

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**HARDNESS REMOVAL FROM WATER THROUGH ZEIN MEMBRANES
OBTAINED BY ELECTROSPINNING**



M.Sc. THESIS

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Department of Food Engineering

Food Engineering Programme

JUNE 2019

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**SUYUN SERTLİĞİNİN ELEKTROEĞİRME YÖNTEMİ İLE ELDE EDİLEN
ZEİN MEMBRANINDAN GEÇİRİLEREK UZAKLAŞTIRILMASI**

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To my family,



FOREWORD

I would like to express my sincere gratitude to my thesis advisor, Assoc. Prof. Dr. Filiz ALTAY for her support to my master thesis research and study.

I would like to thanks to my family for their support and patience during this time period.

May 2019

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ABBREVIATIONS

MF	: Microfiltration
UF	: Ultrafiltration
NF	: Nanofiltration
RO	: Reverse Osmosis
TFNC	: Thin-Film Nanofibrous Composite
FTIR	: Fourier Transform Infrared Spectroscopy
NMR	: Nuclear Magnetic Resonance
PAN	: Polyacrylonitrile
PSU	: Polysulfone
PES	: Polyethersulfone
PVDF	: Polyvinylidene fluoride
CA	: Cellulose acetate
PA	: Polyamide
ENMs	: Electrospun nanofibrous membranes
CDI	: Capacitive deionization
TDS	: Total dissolved solid
PVA	: Polyvinyl alcohol
SD	: Standart deviation
CaCl₂.2H₂O	: Calcium chloride dihydrate
MgCl₂	: Magnesium chloride



SYMBOLS

mS	: Millisiemens
m	: Meter
kV	: Kilovolt
nm³	: Normal cubic meter
kDa	: Atomic mass unit
cm	: Centimeter
cm⁻¹	: Wavenumber
°C	: Centigrade
mL	: Mililiter
h	: Hour
A	: Phenomenological coefficient
dX/dx	: Gradient of X
J_m	: Mass flux
J_v	: Volume flux
J_h	: Heat flux
J_n	: Momentum flux
J_i	: Electrical flux
D	: Diffusion coefficient
Dc/Dx	: Concentration gradient
R	: Rejection ratio
C_p	: Final permeate concentration
C_f	: Initial feed concentration



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HARDNESS REMOVAL FROM WATER THROUGH ZEIN MEMBRANES BY ELECTROSPINNING METHOD

SUMMARY

In this study, hardness removal from water was investigated by filtration method by using zein membrane. It is thought that there may be very large water shortages in the future of our world. Almost all of the water (97%) on earth is salted water in the oceans. Therefore, alternative methods should be developed for water filtration. Waters contain organic or inorganic materials that can soluble and insoluble in water. Mg^{2+} and Ca^{2+} ions are the most common minerals that cause water hardness. Ion exchange, lime-soda softening, adsorption, electrocoagulation, reverse osmosis and nanofiltration methods are the most known methods to remove calcium and magnesium ions from water. The traditional methods for the hardness removal are chemical treatments and it can cause water pollution. So, filtration methods with electrospun membrane can be investigate to develop new techniques or improve current methods. According to studies, filtration method was carried on nanobrane obtained from synthetic polymers or cellulose to remove hardness from water. However, a filtration system was not found in the membrane obtained using zein protein, a natural biopolymer. Moreover, it has high hydrophobic properties and mechanical strength. Therefore, zein protein is preferred to remove hardness from water in this study.

Firstly, zein membrane was obtained with electrospinning method. There are a few published researches about zein nanofiber production by electrospinning. Process conditions were defined to obtain zein nanofiber. Then, filtration process with different salt concentrations was performed with zein membranes and results of electrical conductivity and zeta potential were recorded. There are many studies about hardness removal from water with different method. However, there are no studies about hardness removal from water by filtration method using zein membrane that obtained by electrospinning method. Therefore, after zein membrane is obtained, a study has been carried out to see if this membrane holds the salt ions dissolved in water. For this aim, water solutions were prepared with different salt concentrations. Calcium and magnesium cations are the most common materials that shows the degree of water hardness. Therefore, magnesium chloride and calcium chloride dihydrate were used to obtain salty water at different ratios (1%, 5%, 10% and 15% (v/w)) separately. Pure water (electrical conductivity: 0.083 mS/cm) was used to prepare salty solutions. The electrical conductivity and zeta potential of zein membrane was measure before and after filtration and compared with each other statistically to investigate the membrane hold salt ions. Also, zeta potential and electrical conductivity of water was measured before and after filtration of samples to determine whether the amount of salt in the water content decreases or not. To investigate the membrane performance, rejection rate was calculated. Moreover, scanning electron microscope (SEM), fourier transform infrared spectroscopy (FTIR) analysis were carried out for the characterization of zein membrane.

The results of this work showed that the zein membrane obtained by electrospinning method may be used for hardness removal from salty water. However, optimization studies should be carrying on for further investigation.





SUYUN SERTLİĞİNİN ELEKTROEĞİRME YÖNTEMİ İLE ELDE EDİLEN ZEİN MEMBRANINDAN GEÇİRİLEREK UZAKLAŞTIRILMASI

ÖZET

Bu çalışmada, elektroegirme yöntemi ile elde edilen zein membranından sudaki sertliği gidermek amacıyla filtrasyon prosesi gerçekleştirilmiştir. Yapılan araştırmalara göre, dünyada ileride çok fazla su kıtlığı yaşanacağına ve su kaynaklarının giderek azaldığına dair bulgular bulunmaktadır. Yeryüzünde yer alan suyun %97'si tuzlu sulardan oluşmaktadır ve bu tuzlu sular da okyanuslarda bulunmaktadır. İleride yaşanacak su kıtlığı düşünüldüğünde, mevcut su arıtma sistemlerinde iyileştirmeler yapılması ya da yeni alternatif metotların geliştirilmesi gerekmektedir. Yeryüzündeki suların %97 si tuzlu sulardan oluştuğu için suyun kullanılabilirliğini sağlamak adına özellikle sulardaki tuzların azaltılmasına yani sudaki sertliğin giderilmesine yönelik çalışmalar yapılması gerektiği düşünülmektedir. Suda çözünmüş olan organik ve inorganik maddelerden özellikle magnezyum ve kalsiyum katyonları su sertliğinin belirlenmesinde önemli bir faktördür. Yapılan araştırmalara göre su sertliğinin giderilmesinde en yaygın kullanılan metotlar; iyon değişimi, kireç soda yumuşatma, adsorpsiyon, elektrokoagülasyon, ters osmoz ve nanofiltrasyondur. İyon değişimi ile su sertliğinin giderilmesi metodunda, sentetik polimerler (HCl ve NaOH) atık su olarak toksik suyun üretimine neden olmaktadır. Bu nedenle endüstri için uygun bir metot değildir. Kireç soda ile yumuşatma metodu ise, oldukça eski bir metot olup prosesin gerçekleşmesi çok fazla zaman gerektirdiğinden dezavantaja sahiptir. Elektrokoagülasyon metodunda ise sudaki sertlik iyonları çöktürülerek emilimi sağlanır, ancak proste sentetik polimer kullanımını gerektirir. Diğer metotlar ise ters osmoz ve nenofiltrasyondur. Bu metotlarda ise çok fazla basınç kullanımı gerektirdiğinden maliyetli metotlardır. Yapılan çalışmalara göre sentetik polimerler ya da selüloz kullanılarak elde edilen nanoyüzeylerden su sertliğini gidermek amacıyla filtrasyon işlemi gerçekleştirilmiştir. Ancak, doğal bir biyopolimer olan zein proteini kullanılarak elde edilen membranda gerçekleştirilen bir filtrasyon sistemi bulunamamıştır. Bu nedenle yüksek hidrofobik özelliği sahip olan zein proteini filtrasyon için tercih edilmiştir.

Membran yüzeyi elde etmek için elektroegirme yöntemi kullanılmıştır. Zein nanolifi eldesine ilişkin yapılan çalışmalar sınırlı miktardadır. Zein proteini %80 (v/v) etanolde 30% (w/v) oranında oda sıcaklığında (25 °C) 30 dk karıştırılarak elektroegirme besleme çözeltisi elde edilmiştir. Çalışmada filtrasyon için farklı kalınlıklara sahip olan yüzeyler elde edilmiştir ve farklı kalınlıklarda filtrasyon işlemi gerçekleştirilerek yüzeyin suda yer alan kalsiyum ve magnezyum iyonlarını tutup tutmadığı incelenmiştir. Filtre edilecek olan su laboratuvar ortamında hazırlanmıştır. Sertlik vermesi amacıyla saf suya (elektriksel iletkenlik: 0,083 mS/cm) farklı oranlarda kalsiyum katyonu içeren kalsiyum klorür dihidrat ile magnezyum katyonu içeren magnezyum klorür eklenmiştir. Saf suya eklenen tuzların oranı sırasıyla %1, %5, %10 ve %15 (w/v) (g/ml). Kalsiyum ve magnezyum tuzlarının etkisini ayrı görebilmek adına çözeltiler ayrı ayrı hazırlanmıştır.

Gerçekleştirilen çalışmanın sudaki sertlik gideriminde etkili olup olmadığını anlamak amacıyla suda filtrasyon öncesi ve sonrası zeta potansiyel ve elektriksel iletkenlik ölçümleri gerçekleştirilmiştir.

Filtrasyon öncesi ve sonrası suda gerçekleştirilen ölçümlerde alınan sonuçlara göre; %1 Ca^{2+} , %1 Mg^{2+} veya %5 Ca^{2+} iyonu içeren su numunelerinde filtrasyon sonra elektriksel iletkenlik değişmemiştir, hatta az da olsa bir artış gerçekleşmiştir. Filtrasyon için kullanılan membranın sudaki iyonları azaltmada etkili olmadığı görülmektedir. %5 Mg^{2+} , %10 Mg^{2+} , %10 Ca^{2+} , %15 Mg^{2+} veya %15 Ca^{2+} içeren su numunelerinde filtrasyon sonrası elektriksel iletkenliğin ve zeta potansiyelin önemli ölçüde azaldığı, yani sudaki iyonların azaldığını göstermektedir. Elde edilen membranın %5 Mg^{2+} iyonundan veya %10 Ca^{2+} iyonundan daha fazla tuz içermesi durumunda membranın etkili olabileceği gözlenmiştir. 3 farklı kalınlıkta elde edilen membranlar çalışmada kullanılmıştır: 0,04 mm, 0,12 mm ve 0,28 mm. 0,04 mm ve 0,12 mm kalınlığında elde edilen membranlarda filtrasyon işlemi gerçekleştirildiğinde membranın zarar gördüğü ve kullanılamadığı tespit edilmiştir. 0,28 mm kalınlığında üretilen membran ile filtrasyon işlemi gerçekleştirildiğinde ise filtrasyon işlemi gerçekleştirilebilmiştir ve ölçümler yapılarak sonuçlar kaydedilmiştir. Zeinden elde edilen membranın performansını değerlendirebilmek için süzülme akısı ve geri çevrilme oranları hesaplanmıştır. 1% magnezyum klorür ve %1 kalsiyum dihidrat ile hazırlanan çözeltilerde elektriksel iletkenlik azalmadığı için suydaki tuz iyonlarının azalmadığı düşünülmektedir. Bu nedenle geri çevrilme oranı hesaplanamamıştır. Tuz oranı ile elektriksel iletkenlik arasında doğru orantı olduğu için 15 farklı konsantrasyonda elde edilen çözeltinin sonuçlarına göre konsantrasyon-elektriksel iletkenlik grafiği elde edilmiştir. Filtre edilen suda ölçülen elektriksel iletkenlik değerine göre, filtre edilen suyun konsantrasyonu hesaplama yöntemiyle elde edilmiştir. Sonuçlara göre, %5 kalsiyum klorür dihidrat ile hazırlanan çözeltide filtre edildikten sonra konsantrasyon %4,06 tespit edilmiştir ve geri çevrilme oranı %18,80 olarak hesaplanmıştır. %10 kalsiyum klorür dihidrat ile hazırlanan çözeltide filtre edildikten sonra konsantrasyon %1,66 tespit edilmiştir ve geri çevrilme oranı %83,40 olarak hesaplanmıştır. %15 kalsiyum klorür dihidrat ile hazırlanan çözeltide filtre edildikten sonra konsantrasyon %7,75 tespit edilmiştir ve geri çevrilme oranı %48,33 olarak hesaplanmıştır. %5 magnezyum klorür ile hazırlanan çözeltide filtre edildikten sonra konsantrasyon %0,73 tespit edilmiştir ve geri çevrilme oranı %85,40 olarak hesaplanmıştır. %10 magnezyum klorür ile hazırlanan çözeltide filtre edildikten sonra konsantrasyon %4,83 tespit edilmiştir ve geri çevrilme oranı %51,70 olarak hesaplanmıştır. %15 magnezyum klorür ile hazırlanan çözeltide filtre edildikten sonra konsantrasyon %4,21 tespit edilmiştir ve geri çevrilme oranı %71,93 olarak hesaplanmıştır.

Elde edilen membranın karakterizasyonu için SEM görüntüleri alınmıştır. Elde edilen SEM görüntülerine göre nanolifin çapı oldukça geniş bir aralıkta değişmektedir. ImageJ programında yapılan çalışmaya göre elde edilen her iki görüntüde liflerin çapı 515–1572 nm aralığında tespit edilmiştir. Ortalama lif çapı 1082 nm olarak elde edilmiştir. Sonuçlara göre elde edilen yüzey nanolif boyutunda değildir. Zein membranındaki muhtemel etkileşimleri ve bağları tespit edebilmek için FTIR ölçümü gerçekleştirilmiştir. Ölçüm zein membranında ve %5 lik kalsiyum klorür dihidrat ile hazırlanmış çözelti süzülürken kullanılan zein membranın gerçekleştirilmiştir. Sonuçlar literatür ile karşılaştırıldığında, 3200 bandında ortaya çıkan piklerin O-H bağından kaynaklandığı tespit edilmiştir. 2800-3000 bandında görülen piklerin ise C-H bağından kaynaklandığı tespit edilmiştir. 1600-1700

bandının amit I ve 1500–1600 bandı ise amit II grupları arasındaki bağı ifade etmektedir.

Yapılan lüteratür araştırmalarına göre; çalışmalarda tuz giderimi için kullanılan deniz suyu içerisindeki toplam çözünen katı madde miktarı 35000-43000 mg/L arasında değişmektedir. Filtrasyon sonrası elde edilen sular elde edilen suyun sertliğine göre proses suyu, yıkama suyu veya içme suyu olarak kullanılabilir.

Yapılan bu çalışmada sadece zein polimeri kullanılarak membran elde edilmiştir ve sentetik bir polimer kullanılmamıştır. Elde edilen zein membranın proses sırasında basınç uygulandığında mekanik dayanıklılık olarak zayıf ve hassas olduğu görülmektedir. Bu nedenle tekrar kullanıma uygun değildir. Membranın uzun süreli ve büyük çaplı üretimlerde kullanılabilmesi proses parametrelerine ilişkin optimizasyon çalışmalarının yapılması gerekmektedir. Elde edilen sonuçlar, elektreğirme yöntemi ile elde edilen zein membranlarının yüksek miktarda tuz içeren suların filtrasyonunda kalsiyum ve magnezyum katyonlarını tuttuğu ve tuzlu sudaki sertliği azaltabildiğini göstermektedir.





1. INTRODUCTION

Water is the most worth natural resources in the world and is under serious coercion because of the deleterious human activities. In the future, water scarcity can arise because of the atmospheric deposition, domestic, industrial and agricultural implementations. So, current methodologies are needed the optimization to develop new and effective techniques for water filtration processes to increase the usable water resources (Nasreen et al, 2013).

