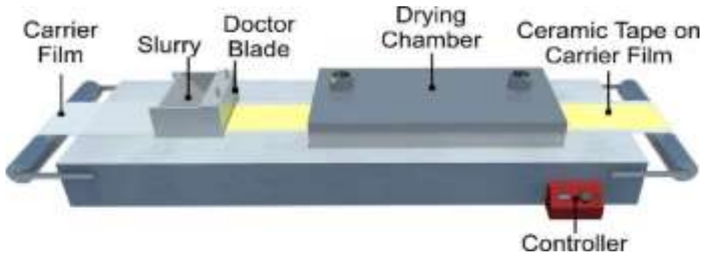

Figure 2.10 : A typical ceramic membrane type-casting manufacturing device (Nishihora, Rachadel, et al., 2018).

Slip Casting

In slip casting method which is defined as an easy and flexible technology of molding, slurries have to be mobile to be able to pour out and have high solid content. After pouring the slurry into casting mold, because of the capillary force solvent is taken away from the slurry and a solid layer with certain strength and thickness is formed. This solid layer is demolded for the sintering process. The properties of the final product depend on the content of binder, particle size in slurry, duration and temperature of firing (Fan et al., 2016). In Figure 2.11, a schematic drawing of slip casting method is given.

Extrusion

After preparing ceramic membrane mixture with suitable additives and dispersant, kneading should be applied to obtain high degree of viscosity. For shaping step, obtained viscous paste is processed in an auger type extruder with vacuum pressure to remove air in the paste. The main logic in extrusion is to put the mixture with a very high viscosity into a mold and form the membrane by applying repulsive force. Final configuration of the membrane is determined by the geometry of the mold, e.g. multichannel tubular, flat, etc. The applied pressure in extrusion process rate of extrusion are the most important parameters for controlling the process. Besides, particle size, dispersant content and material’s character are the significant parameters which are also effect the process (Mestre et al., 2019). In Figure 2.12, simple flow chart of production of ceramic membranes using extrusion or pressing method is given.

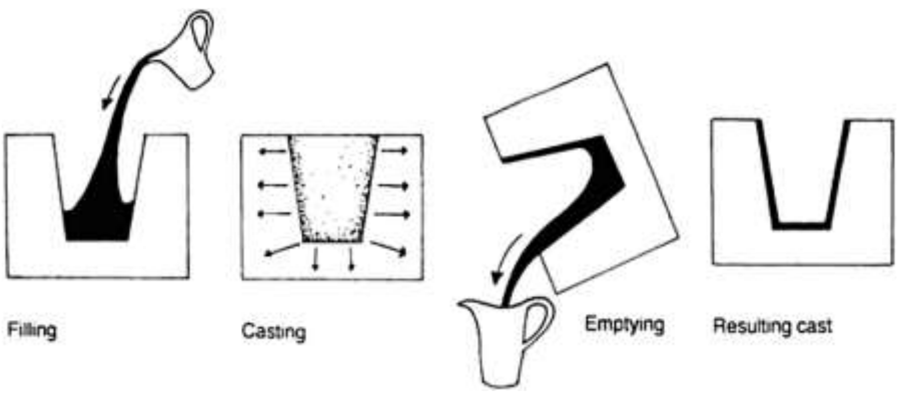

Figure 2.11 : A schematic drawing of slip casting method (Hubadillah, Othman, et al., 2018).

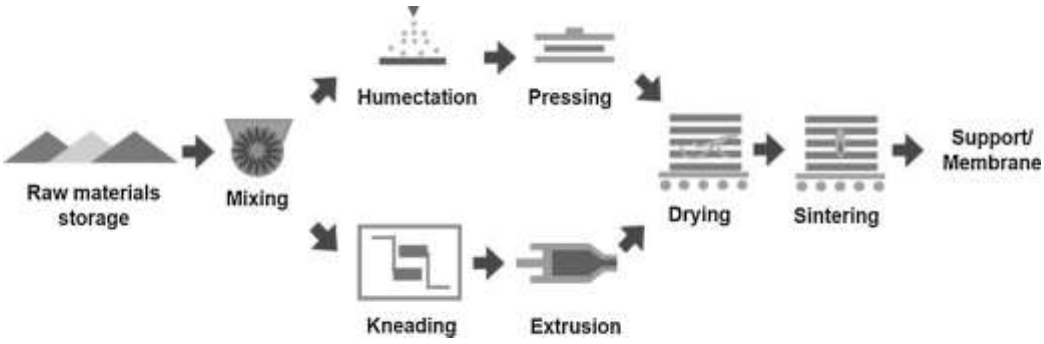

Figure 2.12 : Simple flow chart of production of ceramic membranes using pressing or extrusion method (Mestre et al., 2019).

Pressing

The pressing method can be classified as the most basic and well-recognized fabrication technique. In this method, powders can be used directly since slurry isn't required. First, appropriate powders are weighed according to calculations and placed on the equipment (tungsten carbide or non-flexible steel) to be pressed and preferred pressure is applied (Hubadillah et al., 2018).

Sol-gel

For preparing inorganic membranes, the sol-gel method is defined as the most useful one when considering other preparation methods. This method has many advantages such as providing uniform pore distribution and products with high purity in spite of low temperature requirement. But the occurrence of cracks during drying can be identified as a disadvantage. In order to provide a solution to this situation and to prevent cracks during drying, organic binders are added to the solution and these substances are removed from the membrane during heating (Ahmad et al.,2005).

2.4 Ceramic Membrane Applications in Textile Industry

For membrane processes, two materials are commonly used which are ceramics and polymers. Although polymeric membranes are used more frequently in treatment technologies today, their low stability, easy clogging and short lifetimes limit their use. At this point, ceramic membranes are started to getting attention from both lab and real applications (He et al., 2019). Especially properties like high chemical, thermal and mechanical endurance of ceramic membranes make them an alternative for polymeric membranes (López et al., 2020). When wastewaters with very high temperatures, harsh chemicals and highly contaminated characterization are needed to be treated, ceramic membranes must be used instead of conventional polymeric membranes. In fact, with the start of the production of low-cost ceramic membranes, the use of them on a larger scale has been paved the way for application (Goh and Ismail, 2018). If a comparison is made in terms of flux, it is stated in the literature that ceramic membranes have higher flux than polymeric membranes (Barredo-Damas et al., 2010). Especially when used in hot wastewater treatment in the textile industry, ceramic membrane flux values will increase further, depending on the viscosity decreasing with increasing temperature (Dilaver et al., 2018). In addition, because of the high pH and chemical resistance of the ceramic membranes, the membrane performance can be recovered more efficiently, as the membranes can withstand a more aggressive cleaning process (Cromey et al., 2015). Considering the characteristics of the textile wastewater and the properties of ceramic membranes together, the use of these membranes in textile wastewater treatment is also recommended in the literature (Barredo-Damas et al., 2012).

Despite the increase in ceramic membrane applications in water and wastewater treatment, its real-scale use is very low. The main reason for this is the high initial investment cost of ceramic membranes. This problem is tried to overcome by using lower cost materials such as kaolin and pyrophyllite in membrane production. In addition, aggressive cleaning methods (high concentration of sodium hydroxide or sodium hypochlorite or ozone etc.), which cannot be used in polymeric membranes, are very effective in ceramic membranes in order to eliminate the clogging problem in membranes. However, since these experiments are generally done on lab scale, their effectiveness should be tested in full-scale studies. Hence, the fate of the waste that will come out as a result of this cleaning should be considered (Asif and Zhang, 2021).

In this section, the lab-scale and pilot-scale studies found in the literature are compiled.

2.4.1 Lab-scale studies

Although there are more articles for ceramic membrane production in literature, many studies have been carried out in recent years on a laboratory scale for textile wastewater treatment using ceramic membranes. Within this review, the most recent ones will be compiled.

With the development of the ceramic membrane industry, it has become more accessible in commercial NF membranes. Especially in some studies, treatment of water containing dye and salt was carried out using NF and UF membranes. For instance, Chen et al (2017) used ceramic NF (tubular-MWCO of 900 Da) membrane for treatment of feed water which contains salts (NaCl and Na_2SO_4) and six different dyes with different charges (Evercion red H-E7B, Eriochrome black T, Reactive brilliant blue, Basic Green 4, Methylene blue and Reactive black 5) and compared this ceramic membrane with commercial organic NF membranes. They also investigated effect of salt content on desalination. Ceramic NF membrane showed a better rejection performance (averagely 70% retention) for anionic dyes and Chen et al attributed this to size exclusion and charge effects which are the major separation way for ceramic membranes instead of solution-diffusion mechanism (Chen et al., 2017).

In a study conducted by the authors of this article, it was aimed to recover hot water using commercial membranes with different MWCO values (3, 15, 50 and 300 kDa) and real wastewater. Fouling mechanism of membranes and economic aspects of hot water recovery were also investigated. According to the findings of this research, it can be concluded that treatment of industrial wastewater with ceramic membranes has remarkable potential for recovery and reuse (Dilaver et al., 2018).

In another study, commercial tight ceramic UF membrane (MWCO=2410 Da) was tested to separate reactive dyes form dye-salt mixture by Jiang et al. They reported dye rejection as averagely 98.12% in which seven blue dyes (vary between 626.6-1205.4 Da) were used for experiments. They concluded that accumulation of dyes can be the reason for high rejection rates and they also mentioned that ceramic membrane’s surface was negatively charged (Jiang et al., 2018). Alventosa-deLara et al.(2014) also used commercial UF ceramic membrane for treatment of reactive dye-salt solution which is called simulation of textile wastewater in this paper. Also, in this study, membrane fouling, which is an important issue for membrane processes, was mentioned in terms of various aspects. As stated in many other studies, they found that increasing salt concentration had a negative effect on dye removal (Alventosa-Delara et al., 2014). In their previous study, they investigated transmembrane pressure (TMP), cross-flow velocity (CFV) and dye concentration’s impact on flux and rejection of reactive black 5 by using commercial tubular ceramic membrane. They found that, with lower CFV and higher TMP leads to more significant flux decline (Alventosa-deLara et al., 2012). In addition to studies with commercial membranes, there are many studies in the literature that are conducted after ceramic membrane production.

For fabrication of commercial ceramic membranes, there are common metal oxides which are generally used such as zirconia, titania, silica and alumina. Especially with the increase in ceramic membrane studies, the most used raw material was alumina. However, there have been remarkable developments in the production of ceramic membranes in lab scale studies that have both low cost and high stability, high mechanical strength and selectivity. Examples of the raw materials of these low cost ceramic membranes are starch, clay, sand and apatite which are used for both UF and MF studies. In a recent study, Oun and friends (2017) fabricated tubular ceramic membrane by using alumina powder and natural kaolin clay and coated with TiO_2 nanoparticles to remove a specific dye. As a result of this work, they obtained approximately 99% colour removal (Oun et al., 2017). Because of its high chemical resistance and durability to corrosion, α-alumina membranes are drawing attention recently. In Zou's (2019) study, alumina nanoparticles were used in boehmite sol to obtain small pores on α-alumina membranes. They reported pore sizes as below 5 nm and indicated that membranes have high rejection rates of different dyes such as titan yellow and direct red (Zou et al., 2019). When clay and common metal oxides such as silica, titania, alumina and zirconia are compared, it is known that clay is more resistant and in terms of firing temperature, lower temperatures are sufficient for clay. In a study where ceramic support was produced by mixing clay and banana peel which is used to obtain porosity, MF membrane obtained by covering the support's surface with clay again succeeded in the treatment of textile wastewater. In addition to using clay for low cost fabrication, an ecological friendly approach has been demonstrated by using banana peel (Mouiya et al., 2019). In another clay related study, natural clays were purified before membrane fabrication to obtain richer content of kaolinite and similar materials. After UF membrane production by using purified clay as the coating material, removal performance tests with DR80 (direct red 80 dye) solution were conducted and approximately 97% removal efficiencies were reported. They also remarked that better antifouling results were achieved (Ouaddari et al., 2019). A similar study was carried out by Saja et al. in 2020 by using bentonite clay to ameliorate the membrane's selectivity. The UF membrane produced with clay coating on the perlite support layer has been tested with two different dye solutions, anionic

(DR80- direct red 80 dye) and cationic (RB-rhodamine B). According to results, 97% and 80.1 rejection efficiencies were obtained for DR80 and RB, respectively (Saja et al., 2020). In addition to being used as a perlite support layer, it can also be used without coating. Microfiltration ceramic membrane was also fabricated by Saja et al. and performance tests were conducted by two kinds of industrial effluents. High turbidity removal rates were obtained (Saja et al., 2018). In another study showing that DR80 dye can be removed with UF membrane, MF membrane which was obtained by pressing method, used as support layer is produced from natural bentonite and phosphate and coated with TiO_2. The pore diameter of the membrane obtained was reported as 72 nm (Bouazizi et al., 2017).

In another very interesting study, ceramic hollow fiber membrane was produced using waste cow bone, which can be obtained hydroxyapatite due to its high calcium content. According to efficiency values which are reported as 99.9%, 80.1% and 30.1% for colour, COD and conductivity respectively, it can be understood that it has a potential for treatment of textile wastewater (Hubadillah et al., 2020). Geomaterials which are another option for low cost raw material for ceramic membrane production, has been getting attention in last ten years. Manni and friends (2020) selected Moroccan natural magnesite for fabrication of membrane. One of the magnesite properties is that magnesite decomposes thermally during fabrication because of high temperatures in sintering process and it forms the porosity of the membrane. Thus, there is no need to add an additional pore former during production. After rejection experiments with real textile water, COD and turbidity removal efficiencies were reported as 69.7% and 99.9%, respectively (Manni et al., 2020).

Ceramic and polymeric materials were also used for the production of nanofiltration membranes. Especially ceramic tubular and hollow fiber membranes as a more comprehensive support option for thin film composite applications were studied to take advantage of the durability of the ceramic membrane. Chong and Wang (2019) synthesized polyamide thin films on MF ceramic membranes and obtained nanofiltration level of separation level. Removal of divalent salts and organic dyes were also achieved (Chong and Wang, 2019).

Nanoparticles are also used frequently in membrane production to increase the performance of membranes in wastewater treatment. For example, it is aimed to improve the permeability and permeate quality of membranes produced using metal oxide nanoparticles. In a study where silica nanoparticles obtained from rice husk were used, it was aimed to increase the adsorptive properties of the membrane with silica added to the ceramic membrane. The main material of the membrane is calcium phosphate and ammonium acetate is used to form pores on the ceramic membrane. In the experiments performed with the dye solution, good removal efficiencies have been obtained. It is also stated in the study that the dye adsorbed on the membrane can be removed by calcination and the membrane can be reused (Tolba et al., 2016).

2.4.2 Pilot-scale applications

There are pilot-scale studies related to such as seawater desalination (Cui et al., 2011), oily wastewater treatment (Abadi et al., 2011) and wastewater treatment (Lehman and Liu, 2020). Although laboratory-scale studies are relatively various in the literature, the treatment of textile wastewater treatment on a pilot scale using ceramic membranes is quite limited. This section includes some pilot studies that we were able to investigate in the literature which was very limited.

In 2001 Voigt et al. used titanium NF membranes with 0.9 nm pore size in a pilot-scale ceramic membrane system to remove colour from textile finishing wastewater. They also aimed to recover hot water and reuse as process water in the facility. For this purpose, thirty different wastewaters with different colour were used for experiments during six weeks to evaluate to obtain high rates of flux and low operation costs (Voigt et al., 2001).

In Barredo-Damas et al.’s (2010) study, pilot scale ceramic UF system was tested for a pre-treatment purpose for real textile wastewater treatment which were obtained from a textile manufacturing plant. UF ceramic membranes were tubular with titania support and zirconia active layer and molecular weight cut off values were 150, 50 and 30 kDa. Besides, different cross-flow velocity values were applied to investigate the effect on membrane performance. Approximately 99% of turbidity removal was obtained and colour removal was 98% as the highest removal rate. COD removal values were also considerable. It was reported that ceramic UF membranes can be accepted as a viable option for pre-treatment (Barredo-Damas et al., 2010).

In the study conducted to remove reactive black 5 dye with a pilot-scale ultrafiltration membrane system, the effects of transmembrane pressure and cross-flow velocity parameters, as well as initial dye concentration on membrane performance, were evaluated. Following the studies, flux reduction was more clearly observed in the combination of high transmembrane pressure, low cross-flow velocity and high dye concentration (Alventosa-deLara et al., 2012).

In a study which was conducted by authors of this review, pilot scale UF and NF ceramic membrane systems were used to recover and reuse real textile hot wastewater in-situ. The wastewater was taken from disperse and reactive printing washing baths which were mixing in hot discharge point. UF and NF membrane systems were tested both separately and together in a batch mode. Removal efficiencies for COD, TOC, colour and total hardness (for ultrafiltration + nanofiltration cycles overall average removal efficiencies are 89%, 83.5%, 86.4% and 68% for COD, color, TOC and hardness, respectively, for only nanofiltration cycles, overall average removal efficiencies are 90.1%, 82.2%, 76.8% and 82% for COD, color, TOC and total hardness, respectively) for both operations were quite significant. In addition, fabric dyeing experiments with treated water were also successful for two dyes. According to obtain results, water recovery and energy saving were achieved due to hot water recovery (Ağtaş et al., 2020).

2.5 Conclusion and Suggestions for Future Studies

Gradually decreasing water resources and making access to clean water difficult is perhaps the most important problem facing our world. It becomes mandatory to protect water resources and use them within the framework of logic. In this context, some limitations and solutions are required for industries with high levels of water use. In particular, the high amount of water used in every stage of the textile industry, as well as the water pollution caused by the chemicals and dyes used, make water resources difficult. Therefore, wastewater treatment, water recovery and reuse have become important in the textile industry. Although many traditional methods have been used for textile wastewater over the past years, sufficient efficiency has not been achieved. In this case, membrane processes can be a solution. Ceramic membranes, which can withstand the difficult characteristics of textile wastewater, have become quite prominent in recent years. Cost, which is an important disadvantage of ceramic membranes, has started to decrease as the studies increase.

Based on the literature investigation made within the scope of this review, it is concluded that ceramic membrane production and application studies are given more importance in the laboratory rather than the pilot and real applications. Although laboratory studies are the starting point of many studies and are very valuable, pilot studies are thought to be necessary for real applications. As a result of this study, it can be given as advice for future studies, increasing the studies towards real applications.

3. HOT WATER RECOVERY AND REUSE IN TEXTILE SECTOR WITH PILOT SCALE CERAMIC ULTRAFILTRATION/NANOFILTRATION MEMBRANE SYSTEM[2]

3.1 Introduction

Textile, cosmetic, pulp and paper, carpets and other industries consume a high amount of water and produce highly polluted wastewater (European Parliament, 2019). For instance, studies have shown that the amount of water used per kg of product in the textile industry is between 0.06-0.40 m^3 (Laqbaqbi et al., 2019). The content of textile wastewaters is also toxic. It is stated that of the hundreds of thousands of commercial dyes used in the textile sector, 280,000 tons of dye are discharged annually. This has a serious impact on the environment (Jegatheesan et al., 2016). When wastewater containing dye is discharged to the environment without treatment, it causes aesthetic damage in addition to the mutagenic, carcinogenic and toxic effects that can be observed as well. Moreover, when dyes are broken down, undesired by-products such as naphthalene, benzidine and other aromatic products can be formed (Desa et al., 2019). Another obstacle is high energy costs, as the high rate of consumption of water, especially in dyeing and finishing processes in the textile industry, requires excess energy use for heating. According to Hussain and Wahab (2018), approximately 24.9 % of the thermal energy usage is used in the dyeing process (Hussain and Wahab, 2018). Recovering and reusing hot wastewater in the plant again would not only have environmental and economic benefits, but it would also be important for increasing energy efficiency (Voigt et al., 2001).

Wastewater from the textile industry has variable contents: turbidity, color, chemical oxygen demand (COD), suspended solids, conductivity, high pH, salinity and multifold chemicals values can fluctuate greatly in each facility (Bilińska et al., 2019).