Some materials such as nanoparticles, simple organic compounds, polymers or inorganic clay materials have been used for water filtration. The used materials can be in the form of thin film, membrane or powder. The membrane technology plays a vital role for removal of contaminants due to its easy handling and high efficiency. Though many materials are under investigation, nanofibers driven membrane are more valuable and reliable. Membranes obtained from nanofibrous materials offer high surface area to volume ratio, fine tunable pore sizes. Also, their ease of preparation prompted both industry and academic researchers to study their use in water filtration or purification. Due to innovative thought in the membrane design, novel thin-film nanofibrous composite (TFNC) membranes have been developed and applied for various water purification processes. This technology represents many benefits such as high throughput, high rejection, high durability, low energy consumption and low cost (Nasreen et al, 2013).

According to Ahmed et al., approximately 11% of the people in the world cannot access to drinking water and according to the World Health Organization data, 4 billion of people will be affected from the water shortage by 2050 (Ahmed et al, 2015).

70% of the earth's surface was constituted from water. However, 97% of this water has high salt ratio. So, the world needs treatment methods with low cost to prevent from suffering in the future. Membrane technology has a popularity over the last

years. Because, the membrane systems have high separation effectiveness and low costs (Ahmed et al, 2015).

In order to prevent from water shortages in the future, nanofiltration technique should be investigated in detail. According to the researches only a limited selection of synthetic polymers such as polyacrylonitrile (PAN), polysulfone (PSU), polyethersulfone (PES), polyvinylidene fluoride (PVDF), cellulose acetate (CA) and cross-linked polyamide (PA)) were used for commercial membranes. Natural biopolymers can be used to obtain membranes and there was no academical research about protein membranes for nanofiltration. Zein is a natural protein that obtained from corn gluten and have high hydrophobic properties. According to our findings, membranes that obtained from zein protein through electrospinning process can be option to remove hardness from water that have high salty ratio (ocean, seawater etc.) in the industry.

1.1 Purpose of Thesis

Zein protein have good film-forming ability and it can be a useful material for water softening if it holds salt ions (Mg^{2+} and Ca^{2+}). Electrospinning technique was used to obtain membrane from zein protein. The main objective of the proposed research is to focus on the use of zein which is natural biopolymer to remove hardness from water. It can be a process stage for water filtration of high salty water.

The specific objectives of this thesis study are:

- a) To investigate if it is possible to remove hardness with zein membrane
- b) To define the process conditions: zein membrane thickness,
- c) To measure electrical conductivity and zeta potential of water that have different salt ratio before and after filtration to investigate the effectiveness of the membrane,
- d) To characterize the membrane before and after filtration: Scanning electron microscope (SEM), fourier transform infrared spectroscopy (FTIR), zeta potential, electrical conductivity,
- e) To measure and evaluate the performance of membrane filtration.

1.2 Literature Review

1.2.1 Membrane technology in water treatment

Nanoparticles, nanofibers and nanostructures provide several technological developments in the electronics, catalysis and environmental applications. Different materials are used to obtain nanostructures such as polymeric, inorganic metal/polymer composite with changes in their composition, configuration and assembly. These nanostructures have been manufactured by various techniques such as electrospinning, template assisted synthesis, phase separation, self-assembly, solvent evaporation, drawing-processing method. Electrospinning is the most versatile and simple technique compared to other ones (Nasreen et al, 2013). Moreover, electrospinning process is a high effective method to obtain porous hydrophobic surfaces (Feng et al, 2013).

A number of literature has been reported related to use of electrospun nanofibrous membranes (ENMs) for water treatment applications. ENMs have distinct properties, such as high surface area to volume ratio, large porosity, good mechanical properties and good water permeability, which are very critical for water treatment. Depend on thickness, porosity, and surface roughness of nanofibers, the type of water treatment applications can be changed. The most widely applied filtration methods are microfiltration, ultrafiltration, nanofiltration, reverse osmosis and forward osmosis and pressure retarded osmosis. Among them, the most commonly known ones are microfiltration, ultrafiltration and nanofiltration (Park et al, 2008).

ENMs can also contribute to membrane distillation, an emerging desalination and water treatment technology. These ENM applications for water treatment are summarized in Table 1.1 (Feng et al, 2013).

Table 1.1: Applications of nanofibers fabricated from polymers (Feng et al, 2013).

Polymer	Process	Area of application
PAN	Nanofiltration	Salt removal
Polyvinylidene	Filtration	Pretreatment of water prior to RO or UF
Cellulose/PAN	Filtration	Bacteria and virus removal
PAN/chitosan	Ultrafiltration, nanofiltration	Water filtration
PIP	Ultrafiltration	Water treatment
Polystyrene/beta-cyclodextrin	Nanofiltration	Removal of organic compounds from water
Cellulose acetate	Heavy metal ion adsorption	Water treatment

Water is a fundamental constituent for all living creatures and it is an essential part of human beings for survival. There are wide amounts of water on earth and 71% of the earth's surface is covered by the sea. However, human beings cannot use salt water. So, one of the big challenges in the current and future time is to acquire fresh water with low energy consumption. Some government organizations have reported that approximately 1.2 billion people will be short of access to clean fresh water and about 66% of the world's population may live in water stressed countries by 2025 (Park et al, 2008). Almost all of the water (97%) on earth is salty water in the oceans (Figure 1.1). The remaining 3% fresh water constitute from ice fields (2.06%), groundwater (0.90%) which are not accessible, accessible fresh water (0.04%) which constitute from rivers, lakes and rain and also includes unwanted marsh and sources. To summarize, only 0.01% of total water on the earth is accessible without spend too much energy. The insufficient water on the earth is distributed unequally and these water sources are infected with viruses and bacteria. For this reason, the millions of people are died or illnesses in each year. In addition, the population is rapidly increasing day by day and there was no way for the transportation of water from one country that have high fresh water sources to another country that have low fresh water sources with low cost. Therefore, there was a mandatory requirement for the development of water filtration technologies with low energy and cost are required (Ma et al, 2012).

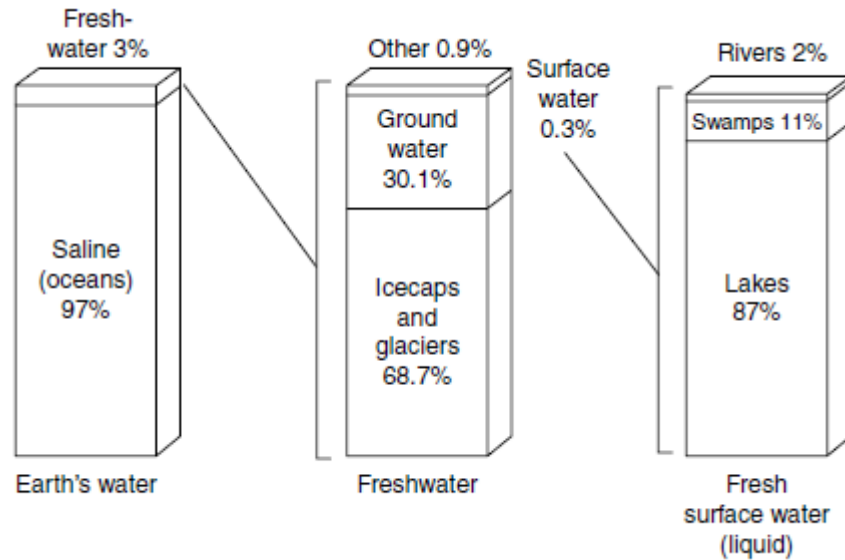


Figure 1.1: Schematic representation of distribution of usable water on Earth (Ma et al, 2012)

Present technologies for water filtration process are distillation, ion exchange, chemical treatment, ultraviolet treatment and filtration. The implementation of distillation, ion exchange and chemical treatment methods are needed high energy. Therefore, these methods are not preferred due to high cost. On the other hand, filtration is more energy-efficient method compared to distillation, ion exchange and safer compared to chemical treatment. Therefore, many new filtration technologies have been developed and many technical academic researches were done on this topic. In general, the filtration process can be classified into four groups according to pore size of the membranes: microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO) and nanofiltration (NF) (Ma et al, 2012).

MF membranes have a pore size larger than 50 nm. These membranes are widely used for potable water purification and have ability to remove particles and waterborne bacteria. The operating pressure of MF membranes is very low, generally less than 2 psi or by gravity. UF membranes have smaller pore sizes comparatively to MF membranes. The pore size is 2-50 nm and they have been used generally for industrial wastewater treatment. The operating pressure of these membranes is between 10–30 psi. For RO membranes, the highly operating pressure is used for desalination of salty water between 150–1000 psi. It can be changed depending on the salt ratio of water. The pore sizes of NF membranes are smaller than 2 nm. These are ideally used to eliminate multivalent ions like lead, chromium, magnesium and

calcium, surfactants or dye molecules from industrial wastewater. The operating pressure is generally under 100 psi. All filtration membranes can be fabricated from inorganic (ceramic), organic (polymer) or hybrid materials (combination of ceramic and polymer materials). The type of material affects the cost which is important issue for industries (Ma et al, 2012).

1.2.2 Hardness removal techniques from water

Water contains organic or inorganic materials that can soluble and insoluble in water. Calcium and magnesium cations are the most common ones that increase to degree of water hardness (Mestre et al, 2016). The hardness of water can change depending on the geology of region (Racho and Namseethan, 2016).

Water hardness is harmful for human health and is a troublesome for the industry. It was reported that 85% of the water source of United States is hard water. The traditional methods for hardness removal are chemical based. However, it can cause water pollution. So, electrochemical treatment can be optional due to its advantages. There are no introducing contaminants to the water source; cause a small amount of concentrated solid waste and it can be easily operated in industry for practical application. There are generally two types of electrochemical methods for removal of water hardness that are electrochemical precipitation and electrocoagulation. Electrochemical precipitation removes hardness ions through creating a high pH environment around the surface of cathode while the electrocoagulation removes hardness ions by scale precipitation on cathode surface and by the adsorption of Ca^{2+} and Mg^{2+} to the $\text{Al}(\text{OH})_3$ (Zhi and Zhang, 2016).

Ion exchange, lime-soda softening, adsorption, electrocoagulation, reverse osmosis and nanofiltration methods are used to remove calcium and magnesium ions from water. However, the ion exchange regenerates unnatural polymers with HCl and NaOH. As a result, this method causes toxic wastewater. Therefore, this method is not useful for the industry. The lime-soda softening is disadvantageous because of time-consuming treatment processes. The other methods are reverse osmosis and nanofiltration. These methods have high cost due to its pressure energy need and treatments of water. According to literatures, some materials were used to remove

the hardness-causing minerals. These are sugar cane bagasse, modified cellulose, modified pumice, activated carbon and coconut shell. These materials have low adsorption capacity or high equilibrium time and cost. Cellulose nanofibers have good adsorption properties in waters due to its biocompatibility, high surface to volume ratio and low cost (Muqet et al, 2018).

Hardness ions cause two detrimental effects. These are formation of deposits and destruction of soap. The deposits of hardness ions formed because of the reaction with soap anions. For the hardness removal, ion exchange is used due to its simplicity operation and high removal activity. The principle of this method is the displacement of sodium ions with hardness ions. The periodic change of resins is required due to the saturation of ion exchange content (Park et al, 2007).

Industries need to soften their water, because hard water can also damage equipment such as pipes, valves and pump. Also, hard water reduces the efficiency of heaters, boiler, cooling towers and similar processes. Lime soda and ion exchange are available processes that used for hardness removal. The lime soda process is old time method and was not efficient for the industry and requires high footprint. Ion exchange is the well-liked method for hardness removal, required low footprint and high efficiency (Racho & Namseethan, 2016).

At the beginning of 21st century, membrane technologies have an important role for desalination of seawater, brackish water and contaminated water sources. The continuous improvement for membrane materials, energy optimization, minimized membrane fouling are important for the future of membrane applications. The most of the minerals are removed from water thorough the desalination process and also remineralization is applied for taste and control of corrosion. The concentration of minerals in desalinated water determined the taste and odor of water (Devesaa & Dietrichb, 2008).

Another method is capacitive deionization (CDI) and it is a potential technology to remove inorganic ions from water and it requires low power consumption. The general principle of this technique is the electrostatic field between the electrodes to force charged ions to move electrodes that have oppositely charges (Li et al, 2008).

Desalination technology has been widely known and ideal process to prevent water scarcity. But, there are some issues for the application of desalination process in plants. The one of the important challenges is fouling of membrane. It affects the productivity of plant adversely and another significant challenge is high energy consumption. The desalination process requires high energy consumption because of the high operating pressure. Therefore, there was a need to research and development to cope with these challenges. Nanofiber membranes are the alternative to overcome the challenges.

NF, which started at the end of the 90s, was tested as one of the pretreatments in the seawater membrane-based desalination plant. This situation causes the decrease of total dissolved solid (TDS) or salts in the water. As a pretreatment, NF cause higher water production and result with low cost. So, further studies about the advantages and application of NF in the industry are needed to investigate this technology deeply. According to the studies, as a pretreatment, NF is a good application to obtain high RO flow to with removal of colloidal particles (Mohammad et al, 2015).

1.2.3 Nanotechnology applications in water treatment

NF membranes have applications in several areas. One of the main applications has been in water treatment for drinking water and a wastewater. NF can be used to treat water including ground, surface and wastewater or used as a pretreatment for desalination. NF membranes can remove turbidity, microorganisms and hardness, as well as a fraction of the dissolved salts. This results in a significantly lower operating pressure and thus provides a much more energy-efficient process (Hilal et al., 2004).

The presence of heavy metal ions in water is a major concern for public health. The waste water in battery manufacturing is one of the main source of heavy metals including lead, copper, cadmium and nickel ions in local water streams. The nanofibrous adsorbents prepared by electrospinning process such as chitosan/titanium dioxide nanocomposite nanofibers due to high surface area and porous structure have been widely used in adsorption of heavy metal ions (Razzaz et al., 2016).

Nanofiltration method has been found to be an appropriate method for the removal of different heavy metals (cadmium, copper, manganese, lead etc.) from aqueous solutions and a few studies have shown that NF membranes can also remove chromium from wastewater. The most known widely used techniques to remove chromium from water are adsorption, chemical reduction or ion exchange resins. In these processes, many different chemical compounds are used. Moreover, they are generally not appropriate to achieve the limit for hexavalent chromium in water. However, membrane based separation techniques may be effective to remove chromium to obtain low concentrations in water. Nanofiltration method should also be considered to obtain higher membrane performance and to avoid the use of any ligand materials. According to the study results, commercial nanofiltration membranes investigated can remove Cr(VI) in drinking water to reach limit in drinking water (Giagnorio et al., 2018).

Ultrafine polysaccharide nanofibers are easily fabricated from many cellulose sources and fewer environmental concerns. In the laboratory environment, polysaccharide nanofibers have been used to modify electrospun nanofibrous scaffolds for the removal of bacteria and viruses for drinking water purification. Highly permeable TFNC membranes with fibrous structures have been produced and applicable to a wide range of water treatment processes. TFNC MF membranes provide 2-5 times higher water permeability than commercial MF membranes. This property was provided with the mean pore size and pore size distribution of the barrier layer by using the electrospun fibrous materials. The fibers that have diameters in the 100 nm range can be achieved by the electrospinning process and these fibers are suitable to produce a cost effective filter to exclude bacteria. Surface modifications of TFNC MF membranes with charged species, such as PEI and polysaccharide nanofibers, have further expanded the application for the removal of viruses and heavy metal ions from contaminated drinking water, while maintaining high retention capability and low pressure drop (Ma et al., 2012).

Moreover, NF hollow fiber membrane was produced and was applied to the process of dye desalination. According to the results, over 95.3% NaCl was removed from the dye/salt mixtures. The results showed that NF hollow fiber membrane could be successfully used to the dye desalination process (Wei et al., 2013).