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[2] This chapter is based on the paper "Meltem Ağtaş, Özgün Yılmaz, Mehmet Dilaver, Kadir Alp and İsmail Koyuncu. Hot water recovery and reuse in textile sector with pilot scale ceramic ultrafiltration/nanofiltration membranes system. Journal of Cleaner Production, 2020.DOI: 10.1016/j.jclepro.2020.120359. "

Each textile factory must treat their wastewater to satisfy stringent standards before discharge to the environment in accordance with local, national and in some cases where there are limited national restrictions, international regulations (Desa et al., 2019). There are a variety of methods to treat wastewater, such as conventional treatment procedures, chemical, biological and advanced treatment processes (Dilaver et al., 2018). Coagulation-flocculation (Cinperi et al., 2019), activated carbon adsorption (Holkar et al., 2016), advanced oxidation processes such as ozonation, fenton treatments, electro-Fenton methods (Lafi et al., 2018), bacterial degradation (Liang et al., 2018), anaerobic SBR (Shoukat et al., 2019) are some examples of conventional treatment processes which have been used. However, conventional methods are not sufficient in many ways. For instance, coagulation-flocculation processes generally produce toxic sludge and biological treatment methods are not enough for the complete elimination of dyes (Liu et al., 2017). To address these issues, the use of membrane processes is gaining popularity and is becoming more widely recognized since they are recommended for textile wastewater treatment in the BAT reference document (Barredo-Damas et al., 2010). In a study conducted by Kamali et al., treatment methods were evaluated and ranked according to technical, environmental, economic and social criterias by using the Fuzzy-Delphi approach. When all criterias are taken into consideration, membrane-based technologies have been determined as the most sustainable technology to treat industrial wastewaters (Kamali et al., 2019a).

For the treatment of industrial effluents, both polymeric and ceramic membranes have been used so far (Kamali et al., 2019b). Although in the market, polymeric membranes are more widely used. However, when ceramic and polymeric membranes are compared, it can be said that ceramic membranes are having more advantageous in terms of high thermal, mechanical and chemical stability, well defined pore size distribution and high flux (He et al., 2019). The pulp and paper industry produces wastewater with temperatures that vary between 60-70°C while the textile industry produces wastewater with temperatures that can go up to 90-95°C. Generally, wastewater must be cooled down before membrane treatment. For efficient treatment, membranes have to be thermally stable; most polymeric membranes tend to degrade at high temperatures and therefore, they are not suitable for hot wastewater treatment

(Cromey et al., 2015). Moreover in recent years, inorganic membranes have gained interest in the treatment of industrial wastewaters (Kamali et al., 2019b).

In study conducted in 2017 by Chen et al., a ceramic nanofiltration (NF) membrane with MWCO of 900 Da and two commercial membranes were used to treat dye solutions containing NaCl and Na_2SO_4. Dye rejection was obtained as 99% when pH was under 6 (Chen et al., 2017). In another study, a ceramic tight UF membrane with a MWCO of 2410 Da was used to separate reactive dyes from dye/Na_2SO_4 mixtures. High rejections for all the reactive dyes (> 98.12%) were achieved (Jiang et al., 2018).

Although the studies carried out in the laboratory are very valuable, they do not fully reflect the systems in real conditions. Pilot scale studies are very important for the design of full scale systems. Furthermore, the data obtained from pilot scale studies will be more realistic in determining the configuration of membrane systems (Kurt et al., 2012). In this respect, the importance of this study emerges.

In a recent review article, there is a table of an overview of some investigations evaluating the application of ceramic membranes to treat effluents from textile industry (Samaei et al., 2018). When this table is examined, it can be seen that the studies are generally made with synthetic dyed wastewater, UF and NF are not used together, or the studies are laboratory scale. This study is kindly thought to be different from other studies.

In this study, the purpose is treating real hot textile wastewater with a pilot ultrafiltration/nanofiltration ceramic membrane technology and recover hot water to reuse in the plant again. Therefore, cross flow ceramic membrane filtration experiments were performed and flux and removal efficiencies were calculated. In addition to this, temperature changes between feed and permeate streams were monitored. The novel contribution of this work aims to increase the application of ceramic membrane processes towards the recovery of textile wastewater and provide data for real-scale studies. In addition, as recovery and reuse issues are becoming more important, it is possible to contribute to these issues with real system data.

3.2 Materials and Methods

In this section, the materials used in our study, the plant where the study is conducted and where the pilot system is located are mentioned. Test methods are also stated.

3.2.1 Materials

Two commercial membranes (ATECH), one ultrafiltration and one nanofiltration membranes were used in the system (Table 3.1). The UF membrane is 450 mm long, 0.05 μm in diameter and has a surface area of 0.09 m^2. The NF membrane is also 450 mm long, has 1 kDa molecular weight cut off and a surface area of 0.09 m^2. Real textile wastewater was taken from Savcan Textile, Bursa, Turkey. The feed stream came from disperse printing and reactive printing washing baths hot discharges mixing point (printing washing baths hot discharges mix) in the factory. From this point on, wastewater used in this study will be called as hot mixing wastewater.

According to the information received from the commercial membrane company, the pore diameter of the nanofiltration membrane is 1 kDa. But by using Eq.(3.1) (Howe and Clark, 2002), the pore diameter of NF membrane was calculated and obtained as 0.00188 μm.

$$d(nm) = 0.09*(Dalton)^{0.44} \quad (3.1)$$

3.2.2 Selected facility for trials

The textile factory selected for this study is located in Bursa Organized Industrial Zone, Turkey. All experiments using the pilot ceramic membrane system were carried out in this factory. All studies were completed in approximately 3 months. In this textile factory, mostly cotton and viskon products which are nearly 15 tons/day are produced and about 3200 m^3/day water consumption is occurred. There are substances such as dyes, several chemicals and cleaning additives in the wastewater resulting from production. Reactive and disperse dyes (reactive blue 72, reactive blue 49, disperse blue 106, disperse yellow 54, and others) are mostly used in the printing processes in this facility.

In Figure 3.1, a flow diagram of selected facility for the trials is given and sample points which wastewater for the trials were taken from are shown. In Dilaver et al.'s study in 2018, wastewater was supplied from the facility mentioned in this study

(Dilaver et al., 2018). Potential sample points were assessed in Dilaver et al.'s study and printing washing baths hot discharge mix sample point was considered to be suitable for pilot scale trials.

Table 3.1 : Multi-channel ceramic membranes properties.

Parameters	**UF**	**NF**
Support layer	Al_2O_3	Al_2O_3/ZrO_2
Active layer	Al_2O_3	TiO_2
Channel number	19	19
Channel diameter (mm)	3.3	3.3
Pore size	0.05 µm	1 kDa
pH resistance	0-14	0-14

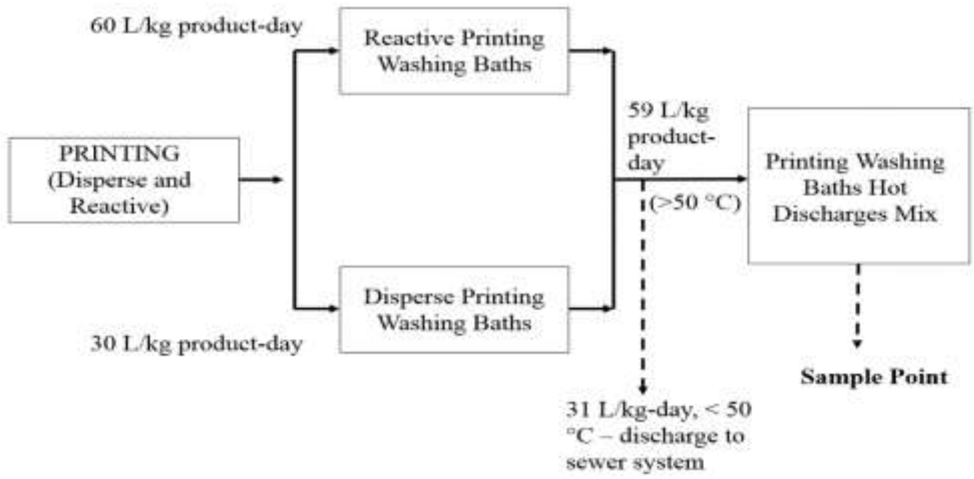


Figure 3.1 : Flow diagram of selected facility for trials (adapted from (Dilaver et al., 2018).

3.2.3 Pilot scale test system

A pilot scale ceramic membrane system was used for the textile wastewater treatment in this study. There are three tanks in the system. The first tank is the main feed (as well as the UF membrane feeding) tank. In the second tank, the UF membrane's permeate is collected (as well as the NF membrane feeding tank) and the final tank is for collection of NF permeate. Two commercial membranes, one UF and one NF membrane were used in the system. Two stainless steel membrane housings (546 mm each) are also available. A real view of the pilot scale ceramic membrane system is given in Figure 3.2.

The pilot scale ceramic membrane system can be operated with both batch and continuous modes and in three different scenarios. With these scenarios; i) only UF membrane, ii) UF + NF membranes together and iii) only NF membrane can be operated (Figure 3.3). Since the wastewater used in the tests carried out within the scope of this study is produced in the factory where the operation is made in a batch, the pilot ceramic system is also operated batch mode. Every batch mode is named as a 'Cycle'.

The pilot scale ceramic membrane system can be followed by SCADA (Supervisory Control and Data Acquisition).

The UF membrane was operated under 2.5 bars. Backwash with air was done once in every 10 minutes for 5 seconds during operation.

Figure 3.2 : Real view of the pilot ceramic membrane test system.

The UF membrane system was operated until the system reached 85% recovery rate. The NF membrane system was operated under 2 bars for the first 5 cycles and 2.5 bars for the other 5 cycles in second scenario. In the third scenario, NF membrane pressure was 2.5 bars. Backwash with air was done once in every 1 hour for 5 seconds during operation. The NF membrane system recovery rate was kept around 60% in both scenarios. Before each operation, it is aimed to clean the system by passing tap water through the system. In the second cycle, the NF membrane could not be operated due to a problem in the system. However, the numbering of cycles has not been altered so that there is no break in the continuity of the experiment and membrane flux values changing can be seen as the cycles progress. UF permeate and NF permeate were recorded every 10-minute and 30-minute interval during the period of filtration, respectively.

Flux was calculated by using Eq.(3.2) where J is permeate flux (LMH), Δm is collected amount of permeate at specified time interval (mL), A is the membrane area (m^2) and the Δt is the specified time interval (second).

$$J = \frac{(60 * 60 * \Delta m)}{(\Delta t * 1000 * A)} \tag{3.2}$$

3.2.4 Characterization and instruments

During the operations, samples were taken from raw water at the beginning of the cycle and from the permeate and concentrate streams at certain intervals and these samples were subjected to some experiments. These experiments are conductivity, pH, temperature, chemical oxygen demand (COD), total organic carbon (TOC), color and total hardness tests. Temperature and pH measurements were performed using pH meter (S220 Seven Compact pH/Ion, Mettler Toledo, USA). Conductivity measurement was performed by conductivity device (HQ40d multi, HACH). Test kits (LCK 1414, LCK514, LCK327, HACH) were used in COD and hardness tests. TOC measurements were made with Shimadzu V-CPN model TOC.

Temperature was one of the key parameters to monitor in this study since we are aiming for hot water recovery. COD, TOC, color and total hardness tests were performed to make sure the treatment of the wastewater met the quality required for reuse in the facility. Textile wastewater has high conductivity and pH values. Conductivity and pH measurements were performed to follow up the developing change throughout the experiments. Flux monitoring was important to understand membrane behaviour during the experiments.

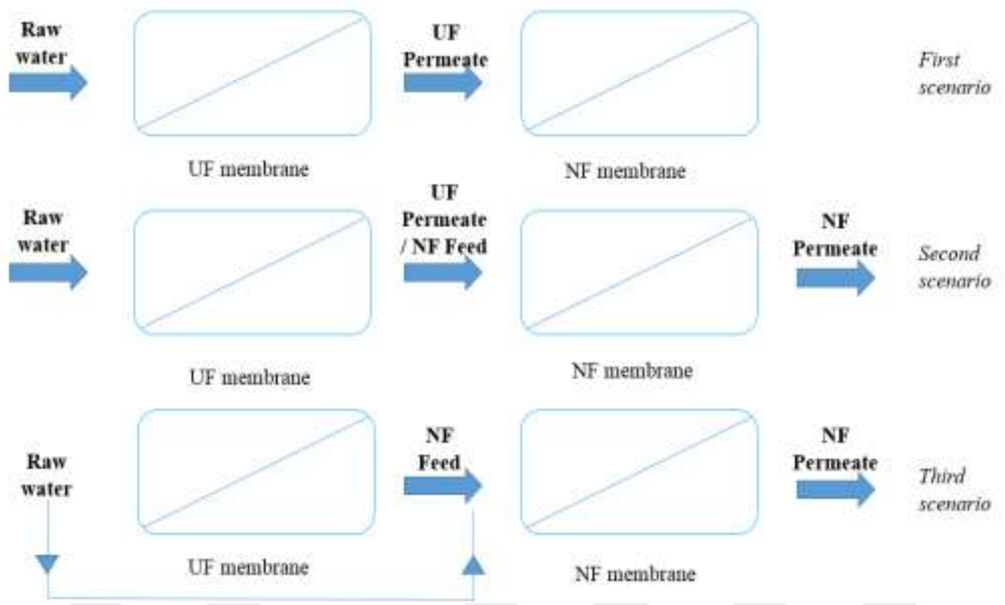


Figure 3.3 : Operation scenarios of pilot scale ceramic system.

Since the pilot-scale ceramic membrane system is operated with different characteristics and color of wastewater in each cycle, the membranes were washed with tap water before the operation in order to prevent the results from being affected when different wastewater is used.

3.3 Results

In the results part, raw water characterization, filtration, treatment efficiency and fabric dyeing experiment results are discussed. Economic evaluation of this study is also stated.

3.3.1 Raw water caharacterization results

Wastewater sample characterization results are provided for each cycle in Table 3.2. It should be noted that changes in production also affect wastewater characterization (Koyuncu et al., 2004). According to Table 3.3, in general, the values obtained from the literature and the values in the study are compatible with each other. However, the average total hardness and color values (49.3 mg/L and 0.33) for mixed hot wastewater was found to be lower than the values given in Table 3.3 for textile wastewater. As it can be seen here, the difference between these values obtained from different studies shows how variable the textile wastewater can be.

3.3.2 Filtration results

Within the scope of this study, 14 ‘cycles’ were performed by using the pilot scale ceramic membrane system. During these operations, hot mixing wastewater was used. The purpose of treating this wastewater is hot water recovery. The character of the hot mixing wastewater used in the experiments differs in each cycle due to the usege of different dyes. In first 10 cycles, UF + NF membranes were used for treatment purposes respectively and only NF membrane was used between 11th and 14th cycles. The results of the studies are given below. In Figure 3.4 and Figure 3.5, starting and ending flux and temperature of UF membranes system during every cycle is given, respectively.

Table 3.2 : Wastewater characterization for each cycle.

Parameter	COD (mg/L)	Hardness (mg $CaCO_3$/L)	Colour (525 nm)	Conductivity (µs/cm)	TOC (mg/L)
C1	389	35.17	0.088	4880	110.1
C2	472	32	0.181	14820	116.38
C3	363	38	0.197	6234	112.2
C4	483	32.8	0.067	9924	104.6
C5	377	25	0.125	7004	108.6
C6	988	42.5	0.484	12482	345.5
C7	734	73.03	0.25	13602	200.4
C8	472	51.95	0.342	1893	155.88
C9	316	34.3	0.364	2345	162.4
C10	666	62.3	0.75	17470	269.6
C11	836	71.5	0.338	3070	65.18
C12	683	63.92	0.115	15786	153.3
C13	563	50.53	0.541	5496	160.55
C14	790	76.96	0.777	21610	189.4

Table 3.3 : Wastewater characterization (average values) in the current study and literature values.

Parameter	This study	Literature values
COD (mg/L)	580 ± 197.36	1017[a],1315[b],1560[c], 185.6[d],281[e],1581[e],329.4[f]
Total Hardness (mg $CaCO_3$/L)	49.3 ± 16.85	500[c]
Color (525 nm)	0.33 ± 0.22	2.98[d]
Conductivity (µs/cm)	9758 ± 6021	57.56[b], 568[d], 27,700[e], 92,200[e], 8620[f]
TOC (mg/L)	161.01 ± 70.89	158[a], 264[b], 390[c], 49.05[d]

[a] (Tomei et al., 2016); [b] (Bilińska et al., 2019); [c] (Blanco et al., 2014); [d] (Güyer et al., 2016); [e] (Ozturk et al., 2016); [f] (Fersi and Dhahbi, 2008)

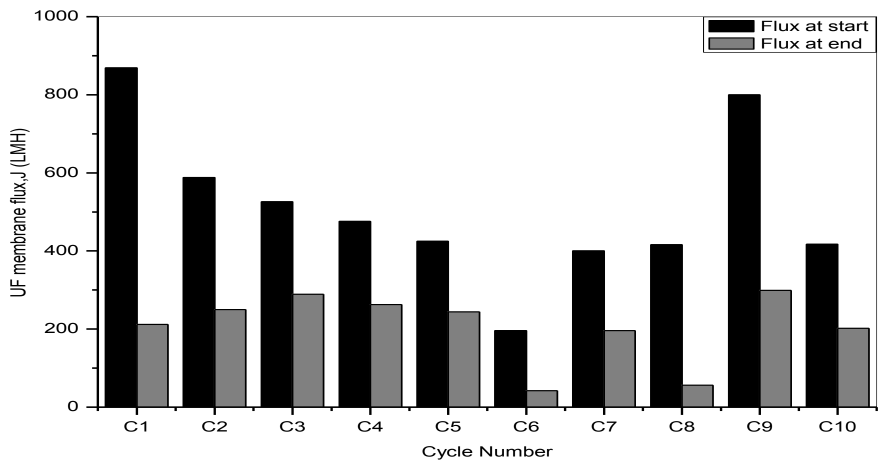


Figure 3.4 : Starting and ending flux of UF membranes during every cycle (UF+NF operation mode).

As can be seen in the UF flux graph, the highest and lowest initial flux was obtained as 869 LMH and 196 LMH respectively, and it is 299 LMH and 42 LMH in the ending of the operations. In Barredo-Damas et al. (2010) study, performance of ceramic membranes was tested with three commercial ceramic membranes with molecular weight cut-offs (MWCO) of 30, 50 and 150 kDa, respectively. For the 150 kDa ceramic membrane, which has the closest pore size value to our UF membrane, pure water flux was obtained as around 450 LMH under 2.5 bar (Barredo-Damas et al., 2010). Considering the average flux of 10 cycles, variable characteristics and temperature of hot mixing wastewater, it can be said that values are compatible with each other. In another study, Moazzem et al. (2018) tested ceramic ultrafiltration and reverse osmosis membranes in treating car wash wastewater for reuse (Moazzem et al., 2018). They used commercial UF membrane with pore size 0.02 µm and average flux of ceramic membrane was found to be 100 LMH. Although 100 LMH may seem low according to the results obtained in this study, because Moazzem's UF membrane pore size is almost half of the membrane used in our study, it can be said to be expected.

However, in another study, commercial tubular MF membrane with 1.5 µm mean pore size was used in a pilot plant of a hybrid microfiltration (MF) and electrodialysis (ED) system for pretreatment step for ED to treat paper industry effluent. In the view of obtained results, MF membrane's flux values varied between 60-130 LMH at 60°C. Although it had larger pore size than our UF membrane, flux values are lower than ours. It may be attributed to different types of wastewater that were dealt with and different temperature values (Nataraj et al., 2007).

The highest flux was obtained in the first cycle. Considering that this is the first cycle using commercial UF membranes, it is expected that the flux in the clean membrane is high.

As the cycles progressed, the start and end fluxes also decreased. Only in cycle 9, there was an increase in flux which is almost same with first cycle. As mentioned previously, the type of dye and the recipe used in the raw water in each cycle vary. Accordingly, the raw water characteristics change. In addition, the water temperature is not likewise unchanged during operation. Therefore, the reason for the flux increase in cycle 9 can be attributed the use of raw water with a recipe that can pass through the membrane more easily. However, it is known that increasing temperature also has a positive effect on flux. In addition to these, cycle 10 which was operated right after cycle 9, has lower flux values than cycle 9. Therefore, it can be understood that there are no cracks in the membrane.

When Figure 3.5 is examined, it can be seen that temperature is changing between 52-72 ^{0}C. Hot mixing wastewater was cooled down to approximately 70 ^{0}C before treatment to prevent damage to electronic components (pH probes etc.). Looking at all of the cycles, it can be seen that the difference between the temperatures of the input and output flows is not significant. The highest difference is at 14^{o}C in ‘cycle 6’. Since one of the main ideas of this study is recovering hot water to use in the factory again, it can be said that these results are quite promising. Instead of heating the process water from the 0 °C to the required temperature, heating the treated hot water to the desired temperature will provide energy gain.