1.2.4 Nanofiber production by electrospinning

1.2.4.1 Working principle of electrospinning device

Nanofibers can be obtained by using electrospinning device that applies high electric voltage to a capillary droplet of polymer solution or a melt to overcome liquid surface tension. Applied voltage to the polymer solution creates a jet of solution to be extracted toward a grounded collector and the fine jets dry to form polymeric fibers which collected as a web (Haghi & Zaikov, 2011).

Electrospun nanofibers shows attractive properties such as high porosity with very small pore size, large surface area to volume ratio, high gas permeability and small pore size (Okutan et al, 2014). Various technical researches have been done to detect the spinnability of a polymer solution. For generally, the mechanisms of fibre formation is defined as the spinnable solution if the polymer jet remains unbroken until dry nanofibers are formed (Rosic et al, 2012).

During the electrospinning, bead formation may occur in which bead formation interrupt the uniformity of nanofibers. Too low molecular weight, lower polymer concentration, feed solution with high surface tension, high voltage, high viscosity of solution and high feeding rates lead to bead formation in nanofiber (Huang et al, 2003; Okutan et al, 2014). Nanofiber diameter is also affected by the parameters influencing the electrospinning, high solution concentration, reduce voltage application and high feeding rate (Haider et al, 2010; Huang et al, 2004).

Nanofibers have many interesting properties due to their nanoscale diameters and large aspect ratio. They have a great mechanical property and their surface can be easily modified based on their high surface to volume ratio. Nanofibers can be obtained with different methods such as drawing, template synthesis, phase separation, self-assembly or electrospinning. Electrospinning method is more easy and reliable to obtain smooth nanofibers with wide variety polymers. For the electrospinning method, it was applied high electrical field to a charged solution to obtain nanofiber (Ahmed et al, 2015).

A schematic of the electrospinning process of polymer nanofibers is shown in Figure 1.2. There are fundamentally three components to fulfill the process: a high-voltage

supply, a capillary tube with a pipette or needle of small diameter, and a metal collecting screen (Haghi & Zaikov, 2011).

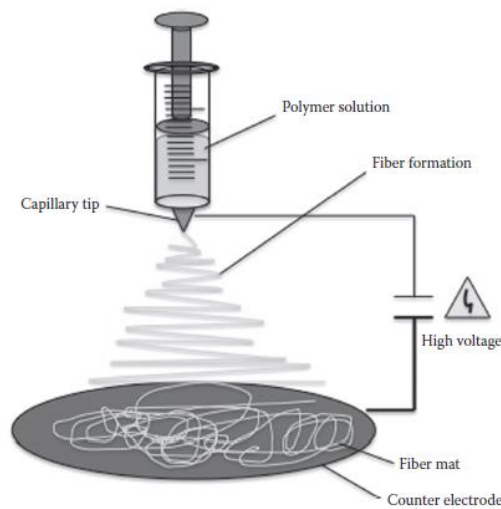


Figure 1.2 A scheme illustrating the basic principles of electrospinning process
(Unser & Xie, 2012)

1.2.4.2 Affecting process parameters

Electrospinning process is affected from various factors. These factors are mainly divided into three groups: polymer solution effects, process conditions and environmental factors. These parameters affect the quality and the morphology of nanofiber (Unser & Xie, 2012). Each parameter affects the morphology of fibers. When those parameters are kept on control, electrospun fibers can be produced with optimum properties by electrospinning technique (Li & Wang, 2013). The parameters that effect the electrospinning process are below;

- Solution properties: Viscosity, electricity, conductivity, surface tension, molecular weight of solution, concentration of solution
- Process conditions: Applied voltage, feed rate/flow rate, types of collector, tip to collector distance and diameter of needle
- Ambient parameters: Temperature, humidity, air velocity in the electrospinning area (Bhardwaj & Kundu, 2010).

The concentration of feeding polymer solution, properties of solvent, electrical conductivity of solution, surface tension and dielectric coefficient have impact on

diameter of nanofiber. The concentration of solution has an important impact on fiber production and it affects fiber morphology and diameter. If the other parameters are hold as constant, as the concentration is increased, fiber diameter generally increases (Andrady, 2008). Viscosity also affects electrospinning process significantly. When the solution has very low viscosity, the continuous fiber formation is not observed or when the solution has very high viscosity, the ejection of jets from polymer solution become very hard, so optimal viscosity is adjusted for electrospinning (Bhardwaj& Kundu, 2010). Choice of solvent is another parameter that affects electrospinning process and morphology of membrane. Ideal solvent vaporizes by the time reach to collector plate from feeding tip. If vaporization of solvent does not realize completely, nanofibers gather as wet and flat strip. For this reason, volatile solvents are preferred in electrospinning process. Also, environment temperature affects the volatilization of solvent (Andrady, 2008). If a solvent used in electrospinning process has low volatility, solvent loss does not occur very fastly and wet fibers form. On the other side, if the volatility of solvent is too high, fibers will not form because the polymer will solidify after the jet exits the needle (Ahmed et al, 2015).

Nanofiber morphology is mainly affected from the solution properties such as conductivity, surface tension, dielectrical properties and volatilization. However, the required criterias were not defined exactly for solvent choice (Andrady, 2008). Polymers are generally conductive and the charged ions in the polymer solution are highly effective in jet formation (Bhardwaj & Kundu, 2010). The movement of electric charge from the electrode to the spinning droplet at the tip is required to achieve the electrospinning process. For this reason, a minimal electrical conductivity in the solution is necessary for electrospinning. Solutions that have zero conductivity cannot be electrospun. Solvents that are used in electrospinning have conductivities lower than distilled water, such as dichloromethane has 0.03 mS/m value (Jun et al, 2003). When the polymer has ionic structure, the conductivity of solution will be much higher comparatively to uncharged polymers. Also, it depends on concentration (McKee et al, 2006). There is a linear relationship between concentration and electrical conductivity in most cases. However, if the polymer has not ionic components, there is a non-linear relationship between concentration and electrical conductivity. In this case, inorganic salts such as sodium chloride can be added into solution to increase electrical conductivity (Andrady, 2008).

The other parameter is surface tension which has an essential role in the electrospinning process. Fibers can be obtained without beads throughout reducing the surface tension of a nanofiber solution. Distinct solvents affect surface tensions differently. In most cases, the high surface tension of a solution prevents the electrospinning process because of inconstancy of the jets and the production of sprayed droplets (Bhardwaj & Kundu, 2010). The formation of droplets, bead and fibers depend on the surface tension of solution. A lower surface tension of the spinning solution helps to electrospinning process to perform at a lower electric field (Haghi & Akbari, 2007). However, a lower surface tension always cannot be convenient for electrospinning. Consequently, when all other variables are held constant, surface tension of feeding solution determines the upper and lower boundaries of the electrospinning (Bhardwaj & Kundu, 2010).

Another parameter is dielectric constant that indicates the electrical charge holding capacity of solution and changes with the type of solvent and polymer. High dielectric constant provides more formation of nanofibers in unit area. Some additives or different solvents can be added to solution to change dielectric constant. But, in this case, conductivity and surface tension is affected, so all parameters should be considered (Andrady, 2008).

The applied electrostatic potential is another critical parameter in the electrospinning process and fiber morphology. Until reach to threshold voltage, fiber formation does not observe. After exceeding to threshold voltage value, the charges reduce on the solution along with electric field and realized electrospinning process. The applied voltage provides charging of solution with electrical charges during process. As the applied voltage increase, the fiber diameter decreased due to high charge and increased jet distance. However, this situation does not valid for every polymer solution. The other parameters are considered while evaluate the effect of applied voltage (Bhardwaj & Kundu, 2010). In the study, when the voltage between 28 kV and 35 kV applied for polyvinyl alcohol and sodium alginate electrospinning fibers, broken fibers were formed at 28 kV and fibers are more continuous at 35 kV. However according to study, they couldn't find any directly correlation between voltage and diameter of fiber. Some studies showed that thinner fibers are formed with high voltage. However, higher voltages lead to increased bead formation (Ahmed et al, 2015).

The flow rate of the polymer from the syringe is also significant process factor due to effect on the jet velocity and the material transfer rate. A lower feed rate is better to provide enough time for evaporation of solvent (Yuan et al, 2004). There should always be a minimum required flow rate of the spinning solution (Bhardwaj & Kundu, 2010).

Another important parameter of the electrospinning process is the type of collector. Aluminium foil is mostly used as a collector. However, the transfer of collected fibers is difficult. Other collectors are conductive paper, conductive cloth, wire mesh, pin, parallel or grided bar, rotating rod, rotating wheel, liquid non solvent such as methanol coagulation bath (Bhardwaj & Kundu, 2010).

The distance between the tip and the collector is another factor to control the fiber diameters and morphology. A minimum distance is adjusted to supply sufficient time to dry the fibers before gathering on the collector. If distances become too close or too far, beads are observed (Bhardwaj & Kundu, 2010).

The diameter of the syringe needle is another process parameter. When the diameter of the needle increased, it does not affect the structure of the fibers. However, when the diameter of syringe needle was decreased, it causes polydispersity of the fiber diameters. It means that the nanofibers have big and small diameter at the same time during the production. According to researches, there was no important relation between syringe needle diameter and nanofiber diameter (Ashraf et al., 2019).

Also ambient parameters such as humidity, temperature, air velocity in the electrospinning area affect the diameter and morphology of fiber (Bhardwaj & Kundu, 2010). The optimum conditions should be adjusted to obtain dry nanofiber, because of their effect on volatilization of solvent from solution. In general, jet formation occurs rapidly with the circulation of heated air that of 25-57°C. However, the circulation velocity of heated air should be equal to volatilization velocity of solvent from nanofiber jet (Andrady, 2008).

1.2.5 Novel membranes produced by electrospinning

Highly permeable TFNC membranes have been manufactured, characterized and used for water treatment. The TFNC MF membrane has a PET layer as the bottom

support and a layer of cross-linked polyvinyl alcohol (PVA), PAN or PES electrospun as the barrier layer. The highly porous and interconnected structure of the layers in TFNC MF membranes provides high water permeability 2-5 times more than commercial MF membranes and also has high retention capacity. The main reason of this property was the pore size and pore size distribution of the barrier layer that maintained by electrospun. The small fiber diameters approximately 100 nm can be obtained by the electrospinning process. The pore sizes are proper to produce a filtration membrane with low cost in an attempt to remove most known bacteria. Surface modifications of TFNC MF membranes with charged polymers and polysaccharide nanofibers, provide the exclusion of viruses and heavy metal ions such as chromium, arsenic and lead from water, while maintaining high retention capacity and low pressure drop (Ma et al, 2012).

TFNC UF membranes were composed of a three layers. The first layer was PET nonwoven as the bottom support layer. The second layer was electrospun scaffold such as cross-linked PVA, PAN and PES as the middle layer. Finally, cross-linked PVA, chitosan, cellulose or ultrafine polysaccharide nanofibers are used as the barrier layer. The third layer could be integrated with the middle layer support to enhance the mechanical stability and to enter directed water channels. The materials used in the barrier layers should be hydrophilic, mechanically durable and have antifouling characteristics to use for water purification. Between 2-10 times higher water permeability was accomplished comparatively to commercial UF membranes. Also, same retention capability can be achieved. Moreover, the polysaccharide barrier layer in TFNC membranes can be further developed for adsorption of bacteria, viruses and heavy metal ions. There is a necessity to improve high cost effective and energy efficient membranes through new and innovative approaches. The development of TFNC membranes offers an encouraging attempt to achieve this target. Because, these membranes have high flux rate, high retention capability, low fouling capability and low cost (Ma et al, 2012).

1.2.6 Characteristic properties of natural zein protein

A zein is a protein that obtained from corn gluten throughout solvent extraction method. It is 50% or more than 50% of the total endospermic proteins in maize. The

zein is a crucial sub-product for the corn starch industry because of its economic advantages. The zein has hydrophobic property and does not soluble in water. So, ethanol at high concentrations between 60–95% was used to dissolve zein and to maintain its molecular structure. Because of its hydrophobic properties and containing sulfur amino acid content, zein is not commonly used in the food industry as an ingredient (Sun et al, 2016). This plant protein has low biological value due to the amino acid derangement. The important advantage of zein is its polymerization attributes (Barbosa de Almeida & Lopes Filho, 2011).

Zein is classified into 4 groups based on its solubility and amino acid sequence in its structure. These are α , β , γ and δ zein. α -zein is the most common type and it can be soluble in aqueous-alcohol. It includes hydrophobic amino acid and hydrophilic amino acid residues in its structure. The structure of zein amino acid was defined by Pomes in 1971. It was published that zein contains 21.4% glutamine, 19.3% leucine, 9.0% proline, 8.3% alanine, 6.8% phenylalanine, 6.2% isoleucine, 5.7% serine and 5.1% tyrosine. The zein has a dimension approximately $17 \times 4.5 \times 1.2 \text{ nm}^3$ and a molecular weight between 19-21 kDa and it has amphiphilic properties. Due to its amphiphilic characteristic, it can create colloidal nanoparticles that have spherical shape and it is generally implemented for controlled or targeted delivery of bioactive in foods (Sun et al, 2016 & Zhang et al, 2011).

Zein is generally known for its film-forming ability, biodegradability and biocompatibility. Thus, zein have many applications in food and pharmaceuticals sectors as emulsifier, chewing-gum base, antioxidant, drug encapsulant and tissue scaffold (Zhang et al, 2011).

Structural studies for zein generally focused on α -zein and γ -zein because of their high ratio in total zein. The secondary and primary structures of zein can be investigated by chromatography, circular, Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) techniques. α -zein have α -helix content between 35-60% and it changes with temperature, pH and type of solvent. γ -zein have 33% α -helix and 31% β -sheet content (Yonga et al, 2016).

The United States Food and Drug Administration accept zein as safe material. More than half of amino acids are non-polar in zein. Due to this property, it was not

dissolved in water and in ethanol (60-90%) solution. Zein was used as a good carrier for encapsulation and to protect the bioactive compounds. It is useful for the delivery of hydrophobic components, such as resveratrol, atocopherol, lutein and quercetagenin. Unfortunately, zein nanoparticles have tendency to aggregation and it has sensitivity for environmental conditions such as pH, high ionic strength and temperature and it displays loading performance and low encapsulation (Dai et al, 2018).

1.2.7 Characterization of membrane and water

1.2.7.1 Scanning electron microscope (SEM)

Microscopic devices are significant to analyze the membrane structure. There are three types electron microscopy devices that generally used for investigating membrane properties. These are scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). These different microscopic devices provide several resolutions according to the working principle of device (Jye & Ismail, 2017). Also SEM device provide the observation of the fouling layer on surface or cross-sectional view of the surface of membrane. During analysis, an electron beams scan the surface of membrane and provide the interaction between beam and surface (Mai, 2014). Overly high electron beam energy was not used during analysis because of its damaging effect. Generally, 10-20 kV was applied to membrane sample. The analysis sample should be completely dry during SEM analysis. If the sample obtained from hydrophilic material, the drying can affect the membrane (Jye & Ismail, 2017).

1.2.7.2 Fourier transfer infrared spectrophotometer (FTIR)

Infrared spectroscopy (IR) is a method to specify the chemical structure of membranes and to detect the positions different materials on the membrane samples. It provides both qualitative and quantitative analysis. The membrane sample absorb the energy at different wavelengths. These wavelengths generate signal on the IR detector. The produced spectrum is peerless for every composite. FTIR device is especially used to investigate the membrane modifications and fouling of membrane surface (Mai, 2014). FTIR analysis was used to investigate the functional groups and

bonds on the membranes that obtained from different materials. The membrane sample should be dry before starting FTIR analysis, it can be provided with desiccator and the device should be cleaned with nitrogen to avoid the form the interaction of atmospheric moisture with the spectra (Jye & Ismail, 2017).