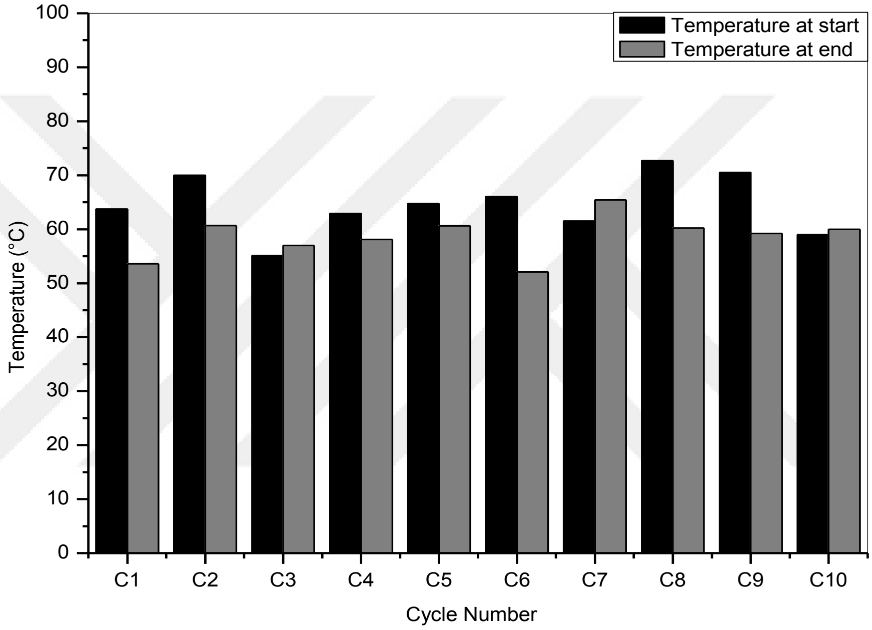


Figure 3.5 : Starting and ending temperature of UF membrane permeate during every cycle (UF+NF operation mode).

In Figure 3.6 and Figure 3.7, the starting and ending flux and temperature of NF membranes system during every cycle is given, respectively. As mentioned previously, data could not be obtained because NF membrane could not be operated in ‘cycle 2’. When the NF flux graph is examined, it is seen that the flow rate is around 100 LMH band. Buekenhoudt et al. (2013) tested different ceramic membranes with pore size diameters ranging from 0.9 nm up to 100 nm (Buekenhoudt et al., 2013). They performed pure water and a variation of 11 different organic solvents filtration experiments. According to results obtained, for 1000 Da membrane, permeability values were between 40-50 LMH bar. Since our NF membrane was classified as 1 kDa, under our operation pressure the results are similar.

Similar to the UF graph, the NF graph showed a greater increase in flux in ‘cycle 9’ than normal. This supports the mentioned raw water’s variable characteristics above.

As it seems in Figure 3.7, there are some fluctuations in temperature. Because of the ambient temperature change, water temperature in the tanks may not be stable. But still, hot wastewater recovery potential can be understood from the obtained result.

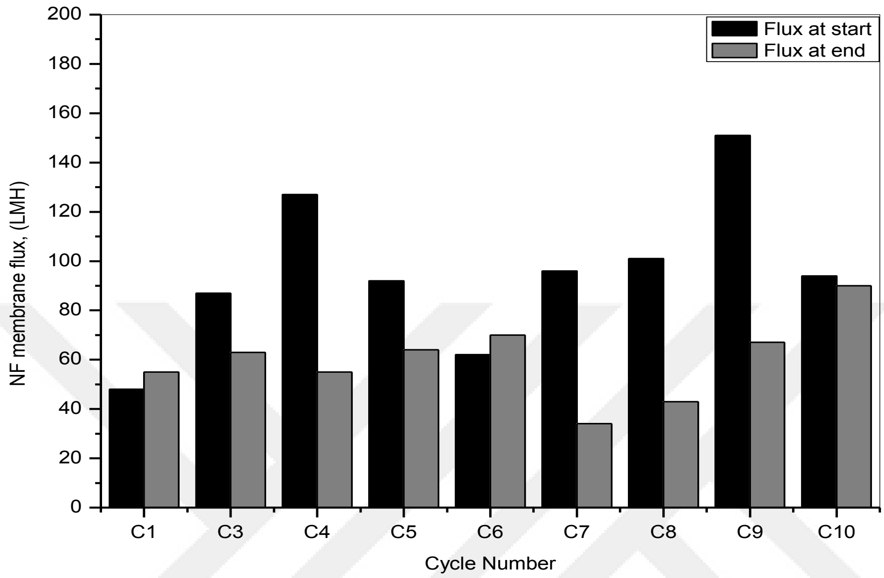


Figure 3.6 : Starting and ending flux of NF membranes during every cycle (UF+NF operation mode).

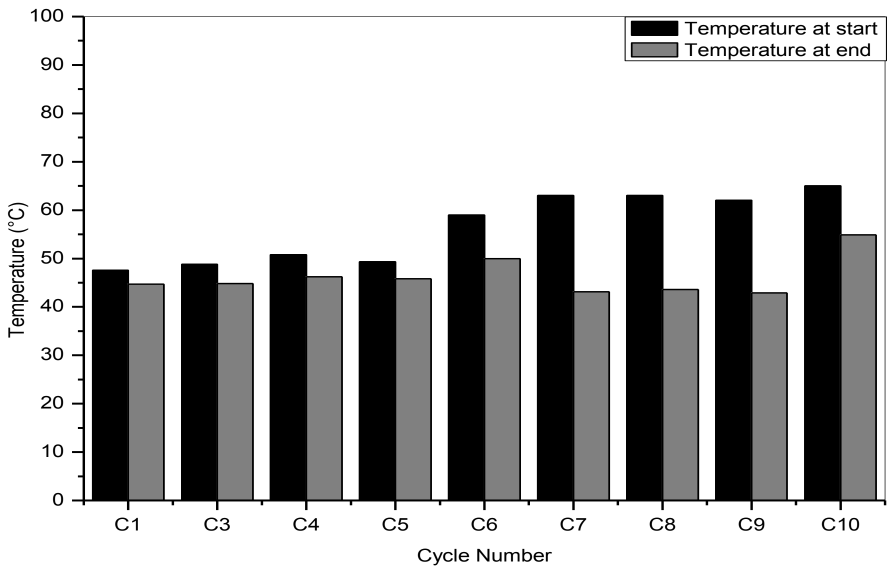


Figure 3.7 : Starting and ending temperature of NF membrane permeate during every cycle (UF+NF operation mode).

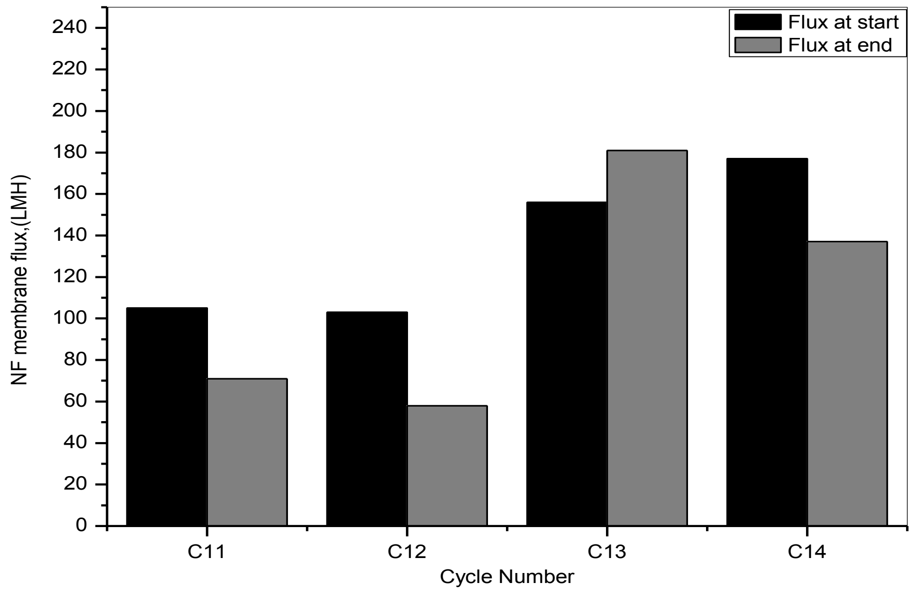


Figure 3.8 : Starting and ending flux of NF membranes during every cycle (only NF operation mode).

In Figure 3.8 and Figure 3.9, the starting and ending flux and temperature of NF membrane system during every cycle is given. In these four cycles, raw wastewater was directly and only treated by NF membrane. The average flux of four cycles is approximately 135 LMH for the start and 111 LMH in the end. Unlike the first 10 cycles, the effect of pre-treatment with UF was observed by using only NF membrane. The flux was expected to be lower since there was no pre-treatment when only NF was used. However, the graphs show that the fluxes are similar to NF fluxes after UF pre-treatment. This can be attributed to real operation conditions in the factory and different types of wastewater usage.

When Figure 3.7 and Figure 3.9 is compared, it can be seen that temperature differences between feed and permeate flows is less severe in only NF operation mode. From this point of view, since both NF flux are similar in two operation modes, only NF membrane usage for hot wastewater recovery may be sufficient. But in the long term operations, usage of UF membrane before NF membrane can prolong the service life of the membrane.

3.3.3 Treatment efficiency results

In Figure 3.10 and Figure 3.11, overall removal efficiencies for UF+NF cycles and for only NF cycles were given. For UF+NF cycles, real wastewater was filtered through UF and NF membranes sequentially and experiments were applied to both UF and NF permeates but only NF permeate results are reported in Figure 3.10 in order to compare with Figure 3.11. When Figure 3.10 is examined, it can be seen that removal efficiencies are generally over 70% for all analysis types (COD, color, TOC and total hardness). Especially COD and TOC removal efficiencies did not droop down below 70%. In Voigt et al.'s study (2001), they used 400 Da ceramic NF membrane for the treatment of 30 different colored textile wastewater samples; they obtained 45-80% COD removal efficiencies. The variety of removal efficiencies was explained by the difference between dye baths in their report (Voigt et al., 2001).

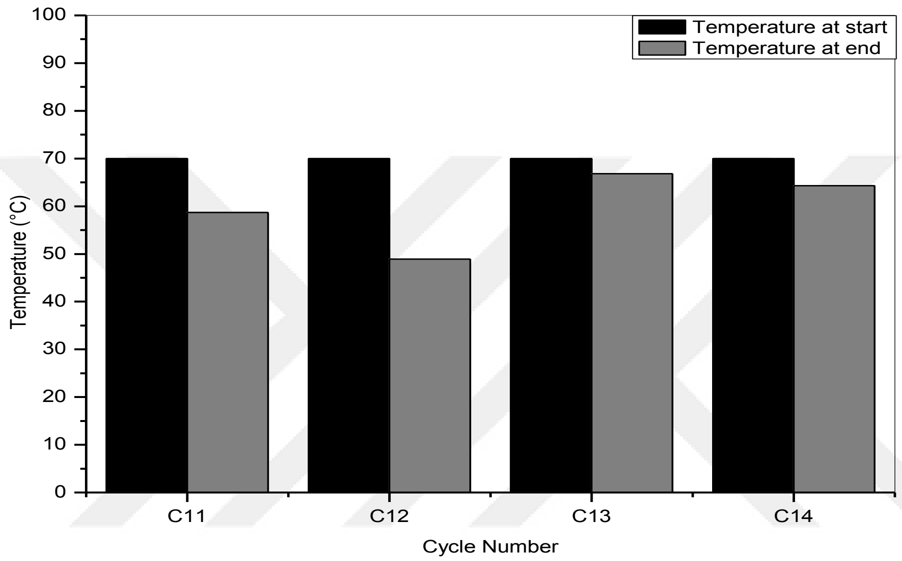


Figure 3.9 : Starting and ending temperature of NF membrane permeate during every cycle (only NF operation mode).

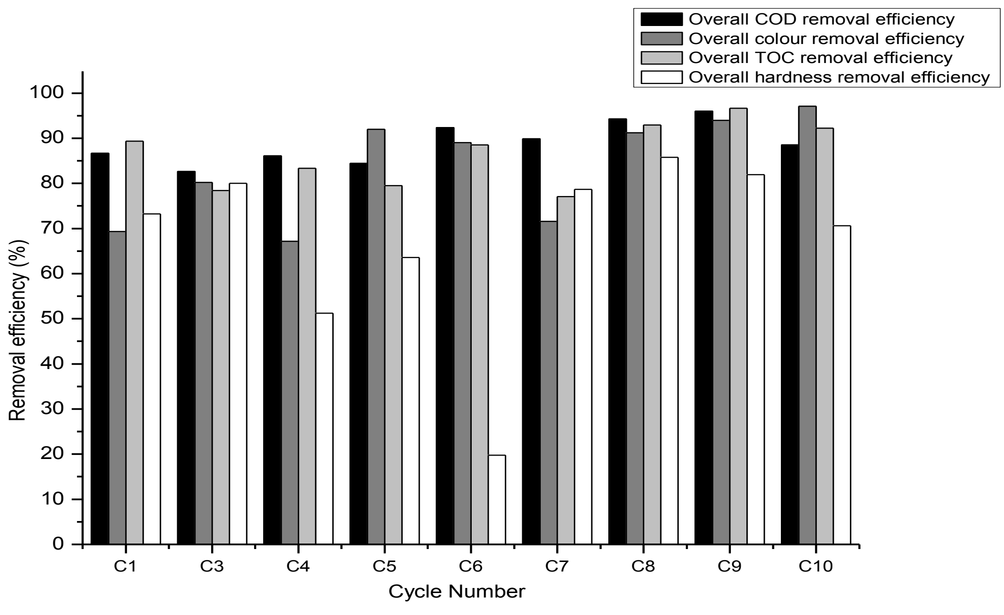


Figure 3.10 : Overall removal efficiencies for UF+NF cycles (second scenario).

Color removal was alternating throughout the cycles. This can be attributed to the variation of wastewater characterization and dye type used in each cycle. In addition, it is stated that textile companies can make use of treated wastewater with acceptable dye content in some processes, for example, in dense dye washing (Dilaver et al., 2018). Also in a recent study, Nadeem et al. (2019) applied different combination ultrafiltration (UF) and nanofiltration (NF) membranes for investigating the treatment and recycling potential of textile wastewater. According to their results, the configuration of UP005 + NF200 + NF90 in a sequential arrangement provided 99.4% color and 99.1% COD removal (Nadeem et al., 2019). In Nadeem's study, polymeric membranes were used. But since pore sizes are similar with ceramic membranes, it can be said that the results of the two studies are similar in some points. It is clear that only the pore size is not sufficient to comment. But it was thought that pore size could be shown as the common point of the two studies. In addition, the membrane type and other parameters are of great importance.

In Fgure 3.11, it can be seen that COD removal efficiencies are approximately 90% for each cycle. It means that organic pollutants are almost eliminated. Color, TOC and total hardness removal efficiencies are also found to be acceptable. As previously mentioned, Nadeem et al. (2019) used the NF membrane (NF200 membrane) for recovery of textile wastewater. They obtained COD and color rejection as 94.3% and 97.7% respectively (Nadeem et al., 2019). In Fersi's (2008) study, they used NF membranes for treatment of textile wastewater. They observed dye retention over 95% even at low pressure in permeate stream (Fersi and Dhahbi, 2008). In Nataraj et al.'s (2009) study, nanofiltration and reverse osmosis thin film composite polyamide membrane modules in a pilot scale system were used to remove the color from synthetic dye solution. Color removal by NF with a rejection of 99.80% was obtained (Nataraj et al., 2009). Whereas only a certain wastewater is used in the studies shown as examples, it should be remembered that more than one wastewater is tested under the real conditions in this scope of study.

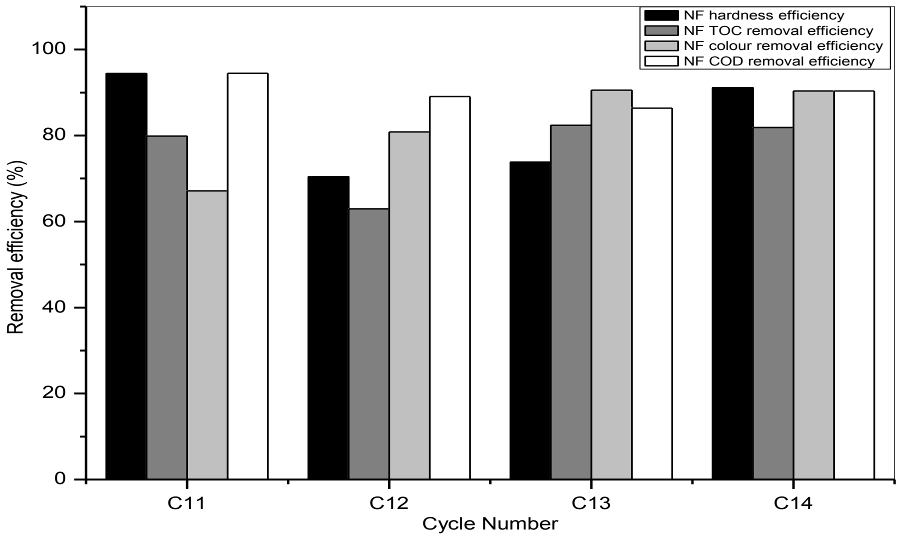


Figure 3.11 : Overall removal efficiencies for only NF cycles (third scenario).

According to obtained results, for UF+NF cycle overall average removal efficiencies are 89%, 83.5%, 86.4% and 68% for COD, color, TOC and total hardness, respectively. For only NF cycles, overall average removal efficiencies are 90.1%, 82.2%, 76.8% and 82% for COD, color, TOC and total hardness, respectively. When results are evaulated, it can be said that similar efficiencies were obtained for both scenario. However, in the long term, the use of UF membrane may be recommended to protect the NF membrane, to maintain membrane yield stability and to prolong membrane life by minimizing fouling.

3.3.4 Fabric dyeing experiment results

Dyeing experiments were carried out with treated water obtained from the UF+NF operation mode which were made with hot mixing wastewater, where commercial ultrafiltration and nanofiltration ceramic membranes were used and applied successively. The dyeing experiments were carried out by Savcan Tekstil and the results are as shown in the Figure 3.12. The fabric used in all experiments is viscose. It was stained according to the reactive staining method. The dye inlet pH is between 6.5-7.5. Acid buffer solutions were added to all dyes and pH adjusted. As shown in the figure, fabric samples are labelled as original and trial in two ways.

According to the results obtained from the dyeing experiments, the beige dyeing experiment was not successful. On the other hand, dyeing with khaki colored dye was classified as ‘usable’, while dyeing with navy colored dye was classified as ‘suitable’ for use. Based on these results, it can be understood that the hot mixing wastewater treated with ceramic membrane can be reused in the plant and will contribute to water recovery. The results of this study are very promising.

3.3.5 Economic evaluation

Because of the intensive water consumption in the textile industry, it is vital to lower water usage and wastewater amount with an integrated approach to protect the environment and water resources (Ozturk and Cinperi, 2018). Hence, many industries have to reduce their water use by reusing the wastewater they produce within the facility for several reasons (Sahinkaya et al., 2018). Turkey pays $0.2 per cubic meter for wastewater discharge and $0.3 for per cubic meter for treated wastewater. In addition to water consumption, textile industry needs high amount of energy for heating baths in wet processes (Kocabas et al., 2009). Thus, recovery of hot wastewater is vital considering both energy efficiency and reduction of the wastewater amount, and thus may decrease energy, water and wastewater costs (Voigt et al., 2001). Considering all this, treating and recovering hot wastewater is aimed in this study. The applicability of in situ pilot scale ceramic membrane technology for hot water recovery has been demonstrated in this study. Based on this study's results, economic analysis was carried out with a rough approach in order to give ideas to the researchers and to the textile industry that those with the potential to research and apply this technology. In Figure 3.13, raw water, NF permeate temperature and the temperature difference between two stream for every cycle is given. It can be seen that temperature difference changed between 4.1-29.1. But on average, it can be considered as 15 °C. Hot waters used in textile industry is around 95±5°C. In this context, required heat can be calculated with Eq.(3.3) where Q is required heat (joule), m is mass (g), c is specific heat capacity (4.184 j/g°C for water) and Δt is temperature difference between inlet and outlet (°C).

$$Q = m * c * \Delta t \tag{3.3}$$

For in-situ pilot scale filtration experiments, directly NF membrane should be used due to flux advantage. Due to absence of real case data, the costs for ceramic membrane installation and operation related expenses were adapted and assumed in this study as the following. Ceramic membrane costs are around 2000 USD $/m^2 and the module cost is 16 to 32 USD $/m^2 (Dilaver et al., 2018). For treatment of 885 m^3/d water and 111 LMH flux (Figure 3.8) the required membrane area is 340 m^2 which corresponds to 680000 USD $ for the membranes and approximately 8160 USD for the membrane module. A summary of expenditures is given in the Table 3.4.

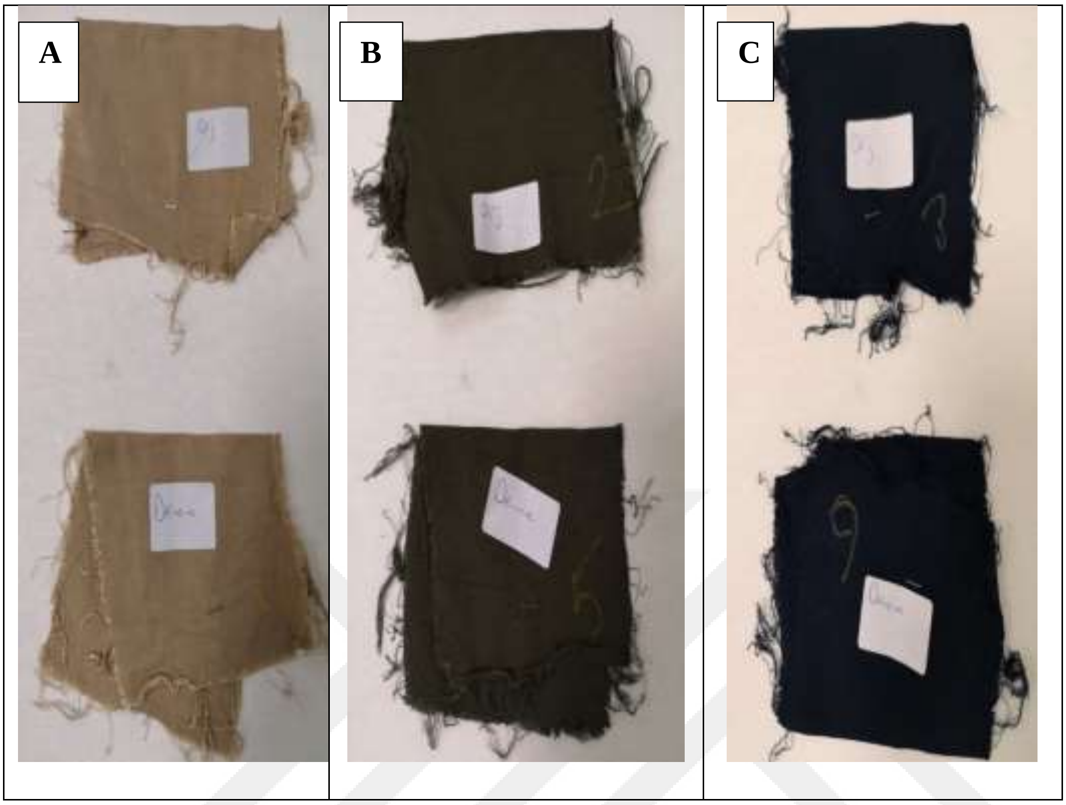


Figure 3.12 : Dyeing experiments with treated hot wastewater (A: Beige dye, B: Khaki dye, C: Navy blue dye, original dyeing on top).

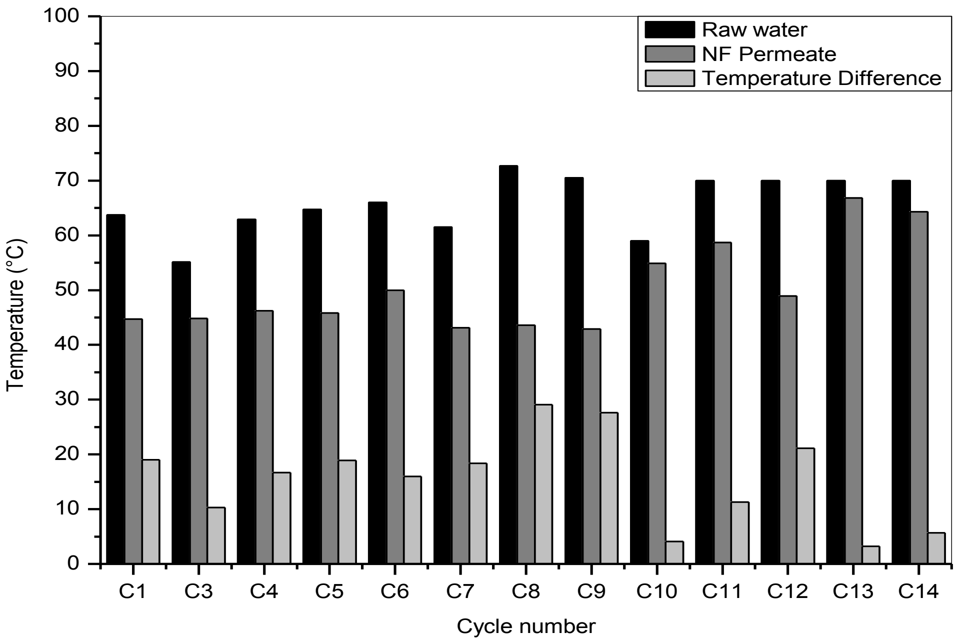


Figure 3.13 : Raw water, NF permeate temperature and temperature difference between two stream for every cycle.

Accordingly, the required heat for heating 258420 m^3/year permeates from 65°C to 95°C is 3,24369*10^{13} Joule or 9082326 kWh. The electricity costs for this would be approximately around 0.1 USD $/kWh which in turn lead to an annual energy cost of 908233 USD $. If the company would have used a water of 25°C, the cost for heating would be approximately 2119210 USD $ which is 2.3 times higher. Thus, the net energy benefit would be approximately 1210977 USD $. As water consumption also has a cost, the expense for 258420 m^3/year water which is around 129210 USD $ can also be saved.

Some operational and specific costs were adapted from TECHNEAU Report (Heijman and Bakker, 2007). As Heijman and Bakker mentioned in this report, in the installation of a 200 m^3/h ceramic membrane filtration system, the initial investment including mechanical, electrical and labor is around 1512000 € (1799280 USD $) with a yearly cost of 165730.09 € (197218 USD $). The exploitation costs including depreciation, energy, chemicals, maintenance and concentrate disposal are approximately 238980.09 € (287386 USD $) leading to a specific cost 0.14 € (0,166 USD $) per cubic meter.

In our case, costs are adjusted as the studied flow rates are 0.18 times of the given references (Heijman and Bakker, 2007). Thus, ceramic membrane installation, operation and specific costs would be roughly 411246 USD $/year and membranes and module would cost around 688160 USD $. The total investment cost would be approximately 1099406 USD $.

When the annual 258420 m^3 permeate is heated from 65°C to 95°C, the annual electricity saving is expected to be 1210977 USD $ together with 129210 USD $ annual water saving. Thus, the total annual saving amount is 1340187 USD $. Accordingly, a return of investment is expected in less than 2 years. These cost calculations were based on assumptions of the water consumption of the medium size industry we have studied.

Table 3.4 : Cost analysis for hot water recovery with ceramic membrane system.

Parameters	Costs (USD $)
Capital cost	
Membrane (340 m^2)	680000
Membrane module	8160
System installation, operation and specific cost	411246
Operating cost	
Heating (With ceramic membrane - from 65°C to 95°C)	908233
Heating (Without ceramic membrane - from 25°C to 95°C)	2119210
Savings	
Electricity*	1210977
Water saving (m^3/year)	129210
Total savings	1340187
Payback period	Less than 2 years

*0.1 USD $/kWh

As mentioned before, although the use of UF and NF membranes together provides advantages in terms of operation, the use of NF alone seems to be more applicable in terms of hot water recovery. When UF and NF are used together, since the flux from the UF is high, there is a high probability that it will cool down by the time it enters nanofiltration. It can be said that one stage is recommended because of the advantage of ceramic membranes and because the flux is higher, it does not clog unlike polymeric membranes.

3.4 Conclusion

In high water consuming industries, water recovery and water reuse will ensure both water conservation, wastewater reduction and energy savings. At this point with ceramic membrane technology, hot textile wastewaters can be treated and it can maintain its temparetaure at the same time.

In this study, a pilot scale UF/NF ceramic membrane system was used to hot wastewater recovery and reuse. All the trials were carried out with real wastewater in a real facility under real conditions. A total of 14 trials were performed and 10 of these experiments were performed with UF + NF process and 4 of them were performed only with NF process. The aim is to see the effect of UF membranes on treatment efficiency. The obtained results show that, with or without UF, there is no severe difference in terms of removal efficiencies and treatment can be said to be sufficient. On the other hand, UF membrane usage can be recommended to provide longer membrane service life for NF membrane.

The main purpose of this study is the hot wastewater recovery as mentioned previously. From this point of view, the outputs of the study showed that temperature difference between feed and permeate streams were not so sharp. In terms of economic evaluation, when annual 258420 m^3 permeate was heated from 65°C to 95°C, the annual electricity saving is expected to be 1210977 USD $ together with 129210 USD $ annual water saving. Thus, the total annual saving amount is 1340187 USD $. Accordingly, a return of investment is expected in less than 2 years.

The applicability of ceramic membrane technology has been found in the laboratory scale hot textile wastewater recovery studies conducted by Dilaver et al. (Dilaver et al., 2018) and, within this study, it was proposed to verify the obtained results with a pilot study. This study confirms that hot water can be recovered using a pilot scale ceramic membrane system. In addition, 2 of 3 fabric dyeing experiments with NF permeate were successful. In light of all of this data, it is seen that full scale ceramic membrane systems can be used in hot water recovery in textile industry. Thus, with the potential for water, energy recovery, and ceramic membrane technology can be counted as one of the Best Available Techniques. A BAT, BREF document is proposed with different methods of reducing water, raw material, and energy use reduction. Pilot scale results and economic evaluations are thought to be a good guide for future studies. Trials with other water and heat consuming industries, trials with domestic ceramic membranes and a more detailed economic evaluation can be recommended for researchers for future studies. As a result of this study, it is thought that a useful resource has emerged for full scale systems that can be installed in the future. Furthermore, it is believed that the results will contribute to existing literature, as it is one of the few pilot studies for hot water recovery.

4. PILOT SCALE CERAMIC ULTRAFILTRATION/NANOFILTRATION MEMBRANE SYSTEM APPLICATION FOR CAUSTIC RECOVERY AND REUSE IN TEXTILE SECTOR[3]

4.1 Introduction

The textile sector has one of the most polluted wastewater outputs of all industries, with high levels of organic compounds and various organic pollutants (Korenak et al. 2019; Kiani et al. 2020). Because of the strict regulations of textile wastewater discharge, recovery of chemicals and water has become a prominent issue (Dilaver et al. 2018). In addition, the increase in water costs and the valuable chemical content of textile wastewater makes recovery and reuse more important, both economically and ecologically (Son et al. 2000). Approximately 3600 kinds of dyes and nearly 8000 different chemicals are used in the manufacturing processes in the textile industry. Most of these chemicals cause serious danger to human life, aquatic life and the overall ecosystem. An average textile factory with a capacity of approximately 8000 kg of product uses 1.6 million liters of water per day (Hussain and Wahab 2018). High amounts of wastewater are also generated due to intensive water use in the textile sector. Therefore, textile wastewaters must be treated before discharge to receiving water bodies. Additionally, high consumptions in this sector lead to the depletion of groundwater. Moreover, reuse of water can play an important role in protecting water resources, also supporting the concept of zero and/or near zero liquid discharge; the use of recycled water has been mentioned in the literature over the past few decades. Considering all this, water consumption, wastewater production and pollution load should be reduced with an integrated approach and the protection of water resources

[3]This chapter is based on the paper "Meltem Ağtaş, Özgün Yılmaz, Mehmet Dilaver, Kadir Alp and İsmail Koyuncu. Pilot scale ceramic ultrafiltration/nanofiltration membrane system application for caustic recovery and reuse in textile sector. Environmental Science and Pollution Research, 2021.DOI: 10.1007/s11356-021-13588-0"

and the environment should be ensured (Ordóñez et al. 2011; Moazzem et al. 2018; Ozturk and Cinperi 2018). At this point, the importance of cleaner production techniques becomes apparent. Cleaner production practices include conservation of raw materials and energy, reduction of toxic substances, and reduction of toxic emissions during production processes. For cleaner production implementation, textile applications gain priority. Most studies on cleaner production practices are carried out in the textile industry in Turkey (de Oliveira Neto et al. 2019).

The textile industry has various processes such as scouring, bleaching, warping, washing, desizing, printing, rinsing, mercerizing, dyeing and finishing (Bisschops and Spanjers 2003; Ordóñez et al. 2014). In the mercerization process, which is generally used in cotton fabrics, fabrics are treated with caustic solution to increase their brightness, dye absorbing capacity and strength of the fabric. The reason for these improvements in fabric is that the caustic solution re-regulates the cellulose molecules in the fibers (Yang et al. 2007). Textile wastewaters also have lots of constituents such as heavy metals, salts, dispersing agents, different types of dyes and lots of organic chemicals. In addition, 10,000 different dyes are used in the processes and only 10-15% of the dyes come out of the process without being used. When all these contents are considered, the harm that textile wastewater can cause to human health and aquatic ecosystem can be estimated (Cinperi et al. 2019).

Biological and physicochemical procedures are mostly applied for textile wastewater treatment. Even though these methods provide discharge limits, because of the limitations of these technologies, they generally do not allow for wastewater reuse or recovery (Barredo-Damas et al. 2011; Kuleyin et al. 2020). In Kamali's (2019) study, they investigated the fuzzy-Delphi approach to analyze seventeen parameters for combining environmental, economic, social and technical criteria to evaluate nine technologies that are physico-chemical and biological treatment processes. According to the obtained outcomes, for technical and environmental criteria, technologies which include membrane processes have the highest ratings while other treatment methods are better, in regard to social and economic criteria. In addition, in view of all of these criteria, membrane processes have been determined as the most sustainable method for industrial wastewater (Kamali et al. 2019a). Over the past few decades, membrane processes that have been used for separation and purification purposes have evolved considerably. Without any phase change, membranes, using their pores, can realize mechanical separation and concentration of impurities (Hubbe et al. 2016; Park and Song 2019). Membranes with ultrafiltration (UF-low pressure membrane process with pore size 10-1000 Å) and nanofiltration (NF-pore size < 2 nm) levels are successfully used in textile wastewater treatment (Gao et al. 2011; Alventosa-deLara et al. 2012; Guo et al. 2020).

Different polymeric and inorganic materials have been put to use to produce membranes in order to treat industrial wastewater. For instance, various types of inorganic ceramic membranes have been put to use frequently in industrial wastewater treatment studies in recent years. This can be attributed to the fact that ceramic membranes have higher chemical resistance and are easier to clean than polymeric membranes (Issaoui et al. 2017; Kamali et al. 2019b). In a study by Fersi and others (2005), textile industry effluents, previously biologically treated by activated sludge, were treated by lab scale membrane processes using different membranes (both polymeric and ceramic membranes). Obtained results showed that membrane processes are very up and coming advanced treatment alternatives for textile industry wastewater (Fersi et al. 2005).

Not only for treatment but also for recovering water and chemicals, membrane processes have come to the forefront in recent years (Harane and Adivarekar 2017). For instance, by using NF membranes, water and NaOH can be separated from organic compounds and therefore this process can be considered a specifically useful separation technology for recovering alkali compounds (Choe et al. 2005). Caustic soda recovery has been carried out since 1994 using commercial systems. Koch MPT-34 tubular polymeric membranes were used in these systems and the operation life of membranes was reported to be more than one year. Ceramic membranes can also be used for recovering caustic soda, while standard polymeric NF membranes can be operated for low sodium hydroxide content solutions (0.1-0.4%) (Schlesinger et al. 2006). Using ceramic membranes for textile effluents, however, has more advantages than using polymeric membranes since ceramic membranes have higher resistance to chemicals and temperature mechanical durability (Barredo-Damas et al. 2010).

This study was carried out for 3 main purposes. First of all, the aim was to treat the real caustic bath wastewater (pH>13) from other impurities in the wastewater by using ceramic membranes in a way that is convenient for reuse. As a second step, the study attempted to determine whether the permeate water coming out of the ceramic membrane has a sodium concentration suitable for reuse in the causticization process in the facility. Finally, a determination of how the obtained permeate will be used in the facility and whether the whole process is economically viable was carried out. To achieve these goals, a pilot scale ceramic UF/NF membrane system was operated in the facility. Considering that there are not many pilot studies related to this subject, this study is thought to contribute significantly to the existing literature.

4.2 Experimental

In this section, the materials used in the study, the facility where the study was carried out, the system used in the study, and the test systems applied to all samples are explained.

4.2.1 Commercial membranes

UF and NF commercial ceramic membranes (ATECH) were used for this study and their properties are given in Table 4.1. As can be seen from the table, the support layer of both membranes is alumina, and the active layer performing the separation process is titania material for the NF membrane. Since the pH range within the two membranes is between 0-14, it is understood that these membranes will be resistant to the high pH values of the wastewater used within the scope of the study.

4.2.2 Pilot scale UF/NF ceramic membrane system

A pilot scale UF/NF ceramic membrane system consists of three tanks, two pumps, a SCADA (Supervisory Control and Data Acquisition) system and other necessary equipments. The pilot scale UF/NF ceramic membrane system has two operation modes,batch and continuous,with three different scenarios. With these scenarios, only UF membrane, UF+NF membranes together and only NF membrane can be operated (Figure 4.2).

In the first tank, wastewater was collected. For the first scenario, wastewater from the first tank passed through the UF membrane and the UF permeate entered the second tank. In the second scenario, the permeate in the second tank was collected in the third tank through the NF membrane. In the third scenario, the UF membrane was deactivated and the wastewater from the first tank passed directly through the NF membrane to the third tank. The membranes used in the system are commercial and contain one UF and one NF membrane. Membrane housings (546 mm each) are stainless steel and also part of the pilot scale system. Two images of the system taken in place is given in Figure 4.1.

In the facility, wastewater is produced in batch mode. Accordingly, the pilot ceramic membrane system was also run batch mode. Every batch mode was defined as a 'Cycle.'

Table 4.1 : Properties of multi-channel ceramic membranes.

Parameters	**UF**	**NF**
Support layer	Al_2O_3	Al_2O_3/ZrO_2
Active layer	Al_2O_3	TiO_2
Channel number	19	19
Channel diameter (mm)	3.3	3.3
Pore size	0.05 µm	1 kDa
Membrane length (mm)	450	450
Membrane area (m^2)	0.09	0.09
pH resistance	0-14	0-14

*This table is adapted from ATECH innovations gmbh technical data sheet.

The filtration system can be monitored by SCADA (Supervisory Control and Data Acquisition).

The UF membrane's operation pressure was 2.5 bar. Once in every 10 minutes for 5 seconds during operation, air was used for backwash. The NF membrane's operation pressure was also 2.5 bar. For NF membrane, air backwash was applied once every 1 hour for 5 seconds during operation. Before each operation, to clean the system, tap water was passed through the system. UF permeate and NF permeate were recorded at every 10-minute and 30-minute interval during the period of filtration, respectively.

Cycle 1,3 and 4 was operated according to the second scenario. For cycle 2, only a UF membrane (first scenario) and for cycle 5, only an NF membrane (third scenario) was used for treatment and caustic recovery. During cycles, operation time for UF membrane varied between 3-5.5 hours,and for NF, it decreased to 1.5-2.5 hours. Only for cycle 5, the NF membrane was operated for approximately 7 hours.

Flux was calculated by using Eq.(4.1) where J is the permeate flux [L/m^2/h], Δm is permeate amount at specified time interval [g], ρ is the feed density [g/cm^3], A is the membrane filtration area [m^2] and the Δt is the specified time interval [minute].

$$J = \left. \left(\frac{\Delta m}{\rho}\right)/1000 \middle/ A * \left(\frac{\Delta t}{60}\right) \right. \tag{4.1}$$

4.2.3 General information about selected facility

The textile factory, where all pilot trials were conducted, is located in Bursa Organized Industrial Zone, Turkey. All membrane filtration studies were completed in about 1.5 months. According to the information obtained from the factory, products from this factory are mostly cotton and viscon. Daily production is aprroximately 15 tons/day and about 3200 m^3/day water is consumed. Studied wastewater contains several chemicals, dyes and cleaning additives.