1.2.7.3 Electrical conductivity

An electrical conductivity is a parameter that used to investigate water quality. It is the measure of the water capacity to transmit the electric flux and it is an indicator about the amount of salt in water. It changes with dissolved ion concentration, ionic strength in water and analysis temperature (Rusydi, 2018).

1.2.7.4 Zeta potential

Zeta potential analysis was performed to investigate the characteristics of membranes surface charge for different pH values. The analysis is also important to investigate acid or base characteristics of membranes and filtration effectiveness. Moreover, the tendency of membrane to fouling at different pH can be researched with the zeta potential analysis (Jye & Ismail, 2017).

According to the researches, the NF membranes have more positive charges at lower pH values (<3.5) when the analysis performed at different pH values. This is due to the protonation functional groups of amine. In opposition to, NF membranes have negative charges at higher pH values and this is due to the deprotonation functional groups of amine. Also, zeta potential measurement can show the isoelectric point of membrane surfaces (Jye & Ismail, 2017).

1.2.8 Performance of membrane filtration

The most important limitation for water desalination by filtration is membrane fouling which causes a rapid flux decline. Membrane selection and operating conditions are important issues to minimize the membrane fouling (Gönder et al, 2011).

The membrane has the ability to transport a component due to physical or chemical properties differences between the membrane and the permeating components.

Transport through the membrane takes place as a result of a driving force acting on the components in the solution. In most cases, the permeation rate through the membrane is directly proportional with the driving force. The relationship between flux and force can be described by a linear phenomenological equation. Proportionality between the flux (J) and the driving force is given by:

$$J = - A \frac{dX}{dx} \quad (1.1)$$

As seen in equation 1.1, A is called the phenomenological coefficient and (dX/dx) is the driving force, expressed as the gradient of X (temperature, concentration, pressure) along a coordinate x perpendicular to the transport barrier.

The phenomenological coefficient relating flux and force is known as the diffusion coefficient (Fick's law), permeability coefficient (Darcy's law), thermal diffusivity (Fourier's law), kinematic viscosity (Newton's law), and electrical conductivity (Ohm's law). Phenomenological equations are summarised in Table 1.2. Driving forces can be gradients in pressure, concentration, electrical potential or temperature (Mulder, 1991).

Table 1.2: Phenomenological equations (Mulder, 1991).

Flux type	Equation	Law
Mass flux (J_m)	$-D (dc/dx)$	Fick
Volume flux (J_v)	$-L_p (dP/dx)$	Darcy
Heat flux (J_h)	$-a (dT/dx)$	Fourier
Momentum flux (J_n)	$-v (dv/dx)$	Newton
Electrical flux (J_i)	$-1/R (dE/dx)$	Ohm

1.3 Hypothesis

This study was carried out to test the following hypothesis for filtration systems. Development of zein protein fiber with electrospinning by dissolving zein in ethanol and obtain membrane to use for the hardness removal from water by filtration. It is assumed that during filtration, membrane can hold the cation ions, namely Mg^{2+} and Ca^{2+} that cause water hardness. Thus, this process can be used as a step for hardness removal from water that have high salt ratio.

Zein contains three-fourths no-polar hydrophobic amino acids such as alanine and one-fourth hydrophilic amino acids like glutamic acid. On the base of the fact that, a

hypothesis was proposed that potential interaction may take place between zein and Ca^{2+} and Mg^{2+} . The incorporation of salt ions will modify the physicochemical properties of zein, which may be adapted to the requirement of processes.



2. MATERIALS AND METHODS

2.1 Materials

Zein (CAS number: 9010-66-6, Sigma Aldrich, USA), ethanol (C₂H₆O, Cas number: 64-17-5, density: 0.805 gr/cm³, purity: %95-96, molecular weight: 46.07 g/mol), calcium chloride dihydrate (CaCl₂.2H₂O, molecular weight: 147.01 g/mol, CAS number: 10035-04-8, Sigma Aldrich, USA), magnesium chloride (MgCl₂, molecular weight: 203.31 g/mol, Tuluçe inorganics), pure water (conductivity: 0,1-0,5 µS, pH: 5-7.5, GreenX) materials were used in all experiments.

2.2 Methods

2.2.1 Preperation of electrospinning feed solution and electrospinning process

Solution of zein was prepared with 80% ethanol solution for concentrations of 30% at 25°C for 1 hour by magnetic stirrer. In electrospin, the flow rate of each solution was adjusted to observe best values in a range of 0.6-1.0 mL/h and applied voltage were between 1.2-5 kV. Electrospinning process were carried in room temperature (25 °C) and aluminium foil was used as collector. All process conditions were presented in Table 2.1.

Table 2.1: Process conditions of zein electrospun production

Process parameters	Experimental values
Flow rate (mL/h)	0.6-1.0
Applied voltage (kV)	1.2-5
Tip to collector distance (cm)	19

2.2.2 Characterization of produced membrane

2.2.2.1 Scanning electron microscope (SEM)

Morphological analysis zein membrane were conducted by the use of Vega3 Tescan (UK) with accelerating voltages of 10 kV and 20 kV. The minimum, maximum and mean size of the particles from the obtained images were recorded with a ImageJ 1.52A programme (Wayne Rasband National Institutes of Health, USA).

2.2.2.2 Fourier transfer infrared spectrophotometer (FTIR)

FTIR device was used to investigate the interactions in the membrane including zein and ions (Ca^{2+}). Infrared spectra of samples were recorded at room temperature on a Spectrum 100 Fourier transform spectrophotometer (Perkin-Elmer, UK). The crystal area has been cleaned and the background collected, the solid material is placed onto the small crystal area. Analysis were carried out for produced zein membrane before filtration and after filtration of water that have 5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ salt concentration.

2.2.2.3 Thickness measurement

The thicknesses of the membranes were measured by micrometer (Alpha Tools, BAHAG AG Gutenbergstr.2168167, Germany).

2.2.2.4 Zeta potential and electrical conductivity

The zeta potential measurement of the zein membrane was carried out using a dynamic light scattering instrument (Malvern Zetasizer Nano ZS, Worcestershire, UK) at 25°C in triplicate. Since zein was not dissolved in water, distilled water was used as a dispersant for all samples during measurements. Zein fiber was dispersed at 0.1% (w/v) in distilled water through mechanical mixer.

The electrical conductivities of the zein membranes before and after filtration were measured with a dynamic light scattering instrument (Malvern Zetasizer Nano ZS, Worcestershire, UK) at 25°C in triplicate. The membrane samples were mixed with distilled water at 0.1% (w/v) ratio through mechanical mixer. Also, some results were verified with a conductometer (WTW LF95, Germany) at room temperature.

2.2.3 Preperation of filtration solution

Filtration solutions were prepared with the addition of calcium chloride dihydrate and magnesium chloride to pure water artificially. The different calcium chloride dihydrate and magnesium chloride concentrations were used to prepare filtration solutions. The ratio of salts added to pure water were presented in Table 2.2. The calcium chloride dihydrate and magnesium chloride were directly added to pure water separately and mixed with spoon for 2 min. Since the dissolution rate of the matters is high in water, a homogeneous liquid is obtained in a short time.

Table 2.2: The ratio of salts added to pure water

Sample	Calcium chloride dihydrate ratio (w/v) (g/ml)	Magnesium chloride ratio (w/v) (g/ml)
1	1%	-
2	5%	-
3	10%	-
4	15%	-
5	-	1%
6	-	5%
7	-	10%
8	-	15%

2.2.4 Filtration of water through zein membrane

A centrifuge tube was used to collect the filtered water during filtration process, the top of the tube was covered with membrane and water was filtered through membrane. Vacuum pump was also used with nuche erlen during filtration. However, the applied pressure caused the damage of membrane. Therefore, the filtration process was carried out simply as follows. The clean dropper or syringe was used to drain the water.



Figure 2.1: The image of the filtration process

2.2.5 Characterization of membrane after filtration

2.2.5.1 Fourier transfer infrared spectrophotometer (FTIR)

FTIR device was used to investigate the interactions in the membrane including zein and ions (Ca^{2+}). Infrared spectra of samples were recorded at room temperature on a Spectrum 100 Fourier transform spectrophotometer (Perkin-Elmer, UK). The crystal area has been cleaned and the background collected, the solid material is placed onto the small crystal area. Analysis were carried out for produced zein membrane before filtration and after filtration of water that have 5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ salt concentration.

2.2.5.2 Zeta Potential

The zeta potential measurement of zein membrane were carried out using a dynamic light scattering instrument (Malvern Zetasizer Nano ZS, Worcestershire, UK) at 25°C in triplicate. Distilled water was used as a dispersant for all samples during measurements. Because, zein was not dissolved in water. Zein fiber was dispersed at 0.1% (w/v) in distilled water through mechanical mixer.

2.2.5.3 Electrical conductivity

The electrical conductivities of zein membranes after and before filtration were measured using a dynamic light scattering instrument (Malvern Zetasizer Nano ZS, Worcestershire, UK) at 25°C in triplicate. The membrane samples are mixed with pure water at 0.1% (w/v) ratio through mechanical mixer. Also, some results were verified with a conductometer (WTW LF95, Germany) at room temperature.

2.2.6 Characterization of water before and after filtration

2.2.6.1 Electrical conductivity

The electrical conductivities of water before and after filtration were measured using a dynamic light scattering instrument (Malvern Zetasizer Nano ZS, Worcestershire, UK) at 25°C in triplicate.

2.2.6.2 Zeta potential

The zeta potential measurement of water before and after filtration zein membrane were carried out using a dynamic light scattering instrument (Malvern Zetasizer Nano ZS, Worcestershire, UK) at 25°C in triplicate.

2.2.7 Performance of membrane filtration

The filtration performance of the membrane is evaluated by the percent rejection (R%) of feed materials, which is calculated as:

$$R (\%) = \left(1 - \frac{C_p}{C_f} \right) \times 100 \quad (2.1)$$

As seen in equation 2.2, C_p represents the concentration of a particular component in the composite permeate at the end of the experiment and C_f is its feed concentration.

To calculate the final concentration of water after filtration, Ca^{2+} and Mg^{2+} analysis was not carried on. The electrical conductivity of the solutions prepared at different concentrations of magnesium chlorur and calcium chloride dihydrate (1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, 11%, 12%, 13%, 14%, 15%) were measured by a dynamic light scattering instrument (Malvern Zetasizer Nano ZS, Worcestershire, UK) three times at 25°C. The graphs and equations were obtained according to the results and the concentration of water after filtration was calculated based on equations.

2.2.8 Statistical analysis

Electrical conductivity and zeta potential analysis results of water and membrane were analyzed by IBM SPSS Statistics Program (21th version) by using one-way analysis of variance (ANOVA) at 0.05 significant level and Tukey's range test was

applied as post hoc test. The differences between all results were evaluated statistically. Tukey's range test was applied to exact values to observe the differences between samples ($p < 0.05$). The results were reported as mean value $\pm$ SD. Statistical analysis results of samples were given at Appendix A, B, C, D, E, F, G, H, and I.



3. RESULTS AND DISCUSSION

3.1 Nanofiber Production by Electrospinning

To prepare electrospun solution, 30% zein (w/v) was dissolved with 80% ethanol (v/v) at 25°C for 1 hour by magnetic stirrer. Flow rate of this solution was determined 0.8 ml/h, the applied voltage was 1.8 kV and the distance between tip and collector distance 19 cm during electrospinning process.

3.2 Characterization of Produced Nanofiber

3.2.1 Scanning electron microscope (SEM)

SEM images of zein nanoparticles electrospun at a 30% zein concentration is seen as below Figure 3.1. Two different images are taken from the analysis with accelerating voltages of 10 kV (first image) and 20 kV (second image).

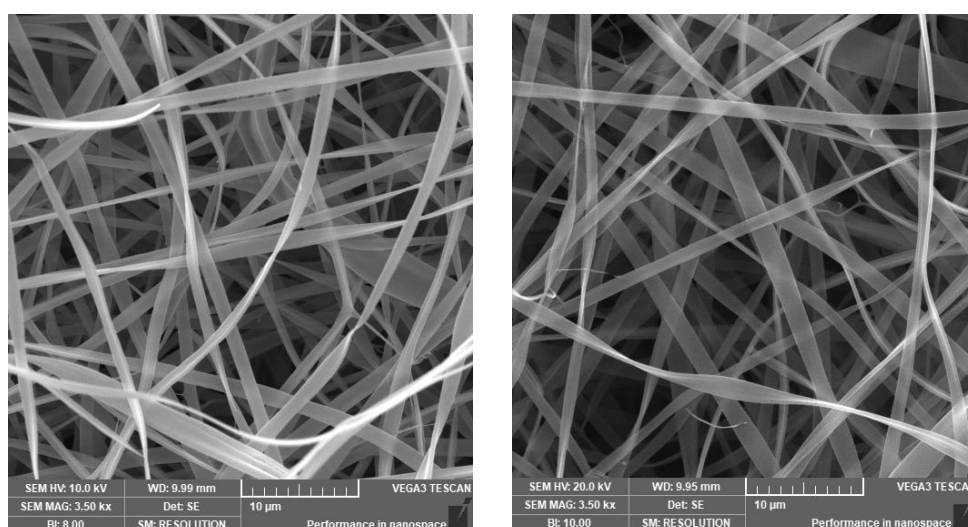


Figure 3.1: SEM images of zein prepared with 30% (w/v) zein

The images were analysed with ImageJ programme by chosen 20 different point from the images. According to the results, average diameter of zein particles was

1082 nm and its distribution was in the range of 515–1572 nm and standard deviation is 250 nm when the accelerating voltage is 10 kV. For 20 kV, average diameter of zein particles was 1128 nm and its distribution was in the range of 652–1508 nm and standard deviation is 273 nm.

The SEM images showed that variations in the fiber diameter could change the porosity under our experimental conditions and fiber diameters should be closer to each other to obtain more accurate results. The fibers are not at nanoscale according to results.

3.2.2 Fourier transfer infrared spectrophotometer (FTIR)

FTIR is applied to unravel the potential interactions in such a system including different materials. In this study, FTIR was applied to detect the potential interactions in such a system including zein and calcium ions. As shown in Figure 3.2 and 3.3, zein membrane before and after filtration exhibited a broad peak band at 3290 cm^{-1} and 3285 cm^{-1} , respectively. According to the researches, $3100\text{--}3500\text{ cm}^{-1}$ peaks were caused by the strong O-H stretching vibration of hydroxyls- bound water (Sun et al, 2017). The result indicated that hydrogen bonds were formed between zein and calcium chloride dihydrate because hydrogen bonds could be formed between amide groups of glutamine in zein and hydroxyl groups. Besides, the band of $2800\text{--}3000\text{ cm}^{-1}$ was attributed to C-H stretching vibrations. The range of peak band from $1500\text{ to }1700\text{ cm}^{-1}$ represented amide I ($1600\text{--}1700\text{ cm}^{-1}$) and amide II ($1500\text{--}1600\text{ cm}^{-1}$) groups. There was a decreasing of wavelength for amide I and increasing for amide II groups after filtration with Ca^{2+} ions. These results suggested that Ca^{2+} addition resulted in a decrease of α -helix and an increase of β -sheet of zein. The presence of Ca^{2+} strengthened the hydrophobic effects due to the fact that Ca^{2+} caused the electrostatic screening and impaired the electrostatic repulsive forces among zein particles.