The wastewater treated in the membrane system was taken from caustic main bath discharges. Concentrated caustic solution is used to swell the fibers and make the raw material more robust. Thus, the fabric treated with this caustic solution can be more ready for absorbing the dye. In causticization process in the selected facility for trials, viscon fabric is treated with ±21g/L NaOH solution within the caustic bath. After this process, the fabrics are rolled and left to stand for a few hours. Following this process, the fabric is washed in seven successive rinsing baths with water at a temperature of 90-95 degrees to remove residues. Caustic main bath and rinsing baths’ photos are given in Figure 4.3. The concentration of caustic solution in the caustic bath must remain constant to maintain the fabric quality.

(a) (b)

Figure 4.1 : In situ pilot ceramic membrane filtration system (a:front view b:back view).

4.2.4 Characterization of streams and instruments

Throughout the operations, samples were collected from the feed (viscon caustic bath discharge) at the beginning of the cycle and from the permeate stream at certain intervals and some experiments were performed using these samples. Considering the previous literature studies, some tests that are thought to be important in wastewater characterization have been selected. Since the aim was to purify the impurities and keep sodium in the wastewater, the specified experiments were conducted to determine whether the goal was acheived. These experiments are temperature, pH, total organic carbon (TOC), total hardness, chemical oxygen demand (COD), color, sodium tests and metal ions measurement. Temperature and pH were obtained by using a pH meter (S220 SevenCompact pH / Ion, Mettler Toledo, USA). For COD and total hardness experiments, test kits (LCK327, LCK514, LCK 1414 HACH) were applied to samples. For TOC measurements a Shimadzu V-CPN model TOC analyzer was used. For sodium elemental measurement, a Dionex ICS-3000 ion chromatography analyzer was used. Colour measurements was conducted by a Hach Lange DR 5000 UV spektrofotometer. For metal ions determination, an ICP-OES (Perkin Elmer OPTIMA 8300 DV Model) following the ISO 11885 method was used.

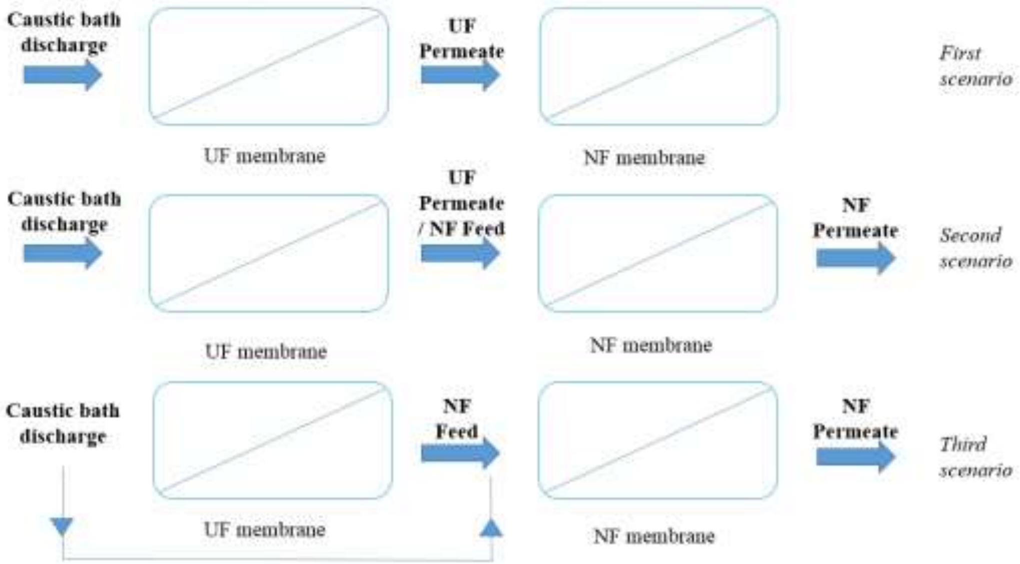


Figure 4.2 : Operation orders of in situ pilot scale ceramic membrane filtration system.

Figure 4.3 : Caustic main bath and rinsing baths.

4.3 Results and Discussion

Within the scope of this study, firstly, the characterization process was applied by sampling the inlet wastewater before each cycle. Then, the flux values for each cycle were monitored and the permeate obtained as a result of filtration was characterized and the removal efficiency was calculated. Finally, caustic recovery, which is the main purpose of this study, was investigated. In addition, aluminum and titanium tests were carried out on the obtained filtrate to determine whether the membranes were worn during the operation. In addition, an economic evaluation was added to the results in order to help the study to be used on a real scale.

4.3.1 Characterization of wastewater

First of all, wastewater characterization tests were applied in order to determine the characteristics and properties of the wastewater taken from the factory, to be treated.

In Table 4.2, the wastewater sample characterization is given. As shown in Table 4.2, the maximum and minimum values were 19110 and 8936 mg/L for COD, 4530 and 2048 mg/L for TOC, 0.846 and 0.264 for color, 453.8 and 68.7 mg $CaCO_3$/L for total hardness, respectively. Except for a few differences, the results were found to be similar. Although the caustic solution concentration in the feed is the same, it can be said that these differences are normal because the treated product changes. Furthermore, according to the information obtained from the plant, the test results may vary depending on how many meters of fabric is processed and the time of sampling. There are not enough studies related to caustic recovery in the literature. However, some studies involving wastewater characterization are as follows. For example, in a recent work, the performance of three UF membranes (submerged PE hollow fiber membrane, PES membrane and tubular ceramic membrane) were tested in the textile mercerization wastewater treatment. In the feed stream, pH and TOC values was reported as 13.3 and 366.9-499.2, respectively. Also, NaOH content was 1.4% in this wastewater (Zebić Avdičević et al. 2019). In another study, Varol and his companions (2015) intended to evaluate caustic recovery with polymeric membranes from mercerizing wastewater originating from a denim textile producing plant. They obtained COD values between 0.5-8.5 g/L and NaOH content was between 1.4-67.5 g/L; pH varied between 8.9-12.3 (Varol et al. 2015).

In Tunç's (2014) study, membrane processes were used for purifying the highly alkaline textile mercerization wastewater. According to the article, COD values were between 448-748 mg/L and pH varied between 12.65-12.96. The NaOH concentration in their mercerization process wastewater was 2.71 and 13.5 g/L for two different feed streams (Tunç et al. 2014).

Table 4.2 : Wastewater characterization results.

Parameter	COD (mg/L)	TOC (mg/L)	Colour (436 nm)	Total Hardness (mg $CaCO_3$/L)	pH
C1	19110	4530	0.264	68.7	>13
C2	9532	2592	0.279	453.8	>13
C3	8936	2842	0.846	95.5	>13
C4	9272	2946	0.763	91.6	>13
C5	9024	2048	0.452	86.3	>13

4.3.2 Filtration results

The aim of this study was real caustic wastewater treatment and recovery of NaOH. Therefore, UF and NF ceramic membrane technology have been used both together and separately. Membrane processes were used to remove impurities in the used caustic solution to obtain the desired denser base solution by recovering NaOH. A total of five cycles were performed. Cycle 1,3 and 4 were operated according to the second scenario. For cycle 2, only an UF membrane (first scenario) and for cycle 5, only a NF membrane (third scenario) was used for treatment and caustic recovery. By performing different scenarios, the difference between the processes could be compared. In Figure 4.4 and Figure 4.5, the UF membrane and NF membrane flux at the start and at the end of the cycles are given. No extra heat was applied during operations and all tests were carried out under real conditions in facility. The permeate temperature values ranged from about 24 to 45 °C for UF and NF.

In Figure 4.4, it can be seen that, UF membrane flux at the start and flux at the end varied between 56.7-32.4 LMH and 17.94-5.33 LMH, respectively. Since the caustic solution is quite dense, the flux values obtained are normal values. Furthermore, the decrease in the end flux indicates that the membrane can be clogged. In terms of flux, a consistency between the cycles can be observed.

In Yang et al.’s (2007) study, different membrane process combinations were tested to recover caustic solution from mercerization wastewater in textile industry. When the study is examined, it can be said that the flux results are similar. For 0.05 µm membrane and 2.5 bar pressure, as can be read from the graph in the article, the flux is below 100 LMH. Temperature is also an important factor affecting flux due to viscosity. It is also stated that the operating temperature is 30 °C which is also similar to the operational conditions of this study (Yang et al. 2007).

In a study conducted in 2004, the membrane-alkali recovery process was tested. For this study an inorganic MF membrane was used. The rejection of silica, lignin and sodium salts by using inorganic MF membrane was examined.

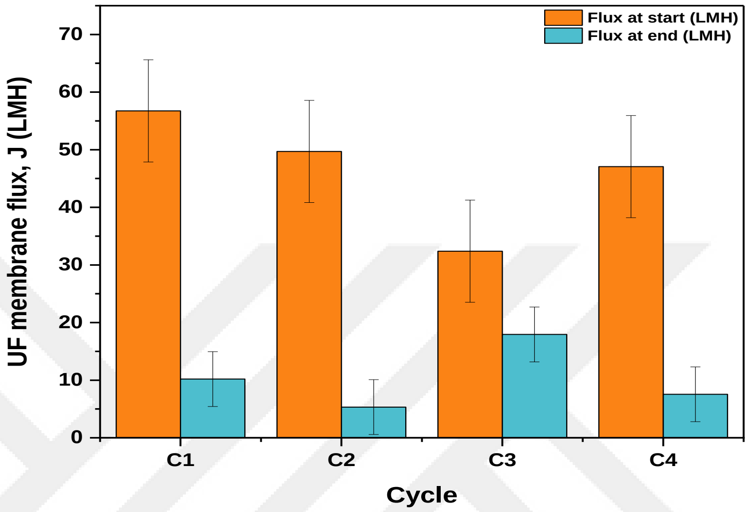


Figure 4.4 : UF membrane flux at the start and end of the cycles.

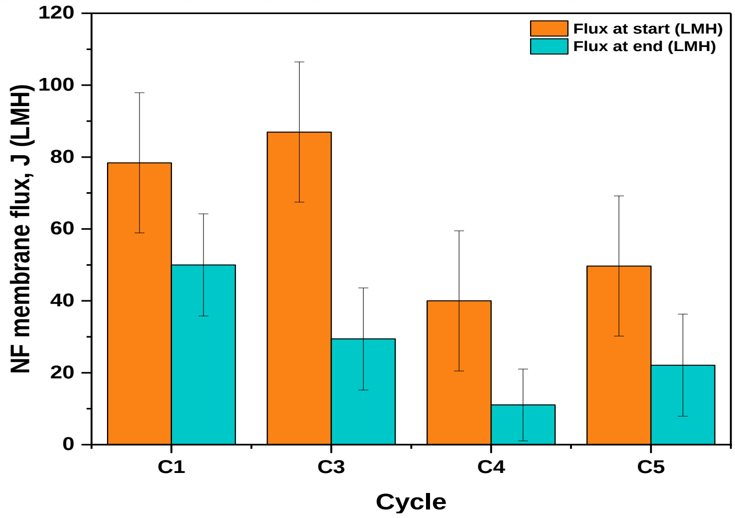


Figure 4.5 : NF membrane flux at start and at end during cycles.

According to obtained wastewater flux for 50 nm MF membrane, flux varied between approximately 35-70 LMH under 2 bar pressure (Liu et al. 2004). Because the studied industry was not textile, the wastewater characterization was different from our work; regardless, the flux values are similar to those obtained from this study.

Flux values for the NF membrane flux at the start and end varied between 78.4-40 LMH and 50-11.05 LMH, respectively, as can be seen from Figure 4.5. C1, C3 and C4 were operated according to scenario 2. This means that raw wastewater went through the UF membrane and UF permeate went through NF membrane, respectively. C5 was operated according to scenario 3 which means raw water filtered by only the NF membrane. When the obtained flux results are examined, it can be seen that C1 and C3's flux values are higher than C5 and C4 is very similar. This can be attributed to the UF membrane, which was used as pre-treatment process and the introduction of less contaminated water into the NF membrane. When only the NF membrane was used, the decrease in flux can be shown as evidence of this.

4.3.3 Treatment efficiency results

In this study, the aim was to treat wastewater from caustic bath and to obtain a caustic solution with minimum sodium lost that is usable for processes in the factory again. Thus, instead of preparing a new solution, it would be economically beneficial to add NaOH to the treated caustic bath wastewater. Moreover, recovery of caustic solution can achieve one of the Textile BAT targets (European Commission 2003). As a result of the experiments carried out in this context, removal efficiencies for only UF operation and overall efficiencies with error bars are given in Figure 4.6 and Figure 4.7, respectively. For only UF cycles, overall average removal efficiencies were 22%, 36%, 25% and 63% for total organic carbon, chemical oxygen demand, total hardness and color, respectively. Obtained results showed that, for UF+NF cycles, overall average removal efficiencies are 67 %, 71%, 42% and 92% for total organic carbon, chemical oxygen demand, total hardness and color, respectively. When Figure 4.6 and Figure 4.7 are analyzed, it can be understood that removal efficiencies are higher for UF+NF operation, rather than only the UF mode operation. This result is expected since NF membrane has narrower pore size distribution.

There are a limited number of studies in the literature including treatment of highly alkaline textile wastewater and recovery of caustic soda. In a study from 2016, Avdičević and his colleagues used 3 different MWCO of ceramic UF membranes (1, 2 and 500 kDa) to treat textile mercerization wastewater from a textile mill under different operating conditions. For 1 kDa ceramic membrane, they obtained rejection efficiencies of 98% for color and 53% for total organic carbon which are similar with our results (Zebić Avdičević et al. 2017).

To summarize this section, it is known that one of the most important steps in wastewater recovery is efficient treatment. Considering that chemical and water recovery is important, especially in the textile industry, where a large amount of water is consumed, it can be seen from the results obtained that sufficient treatment can be achieved by applying ceramic membrane processes. As mentioned above, although there are not enough studies in the literature, it is thought that studies conducted on a pilot scale will yield results very close to the real scale.

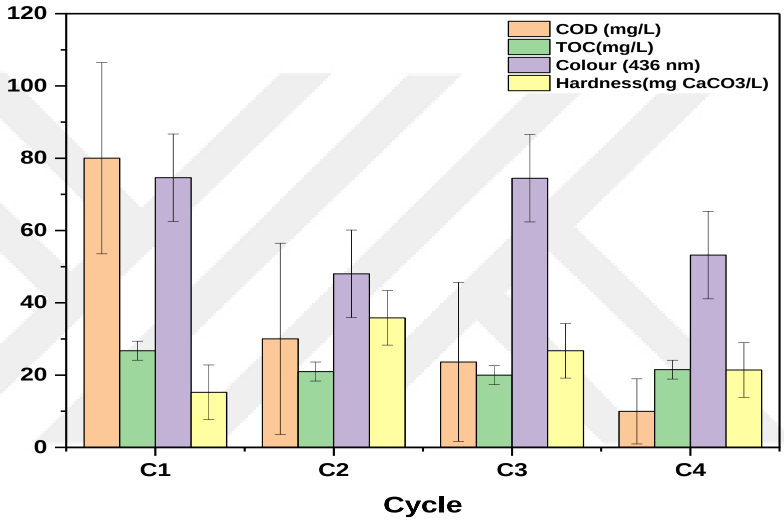


Figure 4.6 : UF membrane removal efficiencies.

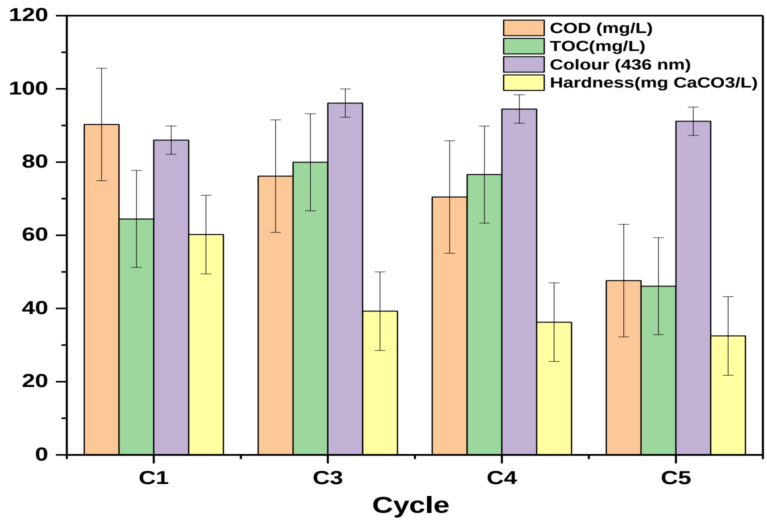


Figure 4.7 : Overall removal efficiencies.

4.3.4 Caustic recovery

The major expenditures for all water consuming industries are water and energy consumption, together with wastewater discharge. To reduce the cost of water, wastewater production and all water related energy consumption, water recovery is essential. The main purpose of the application of ceramic membrane processes to the wastewater taken from the caustic bath is to remove the impurities in the wastewater and to reuse the sodium-containing membrane effluent in the caustic process again. When Table 4.3 is examined, sodium values in the input wastewater are around 12 mg/L on average. The NF membrane output changes between 7-11 mg/L. Since the caustic solution used in the plant is expressed on the basis of sodium hydroxide, the sodium values obtained were also calculated as sodium hydroxide and are indicated in the table. It is observed that sodium loss is higher in the operations where UF and NF were applied consecutively. However, the resulting membrane permeate has the potential to be reused with the addition of higher concentrated sodium hydroxide. This would normally be less than the amount of sodium hydroxide added to the caustic process, which would be economically and environmentally beneficial.

Table 4.3 : Sodium concentrations for all cycles' inlet and outlet streams.

Cycle number	Na^+ (mg/L)	NaOH* (mg/L)
Cycle 1 UF Feed	13,776	23,959
Cycle 1 NF Feed	11,645	20,252
Cycle 1 NF Permeate	7,188	12,501
Cycle 2 UF Feed	14,076	24,480
Cycle 2 UF Permeate	12,319	21,425
Cycle 3 UF Feed	11,390	19,809
Cycle 3 NF Feed	11,060	19,235
Cycle 3 NF Permeate	7,174	12,477
Cycle 4 UF Feed	12,630	21,965
Cycle 4 NF Feed	11,780	20,487
Cycle 4 NF Permeate	7,276	12,654
Cycle 5 NF Feed	12,000	20,870
Cycle 5 NF Permeate	11,690	20,330

* NaOH concentration is calculated with Na molar ratio. Caustic content can be calculated using Na concentration in samples since NaOH is the only source for Na^+ in samples.

Before using the recovered caustic solution, some amount of concentrated commercial caustic solution needs to be added to caustic bath. In this way, both the commercial caustic use has been reduced and the near zero discharge concept which is currently on the agenda can be applied. In light of the results obtained, this study demonstrated that caustic recovery can be achieved and how the recovered wastewater can be used.

In Figure 4.8, overall sodium recovery for all cycles is given. It can be seen that at least 50% recovery was obtained for all cycles. When removal efficiencies and sodium recovery results are evaluated together, it can be said that the best treatment option is the combination of UF and NF membranes. Since the purpose of this study is to reuse the permeate water in caustic bath, the most efficient one should be selected by evaluating the removal efficiency and sodium recovery rate in the permeate together. It is thought to be more reasonable to use UF and NF membranes, since when only the UF membrane is used, the treatment does not reach a sufficient level for reuse.

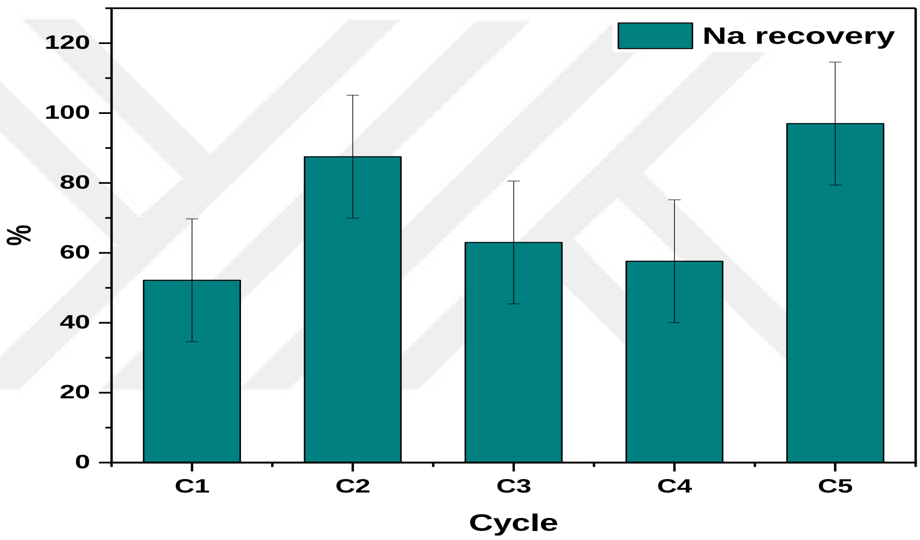


Figure 4.8 : Overall Na+ recovery for all cycles.

When Figure 4.8 is analyzed, it can be observed that the recovery rates in Cycle 2 and Cycle 5 do not correspond to the normal graph trend and the values are approximately above 60%. Since only a UF membrane was applied in Cycle 2 and normally, UF membranes have pore sizes that are not narrow enough to retain Na+ ions, this is an expected situation. However, in Cycle 5, the NF process was applied, and although complete sodium retention was not expected, it was anticipated to be consistent with other NF cycle results.

As mentioned earlier, the membranes used in the pilot system consist of alumina, titania and zirconia. In order to explain the situation in Cycle 5, alumina and titania analysis were done for the feed and permeate samples with the help of the ICP analyzer. Thus, the potential corrosion of the membrane's active layer can be determined. It is possible that the corroded and deformed membranes' active layer could not retain sodium ions. Also, when Figure 4.7 is examined, it can be seen that COD and TOC removals are the lowest among all cycles.

In Figure 4.9 and Figure 4.10, aluminium and titanium concentrations for all cycles' inlet and outlet streams are given. The aluminium values obtained varied between 60.3 and 361 ppm, while titanium values ranged between 41.8 and 145 ppm. Alumina was used as a support layer and titania was used as an active layer for the membranes. For this reason, stripping of the titania from the surface should be examined as a priority. As it can be seen in Figure 4.10, titania levels in permeate streams are almost the same or higher than the concentration found in feed streams.Thus, it can be said that the titanium on the surface decreased and therefore the removal in the last cycle is not sufficient and sodium passed through membrane and entered the permeate stream completely.

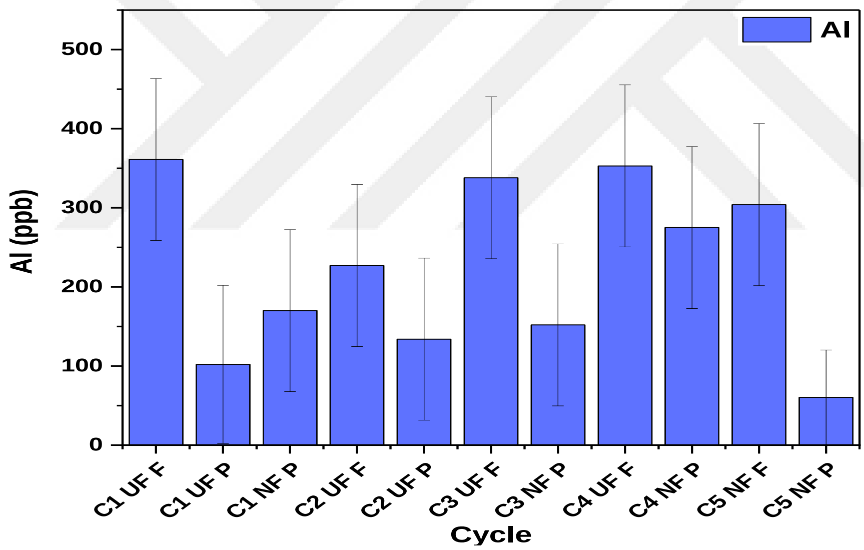


Figure 4.9 : Aluminium concentrations for all cycles' inlet and outlet streams (F: feed, P: permeate).

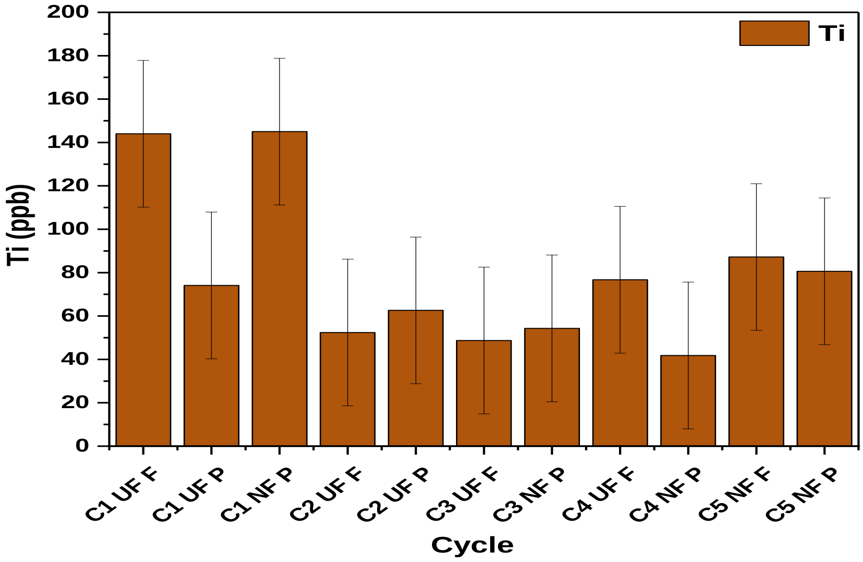


Figure 4.10 : Titanium concentrations for all cycles' inlet and outlet streams (F: feed, P: permeate).

4.3.5 Economic assessment

Within the scope of this study, 3 different scenarios have been tried for caustic recovery. Only UF, only NF and both UF and NF together were applied consecutively to the wastewater. In order to make the economic evaluation more accurate, the calculations were made according to the scenario where UF and NF are used together. The discharges of the viscon caustic main bath should be collected at a separate tank due to batch causticization process and this waste stream will be used up on a request.

In this work, the daily caustic recovery feed volume 1.3 m^3/day and a filtration time of 8 hours were assumed. The two stage membrane filtration total membrane area was calculated as 16 m^2, based on average wastewater flux that reached a steady flow around 20 LMH based on pilot scale experiments and the recovery rate was assumed as 80% .

In Table 4.4, cost analysis for caustic recovery is given. The studied textile industry pays \$0.18 and \$0.25 per cubic meter for wastewater discharge and RO product water for the process, respectively. Studied textile factory discharges were approximately 600 m3/year caustic solution from viscon caustic main bath and the factory spends 27 € for one tonne commercial caustic solution (48 Be^0). Yearly caustic solution recovery potential is around 480 m^3/year when the ceramic membrane filtration technology applied. It should be noted that this recovered caustic solution must be concentrated with commercial caustic solution in order to meet 21.0 g NaOH/L.

Although it is quite difficult to treat chemically dense wastewater, direct discharge to the environment causes huge problems in terms of both ecological and human health. The aim of this study is to protect the environment by recovering substances and water in addition to economic recovery. The important point is, by using ceramic membrane system; the factory may get rid of heavily organic matter and highly caustic waste stream. In addition, an economic evaluation was carried out in order to determine the financial viability of this study. According to the results shown in Table 4.4, it is considered to be viable according to the authors.

Table 4.4 : Cost analysis for caustic recovery.

Parameters	Real scale application (approach*)
Capital cost	(€)
Membrane elements	48000
System installation, operation and specific cost	27000
Operating cost	(€)
Caustic usage (With ceramic membrane-year)	6480
Water consumption (With ceramic membrane-year)	120
Caustic usage (Without ceramic membrane-year)	12960
Water consumption (Without ceramic membrane-year)	150
Savings	
Chemical saving (tone)	240
Water saving (m^3/year)	480
Wastewater discharge (m^3/year)	120
Payback period (year)	Approx. 5 years

* A quote was received from a company for the membrane element and the real scale system. Information was obtained from the factory studied for caustic price and water price.

4.4 Conclusion

Textile BREF documents give some advice for the best available techniques for recovery of caustic wastes, such as evaporation and membrane filtration. Although polymeric membranes are generally used more frequently in membrane processes, it is known that ceramic membranes are more suitable for textile industry wastewaters because of their high temperature and mechanical resistance. These advantages may allow for the direct reuse of the caustic solution to achieve near zero discharge.

In this study, when the results are evaluated, it is seen that at least 50% sodium was recovered in all cycles. Providing 50% recovery means that the sodium cost used in the process, at least, will be saved at this rate. In addition to chemical recovery, another important point is that water recovery also takes place at the same time. Since the permeate obtained as a result of membrane filtration is treated in sufficient amounts and contains caustic, it can be reused in appropriate processes within the facility. This situation is considered to be a very promising result for real-scale use.

This study is considered to be a useful starting point and data source for real-scale systems that can be carried out in the future. Furthermore, it is believed that the results will contribute to existing, limited literature, as it is one of the few pilot studies for sodium recovery. In addition, it is thought that this study contributes to this process' technology readiness level as 5.

5. HALLOYSITE NANOCLAY DOPED CERAMIC MEMBRANE FABRICATION AND EVALUATION OF TEXTILE WASTEWATER TREATMENT PERFORMANCE[4]

5.1 Introduction

In the last century, the quality and quantity of water resources has decreased as a result of the rapid increase of industrialization and population growth. Therefore, new methods have emerged to preserve these resources, and in recent years, membrane technologies, in particular, have become the most prominent method in water and wastewater treatment and the desalination of seawater and brine. Compared to traditional methods, membrane technologies have many advantages, such as high treatment efficiency, low sludge production, and a smaller carbon footprint (Li et al., 2020). The most used membrane types, in terms of manufacturing materials, are polymeric and ceramic membranes. Ceramic membranes are usually fabricated by using inorganic materials such as , zirconia, aluminium and titania oxides. Due to their raw materials and production methods, ceramic membranes are generally more expensive than polymeric membranes (Mestre et al., 2019). Although the use of polymeric membranes is more common in the market, ceramic membranes have many advantages over polymeric membranes, such as higher thermal and chemical resistance, mechanical stability, and higher flux values (Ağtaş et al., 2020).

One of the industries that uses large amounts of water is the textile industry. Due to the large amount of water usage (around 200 to 400 m^3/ton product), the amount of wastewater generated is quite high. Being able to treat textile wastewater effectively is important in order to reduce the amount of wastewater that is discharged into the environment. In addition to the volume of wastewater generated, there are many types

[4] This chapter is based on the paper "Meltem Ağtaş, Mehmet Dilaver and İsmail Koyuncu. Halloysite nanoclay doped ceramic membrane fabrication and evaluation of textile wastewater treatment performance. Process Safety and Environmental Protection, 2021.DOI: 10.1016/j.psep.2021.08.010"

of chemicals within it. Furthermore, the textile industry uses approximately 10,000 different dyes, 10-15% of which pass into wastewater. Dye removal from textile wastewater is difficult. Absorption, flocculation, ozonation, and biological decomposition, which are generally used in textile wastewater treatment, do not provide sufficient treatment efficiency for these dyes. Additionally, in terms of recycling and sustainability, these methods seem to be inadequate. Therefore, the use of membranes stands out. Also, membrane processes for textile wastewater treatment are recommended in the reference document of Best Available Techniques (BAT) (Barredo-Damas et al., 2012; Cinperi et al., 2019; Jiang et al., 2018a; Lin et al., 2019, 2016; Lu et al., 2020). There are many dye removal studies using ceramic membranes in literature.

Alventosa-deLara et al. (2012) used a ceramic tubular ultrafiltration membrane with 150 kDa molecular weight cut off to remove Reactive Black 5 dye from synthetic wastewater, containing concentrations of 50 and 500 mg/L. Over 70 percent removal efficiency was obtained for both concentrations (Alventosa-deLara et al., 2012). In a recent study, a commercial ceramic tight ultrafiltration membrane was used to treat synthetic dye solutions. The ceramic membrane's molecular weight cut off was reported to be 2410 Da. Seven different reactive dyes were tested. According to the obtained results, removal efficiencies for all reactive dyes were higher than 98% (Jiang et al., 2018b). In another study, a 1.5 nm pore sized ceramic membrane and commercial polymeric membranes were tested to remove dyes from a synthetic solution that contained salt as well. It was reported that the dye removal efficiency for different dyes varied between 57% and 97% for the ceramic membrane. It was also stated that in the separation mechanism for the ceramic membrane, charge effects and size exclusion were the main parameters whereas solution-diffusion was the key parameter for polymeric membranes (Chen et al., 2017). In addition to studies done with commercial membranes, ceramic membrane production has become a frequently studied topic in the literature recently.

Low-cost ceramic membrane fabrication has been getting special attention in order to expand its use in the industry. Natural clays also play an important role among the many raw materials used (Ouaddari et al., 2019). In Saja et al.'s (2020) work, bentonite clay was coated on a perlite support by using spin-coating; thermal treatment was then applied to the prepared membrane. For evaluating membrane performance, Rhodamine B and Direct Red 80 solutions were used. Obtained results showed that over 80% removal efficiency was achieved for both solutions (Saja et al., 2020). In an interesting study, natural red Moroccan clay and banana peels were used to fabricate membranes by using solid-state and spin-coating methods. After industrial wastewater filtration, high dye and turbidity removal were attained (Mouiya et al., 2019).

Halloysite nanoclay (HNT) is comprised of aluminium silicate clay nanoparticles with a tubular structure that can be found in excess in nature (Ormanci-Acar et al., 2018). HNT is highly hydrophilic due to the hydroxyl group on its surface. When HNT is compared to other nanomaterials, for example, carbon nanotubes (CNT) and TiO_2, HNT is found to be less expensive and more readily available anywhere in the world. Other advantages of HNT include high stability, easy of disposal and reuse (Ghanbari et al., 2016). Since the outer surface of HNT has SiO_2, it gives negative charge properties to HNT's surface. On the other hand, HNT's inner surface has Al_2O_3, which makes the inner surface positive. Thus, while a negatively charged substance is repelled by the outer surface of the HNT, it can accumulate on its inner surface (Zahidah et al., 2017). Reactive dyes are generally used in the textile industry. Reactive dyes, such as direct and acidic dyes, are also classified as anionic dyes (Abidi et al., 2019; Yagub et al., 2014). Therefore, it is thought that HNT can be used successfully in dye removal.

The main purpose of this study is the fabrication of HNT-doped ultrafiltration (UF) and tight- ultrafiltration ceramic membranes with the layer deposition method using relatively low temperatures, and the treatment of textile wastewaters with the produced membranes. To the best of our knowledge, fabrication of halloysite nanoclay doped ceramic membranes is quite rare.

5.2 Materials & Methods

5.2.1 Materials

Commercial disc ceramic membranes with two different pore sizes (0.2 and 0.45 μm) were supplied from Sterlitech Ceramic. Disc membranes are 2.5 mm thick and 47 mm in diameter with an effective filtration area of 13.1cm^2; they are classified as microfiltration membranes. The pH range of operation is between 0-14 and the membranes are resistant to high temperatures up to 350^{o}C and pressures up to 4 bars.

The active layer of the microfiltration membrane is TiO_2-ZrO_2. The halloysite nanoclay and fumed silica used in the membrane coating was obtained from Sigma-Aldrich company. Ethanol was supplied from J.T. Baker Company. Bovine serum albumin (BSA) was purchased from Sigma-Aldrich. Distilled water was used in experiments and solutions where water was required. Real textile wastewater was taken from Savcan Textile, Bursa, Turkey.

5.2.2 Characterization methods and instruments

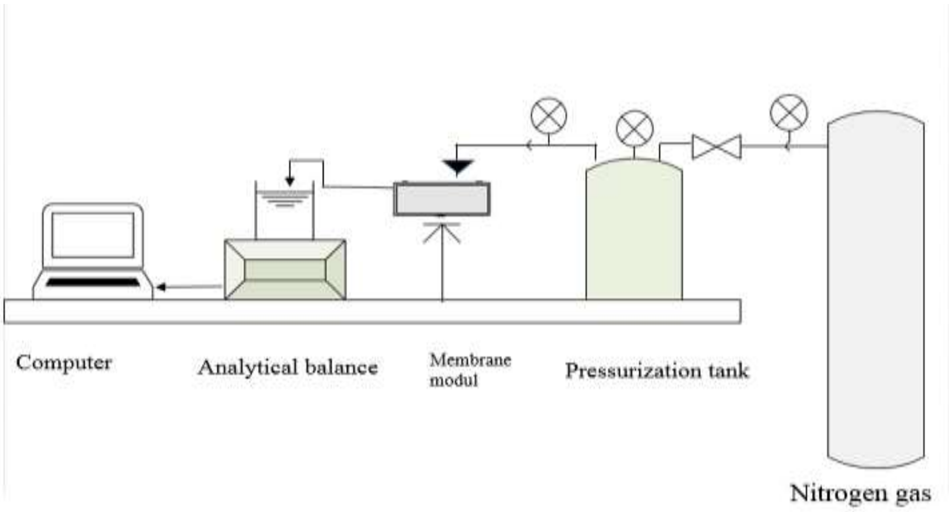
The particle size diameter (PSD) was measured by using a Malvern Mastersizer instrument (Malvern 2000, Worcestershire, UK) with the measurement range of 0.6-6000 μm. The contact angle of the membranes was measured on a KSV Attension Theta contact angle device using the sessile drop technique. The surface and cross-section images of the membranes were obtained using a scanning electron microscope (SEM) (Philips-XL30 SFEG) in ESEM mode after coating membranes with gold-palladium (Au-Pd). A Protherm 442T furnace was used in processes requiring high heat. A Termal brand oven was used for drying processes. Heidolph MR-Hei-Mix D was used as a magnetic stirrer and Everest Cleanex 401 was used for ultrasonication to make the coating solution more homogeneous. Total organic carbon (TOC) measurements were made with a Shimadzu V-CPN model TOC. After filtration, the permeate was collected for color removal performance determination by using UV spectroscopy (Hach Lange). The UV wavelength was chosen to be 525 nm for measuring the sample's color. Test kits (LCK 1014, HACH) were used in chemical oxygen demand (COD) tests.

5.2.3 Membrane coating procedure

For the coating method of membranes, it has been modified based on further studies carried out on the method in Liu et al.'s study (Liu et al., 2018).Since the rate of 0.5 wt% acheived the best result in the article, this rate was also tried in this study. First of all, the fumed silica was stirred in distilled water for 2 hours for complete dissolution at the weight percentage of 0.5%. After continuously stirring for 2 hours, halloysite nanoclay (0.5 wt%) was slowly added to the silica solution. Then, the solution obtained was kept in an ultrasonic bath for 1-5 minutes. The disc ceramic membranes (0.45 and 0.2 μm) were washed with ethanol and distilled water successively, and dried at 60 °C overnight. The dried membranes were then immersed into the silica- HNT containing solution for 2 minutes. After the second drying at 60 °C overnight, the above membranes were immersed in the same solution for 15 minutes with ultra-sonication for the silica and HNT to adhere homogeneously to the membrane surface. Finally, after the third drying overnight at 60 °C, the membranes remained for 30 minutes for calcination at 350 °C.

5.2.4 Membrane filtration and performance tests

Filtration tests were carried out using a dead-end cell filtration system, (Sterlitech, CELLULEDIS47V model) pressurized by nitrogen gas at room temperature. All filtration experiments were applied in dead-end mode and under constant pressure. Pressure was monitored with analog pressure gauges and a digital pressure gauge to maintain filtration under constant pressure. The pressure values were recorded manually. Pressure relief was applied after each set up was finished, using manual valves to control the release of pressure until the pressure gauge showed a zero value. Permeate was collected on a digital balance (AND Fx-5000i) and the cumulative mass of permeate was recorded to a personal computer communicating with the balance via a RsKey Ver.5.40 connection. The time interval between data acquisition can be programmed and the flux was calculated from the difference between two adjacent readings of mass with the specific time interval used for the filtration. We used one external reservoir for feed water. The feed reservoir was connected to a membrane cell to provide continuous feed flow. The feed reservoir was filled out with a feed solution of a certain amount of concentration and volume. Real textile wastewater tests were carried out at 3.5 bar pressure. For hot wastewater filtration studies, the wastewater used was heated up to 72 °C and put into the feed reservoir immediately. Representations of the ceramic membrane dead-end filtration system are given in Figure 5.1 (a) and Figure 5.1(b).



(a)

(b)

Figure 5.1 : Ceramic membrane dead-end filtration system (a) technical drawing (b) real image.