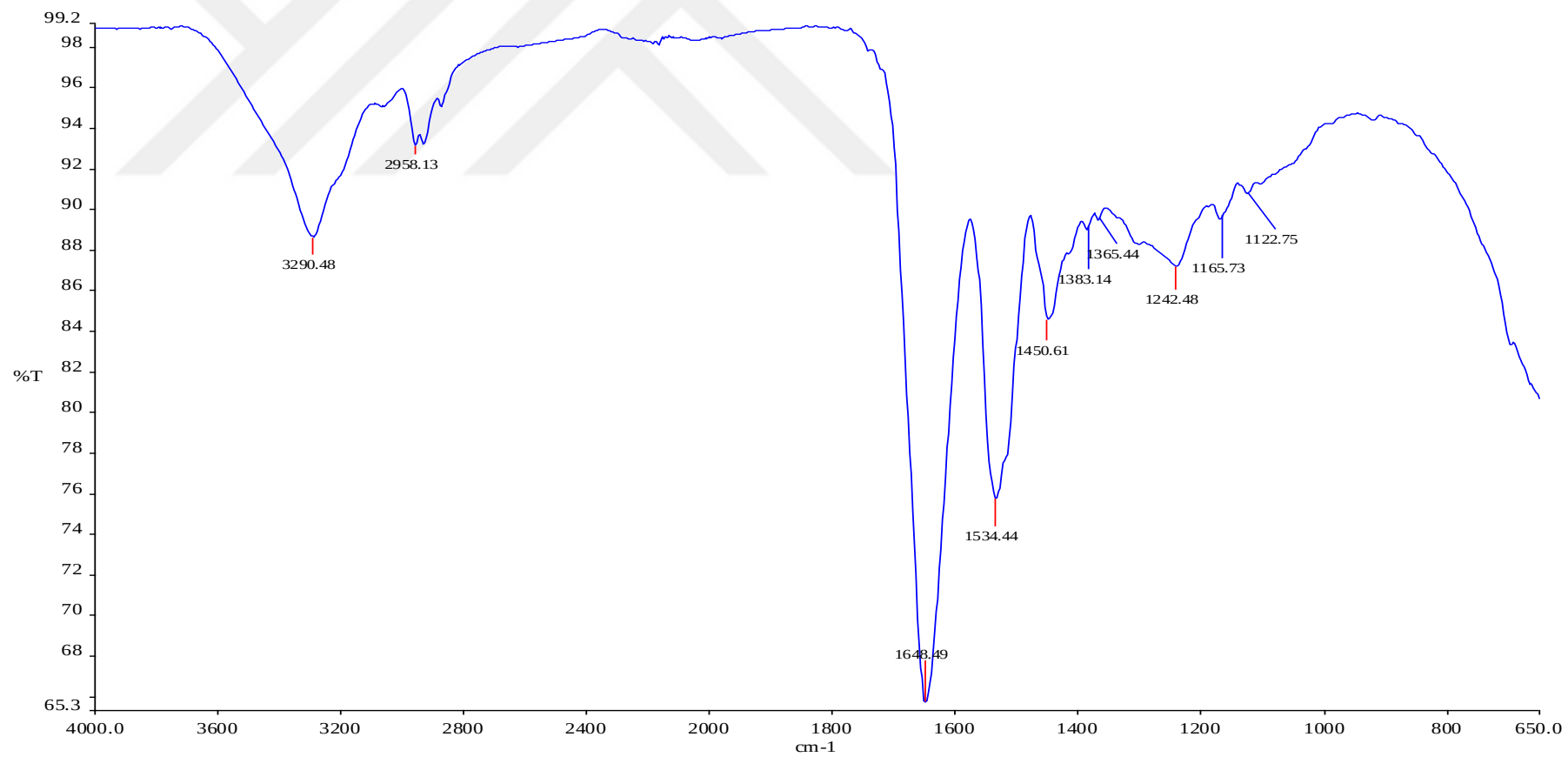


Figure 3.2: FTIR spectra of 30% (w/v) zein membrane before filtration

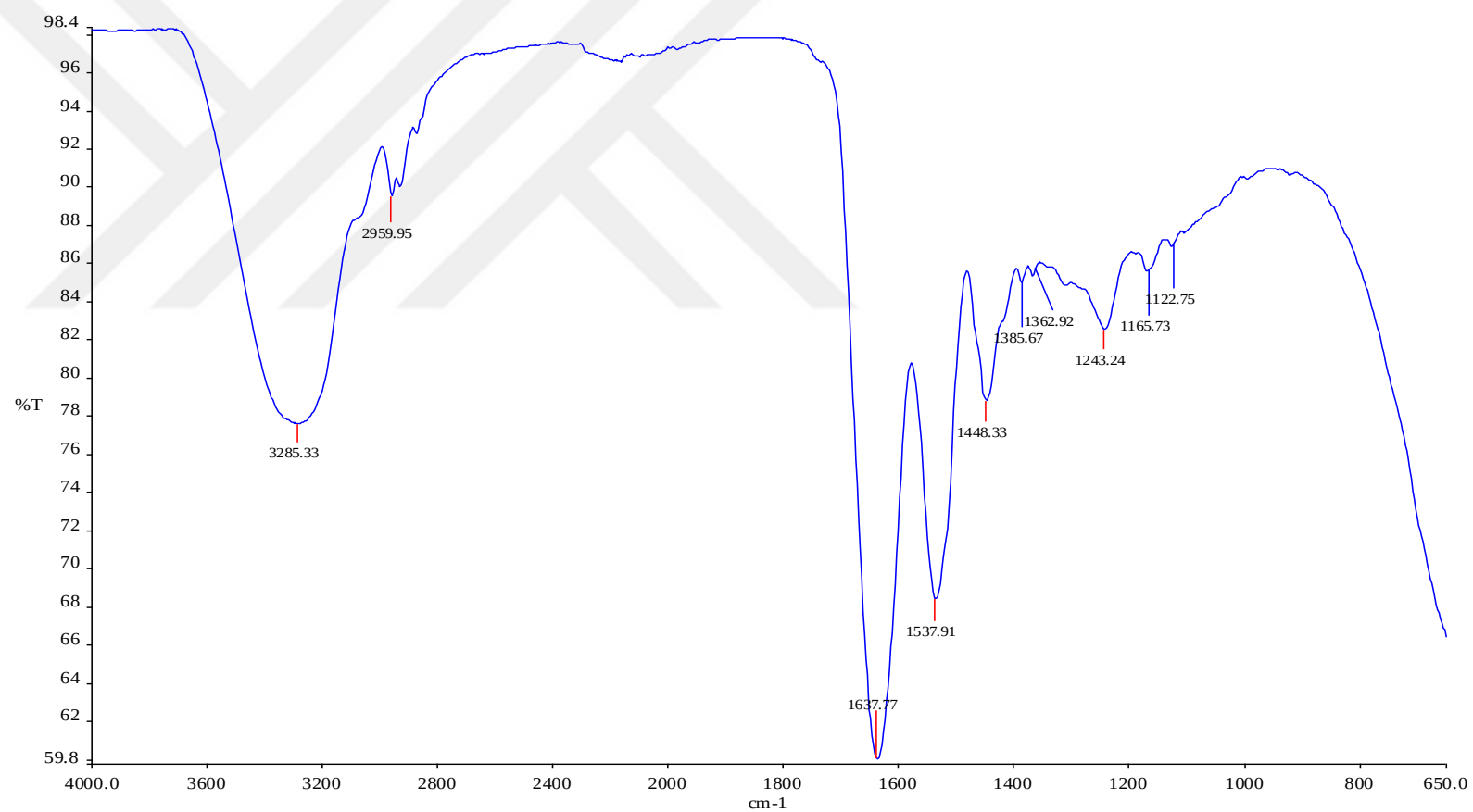


Figure 3.3: FTIR spectra of 30% (w/v) zein membrane after filtration (5% (w/v) CaCl_2 containing water

3.2.3 Zeta potential and electrical conductivity

Zeta potential analysis were performed for zein membrane before and after filtration with 1%, 5%, 10% and 15% magnesium chloride and 1%, 5%, 10% and 15% calcium chloride dihydrate solutions. The results were given in Figure 3.4 and 3.5 for calcium chloride dihydrate and magnesium chloride solutions, respectively. According to the results, for the membrane in which the calcium chloride is filtered, zeta potential value of membrane (1% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution filtered) was higher from zein membrane before filtration. Similar results were obtained for 5% and 10% CaCl_2 solution filtered membrane. However, 15% CaCl_2 solution filtered membrane have lower zeta potential comparatively to 5% and 10% CaCl_2 solution filtered membrane. This may be due to the fact that the fiber diameter is very different for obtained membrane. Even in a small sample taken for the SEM analysis, the fiber has variable diameter. Therefore, the performance of the membrane can vary between samples. Due to the interaction between zein molecules and salt ions, we would expect the zeta potential to increase as the increasing salt concentration of filtered water. Similar findings were obtained for MgCl_2 solution filtered zein membrane. As seen in the graph, for the membrane in which the magnesium chloride is filtered, zeta potential value of membrane (1% MgCl_2 and 5% MgCl_2 solution filtered) was higher from zein membrane before filtration statistically. However, 10% and 15% MgCl_2 solution filtered membrane have almost the same zeta potential value with 5% MgCl_2 solution filtered membrane statistically.

Electrical conductivity analysis was performed on membrane before and after filtration of water to interpret whether the membrane hold salt ions. The measument were realized for membrane before and after filtration of water to understand there was any electrical charge change on membrane. As seen in the Figure 3.4, 3.5 and Table 3.1, 3.2, the conductivity increased with calcium chloride dihydrate concentration. However, 10% and 15% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution filtered membrane had lower conductivity compared to 5% filtered one. As indicated before, this may be due to the fact that the fiber diameter is not dispersed homogenously on the membrane. For MgCl_2 solution filtered membrane, the conductivity increased with increasing MgCl_2 ratio. The results showed that membrane held the salt ions and the electrical charge on membrane increased with increasing Mg^{2+} ions.

Table 3.1: Zeta potential and electrical conductivity for membrane samples that used for water filtration at 1%, 5%, 10% and 15% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (w/v) concentrations

Sample No	Zeta Potential (mV)	Conductivity (mS/cm)
Zein nanofiber membrane before filtration	-30.35 ± 2.28	0.162 ± 0.001581
Filtered zein membrane (1% CaCl_2)	-11.20 ± 0.21	0.218 ± 0.0120
Filtered zein membrane (5% CaCl_2)	-8.99 ± 0.19	0.793 ± 0.0239
Filtered zein membrane (10% CaCl_2)	-1.48 ± 0.49	0.519 ± 0.0257
Filtered zein membrane (15% CaCl_2)	-11.27 ± 0.82	0.52 ± 0.00616

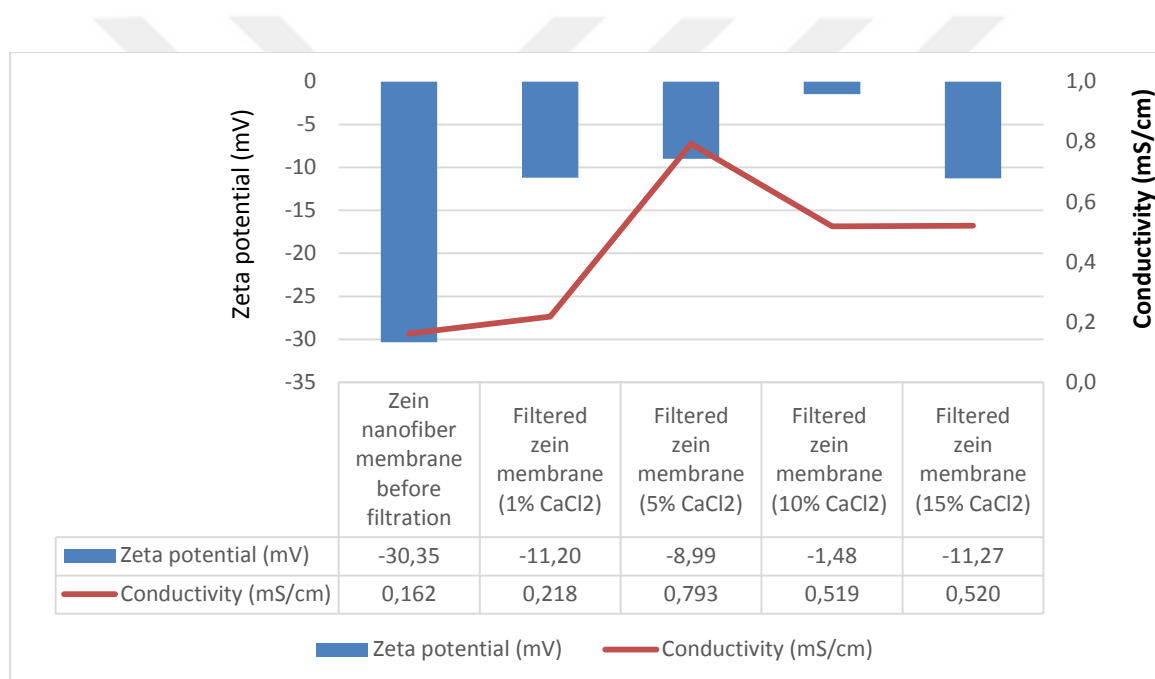


Figure 3.4: Zeta potential and electrical conductivity for membrane samples that used for water filtration at 1%, 5%, 10% and 15% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (w/v) concentrations

Table 3.2: Zeta potential and electrical conductivity for membrane samples that used for water filtration at 1%, 5%, 10% and 15% MgCl₂ (w/v) concentrations

Sample No	Zeta Potential (mV)	Conductivity (mS/cm)
Zein nanofiber membrane before filtration	-30.35 ± 2.28	0.162 ± 0.001581
Filtered zein membrane (1% MgCl ₂)	-19.80 ± 0.92	0.136 ± 0.001247
Filtered zein membrane (5% MgCl ₂)	-14.07 ± 1.13	0.222 ± 0.001247
Filtered zein membrane (10% MgCl ₂)	-14.77 ± 1.11	0.850 ± 0.02671
Filtered zein membrane (15% MgCl ₂)	-14.70 ± 1.59	2.597 ± 0.157551

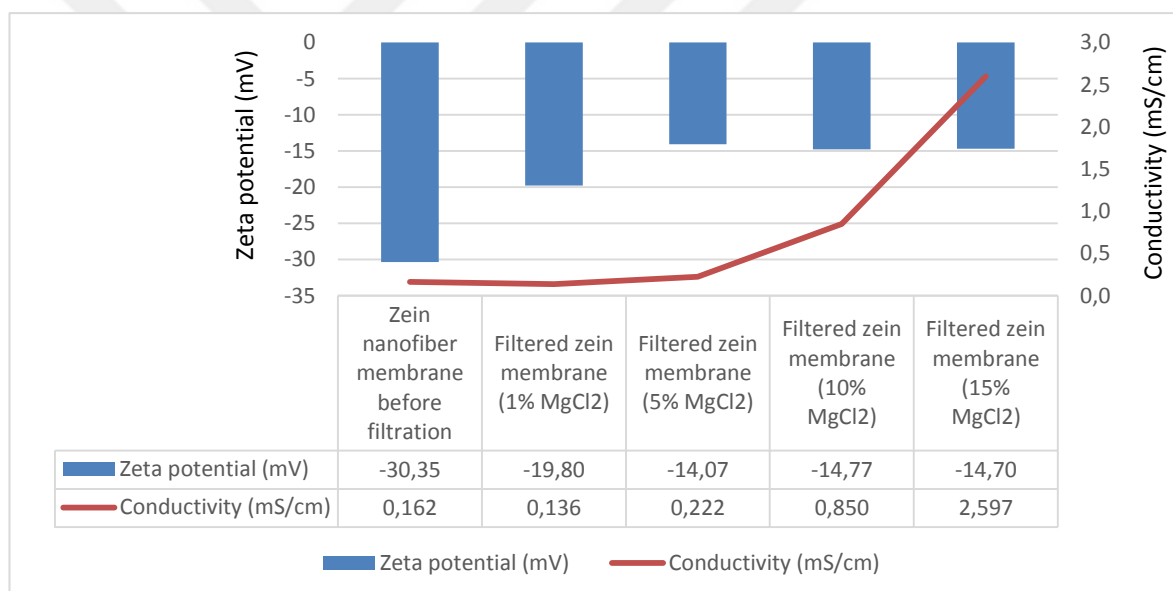


Figure 3.5: Zeta potential and electrical conductivity for membrane samples that used for water filtration at 1%, 5%, 10% and 15% MgCl₂ (w/v) concentrations

3.2.4 Thickness

Three different membrane thickness were used during filtration process. The membranes were obtained with the same feed electrospinning solution. The measurement results are 0.04 mm, 0.12 mm and 0.28 mm. During filtration process, the membranes that have 0.04 mm and 0.12 mm were damaged after a while during filtration. However, membrane that have 0.28 mm thickness have mechanical

strength and not damaged during filtration. Therefore, filtration process carried on only for membrane that have 0.28 mm thickness and water analysis were performed for 0.28 mm thickness membrane.