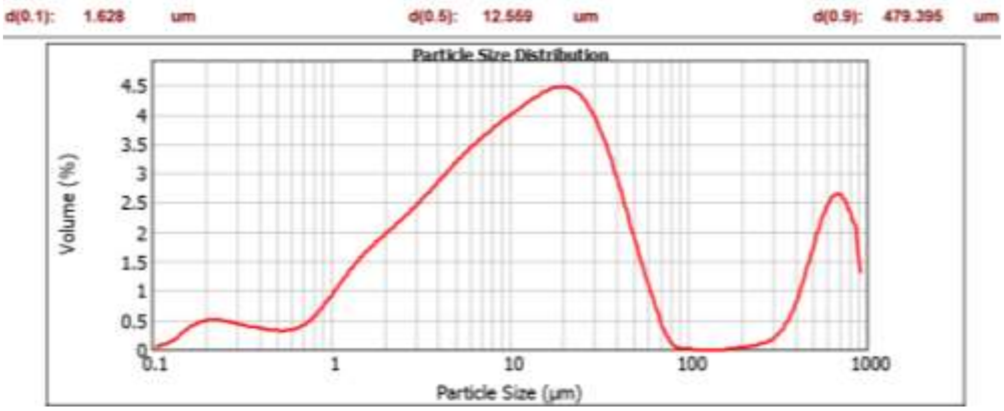
5.3 Results and Discussion

5.3.1 Tests performed before membrane coating

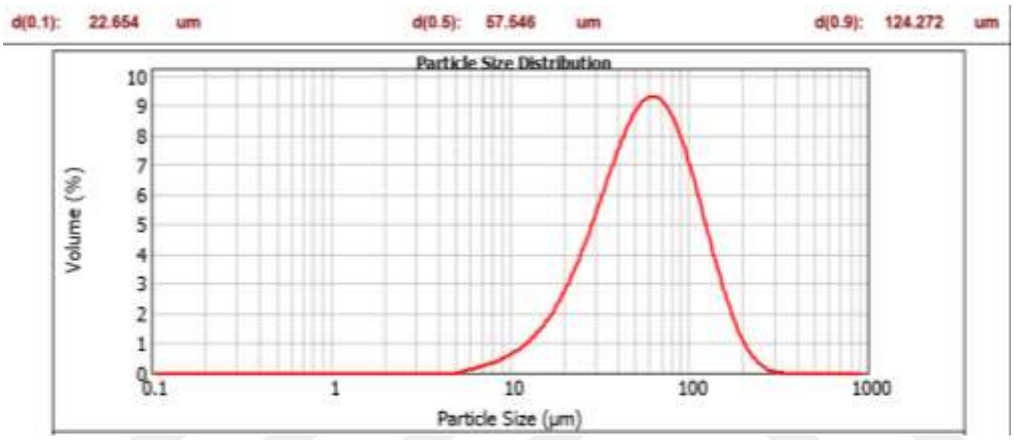
Before the commercial ceramic membranes were coated, some analyses were made of the membranes and the coating solution. First, the particle size distribution of the coating solution and the chemicals used within it were performed separately. Then, contact angle and SEM analyses were applied to the uncoated membranes.

In Figure 5.2, the particle size distributions of HNT, fumed silica and the coating solution are given. The particle size of HNT ranges between 1-100 µm, and the d (0.5) value, i.e. the median particle size, was found to be 12.5 µm. These values for fumed silica are approximately 10-100 μm and 57.5 μm, respectively. Although the particle size distribution of both materials varies in similar ranges, the sizes of the predominant particles are different. A particle size distribution test was applied to the coating solution after the previously mentioned mixing and ultrasonication processes were conducted. Looking at the results obtained, it is seen that the d(0.5) value is 2.4 μm. As it will be understood, the processes applied to the coating solution resulted in a reduction in particle sizes.

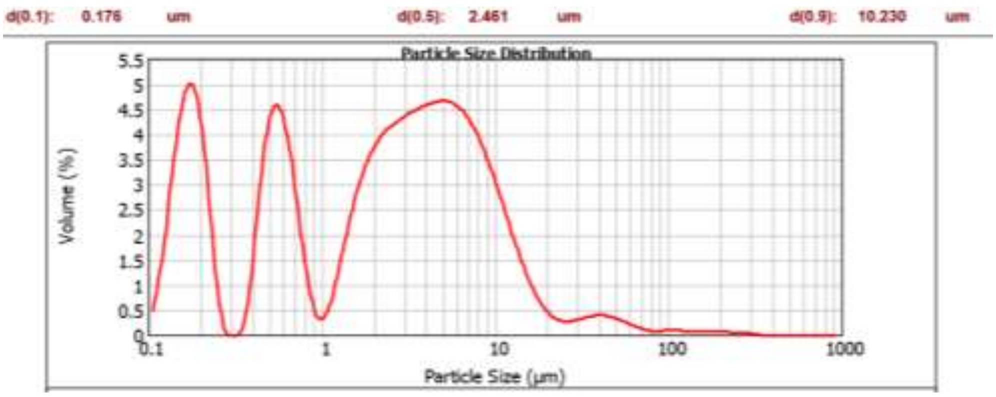
In order to obtain a uniformly distributed coating on the support layer, solutions containing small particles and a narrow particle size distribution are required. Since the spaces between large particles will be large, a smooth coating will not be possible on surfaces covered with solutions with large particle sizes (Monash et al., 2010). It is thought that the coating made in this study will be successful due to the small particle sizes of the coating solution obtained in this study.



a)



b)



c)

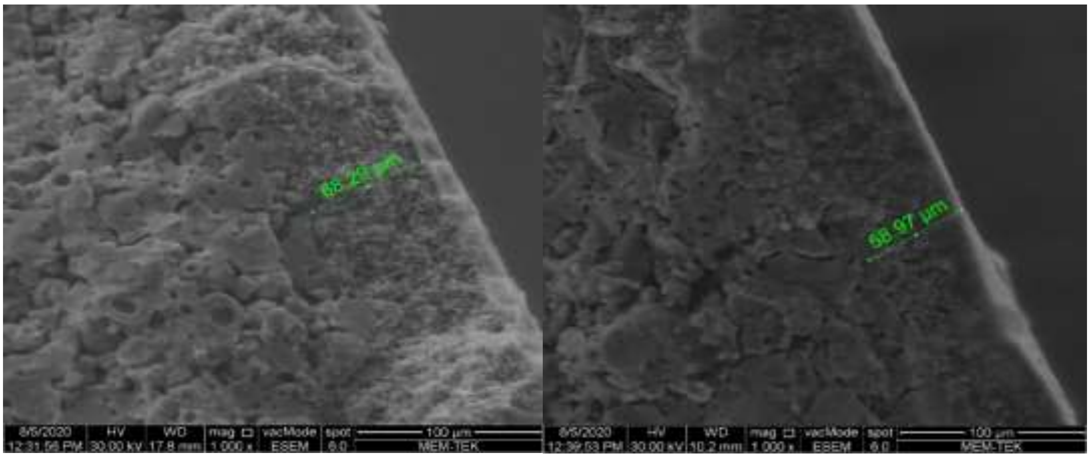
Figure 5.2 : Particle size distribution of HNT(a), fumed silica(b) and coating solution(c).

In Figure 5.3, surface and cross-section ESEM images of uncoated membranes were given. Looking at the cross-sectional views, it can be seen that the membrane structure has an increasingly inhomogeneous structure below the active layer (surface). It can also be understood from the surface measurements that the 0.2 μm membrane has a thicker active surface. This is as expected, as the 0.2 μm membrane has a smaller pore size. For the surface images, it is understood that the 0.2 μm membrane has a smoother surface structure compared to the 0.45 μm membrane. In addition, since the pore size of the 0.45 μm membrane is larger, the pore structure can be seen more clearly.

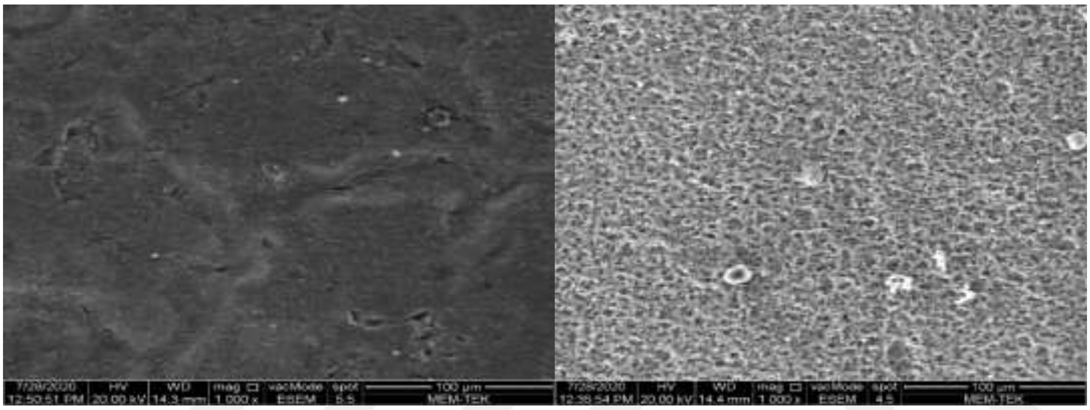
In order to observe how the hydrophilicity changes after coating the surface of the ceramic membranes, the surface contact angles of the uncoated membranes were also measured and the results are given in Table 5.1. A total of 4 measurements were made for each membrane at different points on the membrane surface. As it can be seen from the table, the obtained results for both membranes are similar and quite low.

Table 5.1 : Contact angle values of uncoated membranes.

0.45 μm (3 frame)				
	1	**2**	**3**	**4**
Mean contact angle (°)	34.2	38.63	26.08	27.68
Std dev.	NAN	NAN	0	0
0.2 μm (10 frame)				
	1	**2**	**3**	**4**
Mean contact angle (°)	37.92	45.72	47.96	48.2
Std dev.	17.35	21.26	19.81	8.52



a) c)



b) d)

Figure 5.3 : Cross-section and surface ESEM images of uncoated membranes, a and b) 0.2 µm c and d) 0.45µm.

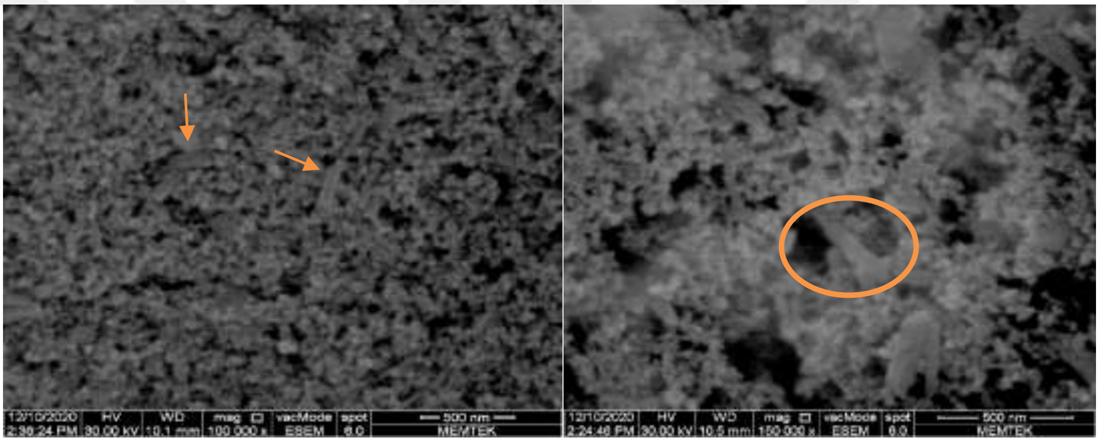
5.3.2 Tests performed after membrane coating

Some tests have been applied to the coated commercial membranes to determine the membrane performance and properties. These include contact angle analysis, SEM analysis, pure water flux, bovine serum albumin (BSA) removal, and finally, real wastewater trials on the selected membrane.

Structural characterization of coated membranes

In order to understand the structure of the coated membranes, ESEM images were taken and the contact angle was measured. In Figure 5.4, surface ESEM images were shown. Since fumed silica and HNT are in the coating solution, these materials are expected to be seen on the membrane surface. Tubular structures stand out in the spongy structure formed on the surface. These tubular structures are shown in Figure 5.4(a) with the help of green arrows, and these structures are thought to be HNTs. It is also stated in the literature(Keskin et al., 2021; Ormanci-Acar et al., 2018) that HNT has a tubular shape. These structures can be seen more clearly in Figure 5.4(b). Based on the ESEM images, it can be understood that the coating solution is integrated into the membrane surface using the deposition method.

An attempt to determine the contact angle was made on the coated membranes, but the device could not take the appropriate measurements because the membranes are highly hydrophilic. Contact angle analysis was attempted more than once with the produced membranes. When no results could be obtained from the 3 frame method, the 10 frame method was also tried. Only one result could be obtained, which is 7.80. Considering that the membranes had very low contact angle values before coating, it is understood that fumed silica and HNT further reduce this value.



a) b)

Figure 5.4 : ESEM images of coated membranes (a) 100k zoom (b) 150k zoom.

Pure water flux

First, the pure water fluxes of the membranes to be used for coating were measured under three different pressures (1 bar, 1.5 bar and 2 bar). Then, after each coating procedure, pure water flux was measured for each layer added to the membrane. The pure water flux results of the membranes are given in Figure 5.5 and Figure 5.6. Among the commercial membranes used, the desire was to obtain a UF membrane, by coating a 0.45 μm membrane which has a larger pore size, and a tight UF membrane, by coating a membrane with a pore size of 0.2 μm, and studies were conducted to achieve this goal.

As can be seen in Figure 5.5, the 0.2 μm pore size membrane was coated 6 times. Although the flux reductions are quite significant until 3 coatings, there were also decreases in the flux after other coating processes. These decreases in flux can be more pronounced as pressure increases. After 5 coatings, the flux decreased approximately 12 times compared to the uncoated version of the membrane under pressures of 2 bars. As a result of the 6th coating, since there was no significant decrease in flux compared to the 5th coating, the coating process was completed. Looking at the flux results under 1 bar pressure, it can be seen that the pure water flux value of the uncoated membrane is approximately 400 L/(m^2.h) (LMH), and the flux value after 6 coatings is approximately 23 LMH. Based on this result, it can be understood that the membrane coating is effective.

In a study conducted in 2016, a ZrO_2 nanofiltration (NF) membrane was produced and the effects of glycerol concentration on the produced membrane were examined. Considering the results obtained, the permeability value of the membrane, which was produced and defined as an NF membrane, was found to be 13 LMH for 1 bar pressure (Da et al., 2016). When this result is compared with our result, it is seen that the pure water flux value for 1 bar of the coated 0.2 μm membrane is higher. Therefore, although the membrane obtained in this study is not exactly at an NF level, it is thought that it can be described as a tight UF membrane. In addition, some studies in the literature and the results obtained in this study are compared in Table 5.2. When this table is examined, it can be understood that our coated 0.2 μm membrane is between UF-NF size scales.

Table 5.2 : Comparison with studies in the literature.

Membrane material	Membrane type	Pure water permeability (LMH.bar)	Reference
TiO_2–ZrO_2	NF	3.7–11.4	(Sada et al., 2019)
TiO_2	NF- tubular	8	(Cai et al., 2015)
Al_2O_3-ZrO_2	NF-disc	0.2-0.3	(Qi et al., 2012)
Natural pozzolan	MF- tubular	1444.7	(Achiou et al., 2017)
Zeolite	UF- tubular	80	(Aloulou et al., 2018)
Natural clay	UF-disc	880-2219	(Ben Ali et al., 2018)
ZrO_2-TiO_2-HNT	UF-disc	105.2	This study
ZrO_2-TiO_2-HNT	Tight UF-disc	23.13	This study

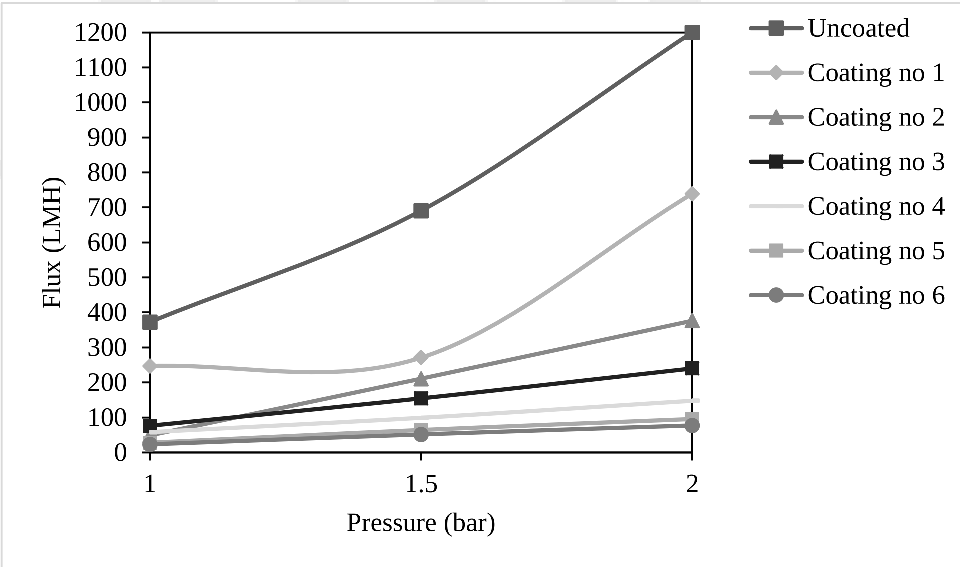


Figure 5.5 : Pure water flux of 0.2 μm membrane for each layer.

As can be seen in Figure 5.6, the 0.45 μm pore size membrane was coated 4 times. Since the flux of the uncoated membrane is very high, the flux values can only be collected at 1 bar for the uncoated membrane. After 4 coatings, the flux decreased approximately 19 times compared to the uncoated version of the membrane under the same 1 bar of pressure. Since there was no significant difference between the third and fourth coating, the coating process was finished after the fourth coating and the UF membrane was obtained. It can be understood that the membrane obtained is at UF level by looking at the literature results in Table 5.2.

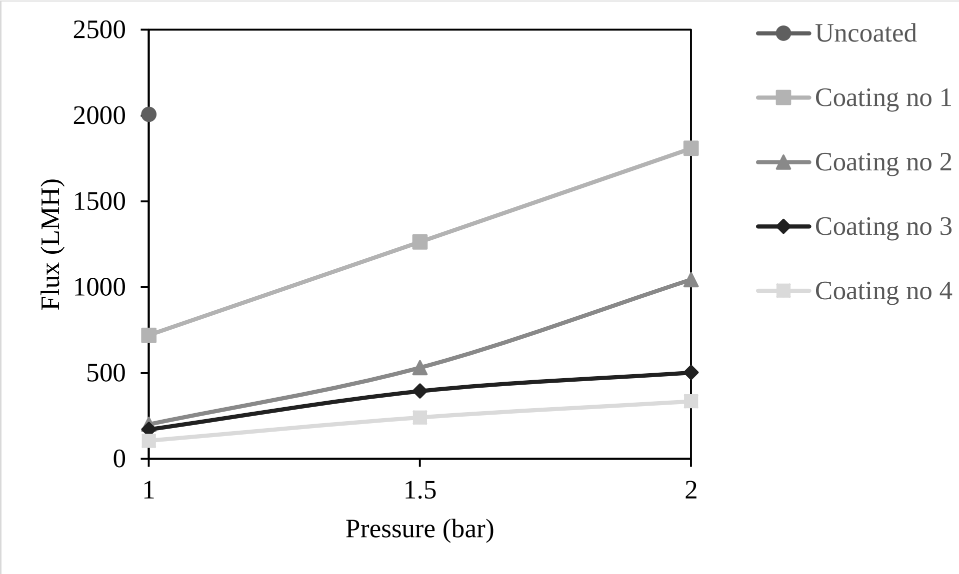


Figure 5.6 : Pure water flux of 0.45 µm membrane for each layer.

Bovine serum albumin (BSA) removal efficiency

After the pure water flux of the fabricated membranes were tested, a BSA solution was used as a model solution to examine the effect of the coating on the membrane surface on pollutant removal. Additionally, filtration experiments were carried out. BSA flux and removal tests were repeated twice for each membrane, and removal efficiency was calculated by measuring the TOC values of the input and output samples.

In Figure 5.7, average BSA flux and BSA removal efficiency values were given. The fluxes of the 0.45 µm membrane, which was coated 4 times and brought to the UF level, were respectively 64 and 96 LMH for the 2 tests, and the best BSA removal efficiency value was approximately 32%. For the 0.2 µm membrane, which was coated 6 times and brought to the tight UF level, the fluxes were found to be 11.2 to 16.2 LMH, and its removal efficiency was calculated as almost 100% for both trials. From the difference in flux and removal efficiency between the two coated membranes, it can be clearly seen that the obtained membranes have different pore diameters and their active surfaces have different levels of separation.

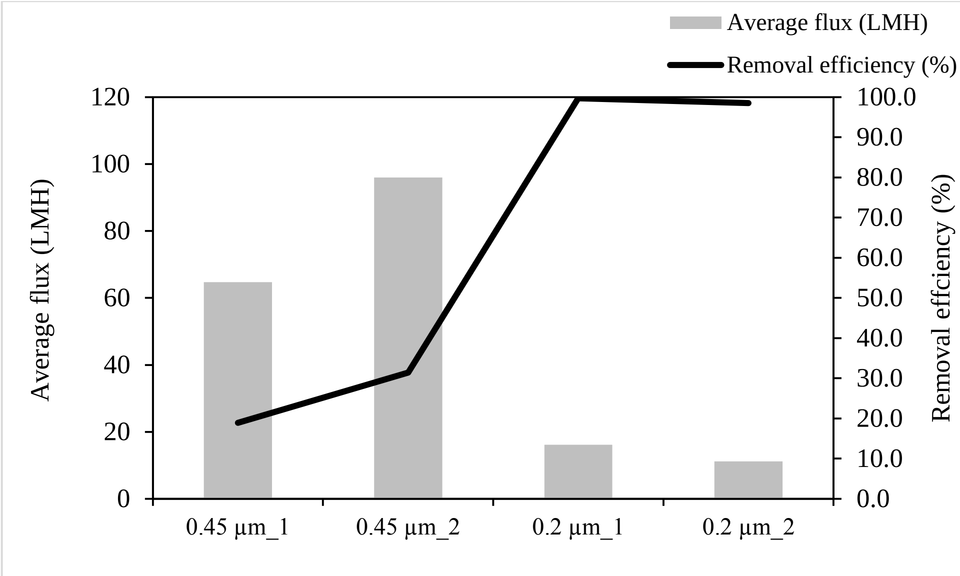


Figure 5.7 : Average BSA flux and removal efficiencies of fabricated membranes.

In a study conducted for low-cost ceramic membrane production, the membrane in question was produced by coating zeolite more than once on the support layer, which was produced using clay. It has been reported that the average pore diameter of the membranes produced ranged from 76 to 215 nm. It was stated that the best BSA removal efficiency value obtained was realized at pH 2.5 and was 80%. It was also underlined that as the pH increases, the BSA removal efficiency also decreases (Vasanth et al., 2017). In a study comparing the natural organic matter removal performances of ceramic UF and polymeric UF membranes, filtration trials were performed for both membranes with solutions containing humic acid, BSA, and alginate. According to the results, the BSA removal efficiency of the ceramic UF membrane was found to be about 84%, and for the polymeric UF membrane, this value was found to be about 77%. Although the removal efficiencies for both membranes are similar, it has been stated that the performance of the ceramic membrane after backwashing is better (Alresheedi et al., 2019). When these results are compared with the results of our study, it is thought that the literature corroborates that 0.45 µm membrane is at the loose UF level, with the coating, and the 0.2 µm membrane is at the tight UF level.

Studies with real wastewater

Treatment studies of 3 different real wastewater samples taken from a textile company located in the Bursa Organized Industrial Zone were carried out with the selected membrane, that is. the coated 0.2 µm membrane, at room temperature. These wastewaters were taken from the printing washing baths' hot discharge (S1), mixed hot wastewater sampling points (S2), and disperse printing washing baths (S3) of the factory. These wastewaters will be named S1, S2, and S3 respectively for the remainder of the text. Firstly, the flux values of all wastewater were obtained, then, the removal efficiencies of the input and output samples were calculated by measuring the COD, TOC and color values. Two trials were conducted for each of the wastewaters to see if the results were consistent.

Figure 5.8 represents flux values obtained in real wastewater trials. The numbers 1 and 2 indicated after the underscore in the sample names indicate the number of trials made. As can be seen from the figure, the flux values vary between approximately 3-4.5 LMH. Although the types of wastewaters tested are different, there is no obvious difference in their flux values.

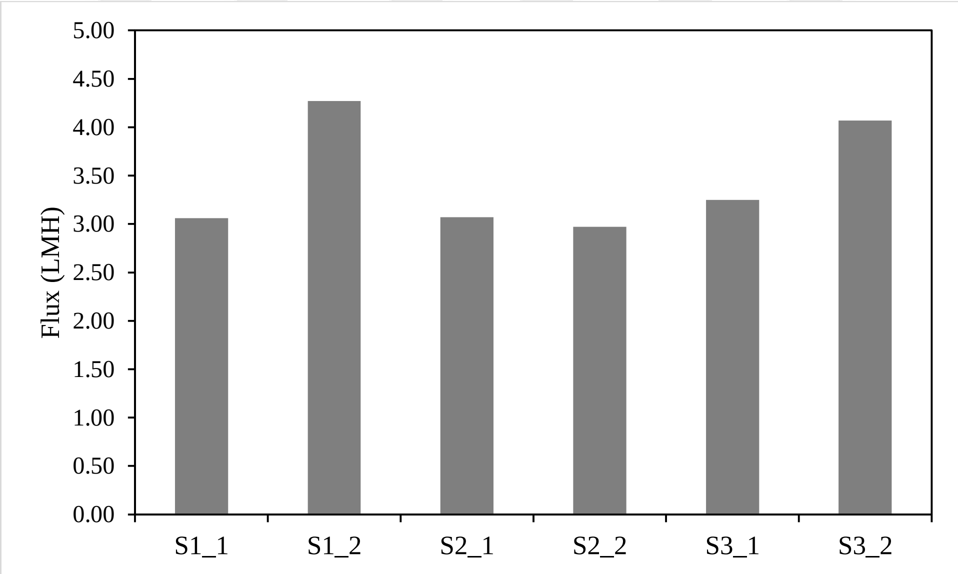


Figure 5.8 : Flux values obtained in real wastewater trials.

In a recent study, removal efficiency experiments of various dyes and salts were performed using a commercial tight ceramic UF membrane. In experiments with different dye concentrations, flux values were monitored under different pressures. In light of the data obtained, the flux value at 3.5 bar pressure was measured to be approximately 20 LMH in the filtration test using RB19 dye. The cross-flow system was used in this experiment, and the dye concentration in the synthetic solution used was reported as 10 g/L (Jiang et al., 2018b). When this study is compared with our study, our flux values seem a little low; however. it is thought that one of the reasons for this can be attributed to the differences in filtration systems used. It is known that there is a certain flux difference between dead-end and cross-flow systems and that the flux is higher in cross-flow systems. It is also considered normal for the flux to be higher, as unforeseen impurities are also present in real wastewater, whereas the synthetic solution only contains dye.

Quaddari et. al (2019) produced ceramic UF membranes using natural Moroccan clay in their study. Filtration tests were carried out with the membranes produced, using 50 ppm Direct Red 80 dye at 3 bar pressure. As a result of the filtration tests, the flux values were found around 12 LMH (Ouaddari et al., 2019). As can be understood from the literature, membrane fluxes used at the UF membrane level may differ from study to study.

Figure 5.9 illustrates the COD removal efficiency values obtained in real wastewater trials. COD removal efficiency values vary between 5-55%. Although removal efficiencies in sample 1 and sample 2 have similar values, removal efficiencies in sample 3 are quite low. Considering these results, it is thought that the impurities causing COD in sample 1 and sample 2 are similar in nature. In addition, this difference in removal efficiency can be attributed to the fact that the COD in samples 1 and 2 may be composed of particulate matter, while sample 3 may contain more dissolved COD.

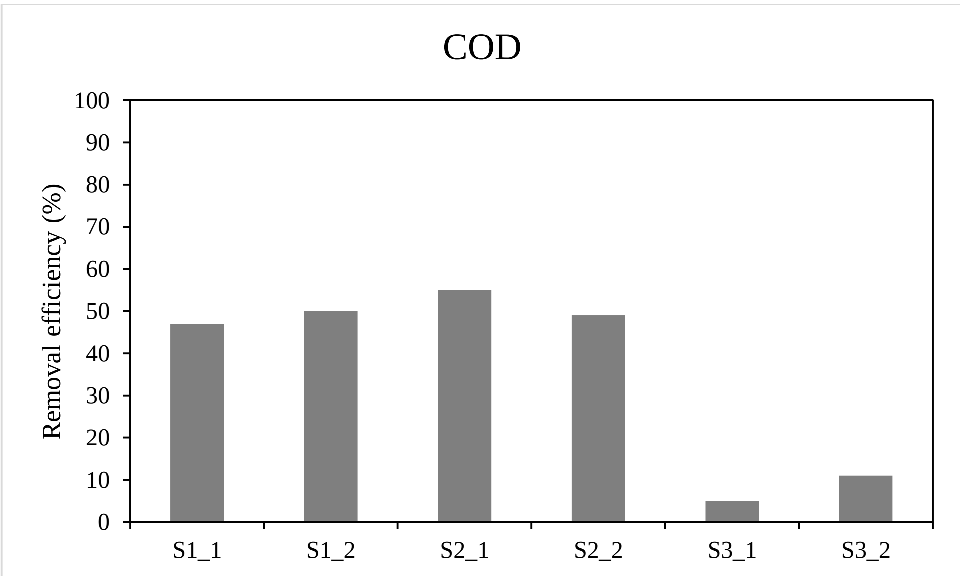


Figure 5.9 : COD removal efficiency values obtained in real wastewater trials.

In a study where a ceramic hollow fiber membrane with hydroxyapatite was produced, membrane production was made by applying different sintering temperatures. In the study, in which the membrane pore size decreased as the sintering temperature increased, the COD removal was found to be 15.1% at 1000°C, 68.9% at 1100 °C sintering temperature and 80.1% at 1200 °C for textile wastewater. Pore size was reported as 0.013 μm on the membrane where 80.1% COD yield was obtained (Hubadillah et al., 2020). In Voigt et. al's (2001) study, NF membranes with an average pore size of 0.9 nm were used in an attempt to treat 30 different textile wastewaters in a pilot system. When the data obtained is examined, it can be observed that COD removal varies between 45-80%, depending on the type of wastewater (Voigt et al., 2001). Different ranges of COD removal were found in different studies. However, in this study, considering that the membrane is tight UF, it is thought that significant COD removal was achieved.

In Figure 5.10, TOC removal efficiency values obtained in real wastewater trials are given. Although TOC removal efficiency values vary between 3-43%, it has a similar pattern with COD removal efficiency values. With TOC removal efficiency, as in with COD, the treatment efficiency of the first two samples is much higher than the last sample. Considering that the relation between COD and TOC is directly proportional to each other, this result is expected and logical. Although the COD and TOC removals for sample 3 were low, the best color removal was seen in this sample, as is shown in Figure 5.11.

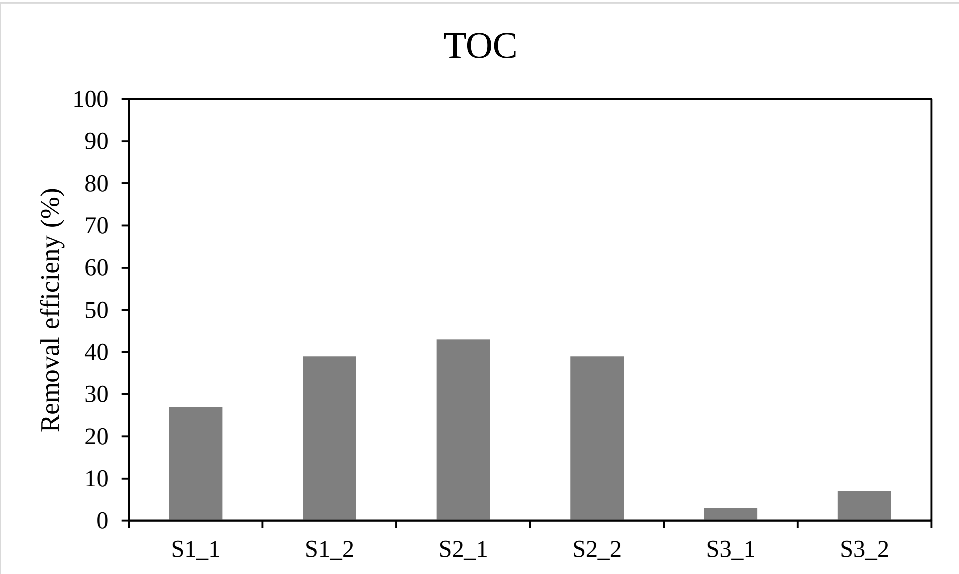


Figure 5.10 : TOC removal efficiency values obtained in real wastewater trials.

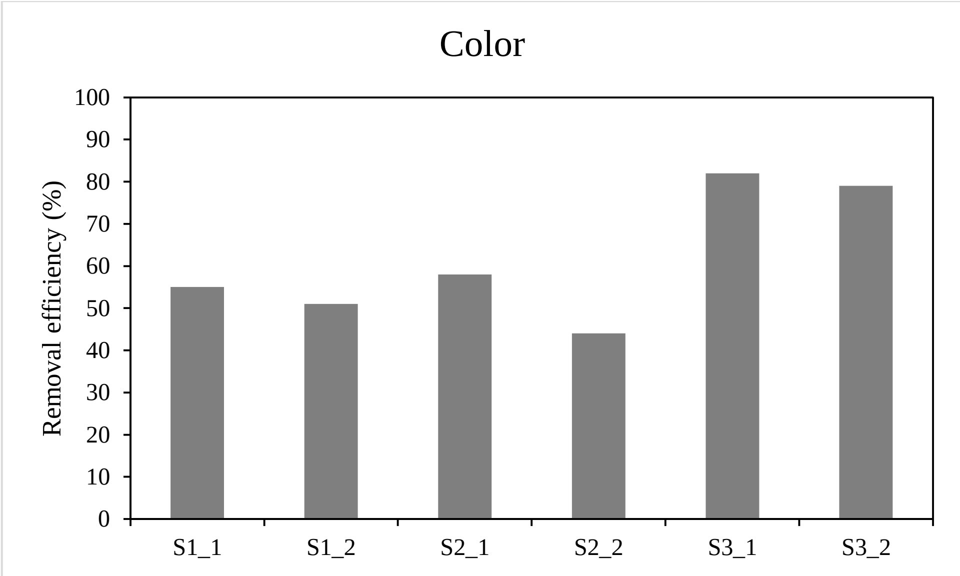


Figure 5.11 : Color removal efficiency values obtained in real wastewater trials.

The same real wastewater samples used in this study were also used in the study of Dilaver et. al. Within the scope of the study, real textile wastewater was subjected to treatment tests using commercial ceramic membranes with 4 different molecular weight cut off (MWCO) values. The obtained COD, TOC, and color removal efficiency results are in line with the results in this study. Dilaver et. al (2018) reported that although COD and TOC removal was low, the high color removal was due to the content of Sample 3. This is attributed to the fact that some small particles found in wastewater, which differ from dyes, cannot be retained by the membrane and that, instead of the types of dyes in the wastewater is what is absorbed onto the membrane surface.(Dilaver et al., 2018). In addition, disperse dyes do not dissolve in water, have low zeta potential distribution and high colloidal structure, which may cause low COD and TOC yields for wastewater taken from disperse baths (Kim et al., 2004). It is thought that the high color, low COD and TOC removal efficiencies obtained for the 3rd sample, which is the disperse printing washing baths wastewater, can be explained in this way.

Finally, since textile wastewater is generally hot, the first sample was heated to about 72 °C and the filtration test was repeated. In the tests performed with hot water, the flux value of the membrane was approximately 10 LMH, and COD and color removal efficiencies were recorded as 40.6% and 46.5%, respectively. Based on these results, it can be said that the flux value has increased approximately 3 times, but there is no significant decrease in removal efficiency. Consequently, it can be seen that the viscosity decreases and the flux increases with the increase in wastewater temperature. However, the temperature increase has no effect on the active surface of the produced membrane and does not affect the removal efficiency performance of the membrane or HNT.

5.4 Conclusion and Further Recommendations

HNT-doped UF and tight-UF ceramic membranes were fabricated using the layer deposition method with relatively low temperature, and analyzed systematically. For the production of the UF membrane, 4 layers with HNT and 6 layers for tight UF are coated on an active layer of a commercial ceramic membrane. Pure water flux was measured for each layer, and the layer deposition process was completed when there was no significant difference between the last two layers. Looking at the pure water flux values, it can be seen that the decrease in flux in both membranes follows a certain trend after each coating. From this, it can be understood that even if membranes with different pore diameters are coated, the coating efficiency is similar, and similar results can be obtained with reproduction. In the BSA removal efficiency test, performed to see the organic matter retention of the membranes obtained, approximately 30% removal was obtained for the UF membrane, and 100% for the tight UF membrane. Since the main purpose of the study was to produce ceramic membranes at a low cost and determine the use of these membranes in textile wastewater treatment, treatability studies were carried out using 3 different real textile wastewater with the tight UF membrane obtained, and noteworthy results were acheived in COD, TOC and color removal. Finally, in the hot water test, it was observed that the permeate flux increased approximately 3 times, but there was no significant decrease in the treatment efficiency. Within the scope of this study, low-cost ceramic membrane production has been successfully carried out and the treatability of textile wastewater has been tested. In light of the results obtained, it was seen that the membranes produced can be used in hot textile wastewater treatment.

In future studies, the aim would be to determine the effects of operating in a cross-flow system with the optimized HNT doped membrane and to study the clogging mechanism of the membrane and the cleaning procedure. It is also valuable to monitor changes in membrane performance with long-term operation.

6. CONCLUSIONS AND RECOMMENDATIONS

Treatment, recovery, and reuse of wastewater are of great importance in order to protect and ensure the sustainability of dwindling water resources. Particularly in industries that use large amounts of water, the adoption of this approach is certain to contribute significantly to the conservation of our resources. Within the scope of this thesis, studies have been carried out for the treatment, recovery, and reuse of wastewater from the textile industry, which is one of the leading industries that consume high amounts of water. In addition to water recovery, the recovery of highly valuable and expensive chemicals has also been studied. In order to achieve all these aims, ceramic membranes were used in the thesis studies. The results obtained as a result of this thesis can be listed as follows.

- A pilot scale UF/NF ceramic system was used for real textile wastewater treatment, reuse and recovery under real conditions.
- Hot water recovery, which is one of the main objectives of this thesis, has been achieved by pilot system operation. In case the obtained hot water is reused in the system, the financial gain to be obtained has been evaluated.
- In terms of economic evaluation, when annual 258420 m^3 permeate was heated from 65 °C to 95 °C, the annual electricity saving is expected to be 1210977 USD $ together with 129210 USD $ annual water saving. Thus, the total annual saving amount is 1340187 USD $. Accordingly, a return of investment is expected in less than 2 years.
- 2 out of 3 fabric dyeing tests conducted to evaluate the reuse of treated wastewater in processes were successful.
- In the studies carried out for caustic recovery, which is another aim of this thesis, at least 50% of sodium was recovered when the results obtained were examined.

- In ceramic membrane production studies, HNT-doped UF and tight-UF ceramic membranes were successfully fabricated using the layer deposition method with relatively low temperature.
- Treatability studies were carried out using 3 different real textile wastewater with the tight UF membrane obtained, and noteworthy results were acheived in COD, TOC and color removal. In addition, in the hot water test, it was observed that the permeate flux increased approximately 3 times, but there was no significant decrease in the treatment efficiency.

To summarize all the work done, hot water and chemical recovery have been achieved with ceramic membranes, and it has been proven that these processes have a serious potential for both the protection of water resources and the protection of the environment by preventing the discharge of wastes to the environment. In addition, it has been shown that HNT added membranes, produced in order to reduce the cost of these studies with commercial membranes, are also suitable for real textile wastewater treatment and recovery.

The following recommendations are made for future work.

- It can be recommended that to repeat these pilot-scale studies at a real level and to use the water obtained in the processes in the facility.
- Trials with other water and heat consuming industries and a more detailed economic evaluation can be recommended.
- The clogging trend of the produced HNT-doped membranes can be examined. In addition, tubular fabrication and testing of the optimized membrane can be suggested.

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PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

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