3.3 Characterization of water before and after filtration

3.3.1 Zeta potential and electrical conductivity

To measure the effectiveness of membrane in terms of hardness removal, zeta potential and electrical conductivity analysis were performed before and after filtration and the results were compared. Firstly, the zeta potential and electrical conductivity analysis were performed before water filtration for samples that have different $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ratio. As seen on the Figure 3.6, 3.7 and Table 3.3, 3.4, with the increase of Mg^{2+} or Ca^{2+} in water, the zeta potential and electrical conductivity of water sample increased.

Table 3.3: Zeta potential and electrical conductivity for water samples before filtration at 1%, 5%, 10% and 15% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (w/v) concentrations

Sample No	Zeta Potential (mV)	Conductivity (mS/cm)
1% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	-1.372 ± 0.13	17.00 ± 1.70
5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	1.505 ± 0.38	51.95 ± 0.05
10% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	3.93 ± 0.23	88.15 ± 1.80
15% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	7.72 ± 0.42	108.00 ± 3.62

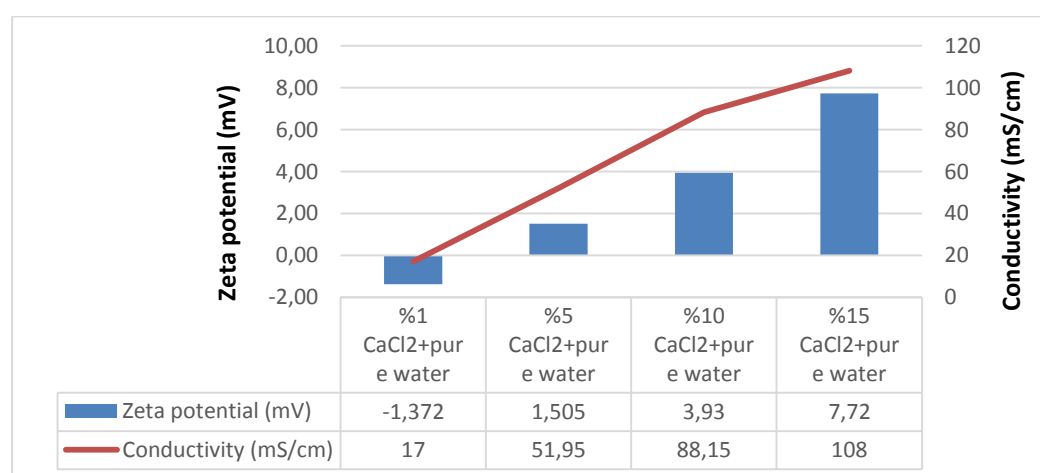


Figure 3.6: Zeta potential and electrical conductivity for water samples before filtration at 1%, 5%, 10% and 15% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (w/v) concentrations

Table 3.4: Zeta potential and electrical conductivity for water samples before filtration at 1%, 5%, 10% and 15% MgCl₂ (w/v) concentrations

Sample No	Zeta Potential (mV)	Conductivity (mS/cm)
1% MgCl ₂ + pure water	-3.17 ± 0.72	10.95 ± 0.45
5% MgCl ₂ + pure water	4.99 ± 0.99	41.43 ± 0.68
10% MgCl ₂ + pure water	11.15 ± 2.63	72.30 ± 1.43
15% MgCl ₂ + pure water	31.14 ± 3.87	95.50 ± 0.49

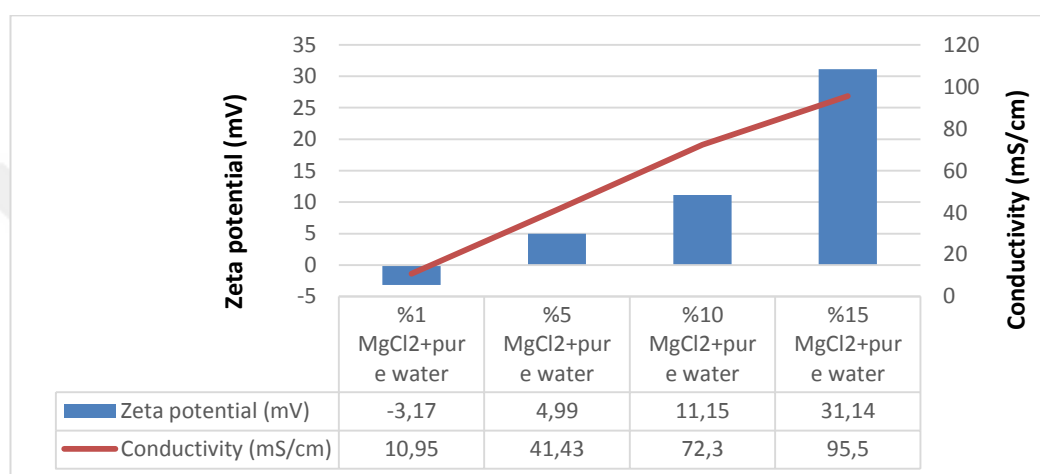


Figure 3.7: Zeta potential and electrical conductivity for water samples before filtration at 1%, 5%, 10% and 15% MgCl₂ (w/v) concentrations

Secondly, zeta potential and electrical conductivities of water samples were measured after filtration and then compared with initial solution. According to the results, as seen in Table 3.5 and Figure 3.8, zeta potential and electrical conductivity did not significantly ($p < 0.05$) change after filtration at 1% CaCl₂ (w/v) concentration. This situation showed that zein membrane could not hold Ca²⁺ ions at this concentration.

Table 3.5: Zeta potential and electrical conductivity of water samples prepared with 1% CaCl₂.2H₂O (w/v) before and after filtration

Sample No	Zeta Potential (mV)	Conductivity (mS/cm)
1% CaCl ₂ .2H ₂ O + pure water- before filtration	-1.372 ± 0.13	17.00 ± 1.70
1% CaCl ₂ .2H ₂ O + pure water- after filtration	-1.34 ± 0.19	18.75 ± 1.30

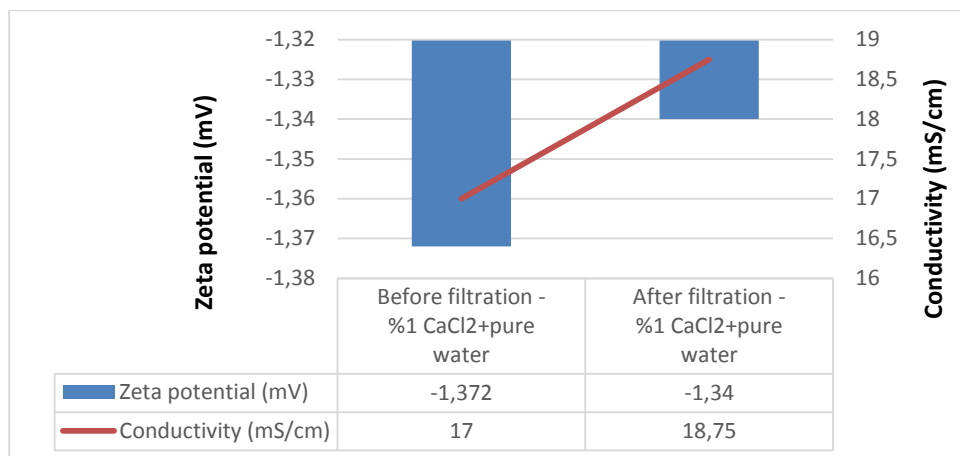


Figure 3.8: Zeta potential and electrical conductivity of water samples prepared with 1% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (w/v) before and after filtration

For 5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (w/v), as seen in Table 3.6 and Figure 3.9, zeta potential increased significantly ($p < 0.05$) and electrical conductivity decreased after filtration significantly ($p < 0.05$).

Table 3.6: Zeta potential and electrical conductivity of water samples prepared with 5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (w/v) before and after filtration

Sample No	Zeta Potential (mV)	Conductivity (mS/cm)
5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water- before filtration	-1.505 ± 0.54	51.95 ± 0.05
5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water- after filtration	7.91 ± 0.94	45.97 ± 0.84

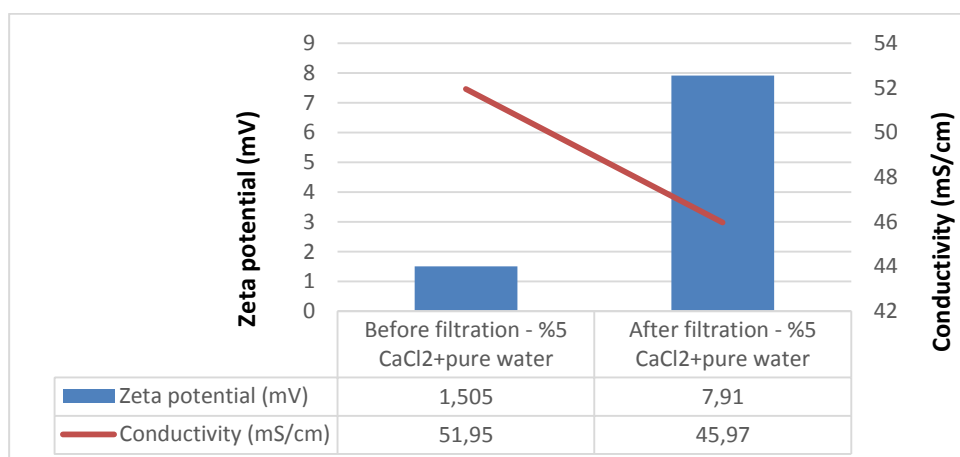


Figure 3.9: Zeta potential and electrical conductivity of water samples prepared with 5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (w/v) before and after filtration

For 10% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (w/v), zeta potential and electrical conductivity results changed significantly after filtration. As seen in Table 3.7 and Figure 3.10, zeta potential and electrical conductivity decreased after filtration significantly ($p < 0.05$).

Table 3.7: Zeta potential and electrical conductivity of water samples prepared with 10% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (w/v) before and after filtration

Sample No	Zeta Potential (mV)	Conductivity (mS/cm)
10% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water- before filtration	3.93 ± 0.23	88.15 ± 1.80
10% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water- after filtration	-0.559 ± 0.14	18.73 ± 1.62

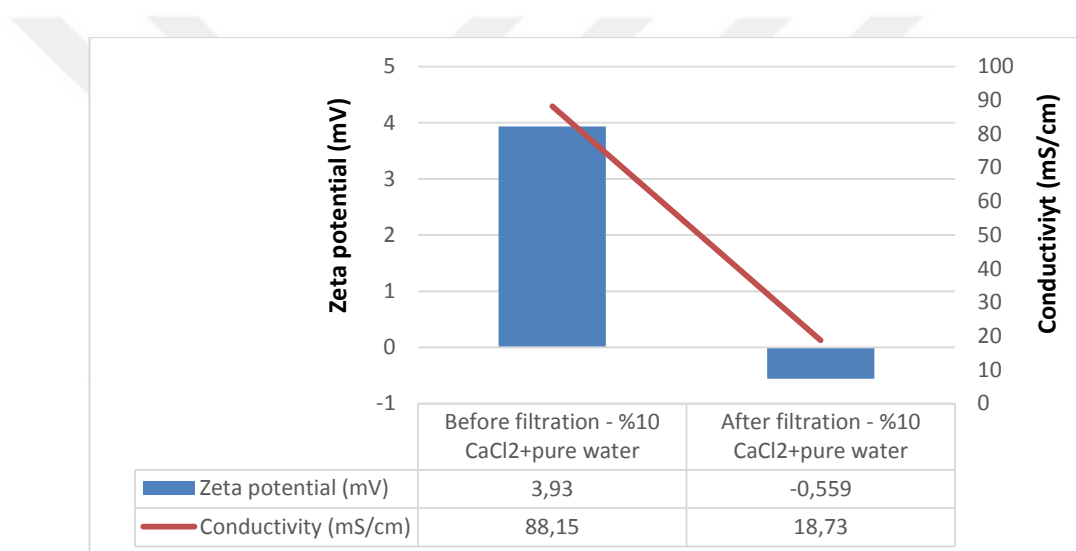


Figure 3.10: Zeta potential and electrical conductivity of water samples prepared with 10% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (w/v) before and after filtration

For 15% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (w/v), as seen in Table 3.8 and Figure 3.11, zeta potential was significantly ($p < 0.05$) lower and electrical conductivity decreased after filtration significantly ($p < 0.05$)

Table 3.8: Zeta potential and electrical conductivity of water samples prepared with 15% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (w/v) before and after filtration

Sample No	Zeta Potential (mV)	Conductivity (mS/cm)
15% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water- before filtration	7.72 ± 0.42	108 ± 3.62
15% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water- after filtration	-3.79 ± 0.14	72.9 ± 3.53

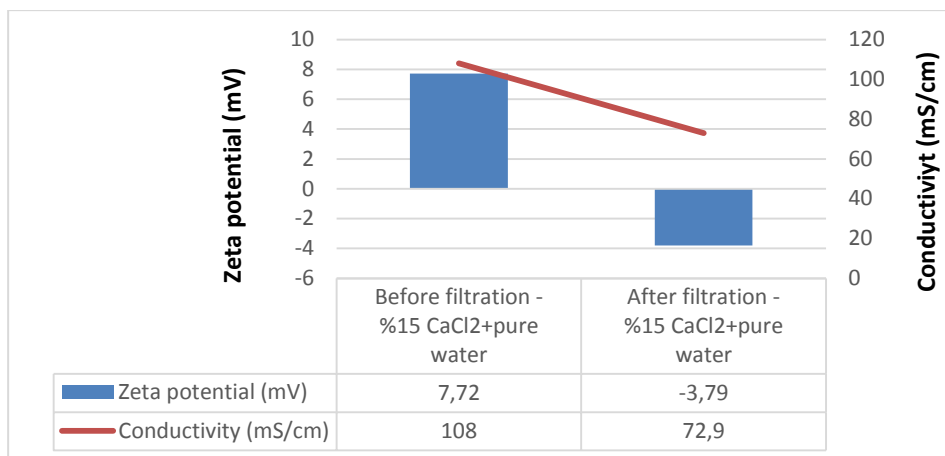


Figure 3.11: Zeta potential and electrical conductivity of water samples prepared with 15% CaCl₂.2H₂O (w/v) before and after filtration

For 1% MgCl₂ (w/v), as seen in Table 3.9 and Figure 3.12, zeta potential and electrical conductivity were not change after filtration significantly ($p < 0.05$). This situation showed that zein membrane can not hold Mg²⁺ ions at this concentration.

Table 3.9: Zeta potential and electrical conductivity of water samples prepared with 1% MgCl₂ (w/v) before and after filtration

Sample No	Zeta Potential (mV)	Conductivity (mS/cm)
1% MgCl ₂ + pure water- before filtration	-3.17 ± 1.02	10.95 ± 0.45
1% MgCl ₂ + pure water- after filtration	-1.788 ± 0.29	11.27 ± 1.90

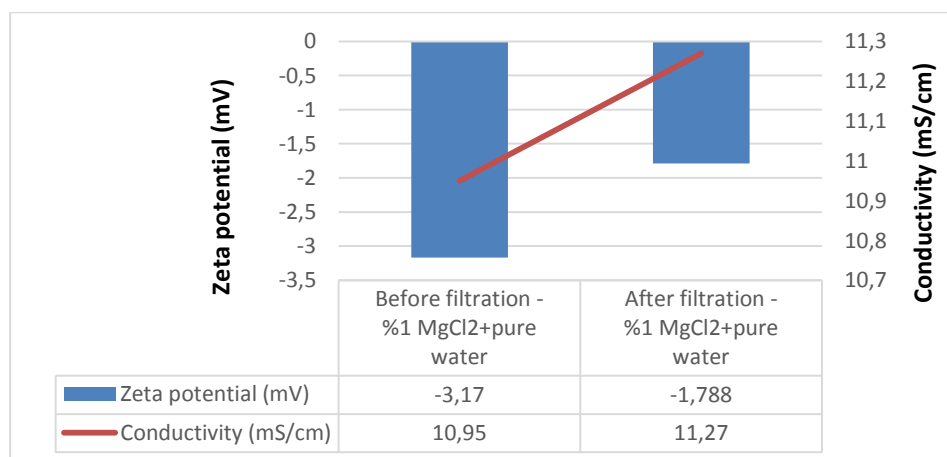


Figure 3.12: Zeta potential and electrical conductivity of water samples prepared with 1% MgCl₂ (w/v) before and after filtration

For 5% MgCl_2 (w/v), as seen in Table 3.10 and Figure 3.13, zeta potential and electrical conductivity decrease after filtration significantly ($p < 0.05$).

Table 3.10: Zeta potential and electrical conductivity of water samples prepared with 5% MgCl_2 (w/v) before and after filtration

Sample No	Zeta Potential (mV)	Conductivity (mS/cm)
5% MgCl_2 + pure water- before filtration	4.99 ± 1.22	41.43 ± 0.68
5% MgCl_2 + pure water- after filtration	-2.36 ± 1.20	8.73 ± 1.04

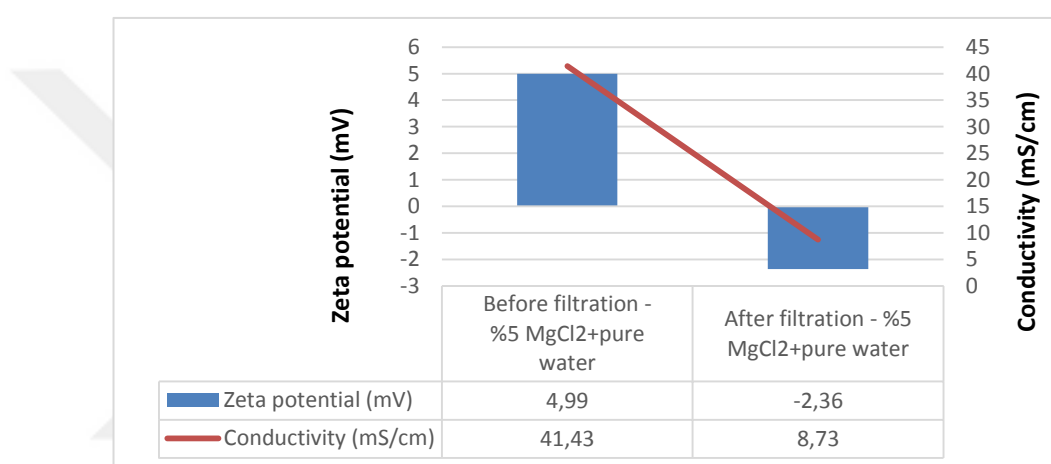


Figure 3.13: Zeta potential and electrical conductivity of water samples prepared with 5% MgCl_2 (w/v) before and after filtration

For 10% MgCl_2 (w/v), as seen in Table 3.11 and Figure 3.14, zeta potential and electrical conductivity decrease after filtration significantly ($p < 0.05$).

Table 3.11: Zeta potential and electrical conductivity of water samples prepared with 10% MgCl_2 (w/v) before and after filtration

Sample No	Zeta Potential (mV)	Conductivity (mS/cm)
10% MgCl_2 + pure water- before filtration	11.15 ± 3.22	72.30 ± 1.43
10% MgCl_2 + pure water- after filtration	-3.83 ± 0.24	35.90 ± 5.16

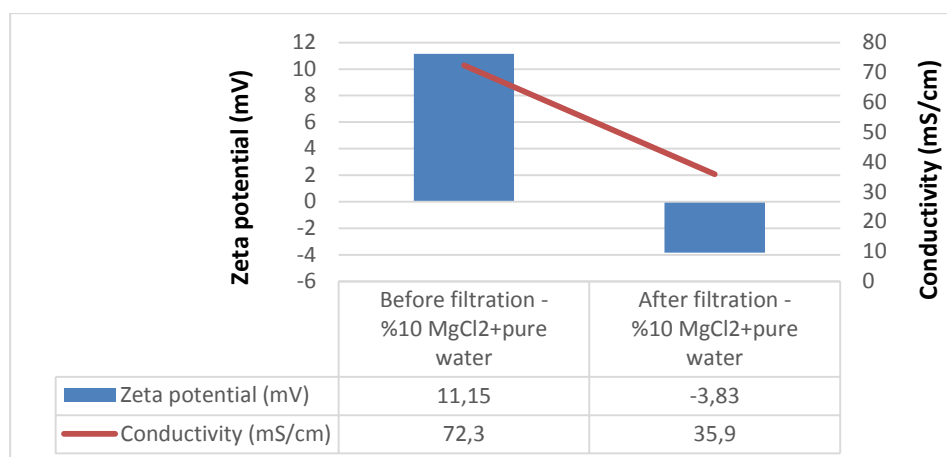


Figure 3.14: Zeta potential and electrical conductivity of water samples prepared with 10% MgCl₂ (w/v) before and after filtration

For 15% MgCl₂ (w/v), as seen in Table 3.12 and Figure 3.15, zeta potential and electrical conductivity decrease after filtration significantly ($p < 0.05$).

Table 3.12: Zeta potential and electrical conductivity of water samples prepared with 15% MgCl₂ (w/v) before and after filtration

Sample No	Zeta Potential (mV)	Conductivity (mS/cm)
15% MgCl ₂ + pure water- before filtration	31.14 ± 3.87	95.50 ± 0.49
15% MgCl ₂ + pure water- after filtration	-1.458 ± 0.07	32.40 ± 0.42

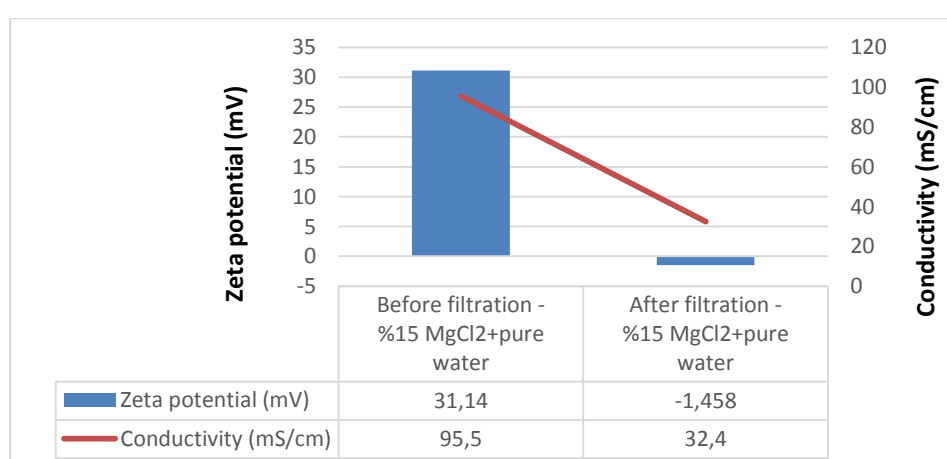


Figure 3.15: Zeta potential and electrical conductivity of water samples prepared with 15% MgCl₂ (w/v) before and after filtration

3.4 Performance of membrane filtration

The filtration performance of the membrane is evaluated by the percent rejection (R%) of feed materials (Table 3.13). According to the results, the rejection rate was high for 10% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ containing water and 5% MgCl_2 containing water between all samples.

Table 3.13: Rejection rate calculation

Sample No	Concentration of water before filtration (%)	Concentration of water after filtration (%) ^{1,2}	Rejection rate (%)
1% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	1	—*	—*
5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	5	4.06	18.80
10% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	10	1.66	83.40
15% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	15	7.75	48.33
1% MgCl_2 + pure water	1	—*	—*
5% MgCl_2 + pure water	5	0.73	85.40
10% MgCl_2 + pure water	10	4.83	51.70
15% MgCl_2 + pure water	15	4.21	71.93

*There was no decrease in concentration after filtration of water. Therefore, the rejection rate could not be calculated.

¹The measured electrical conductivity of samples that prepared with different ration of calcium chloride were shown in Table 3.14.

Table 3.14: Electrical conductivity of water samples ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$)

Sample Name	Electrical conductivity (mS/cm)
1% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	17.00 ± 1.70
2% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	22.70 ± 1.37
3% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	31.87 ± 2.87
4% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	36.73 ± 0.97
5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	51.95 ± 0.05
6% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	56.93 ± 0.17
7% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	67.50 ± 0.43
8% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	75.43 ± 0.31
9% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	82.90 ± 0.36
10% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	88.15 ± 1.80
11% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	90.70 ± 1.00
12% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	92.67 ± 0.69
13% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	96.70 ± 1.08
14% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	104.67 ± 1.24
15% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ + pure water	108.00 ± 3.62

As indicated before, the final concentration of sample was calculated by using the electrical conductivity of water after filtration. A graph was obtained based on the results (Figure 3.16) and polynomial equation was obtained with correction factor (R^2)= 0.9893.

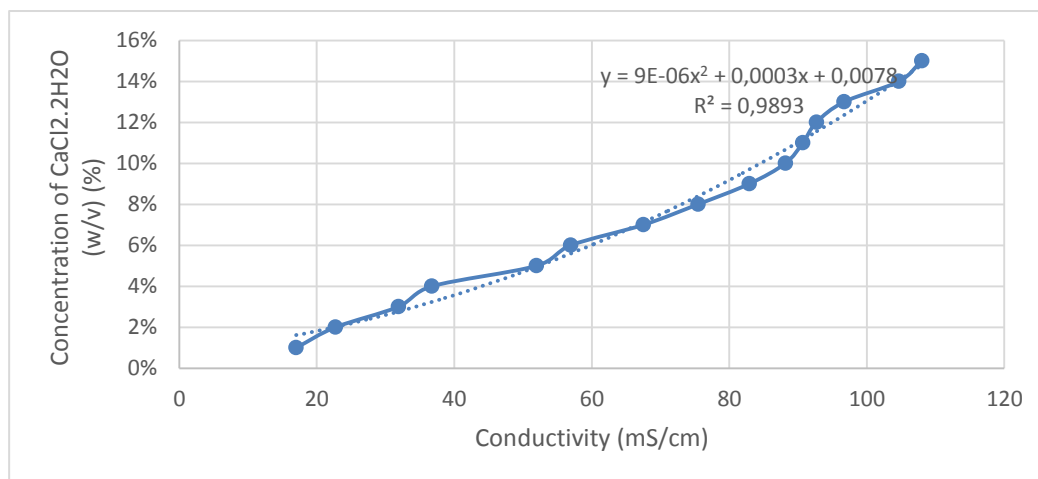


Figure 3.16: Electrical conductivity of water with respect to concentration of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in water

According to the polynomial equation that obtained from graph, approximately calculated concentrations of water after filtration were shown in Table 3.15.

Table 3.15: The concentration of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ containing water after filtration

Initial concentration	Final electrical conductivity (mS/cm)	Final concentration (%)
1% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ *	—*	—*
5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	45.98	4.06
10% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	18.73	1.66
15% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	72.9	7.75

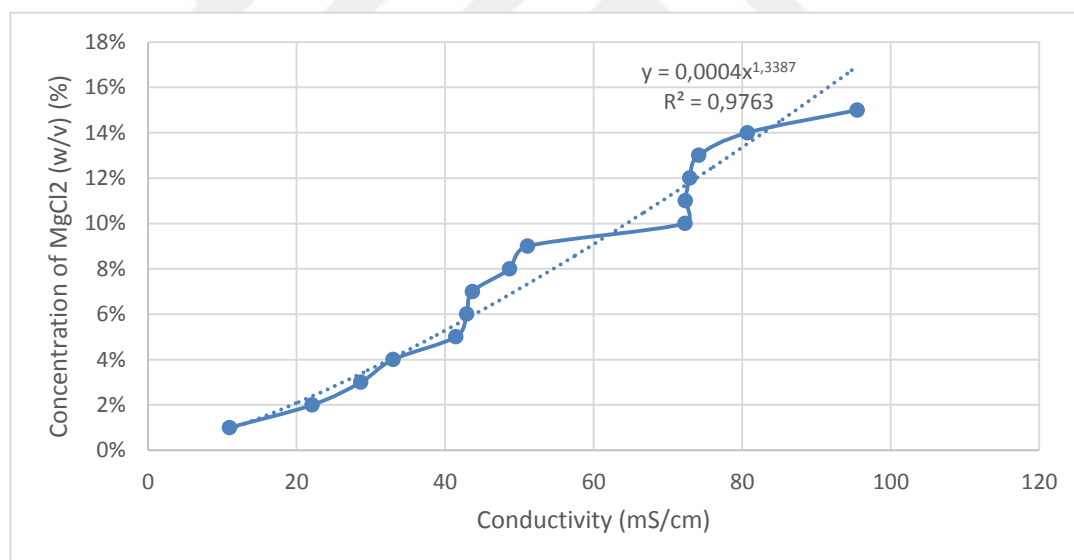
*There was no decrease in final electrical conductivity, so the final concentration of water after filtration could not be calculated.

² The measured electrical conductivity of samples that prepared with different ratio magnesium chloride were showed in Table 3.16.

Table 3.16: Electrical conductivity of water samples (MgCl₂)

Sample Name	Electrical conductivity (mS/cm)
1% MgCl ₂ + pure water	10.95 ± 0.45
2% MgCl ₂ + pure water	22.10 ± 1.60
3% MgCl ₂ + pure water	28.65 ± 0.35
4% MgCl ₂ + pure water	33.00 ± 0.10
5% MgCl ₂ + pure water	41.43 ± 0.68
6% MgCl ₂ + pure water	42.90 ± 2.00
7% MgCl ₂ + pure water	43.70 ± 0.30
8% MgCl ₂ + pure water	48.70 ± 0.20
9% MgCl ₂ + pure water	51.10 ± 0.50
10% MgCl ₂ + pure water	72.30 ± 1.43
11% MgCl ₂ + pure water	72.35 ± 4.45
12% MgCl ₂ + pure water	72.95 ± 0.55
13% MgCl ₂ + pure water	74.15 ± 0.65
14% MgCl ₂ + pure water	80.70 ± 0.90
15% MgCl ₂ + pure water	95.50 ± 0.49

A graph was obtained based on the results (Figure 3.17) and power equation was obtained with correction factor (R^2) = 0.9763.

**Figure 3.17:** Electrical conductivity with respect to concentration of MgCl₂ in water

According to the power equation that obtained from graph, calculated concentrations of water after filtration were showed in Table 3.17.

Table 3.17: The concentration of MgCl₂ containing water after filtration

Initial concentration	Final electrical conductivity (mS/cm)	Final concentration (%)
1% MgCl ₂ *	-*	-*
5% MgCl ₂	8.73	0.73
10% MgCl ₂	35.90	4.83
15% MgCl ₂	32.40	4.21

*There was no decrease in final electrical conductivity, so the final concentration of water after filtration could not be calculated.

According to Wei et al, polysulfone/polyethersulfone hollow fiber UF supporting membranes had different rejection ratio and permeate flux. The results showed that the mean rejection rate of the membrane to different salts follows the sequence of MgSO₄ > Na₂SO₄ > MgCl₂ > NaCl. This finding is hardly explained by the Donnan exclusion effect, because neither Mg²⁺ nor (SO₄)²⁻ exhibits poor rejection. The rejection rates were 96.2, 95.9, 89.2 and 39.8%, respectively (2013).

NF membranes, generally, are able to reject divalent ions up to 98% while the rejection rate of monovalent varies from 30% to 85% depending on the ion size and the type of NF membrane. According to the research, the rejection rate of Filmtec NF membrane NF90-400 to MgSO₄ is > 97%. The concentration of used seawater in this study is varied from 37,000 ppm to 43,000 ppm (AlTae & Sharif, 2011). According to the another study, the applicability of nanofiltration (NF) was investigated as a pre-treatment stage of reverse osmosis (RO) process for seawater desalination. The single SW30-RO membrane showed an average rejection of 98.2% for salinity and the average permeate flux of single SW30-RO membrane was 30.1L/h*m² (Kaya et al., 2015).

3.5 Outcome

Main strategic purpose of utilization of zein membrane that obtained by electrospinning technique in the present work was to remove hardness from water. The main reasons to use zein protein as a membrane material is that it is a natural material and have hydrophobic properties.

Firstly, zein membrane was obtained by electrospinning method. According to SEM images, the obtained fibers were not at a nanoscale. To obtain a fiber at nano scale,

process conditions should be changed, especially applied voltage may be increased to obtain low fiber diameter.

To measure the effectiveness of membrane to remove hardness from water, electrical conductivity and zeta potential analysis were performed on water and zein membrane before and after filtration. Also, rejection rate was calculated to have an idea about the performance of the membrane. As a result of the experiments, it was assumed that zein membrane may hold salt ions when the required conditions were provided and with the optimization studies it may be used as a filtration membrane to remove hardness from salty water (ocean, seawater etc.).





4. CONCLUSIONS AND RECOMMENDATIONS

Water is the most valuable source for humanity and it is under serious coercion. According to the studies, water scarcity will arise in the future because of the atmospheric deposition, domestic, industrial and agricultural implementations. So, current water filtration methods should be the optimized and new techniques should be developed to increase the usable water resources.

Electrospinning process is an effective method to make nanometer scale fibers and highly porous nanofiber membranes with nano- to micro-meter scale pores. Membrane distillations by using nanofiber membranes is a novel approach and have great future in desalination of seawater, water treatment, removal of organic volatile compounds from industrial waste water. In particular, hydrophobicity of polymeric material is enhanced significantly at the nanofiber membrane surface, which is one of the desirable properties for applications for membrane distillation. In recent years, research groups have paid more attention to the functionalities of electrospun nanofibers.

Membrane technology plays an important role to remove the contaminants from water. Although many materials are under investigation, nanofibers driven membrane are more valuable and reliable. Membranes obtained from nanofibrous materials offer high surface area to volume ratio, fine tunable pore sizes. Also, their ease of preparation prompted both industry and academic researchers to study their use in water filtration or purification. This technology represents many benefits such as high throughput, high rejection, high durability, low energy consumption and low cost. There have been many studies to remove hardness from water through filtration by using synthetic polymers such as polyacrylonitrile (PAN), polysulfone (PSU), polyethersulfone (PES) or polyvinylidene fluoride (PVDF). However, there have been no study using the zein membrane obtained by using electrospinning method. As an alternative to current filtration techniques for water softening, zein membrane filtration technique can be an effective option.

According to the electrical conductivity and zeta potential analysis result, zein membrane was effective to remove hardness from salty water. When Ca^{2+} concentration of water is higher than 10% and Mg^{2+} concentration of water is higher than 5%, the electrical conductivity and zeta potential of water decreased after filtration. It shows that the Mg^{2+} and Ca^{2+} ions in the water decreased after filtration. In order to determine the minimum amount of salt that it should have in order to remove hardness from salty water, optimization studies can be carried out by changing the fiber diameter and membrane thickness especially for further studies. The experiments to determine the optimum conditions are generally conducted in such a manner as to study one factor at a time. This means the interactions of factors have been omitted that may result in incorrect conclusions because of ignoring interaction of factors. Statistical experimental designs can be used to investigate the effect of all the possible combinations of the factors by making fewer possible experiments.

According to SEM images of fiber, the average diameter of fiber 1082 nm. The fiber diameter is not at nano scale. To obtain nanofiber, process conditions should be optimized. The applied voltage was 1.8 kV during electrospinning process. It is a very low voltage value to obtain nanofiber. The applied voltage can be increased to obtain nanofiber and SEM images should be taken from more samples.

The membrane charge originates from the dissociation of ionizable groups at the membrane surface and from within the membrane pore structure. These groups may be acidic or basic in nature or indeed a combination of both depending on the specific materials used during the fabrication process. The dissociation of these surface groups is strongly influenced by the pH of the contacting solution and the membrane may exhibit an isoelectric point at a specific pH. In this study, pH was not considered as a parameter. For the optimization studies, pH should be considered and isoelectric point should be determined. Because, the rejection rate was affected from the pH.

The results of this work showed that the zein membrane obtained by electrospinning method may be used for hardness removal from salty water when the required conditions were provided. In this study, only natural biopolymer zein was used to obtain membrane. During filtration, the obtained zein membrane exhibited weak

mechanical strength when the pressure was applied. In order to long-term usage of membrane and usage in large-scale production, optimization studies should be carried out. Synthetic polymers such as PAN may be added as membrane layer to increase the mechanical strength of membrane. Preliminary studies should be carried on with the real salty water. This study showed that the zein membrane obtained by the electrospinning method can retain the calcium and magnesium cations in the water that cause hardness





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APPENDICES

APPENDIX A: Zeta potential and electrical conductivity of pure water, zein nanofiber membrane and zein powder

APPENDIX B: Zeta potential and electrical conductivity of 1%CaCl₂.2H₂O +pure water before and after filtration, zein nanofiber membrane before and after filtration

APPENDIX C: Zeta potential and electrical conductivity of 5%CaCl₂.2H₂O +pure water before and after filtration, zein nanofiber membrane before and after filtration results

APPENDIX D: Zeta potential and electrical conductivity of 10% CaCl₂.2H₂O +pure water before and after filtration, zein nanofiber membrane before and after filtration results

APPENDIX E: Zeta potential and electrical conductivity of 15% CaCl₂.2H₂O +pure water before and after filtration, zein nanofiber membrane before and after filtration results

APPENDIX F: Zeta potential and electrical conductivity of 1% MgCl₂ +pure water before and after filtration, zein nanofiber membrane before and after filtration results

APPENDIX G: Zeta potential and electrical conductivity of 5% MgCl₂ +pure water before and after filtration, zein nanofiber membrane before and after filtration results

APPENDIX H: Zeta potential and electrical conductivity of 10% MgCl₂ +pure water before and after filtration, zein nanofiber membrane before and after filtration results

APPENDIX I: Zeta potential and electrical conductivity of 15% MgCl₂ +pure water before and after filtration, zein nanofiber membrane before and after filtration results

APPENDIX A

Table A.1: Statistical zeta potential and electrical conductivity of pure water (I), zein nanofiber membrane (II) (0.1% (w/v)) and zein powder (III) (0.1% (w/v)) results

Variable	I, II, III samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	279.64	2	139.532	33.106	.000
	Within Groups	33.718	8	4.215		
	Total	312.782	10			
Electrical conductivity	Between Groups	.010	2	.005	1007.976	.000
	Within Groups	.000	8	.000		
	Total	.010	10			

Table A.2: Multiple comparisons of zeta potential and electrical conductivity of pure water (I), zein nanofiber membrane (II) (0.1%) and zein powder (III) (0.1%) results

Variable	(I) result	(J) result	Mean Difference		Sig.	95% Confidence Interval	
			(I-J)	Std. Error		Lower Bound	Upper Bound
Zeta Potential	I	II	12.75000*	1.56798	.000	8.2696	17.2304
		III	7.67500*	1.56798	.003	3.1946	12.1554
	II	I	-12.75000*	1.56798	.000	-17.2304	-8.2696
		III	-5.07500*	1.45167	.020	-9.2231	-.9269
	III	I	-7.67500*	1.56798	.003	-12.1554	-3.1946
		II	5.07500*	1.45167	.020	.9269	9.2231
Electrical Conductivity	I	II	-.0763000*	.0017326	.000	-.081251	-.071349
		III	-.0560500*	.0017326	.000	-.061001	-.051099
	II	I	.0763000*	.0017326	.000	.071349	.081251
		III	.0202500*	.0016041	.000	.015666	.024834
	III	I	.0560500*	.0017326	.000	.051099	.061001
		II	-.0202500*	.0016041	.000	-.024834	-.015666

*. The mean difference is significant at the 0.05 level.

APPENDIX B

Table B.1: Statistical zeta potential and electrical conductivity of 1%CaCl₂.2H₂O +pure water (IV) before and after filtration (V) results

Variable	IV, V samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	.001	1	.001	.002	.970
	Within Groups	1.148	2	.574		
	Total	1.149	3			
Electrical conductivity	Between Groups	3.063	1	3.063	.650	.505
	Within Groups	9.425	2	4.713		
	Total	12.488	3			

Table B.2: Statistical zeta potential and electrical conductivity of zein nanofiber membrane (II) before and after filtration (VI) results

Variable	II, VI samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	657.636	1	657.636	133.769	.000
	Within Groups	34.413	7	4.916		
	Total	692.049	8			
Electrical conductivity	Between Groups	.009	1	.009	31.613	.001
	Within Groups	.002	7	.000		
	Total	.011	8			

APPENDIX C

Table C.1: Statistical zeta potential and electrical conductivity of 5%CaCl₂.2H₂O +pure water (VII) before and after filtration (VIII) results

Variable	VII, VIII samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	49.280	1	49.280	71.334	.003
	Within Groups	2.073	3	.691		
	Total	51.353	4			
Electrical conductivity	Between Groups	42.960	1	42.960	91.297	.002
	Within Groups	1.412	3	.471		
	Total	44.372	4			

Table C.2: Statistical zeta potential and electrical conductivity of zein nanofiber membrane (II) before and after filtration (IX) results

Variable	II, IX samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	827.431	1	827.431	168.446	.000
	Within Groups	34.385	7	4.912		
	Total	861.816	8			
Electrical conductivity	Between Groups	.824	1	.824	1760.310	.000
	Within Groups	.003	7	.000		
	Total	.828	8			

APPENDIX D

Table D.1: Statistical zeta potential and electrical conductivity of 10%CaCl₂.2H₂O +pure water (X) before and after filtration (XI) results

Variable	VII, VIII samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	99.678	1	99.678	264.629	.001
	Within Groups	1.130	3	.377		
	Total	100.808	4			
Electrical conductivity	Between Groups	5782.408	1	5782.408	2705.572	.000
	Within Groups	6.412	3	2.137		
	Total	5788.820	4			

Table D.2: Statistical zeta potential and electrical conductivity of zein nanofiber membrane (II) before and after filtration (XII) results

Variable	II, XII samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	1551.579	1	1551.579	299.572	.000
	Within Groups	36.255	7	5.179		
	Total	1587.834	8			
Electrical conductivity	Between Groups	.271	1	.271	534.669	.000
	Within Groups	.004	7	.001		
	Total	.274	8			

APPENDIX E

Table E.1: Statistical zeta potential and electrical conductivity of 15%CaCl₂.2H₂O +pure water (XIII) before and after filtration (XIV) results

Variable	XIII, XIV samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	170.198	1	170.198	595.580	.026
	Within Groups	.286	1	.286		
	Total	170.483	2			
Electrical conductivity	Between Groups	940.002	1	940.002	20888.926	.004
	Within Groups	.045	1	.045		
	Total	940.047	2			

Table E.2: Statistical zeta potential and electrical conductivity of zein nanofiber membrane (II) before and after filtration (XV) results

Variable	II, XV samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	652.809	1	652.809	125.955	.000
	Within Groups	36.280	7	5.183		
	Total	689.089	8			
Electrical conductivity	Between Groups	.273	1	.273	1145.362	.000
	Within Groups	.002	7	.000		
	Total	.274	8			

APPENDIX F

Table F.1: Statistical zeta potential and electrical conductivity of 1%MgCl₂+pure water (XVI) before and after filtration (XVII) results

Variable	XIII, XIV samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	2.293	1	2.293	2.774	.194
	Within Groups	2.480	3	.827		
	Total	4.773	4			
Electrical conductivity	Between Groups	.120	1	.120	.233	.663
	Within Groups	1.552	3	.517		
	Total	1.672	4			

Table F.2: Statistical zeta potential and electrical conductivity of zein nanofiber membrane (II) before and after filtration (XVIII) results

Variable	II, XV samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	181.769	1	181.769	34.526	.001
	Within Groups	36.853	7	5.265		
	Total	218.622	8			
Electrical conductivity	Between Groups	.000	1	.000	2.022	.198
	Within Groups	.002	7	.000		
	Total	.002	8			

APPENDIX G

Table G.1: Statistical zeta potential and electrical conductivity of 5%MgCl₂+pure water (XIX) before and after filtration (XX) results

Variable	XIX, XX samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	80.953	1	80.953	31.607	.005
	Within Groups	10.245	4	2.561		
	Total	91.198	5			
Electrical conductivity	Between Groups	1603.935	1	1603.935	322.819	.000
	Within Groups	19.874	4	4.969		
	Total	1623.809	5			

Table G.2: Statistical zeta potential and electrical conductivity of zein nanofiber membrane (II) before and after filtration (XXI) results

Variable	II, XXI samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	466.142	1	466.142	85.598	.000
	Within Groups	38.120	7	5.446		
	Total	504.262	8			
Electrical conductivity	Between Groups	.010	1	.010	46.152	.000
	Within Groups	.002	7	.000		
	Total	.012	8			

APPENDIX H

Table H.1: Statistical zeta potential and electrical conductivity of 10%MgCl₂+pure water (XXII) before and after filtration (XXIII) results

Variable	XXII, XXIII samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	336.601	1	336.601	6.663	.061
	Within Groups	202.071	4	50.518		
	Total	538.671	5			
Electrical conductivity	Between Groups	1987.440	1	1987.440	133.565	.000
	Within Groups	59.520	4	14.880		
	Total	2046.960	5			

Table H.2: Statistical zeta potential and electrical conductivity of zein nanofiber membrane (II) before and after filtration (XXIV) results

Variable	II, XXIV samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	424.376	1	424.376	78.257	.000
	Within Groups	37.960	7	5.423		
	Total	462.336	8			
Electrical conductivity	Between Groups	.977	1	.977	1851.763	.000
	Within Groups	.004	7	.001		
	Total	.981	8			

APPENDIX I

Table I.1: Statistical zeta potential and electrical conductivity of 15%MgCl₂+pure water (XXV) before and after filtration (XXVI) results

Variable	XXV, XXVI samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	168.166	1	168.166	184.683	.001
	Within Groups	2.732	3	.911		
	Total	170.898	4			
Electrical conductivity	Between Groups	4777.932	1	4777.932	15580.213	.000
	Within Groups	.920	3	.307		
	Total	4778.852	4			

Table I.2: Statistical zeta potential and electrical conductivity of zein nanofiber membrane (II) before and after filtration (XXVII) results

Variable	II, XXVII samples	Sum of Squares	df	Mean Square	F	Sig.
Zeta potential	Between Groups	428.269	1	428.269	71.628	.000
	Within Groups	41.853	7	5.979		
	Total	470.122	8			
Electrical conductivity	Between Groups	11.966	1	11.966	1101.826	.000
	Within Groups	.076	7	.011		
	Total	12.042	8			

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